

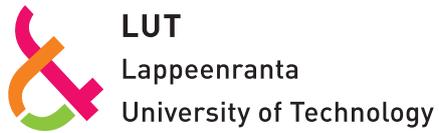
Acta Universitatis  
Lappeenrantaensis  
789



Evgenia Iakovleva

**NOVEL SORBENTS FROM LOW-COST MATERIALS  
FOR WATER TREATMENT**

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Evgenia Iakovleva

## **NOVEL SORBENTS FROM LOW-COST MATERIALS FOR WATER TREATMENT**

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium of the MUC, Mikkeli University Consortium, Mikkeli, Finland, on the 19<sup>th</sup> of January, 2018, at noon.

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## **Abstract**

**Evgenia Iakovleva**

**Novel sorbents from low-cost materials for water treatment**

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Great attention has been paid in many studies to the environmental problems in mining. One of these is how to reduce water consumption during the ore mining and metal extraction process. Another ecological problem of mining includes solid waste management.

The main method for reducing water consumption is recycling water. In this case, problems may be encountered, such as water treatment before reusing it. The purification methods will depend on the set of pollutants that should be removed and the type of water that should be treated. For example, the term “mine water” includes waters with different compositions and quality that depend on the chemical composition of an ore, extraction methods, and environmental conditions. Process water is also a general term for water, which is used for various technological processes and therefore has a different composition. Process water should be treated in accordance with technological requirements before use. Mine water, such as acid mine drainage (AMD), should also be treated before being released into the environment. AMD and process water from metal extraction were investigated in this work as objects for finding new solutions for their treatment and reuse.

Traditional methods for the treatment of mine water are expensive. Adsorption is the most cost-efficient method of water purification. Therefore, adsorption has been applied as a low-cost, efficient, and environmentally friendly methodology for AMD and process water treatment.

Approximately 80% of ore is waste after the extraction of metals. The amount of solid wastes is increasing significantly in mining countries. The development of sorbents from solid wastes is one promising solution to the management of solid wastes. The first part of this paper presents a literature review considering the main points of adsorption theory with a focus on the interaction between the liquid and solid phases. On the basis of the results obtained by numerous research groups, the various methods of modification have been reported with a focus on low-cost materials.

The experimental results and discussion section are presented for the chosen adsorbents, including physicochemical characteristics and capacity to adsorb various pollutants. The chemical composition and structure of the materials were characterized with X-ray diffraction (XRD), X-ray fluorescence (XRF), organic elemental analysis, scanning

electron microscope/energy dispersive X-ray spectroscopy (SEM/EDX), and a Fourier transform infrared spectroscope (FTIR). The determination of pollutant concentration before and after adsorption was conducted with inductively coupled plasma atomic emission spectroscopy (ICP-OES) and high-performance liquid chromatography (HPLC). Various adsorption isotherms were used in the characterisation of behaviour between adsorbent and adsorbate.

The results of this research work show that some low-cost materials and industrial by-products could be used as adsorbents for wastewaters.

Keywords: limestones, by-products, sulphate tailings, coffee waste, iron-based adsorbent atomic layer deposition for powder, metal ions, cyanide, arsenic, sulphates, chlorides

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## List of publications

- I. Iakovleva, E., Mäkilä, E., Salonen, J., Sitarz, M., Sillanpää, M. (2015). Industrial products and wastes as adsorbents for sulphate and chloride removal from synthetic alkaline solution and mine process water. *Chemical Engineering Journal*, 259, pp. 364-371.
- II. Iakovleva, E., Mäkilä, E., Salonen, J., Sitarz, M., Wang, S., Sillanpää, M. (2015). Acid mine drainage (AMD) treatment: Neutralisation and toxic elements removal with unmodified and modified limestone. *Ecological Engineering Journal*, 81, pp. 30-40.
- III. Iakovleva, E., Maydannik, P., Ivanova, T.V., Sillanpää, M., Tang, W.Z., Mäkilä, E., Salonen, J., Gubal, A., Ganeev, A.A., Kamwilaisak, K., Wang, S. (2016). Modified and unmodified low-cost iron-coating solid wastes as adsorbents for efficient removal of As(III) and As(V) from mine water. *Journal of Cleaner Production*, 133, pp. 1095-1104.
- IV. Iakovleva, E., Sillanpää, M., Maydannik, P., Liu, J.T., Allen, S., Albadarin, A.B., Mangwandi, C. (2017). Manufacturing of novel low-cost adsorbents: co-granulation of limestone and coffee waste. (2017) *Journal of Environmental Management*, 203 (2), pp. 853-860.
- V. Iakovleva, E., Sillanpää, M., Mangwandi, C., Albadarin, A.B., Maydannik, P., Khan, S., Srivastava, V., Kamwilaisak, K., Wang, S. (2017). Application of Al<sub>2</sub>O<sub>3</sub> modified sulfate tailings (CaFe-Cake and Sufe) for efficient removal of cyanide ions from mine process water. *Journal of XXX*. Submitted for publication 2017.
- VI. Iakovleva, E., Sillanpää, M., Maydannik, P., Khan, Doshi, B., Kamwilaisak, K., Wang S. (2017). Novel sorbents from low-cost materials modified with atomic layer deposition for acid mine drainage treatment. *Journal of XXX*. Submitted for publication 2017.

## Author's contribution

I-VI. The author carried out all of the experimental work, analysed and collected most of the data, and prepared the first draft of the manuscripts.

## Related publications

- a) Iakovleva, E., Sillanpää, M. (2013). The use of low-cost adsorbents for wastewater purification in mining industries. *Environmental Science and Pollutants Research Journal*, 20(11), pp. 7878-7899.
- b) Ganeev, A., Bogdanova O., Ivanov I., Burakos, B., Agafonova, N., Korotetski, B., Gubal, A., Solovyev, N., Iakovleva, E., Sillanpää, M. (2015). Direct determination of uranium and thorium in minerals by time-of-flight mass spectrometry with pulsed glow discharge. *Royal Society of Chemistry*, 5(99), pp. 80901-80910.
- c) Rivas, E., Urbano, B., Koter, S., Polowczyk, I., Konieczny, K., Figoli, A., Sarkar, S., Iakovleva, E. (2016). Chapter 1, Occurrence and toxicity of arsenic and chromium. Book, Innovative Materials and Methods for Water Treatment: Solution for Arenic and Chromium Removal. *CRC Press, Taylor and Francis Group*.
- d) Iakovleva, E., Louhi-Kultanen, M., Sillanpää, M. (2016). Chapter 7, Low-cost adsorbents for arsenic separation from wastewaters. Book, Innovative Materials and Methods for Water Treatment: Solution for Arsenic and Chromium Removal. *CRC Press, Taylor and Francis Group*.
- e) Shestakova, M., Vinatoru, M., Mason, T. J., Iakovleva, E., Sillanpää, M. (2016). Sonoelectrochemical degradation of formic acid using Ti/Ta<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> electrodes. *Journal of Molecular Liquids*, 223, pp. 388-394.
- f) Iakovleva, E., Sillanpää, M., Khan, S., Kamwilaisak, K., Wang, S., Tang, W.Z. (2017). Synthesis of sorbents from industrial solid wastes by modification with atomic layer deposition (ALD) for mine water treatment. *13<sup>th</sup> International Mine Water Association Congress Mine Water & Circular Economy, 2017*.
- g) Zhao, F., Repo, E., Dulin, Y., Li, C., Kalliola, S., Juntao, T., Iakovleva, E., Kam, C. T., Sillanoää, M. (2017). One-pot synthesis of trifunctional chitosan-EDTA-β-cyclodextrin polymer for simultaneous removal of metals and organic micropollutants. *Scientific Reports*, 7, pp. 1-14.

The author carried out the literature survey (a, c, d, f), analysed data with the co-authors, and wrote the paper (a, d, e). The author did the experimental work related to sample preparation and measurements by TOF MS (b) and HPLC (e, g), and analysed data with co-authors.

## List of symbols

### Latin alphabet

$A$	adsorption	%
$A_f$	Arrhenius's prefactor	
$C$	concentration	mg L <sup>-1</sup> or mmol L <sup>-1</sup>
$D$	desorption	%
$d$	diameter	mm
$E$	potential in specific conditions	
$E_a$	activation energy	
$E^o$	potential in standard-state conditions	
$Eh$	redox potential	mV
$F$	Faraday's constant	C mol <sup>-1</sup>
$f$	compressive force	N
$i$	tests amount	
$k$	constant	
$K$	Henry's constant	L mmol <sup>-1</sup>
$K_L$	Langmuir constant	L mmol <sup>-1</sup>
$K_F$	Freundlich constant	L mmol <sup>-1</sup>
$K_B$	BET constant	L mmol <sup>-1</sup>
$m$	exponent for compound 1	
$n$	exponent for compound 2	
$pH$	hydrogen ion activity	
$pE$	electron activity	
$q$	adsorption capacity	mmol g <sup>-1</sup>
$q_e$	equilibrium adsorption capacity	mmol g <sup>-1</sup>
$q_m$	maximum adsorption capacity	mmol g <sup>-1</sup>
$R$	ideal gas constant	J mol K <sup>-1</sup>
$T$	temperature	°C or K
$t$	time	min
$V$	volume	m <sup>3</sup>
$v$	rate of reaction	
$X$	error	

### Greek alphabet

$\Delta$	(capital delta) usually used for change without slanting: $\Delta$	
$\zeta$	(zeta) is zeta potential	mV
$\Sigma$	(capital sigma) often used for sum without slanting: $\Sigma$	
$\pi$	(pi) usually reserved for mathematical value $\pi = 3.14159...$	
$\sigma$	(sigma) is granules strength	
$\tau$	(tau) is temperature coefficient	

### Abbreviations

a	annually
AC	activated carbon
ALD	atomic layer deposition
AMD	acid mine drainage
ARD	acid rock drainage
BET	Brunauer Emmett and Teller model
DHBA	2,5-Dihydroxybenzoic acid
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy-dispersive X-ray spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
h	hour
HPLC	High Performance liquid chromatography
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ln	natural logarithm
log	logarithm
MB	methylene blue
NTA	Nitrilotriacetic acid
OR	orange II
Ox	Oxidation
Red	Reduction
S	standard deviation
SEM	Scanning Electron Microscope
TMA	trimethylaluminium
USD	United States Dollar
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

### Names of unmodified and modified adsorbents

CaFe-Cake	unmodified sulphate tailing
CaFe <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>	modified with Al <sub>2</sub> O <sub>3</sub> sulphate tailing
CaFe <sub>2</sub> NaOH	modified with NaOH sulphate tailing
CaFe <sub>2</sub> TiO <sub>2</sub>	modified with TiO <sub>2</sub> sulphate tailing
CW	coffee waste
DI-60	by-product of pulp and paper industry
FF	unmodified limestone
FF <sub>NaCl</sub>	modified with NaCl limestone
FF <sub>WW</sub>	modified with process water limestone
FS	unmodified limestone
FS <sub>NaCl</sub>	modified with NaCl limestone
FS <sub>WW</sub>	modified with process water limestone
RH	unmodified industrial by-product

---

RH_ Al <sub>2</sub> O <sub>3</sub>	modified with Al <sub>2</sub> O <sub>3</sub> industrial by-product
RH_ NaOH	modified with NaOH industrial by-product
RH_ TiO <sub>2</sub>	modified with TiO <sub>2</sub> industrial by-product
SuFe	unmodified sulphate tailing



## 1 Introduction

Modern society cannot be imagined without the technological advances that have occurred over the past 100 years. Technology continues to develop and cannot exist without the use of natural resources such as water and metals. Water is one of the most important resources for sustainable life on the planet [1–3].

Water covers more than 70% of the earth, but less than 3% is fresh water, and less than 1% of fresh water is easily available for human consumption [1–3] (Fig. 1). More than a third of the world's population live in conditions of water stress. Industry consumes a fifth of the total water in use, which is about  $750 \text{ km}^3 \text{ a}^{-1}$  [1].

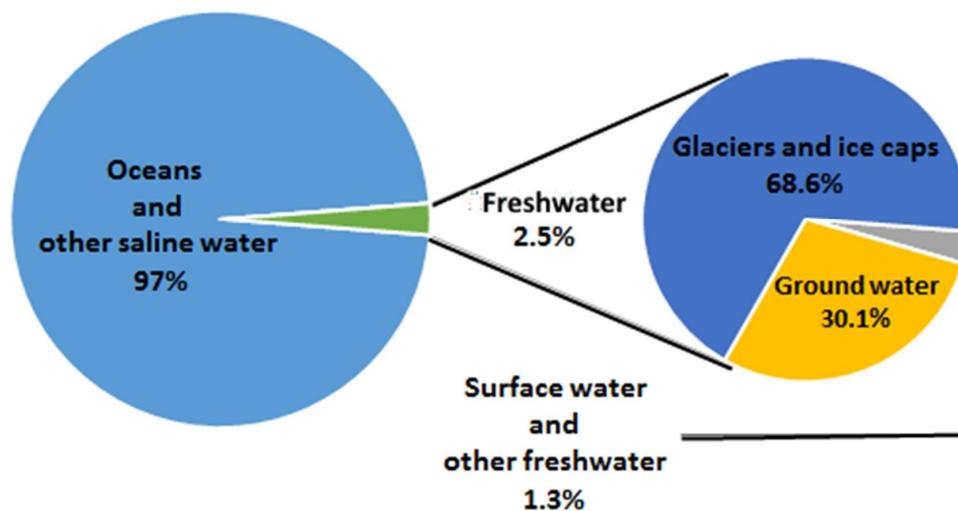


Figure 1. World water resources (modified from references [1–3]).

One of the main tasks of modern science is to find ways to reduce water consumption in industry, through re-use, as well as the search for new water-free technological solutions, or through minimizing water consumption as much as possible. With the support of governments and industries, many research groups are actively working on the challenge of minimizing water consumption [5]. For example, some new methods of mining and metals extraction have been proposed over the past decades, such as desalination of saline water for mining, reusing process water for double extraction of rich metals from

solutions, and waterless methods [4, 6–8]. All of these achievements make a certain contribution to the development of more environmentally friendly mining and extraction. However, these methods are rather expensive and sometimes less effective than the ones already in use [7].

Since this work has been financed by the Finnish Funding Agency for Technology and Innovation (TEKES), data on water consumption and the amount of solid waste will be presented on the basis of the reports of the Finnish Network for Sustainable Mining (FNSM) [9].

Mining activities use fresh and process water for many tasks, such as the extraction of natural gas, petroleum and minerals. Frequently, part of the water is reused after pretreatment; pretreatment procedures and costs vary depending on water quality requirements. However, a lot of challenges remain open. How can the maximum opportunities for water reuse be achieved? How can process water be purified efficiently using economically sustainable methods? Can other opportunities be found to use process water [9]? It was observed by the FNM that mine industries in Finland used 1,798 GWh energy and 65.4 Mm<sup>3</sup> of water, including recycled water, for the period of 2015 [9]; moreover, the percentage of raw water is from 3.6% to 68% (Table A1). Some companies reuse a certain amount of raw water. For example, Agnico Eagle Finland Ltd reported, that water is processed in the process through a closed underground mine located area, which means that no additional water is required (Table A1). However, the challenges of water management are still an open question and the effort to reduce water consumption is in progress.

Another type of water that causes serious concern for the environment is acid mine drainage (AMD) that forms in closed mines due to the oxidation of mine tailings. AMD is one of the main sources of pollution of surface and ground waters with metal, sulfate ions and other pollutants. AMD is especially formed in metal and coal mines. Sulfur containing tailings react with water and oxygen to form sulfuric acid and dissolve in their metal ions. This acid is carried out of the mine site by rainwater or surface drainage and gets into nearby streams, rivers, or lakes, creating environmental risks. Comparative analysis of the two geological maps from the Geological Survey of Finland (GTK) that are presented in Figure 2 shows that a decrease in the quality of water sources is more often observed in the location of mining [10].

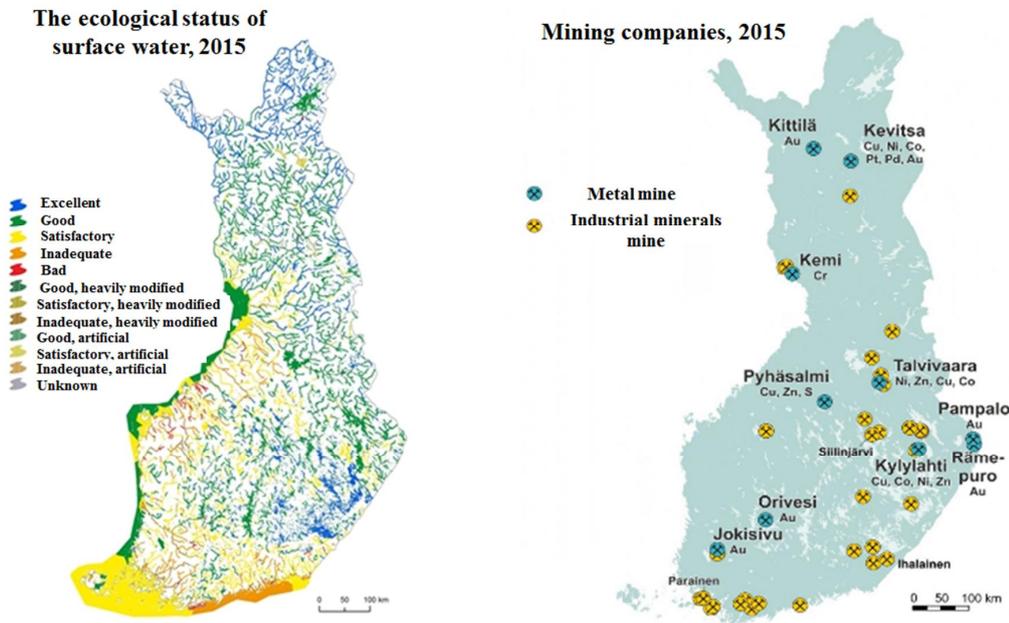


Figure 2. Data on the ecological status of groundwater and the location of mining companies in Finland during 2015 (data were collected from references [9, 10]).

The global challenge also is the daily increasing amount of solid wastes related to human activity. The mining and ore process industries are among the largest water consumers and producers of 60–70 Gt solid waste every year [4]. The remnants of the rock produced as a result of extraction and processing are the main source of the pollution of natural ecological systems. For example, mine tailings, which remain after ore extraction and can account for 20% to 98%, depending on the mined minerals. They can damage the environment by releasing toxic metals with acid drainage. Mining minerals, according to the mining law, extracted from Finland are comprised of metal minerals (Cr, Ni, Cu, Zn, Co, Au, Ag, Pt, Pd, sulfur), industrial minerals (apatite, calcium, dolomite, wollastonite, talc, quartz and ground beet), industrial stone, jewellery, and precious stones (amethyst) [10]. The most significant environmental impacts are usually related to the extraction of sulphide metal ores (Ni, Cu, Zn, Au, Ag, Pt, Pd, sulfur).

According to the FNM report for 2014, total extraction amounted to 73.8 Mt and solid waste was 67.3 Mt, which is approximately 91% of the total amount of ore. Data on some companies for 2015 are shown in Table A1 [9]. It can be seen that the amount of solid waste ranges from 50% to 99% of the total amount of excavation ore. In particular, a large part of the solid waste is the tailings. At the same time, if waste rock is reused, in whole or in part, the tailings are then most often outgoing to dumps. The main environmental impacts of sulfide metal mines are related to the storage and discharge of extractive waste

as tailings are exposed to oxidation at the excision level of extractive waste and cause harmful effects to the environment. Oxidation of tailings can occur on quarry walls, in enrichment processes, in concentrate storage levels, and in areas where sulfide-containing dust has spread. Efficient and low-cost methods for the neutralization of tailings for their further disposal, as well as the possibility of their reuse, remain serious challenges for the mining industry and environmental services.

The mineral processing facilities are also located in Finland, of which the largest is Norilsk Nickel Harjavalta, with an annual production of copper and nickel compounds of about 46 kt, and half of which is sulphates. The consequence of this extraction process is also sulphate tailings, which are not reused. The water consumption during production is approximately 11 Mm<sup>3</sup>/a [11]. The main aim of the sustainable management of mine tailings is to stabilize those mining wastes and to make them inert or to limit their contact with natural water to prevent the oxidation process. It can be seen from the data given in Table A1 that the Finnish gold mine and processing companies have used about 200 tons of cyanides per year, which also must be subjected to neutralization before its disposal.

The food industry is the other main producer of solid waste in the world. As the UN Food and Agriculture Organisation confirm, approximately 30% of all produced food goes to waste, which is about 1.3 billion tons per year [11]. Considering the challenges in the mining and food industry, efforts must be made to optimize and minimize solid waste.

Increasing the efficient use of resources by reuse will allow a decrease in the consumption of energy, water, and chemicals. The most environmentally friendly approach, which is consistent with the principles of green chemistry and ecological aspects, is to search for alternative applications for solid wastes. Utilizing solid waste as potential sorbents for water treatment was taken as main alternative approach for reuse during this research. Industrial and food by-products were applied to different challenges of water treatment in accordance with their chemical-physical properties. The adsorption method with sorbents produced from low-cost materials, such as limestone and by-products, was used in this research work. The theoretical part of this study includes a literature review, which addresses the issue of adsorption theory, mine water composition, and the effects of their physicochemical properties on the behavior and removal of pollutants [12–18]. The various types of low-cost adsorbents and their adsorption capacities and possible methods of modification are described.

The low-cost materials and by-products of various Finnish industries for acidic and alkaline mine water are presented in the experimental part. All of these materials were tested without modification of their surfaces. However, some methods of surface modification are also described. Water and solid waste minimization by the production of low-cost sorbents for mining water treatment in the framework of the Green Mining and Intelligent Mine Water Management projects with the financial support of the Finnish Funding Agency for Technology and Innovation (TEKES) were considered in this study.

## 2 Literature review

### 2.1 Mine water composition

Ground and surface waters in ground and underground mining excavations are exposed to physical and chemical changes during operation. Mine water occurs from the interaction of ground water with the atmosphere and the opened ore. The chemical composition of these differs from that of the ground water surrounding the mine as a consequence of the rocks leaching, the influence of atmospheric gases, bacterial, organic, and inorganic pollutants [19].

The geochemistry of mine water depends on chemical composition, pH, redox potential, origin, and application. Mine waters may be classified by their contamination, quality and applicability. In this manuscript mine waters will be divided into acid mine drainage and process waters.

Acidic mine water is named acid mine drainage (AMD) or acid rock drainage (ARD) [20–27]. The term ARD is used to refer to acid drainage originating from sources other than mines — for example, as a consequence of building activities or after a rise in sea level [23]. The present study is primarily concerned with AMD. AMD is formed in the process of metal mining and associated processes with the oxidative dissolution of sulphide minerals. The chemical composition of AMD is unique to every mine and depends on the rock mineralogy, climate, seasons, geographic location, mining and mineral processing methods, and other factors [23-27]. It can be seen in Figure 3, that the entry of pollutants into surface and groundwater is possible due to rainfall and percolation through the soil.

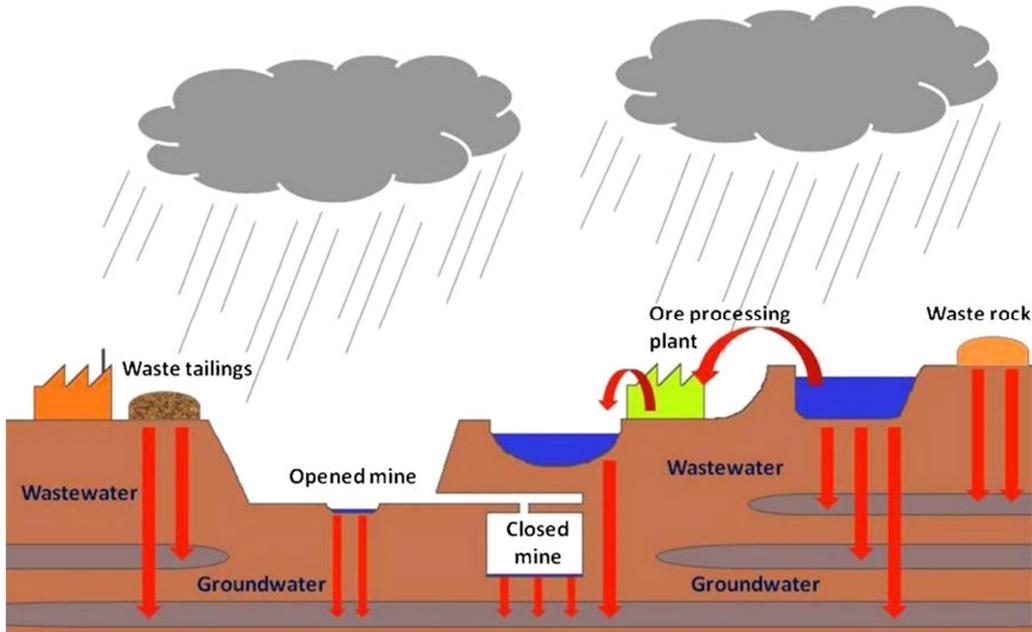
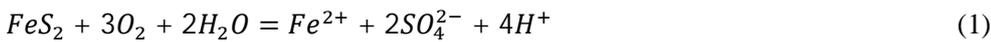
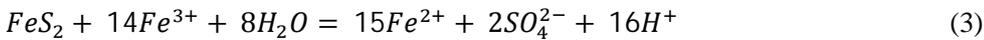
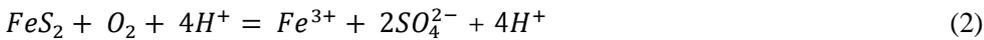


Figure 3. General diagram of pollutants' transfer and AMD formation (modified from references [22-27]).

All AMD is characterized by low pH and a high concentration of metal ions and other toxic elements (As, Hg, Cl etc.) [20–27]. The process of oxidation of sulphide minerals can be described by pyrite oxidation, which is the main step in the AMD formation process. The general equation is:



Continued oxidation can lead to the formation of ferric iron (Eq. 2), which can also oxidize additional pyrite (Eq. 3):



The opened mine has a higher probability of pyrite formation than the closed mine, since the entry of water and oxygen through natural sources are more likely (Figure 3). The general impact of the AMD formation is the release of  $H^+$  and maintaining the solubility of metal ions. Hence, acid neutralization and metal ions removal are general challenges for AMD treatment.

The behaviour of anions and cations in water is related directly to pH and redox potential. pH is a characteristic of the behaviour of hydrogen ions in a solution and can be determined as the reverse decimal logarithm of the hydrogen ion activity:

$$pH = -\log[H^+] \quad (4)$$

Redox potential is a characteristic of the activity of electrons and can be determined as the reverse decimal logarithm of the electron activity in a solution:

$$pE = -\log[e^-] \quad (5)$$

These two parameters are described by the Nernst equation and can be determined simultaneously:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} \quad (6)$$

where  $E$  and  $E^0$  are potentials at specific and standard-state conditions respectively;  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ );  $T$  is ambient temperature;  $n$  is the number of electron moles;  $F$  is Faraday's constant, the charge on a mole of electrons ( $96485 \text{ C mol}^{-1}$ ).

The Nernst equation for the hydrogen value after calculation at temperature 298 K and considered constants  $R$ ,  $T$  and  $F$  is:

$$E = E^0 + 2.3 \frac{RT}{nF} \log aH^+ \quad (7)$$

where  $\log aH^+$  is pH.

As can be seen, these values are related to each other and may vary depending on the conditions. For example, the redox potential of distilled water at pH 7 should be 812 mV, whereas for natural waters, the potential ranges from 300 to 600 mV. The Eh of groundwater decreases from 0 to minus values accompanied with the depletion of  $O_2$  due to the increase in depth (Fig. 4).

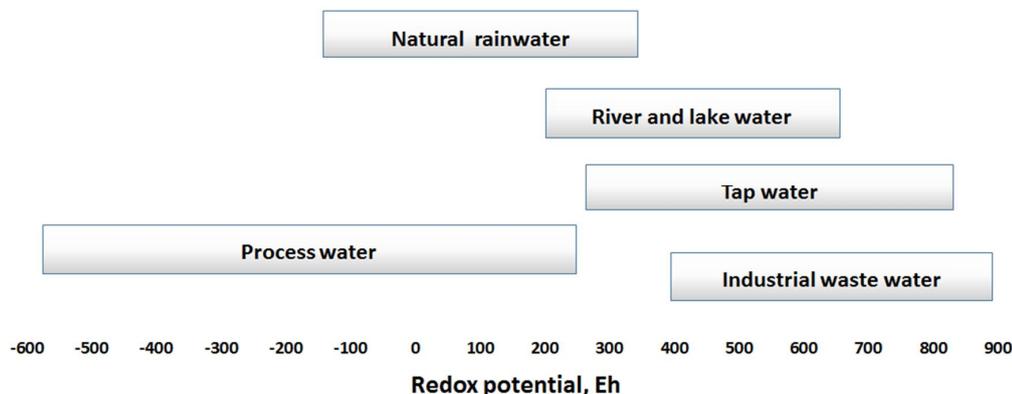


Figure 4. Redox potential of different types of water (modified from reference [27]).

Redox potential and pH are the decisive factors for the availability of the predominant oxidized form of various elements and their behaviour in water. For example, surface waters contain As and its oxidized forms. Arsenic form changes to reduced forms due to decreasing Eh under anaerobic conditions [28] (Fig. 5). There are transition forms of arsenic:  $AsH_3 > AsO_3^{3-} > As_2O_3, As(III) > AsO_4^{3-} > R_4AsX > As(V)$ .

With the lower valence state As(III) and its oxide  $As_2O_3$  is the most toxic form. This form is chemically active. This especially forms bonds with sulphur-containing fragments of protein molecules in the human body [29, 30]. The main source of arsenic(III) oxide is groundwater and gold and copper mining activity. Arsenic(III) oxide is a valuable chemical raw material for the production of other arsenic compounds. It is also used for pulp and paper industry, semiconductor electrical engineering and for the production of collared glass. The gross production of  $As_2O_3$  in the world is 50,000 tons per year [31]. However, the safety of use is questioned due to the high toxicity of this substance. The massive and most common arsenic poisoning occurring through drinking water has been observed in areas of Bangladesh [32], India [33], the Tibetan Plateau [34], Chile [35], the USA [36] and Cambodia [37]. Only strong oxidants, such as ozone, hydrogen peroxide, and nitric acid, are able to convert arsenic(III) oxide to arsenic(V) oxide, which is removed easily from the solution to compare with As (III). Many scientific groups have presented research on the removal of As(III) through its conversion into As(V) by pH exchange [28, 38-44]. However, this methodology is multistep since pH must be controlled by chemicals that are toxic and not cheap, and limits their use in economically underdeveloped countries. The development of a method that would allow the removal directly of both forms of arsenic from water with minimal time and chemical consumption can solve this problem.

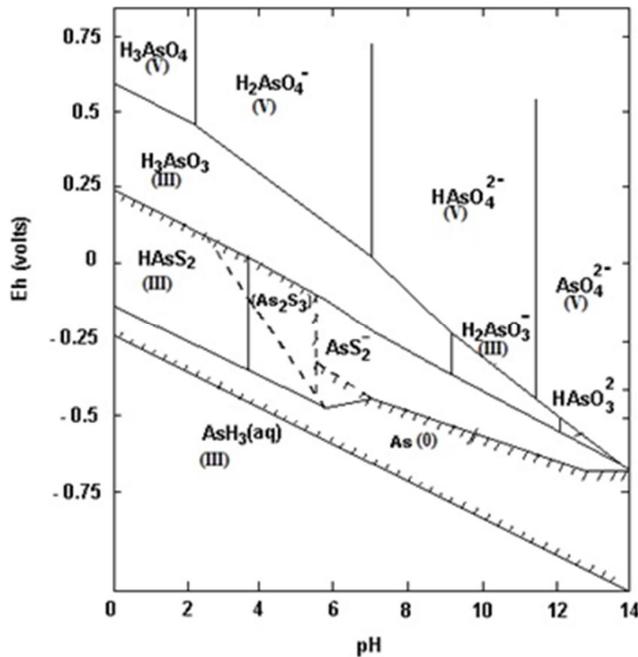
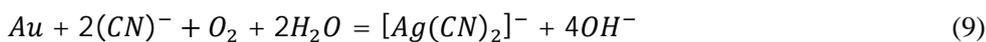
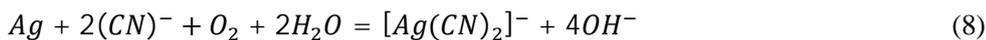


Figure 5. Eh-pH diagram for As compounds in water at 25 °C (modified from reference [42]).

Cyanides are the main pollutants that originate from extraction in the gold and silver industry, because of their high affinity for gold and silver:



The concentration of cyanide and its compounds should be limited to minimize the risk of environmental contamination. Cyanide ions form complexes with metal ions which participate in the biochemical processes and disturb the bio-processes in the cells of humans, animals and plants [29, 30]. The cyanide process is used for extracting precious metals in many countries. However, in some countries, such as the USA and Canada, mercury amalgamation is used instead of cyanides [45, 46].

Process water is water that is used for the extraction of metals from ore [47-55]. Process water for metal extraction is alkaline with a pH of about 10 – 12. Associated metals and salts enter into the process water during the metal extraction. This water must be purified from the excess metals and salt ions after each working cycle. Reuse of process water serves to decrease clean water consumption [56].

## 2.2 Mine water purification

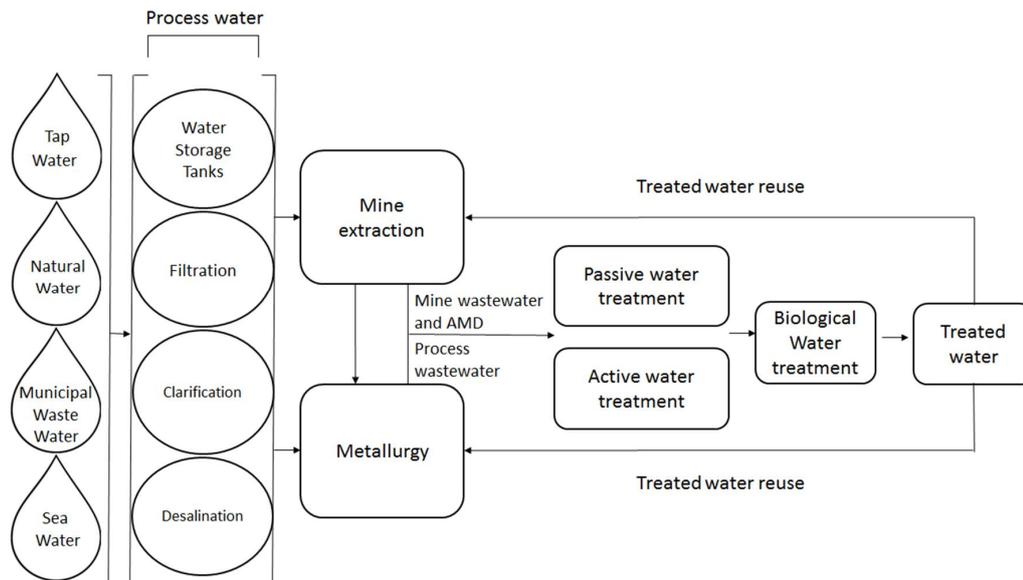


Figure 6. Scheme of mine water consumption and reuse (modified from reference [56]).

Mine water treatment is a complex and multi-step process. Active and passive methods are the main groups of all wastewater purification methods (Fig.6). They can be used both separately and in combination, depending on the technology and issues involved [56]. For example, AMD treatment consists of several challenges, particularly neutralization and metal ions removal [26], whereas process water contains large amounts of salts needed for the extraction of metals [47-55]. However, a certain amount of anions may pass into process water from ore during the extraction process and they should be purified from there. Both active and passive methods are often used in combination depending on the objectives [53].

In this chapter, all mine water treatment methods are divided into two groups, active and passive, and will be addressed according to their applicability.

### 2.2.1 Passive treatment of mine water

Wetlands, biochemical reactors, reactive barriers, and limestone drains are passive methods applied in acidic mine water treatment [26, 58-62].

Wetlands are an effective method for the removal of many metal ions from mine water (Figure 6). The effect of acid mine water treatment can be increased by the addition of

lime for water neutralization and metal ions removal by precipitation. Limestone is a low-cost material, but it can increase the amount of precipitants and form buffer solutions with carbon dioxide at a pH below 6. It may prevent the removal of some elements, such as manganese, which is extracted from solutions with a pH higher than 6 [63-67]. The surface of limestone rapidly becomes covered with iron and the neutralization of large water volumes requires huge amounts of limestone [26, 58-67]. During passive water treatment it is necessary to avoid some possible negative factors, such as rainwater inflow and bacteria deterioration. Rainwater will lead to further oxidation of pyrite and leaching of the more toxic elements from the ore to wastewater [27].

The use of bacteria in metal extraction from ore and for removing various toxins from wastewater has been studied extensively in recent years. This is a low-cost and environmentally friendly method. The ability of bacteria to extract and enrich various metals, including rare earth, from ore was discovered in the middle of the 20<sup>th</sup> century. The most studied bacteria is *Acidithiobacillus Ferrooxidans*, which can oxidize sulphides. At the moment, this process is mainly used for the enrichment of copper from copper-lean ore, when the use of traditional methods of copper extraction are uneconomical. This method is currently used for the industrial production of copper, uranium, molybdenum, and other metals [68-74]. The ability of bacteria to remove trace amounts of metals as well as their affinity to cyanides and arsenic compounds makes them good candidates for water treatment. For example, algae and fungi use the products of pyrite decomposition for their subsistence [75].

The disadvantages of biological methods are an obstacle to their widespread use. There are strict limits of temperature, UV light intensity, and pH ranges which must be maintained throughout the purification process in order to avoid the death of the bacteria [68-82].

Although natural or industrial beds have low investment costs and cost-effective water consumption, these methods have disadvantages limiting their application. The removal of some metals is not effective, for example Zn and Ni [26]. The passive method for mine water treatment is less effective and time consuming than active chemical methods.

### 2.2.2 Active treatment of mine water

Active treatment consists of various steps, such as mechanical, chemical, mechanochemical, and physiochemical methods [61].

The first step in many water purification technologies is the application of the physical methods by mechanical removal of solid and colloidal substances [61]. The main goal of this treatment is separation of coarse particles. This can be done with coarse filters and using gravitational sedimentation. There are three basic methods of mechanical treatment: detention, filtration, and straining. The particles with greater relative density than the specific gravity of water form a sediment. At the same time, the particles with smaller relative density than the specific gravity of water, such as fats and oils, float on the surface

of the water. Mechanical treatment is widely used for mine and metallurgical water treatment, since these waters may be contaminated with solid ore residues and colloids [83, 84].

Chemical purification methods are based on chemical reactions, which help to remove various contaminants from water, such as sorption by ion-exchange reactions, adsorption, and absorption, [83-85]; separation methods by coagulation, crystallization, magnetic separation and precipitation [86, 87], and electrochemical methods [88, 89]. It can also serve as a preparatory stage before the main purification method. For example, AMD should be neutralized before metal ions removal. At the same time, metal ions may partially precipitate during the neutralization process [27].

Sorption is the most widely applied, low-cost, less energy consuming method for removing various types of pollutants. This method may be a good option compared to other more expensive methods.

### 2.3 Key aspects of AMD and process water treatment

Neutralization of AMD is the main and first step for successful mine water treatment. Generally, limestone or other calcareous compounds are used for acid neutralization by dissolution of calcite and silicates decreasing of sulphate concentration.

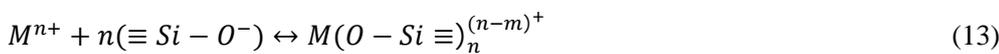
Limestone neutralizes AMD by release of calcium into the solution and precipitation of gypsum as a consequence:



The precipitated gypsum coats rapidly the limestone reactive surface, which leads to slower AMD neutralization, as observed by many investigators [42, 90-97]. This lead to the additional amount of slurries and precipitates generated during the increasing a pH and removal of metal ions with precipitation. On the other hand, some compounds are not precipitate even at a high pH, such as sodium sulfate and can be released into the environment with effluent.

The problem of gypsum precipitation can be solved by using the reagents that realize magnesium, which has approximately a hundred times higher coefficient of solubility equilibrium than gypsum [90, 93]. The use of minerals such as dolomite, diopside, and others, which contains magnesium and other more soluble components, can avoid the coating of active sites of limestone by insoluble components. This phenomenon can be described through the ions exchange mechanism between metal ions and reactive hydroxyl groups that occur on the sorbent surfaces [90-97].

As has been observed by some researchers, silicate reacts with metal ions through adsorption onto active sites of the polymerized silicate, followed by an increase in pH values. If the process of precipitation of metal oxides is understandable, the process of adsorption of metal ions on the surface of silicate is more difficult to characterize [98-103]. Falcone [98], Fripiat et al. [99] and Elizondo-Alvarez et al. [103] have made the assumption about the progress of a sorption mechanism between metal ions and active sites of silica. This phenomena can be described by the following reactions:



The polymerization mechanism of silica in water solution is describe by reversible reaction between molecules of orthosilicic acid and molecules of water (11). Equation 12 describes the dissociation of the hydroxyl group. The interaction of positively charged metal ions with the negative charge of silica surface causes the formation of the surface complexes creation (13). Falcone [98] and Wawrzkievicz et al. [100] mentioned that

metal ions were removed from acid solutions with polymerized silicate at pH values below the equilibrium at which metal should precipitate. Adsorption can take place on binding sites on the external “surface” of clusters of polymerized silicate tetrahedral or the metal ions can be encapsulated within the silicate cluster. Regarding the adsorption site, the metal ions are carried out of the solution with the flocculated silicate.

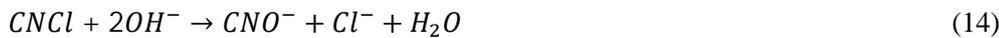
The use of polymerized silicate for the removal of metal ions and acid neutralization of mine waters has the following benefits:

- The alkaline silicate can be used to adjust the pH to higher values
- Silicate reacts with dissolved metal ions or immobilizes them by adsorption on the surface of colloidal silicate particles.

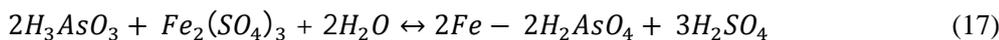
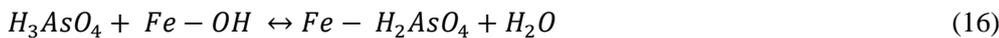
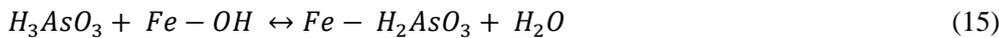
There are large variety of process waters according to their chemical composition, as previously noted. The treatment of alkaline process water with a high concentration of sodium chloride and sulphates and the process water from a gold mine will provide the framework for the investigations of this research.

Process water treatment problems can be solved using a variety of treatment technologies, such as the electro-chemical method [104-107], biological degradation [108], membrane filtration [109, 110], coagulation [111-113], adsorption or ion exchange [114-117]. Low-cost process water recovery is one of the most significant issues facing the industry today. Ion exchange is considered to be one of the best and most efficient methods for removing anions from water due to its high efficiency, simplicity, and low cost. The removal of anions from highly alkaline process water is expensive and quite challenging. Sulphate and chloride removal is often accomplished through an ion exchange mechanism with limestone [110, 118, 119]. This process involves ion exchange between  $\text{OH}^-$  on the adsorbent surface and removed anions. Natural lime is often used for process and wastewater treatment [58-64, 120-126]. Sulphate removal from water by adsorption has not always been successful — for example, in Darbi et al.'s research on sulphate removal from drinking and groundwater by bentonite [110]. Solid waste, however, is similar in composition to limestone and has a demonstrably high capacity to adsorb anions from wastewaters, yet it has received the least amount of research attention [125, 126]. Alkaline mine water can be treated with sorbents based on the ion exchange between  $\text{OH}^-$  ions on the surface of sorbents containing  $\text{H}^-$  groups.

Process water treatment with various reagents is used to purify it from many pollutants, including cyanide. For example, one of the methods is based on the extraction of cyanide ions in the form of hardly soluble complexes salts ( $\text{Fe}_4^{3+}[\text{Fe}^{2+}(\text{CN})_6]_3$  and  $\text{Fe}_3^{2+}[\text{Fe}^{3+}(\text{CN})_6]_2$ ) formed in the alkali solution in the presence of Fe(II) ions [127]. Effective removal of cyanides from process water using this method is possible only in the case of precise monitoring of the pH values and other conditions. Another method used to remove cyanide compounds from process water is based on their oxidation with chlorine or hypochlorite [127]. The reaction of cyanide oxidation to cyanates proceeds in two stages:



Firstly, chlorine is formed (Eq 13), which is hydrolyzed to cyanate (Eq 14). Considering that chlorocyan is a highly poisonous gas, it is necessary to maintain such conditions that the reaction rate (Eq 13) is greater than the reaction rate (Eq 14). The following conditions are observed when the concentration of cyanide in the sewage does not exceed  $1 \text{ g L}^{-1}$  and the process proceeds at  $50 \text{ }^\circ\text{C}$  and the pH value higher than 8.5. Waters with a higher concentration of cyanides are needed to dilute or use another method of neutralization. On the other hand, despite the fact that cyanates are less toxic than cyanides, their further neutralization is required [127].



Equations 15-17 are presented as a possible complexation mechanism between arsenic compounds and iron hydroxides, which are component of the sorbents.

All of the listed methods are complicate and associated with the possible release of toxic by-products. New materials that could be used as a complex agent for the cyanide and their conversion into non-toxic forms is the high priority aim in terms of environmental management in gold exploration.

### 2.3.1 Sorption in liquids

Sorption is a phenomenon that describes the interactions or mass transfer at the interface of two different phases (gas, liquid, or solid) leading to changes in their composition by physical or chemical processes. The first sorption phenomenon between gas and solid or liquid phases was observed and described over 200 years ago by Scheele [128]. The sorption process is divided into two types, adsorption and absorption. Selective adsorption and ion exchange may be specified as particular cases of adsorption. The basic sorption mechanisms are shown in Figure 7. Absorption is a process in which an absorbate completely penetrates the body of a solid or liquid to form a compound or a solution (Fig. 7b). On the other hand, adsorption is a surface reaction in which the molecules of an adsorbate concentrate only on the surface of an adsorbent (Fig. 7a). Frequently, both mechanisms can be present during the phase transfer process, which are not easy to distinguish. Therefore, the term sorption is more useful for both phenomena [128, 129]. These two processes were described in the late 19<sup>th</sup> and early 20<sup>th</sup> centuries. The most important researchers who studied sorption were Scheele and Fontana (1777), Lowitz and

Saussure (early 19<sup>th</sup> century), Chappuis, Kayser, McBain, Langmuir etc. (20<sup>th</sup> century). Their contribution to the study of this research field is described in detail by Dabrowski [128]. Worch described in detail the fundamentals, process, and modelling of adsorption as the technology for water treatment [129].

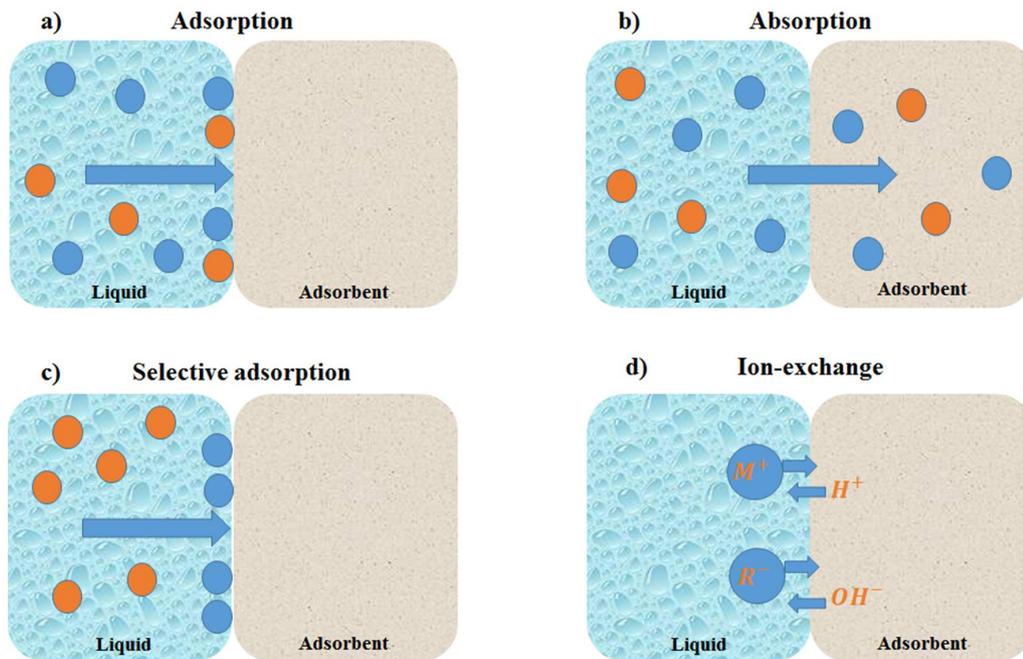


Figure 7. Basic sorption mechanisms between solid and liquid phases (modified from references [128, 129]).

Adsorption can be divided into two basic types of processes, the physical and the chemical.

The physical adsorption process is followed by trapping certain compounds on an adsorbent surface by intermolecular forces that are described by the Van der Waals force. In this case, pollutants desorption from the adsorbent surface follows easily. Chemical adsorption, or chemisorption, is the process of adhering and mass transfer to the surface of the adsorbent compounds in chemical reactions by the valence forces. As a result of this, complex reactions with pollutants may occur or ion exchanges of the contaminant ions and the surface of the adsorbent may take place. Both processes can be observed in some cases, with adsorption due to strong hydrogen bonds and weak charge transfer [128]. Ion exchange is an exchange process between the ions of a solution and the surface area of adsorbents. It is a particular case of chemical adsorption [128, 129].

The purification of mining water by adsorption has been studied in industrial plants for passive (wetland) and active (column) methods [26, 27, 61-64]. The adsorption by batch

method is mainly used in laboratories for the detailed study of adsorbents' and pollutants' properties, adsorption kinetics, and optimization of the pollutant removal process. Removal of pollutants by the column method is the next step for the optimization of adsorption parameters to use the methodology obtained on the industrial scale [58, 64, 71, 124, 127, 130-131]. The materials studied should have a homogeneous structure. Therefore, they are pre-milled before laboratory tests. The potential sorbents should then be prepared for industrial application. The use of powder materials in the column method is limited due to the possible adhesion of sorbent particles. Granulation is the most promising way to solve this problem. In this study, the method of sorbent granulation was studied and applied to cyanide removal [131-133].

The mechanism of the adsorption process can be described with mathematical models that include adsorption kinetics and isotherms of adsorption. Mathematical modelling is an important instrument for understanding adsorption mechanisms. It assists in the selection of the correct process parameters for the better removal of pollutants.

### 2.3.2 Adsorption kinetics

The mass transfer of adsorbate to the sites of the adsorbent during the time is referred to as adsorption kinetics [134, 135]. The rate and intermediate stages of the process are investigated by conducting kinetic studies. The rate of chemical reactions is an important concept of kinetics. The rate of the reactions is defined as the change of the component concentration of the time:

$$v = kC_1^m C_2^n \quad (18)$$

where  $k$  is the constant of the reaction rate;  $C_1$  and  $C_2$  are molar concentrations of reactants;  $n$  and  $m$  are exponents, which indicate the order of the reaction respectively on compounds 1 and 2. The sum of  $n$  and  $m$  is the order of the reaction. This value is always positive.

The chemical kinetic is based on the law of mass action. This law was formulated by Beketov N.N. in 1865 and Guldenberg K.M. and Waage P. in 1867. According to this law, the rate of a chemical reaction at any given time is proportional to the concentrations of the reactants elevated to some degree. An additional point is that the nature of reactants, the presence of a catalyst, temperature, and the interface of the surface area, all influence the chemical reaction rate (Van't Hoff) [128]:

$$V_2 = V_1 \tau^{\frac{T_2 - T_1}{10}} \quad (19)$$

where,  $V_1$  and  $V_2$  are rates of reaction at  $T_1$  and  $T_2$ , respectively;  $\tau$  is the temperature coefficient.

The Van't Hoff equation is applicable only to reactions in the temperature range 10-400 °C. The Arrhenius equation describes the dependence of the reaction rate on temperature more specifically [128]:

$$k = Ae^{\frac{-E_a}{RT}} \quad (20)$$

where  $k$  is the rate constant of a chemical reaction;  $A$  is the prefactor, which characterizes the frequency of collisions of the reacting molecules per second;  $E_a$  is the activation energy;  $R$  is the universal gas constant; and  $T$  is temperature.

It can be seen from Equation (20) that two factors influence the reaction rate, namely temperature and activation energy. An increase in temperature and/or decrease of activation energy can be applied to increase the reaction rate [128].

The order of reaction is the exponent of the substance concentration in the kinetic equation. Because the rate constant is a function of temperature and does not describe the changing of the substances' concentration, the equation of a reaction order takes the form:

$$V = k\Delta C^n \quad (21)$$

As can be seen from Equation 21, the speed of the zero-order reactions does not depend on the concentration of reactants. For the first-order reaction, the speed depends on the concentration of a single reactant. For the reaction of the second order, the concentration of two components changes during the chemical process. If the concentration of one of the reactants remains constant, because it is a catalyst or matrix solution such as water, its concentration cannot be included in the rate constant. In this case, if the concentration of one reactant is not changed during reaction, its concentration cannot be taken into account in the calculation, the pseudo-first-order or occasionally pseudo-second-order rate equation may occur (Table 1) [128].

The reaction can change its order from, for example, second order to first order as the reactant is consumed. Adsorption processes in water with complex composition can be described by mixed-order rate laws. The slowest reaction is decisive if the chemical process has a mixed-order of reactions rate [128].

When it is difficult to predict the order of the reaction studied theoretically, it can be determined experimentally. These experiments make it possible to review the reaction mechanism and may help to identify the rate-determining step [128, 135].

Table 1. Kinetic models.

Order of reaction	Kinetic equation	Half-life of reaction
Zero-order	$v = k_0$	
First-order	$k_1 = \frac{1}{\tau} \ln \frac{C_0}{C_\tau}$	$\tau_{\frac{1}{2}} = \frac{0.693}{k_1}$
Pseudo-first-order	$\frac{dC}{d\tau} = k_1(C_e - C)$	
Second-order	$k_2 = \frac{1}{\tau} \left( \frac{1}{C_\tau} - \frac{1}{C_0} \right)$	$\tau_{1/2} = \frac{1}{C_0 k_2}$
Pseudo-second-order	$\frac{dC}{d\tau} = k_2(C_e - C)^2$	
Third-order	$k_3 = \frac{1}{\tau} \left( \frac{1}{C_\tau^2} - \frac{1}{C_0^2} \right)$	$\tau_{1/2} = \frac{3}{C_0^2 k_3}$

### 2.3.3 Adsorption isotherms

The basic concept of adsorption is adsorption isotherms, which describe the equilibrium between adsorbate and adsorbents at a constant temperature [128]. Adsorption isotherms make it possible to evaluate the adsorbent velocity saturation, selectivity, and efficiency to various pollutants in various conditions, such as temperature and pH. Once the equilibrium is reached at a fixed temperature and pH, the adsorption efficiency is estimated based on the amounts of adsorbate respectively on the surface to the adsorbent and in the solution.

All isotherms are based on Henry's law (Eq. 22). These are the most used isotherms: Langmuir (Eq. 23), Freundlich (Eq. 24), Brunauer, Emmett and Teller model (BET) (Eq. 25), Sips (Eq. 26), Toth (Eq. 27) and BiLangmuir (Eq.28) isotherms.

$$q_e = K q_m C_e \quad (22)$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (23)$$

$$q_e = K_F C_e^{1/n_F} \quad (24)$$

$$q_e = \frac{K_B C_e q_m}{(C_i - C_e) [1 + (K_B - 1) (C_e / C_i)]} \quad (25)$$

$$q_e = \frac{q_m (K_S C_e)^{n_S}}{1 + (K_S C_e)^{n_S}} \quad (26)$$

$$q_e = \frac{q_m C_e}{(a_T + C_e^{m_T})^{1/m_T}} \quad (27)$$

$$q_e = \frac{q_{m1} K_{L1} C_e}{1 + K_{L1} C_e} + \frac{q_{m2} K_{L2} C_e}{1 + K_{L2} C_e} \quad (28)$$

where,  $q_e$  (mmol g<sup>-1</sup>) is the equilibrium adsorption capacity;  $K$ ,  $K_L$ ,  $K_F$ ,  $K_B$ ,  $K_S$  and  $K_{L1,2}$  are Henry's, Langmuir's, Freundlich's, BET's, Sips' and BiLangmuir's constant (L mmol<sup>-1</sup>), respectively, which depends on temperature and pressure;  $q_m$  is the maximum adsorption capacity, mmol g<sup>-1</sup>;  $C_e$  and  $C_i$  (mmol L<sup>-1</sup>) are equilibrium and initial concentrations of adsorbate;  $1/n_F$  is a measure of the intensity of adsorption.  $a_T$  is the adsorptive potential constant (mmol L<sup>-1</sup>), and  $m_T$  the heterogeneity factor of the Toth isotherm.

Several isotherms are used to describe one sorption process for the evaluation of their parameters during comparison. Each isotherm equation serves to describe the properties of adsorbents and understand the type of sorption.

Henry's law is used to calculate the adsorption equilibrium if the adsorption is proportional to the concentration of the adsorbate in the liquid phase.

The Langmuir isotherm is a monomolecular adsorption theory and based on the following assumptions [128, 136-138]:

- Adsorption does not occur on all adsorbent surfaces, but on the active sites. The active sites are bumps or spots on the surface of adsorbents and characterized by the presence of free valences.
- Each active site can be integrated with only one molecule of adsorbate. Consequently, one layer of adsorbed molecules can be formed on the surface.
- The adsorption process is an equilibrium and reversible since an adsorbed molecule is held by an active site for a while and desorbed. In other words, the dynamic equilibrium between the adsorption and desorption processes is established after some time.

- The maximum value of adsorption is achieved when all active sites are occupied by molecules of adsorbate.

The Langmuir isotherm is used to describe some of the adsorption dissolved components with low concentrations. The theoretical concepts of the Langmuir isotherm simplify the adsorption process. In fact, the surface is not uniform for a large amount of adsorbents. Chemical or/and physical interactions between the adsorbed particles take place in most cases. The active sites are not completely independent of each other. Therefore, more detailed mathematical models are required to describe the adsorption process in real systems.

Freundlich isotherm is another theoretical model generally indicating the heterogeneous surface of the studied adsorbent, and the presence of unequal adsorption sites, leading to different affinities with the adsorbates [136-138].

The Brunauer, Emmett and Teller theory describes multilayer adsorption. It was assumed that the adsorbent surface has a uniform localized adsorption site and adsorption on one site has no influence on the adsorption of neighbouring sites, as well as in the Langmuir theory. It was also accepted that the molecules can be adsorbed in the second, third and  $n^{\text{th}}$  layer is a covered area ( $n^{-1}$ ) layer. The aim of this equation is to find a constant, which can be used to calculate the available surface of the adsorbent [136].

The Sips adsorption isotherm is a combination of the Langmuir and Freundlich isotherms, which is suitable for the description of heterogeneous adsorption systems [139].

The BiLangmuir isotherm is a special case of multi-site Langmuir equation. It assumes that the surface contains two divergent active sites with different affinities towards the target compound [140]. The Toth isotherm (three-parameter equation) is the Langmuir theory with a symmetrical quasi-Gaussian surface heterogeneity. The Toth equation is obtained by adding two parameters,  $(aT)$  and  $(mT)$ , to the Langmuir equation [140]. Those two parameters allow for the heterogeneity of the system.

### 2.3.4 Effect of Zeta potential

A double electric layer appears at the interface in dispersed systems. The double electrical layer is a charged particle and layer of oppositely charged ions formed on the surface of the particle as a result of the ions' adsorption from the solution. The layer of oppositely charged ions consists of two layers, such as stern and diffusion layers (Fig. 8). The double electrical layer breaks during the movement of the solid and liquid phases relative to each other and the place of the rupture is called a slipping plane. The slipping plane lies on the boundary between the diffuse and stern layers. The formation of a double electric layer is the appearance of an electric potential that decreases with the distance from the particle and its value at different points corresponds to the surface, stern, and zeta potentials [141].

The zeta potential ( $\zeta$ -potential) is a physiochemical parameter that characterizes the degree of electrostatic repulsion or the potential difference between charged particles of the interfacial double layer and colloidal dispersion stability (Fig. 8). This parameter describes the electrokinetic properties of charged porous materials [141]. The zeta potential described by Henry's and Smoluchowski's laws (Eq. 29), where  $\epsilon$  is a dielectric constant,  $\eta$  is viscosity of liquid,  $\mu_e$  is electrophoretic mobility and  $f(ka)$  is Henry's function [141]:

$$\zeta = \frac{4\pi\eta}{\epsilon} f(ka)\mu_e \quad (29)$$

$\zeta$ -potential is often used for the characterization of double-layer properties to understand the interaction of surface particles of adsorbents and pollutants in solution during adsorption [141]. A high level of  $\zeta$ -potential (negative or positive) indicates the electrically stabilized colloids. On the other hand, colloids with low  $\zeta$ -potential may coagulate or flocculate easily.

There are many factors that impact on zeta potential, such as type and concentration of particles, chemical composition of liquid, and pH. The pH and its changes have the main impact to the zeta potential value. With a change in the pH, it is possible to obtain the necessary zeta potential values, which will most effectively influence the removal of pollutant ions from water by physical or chemical adsorption [141].

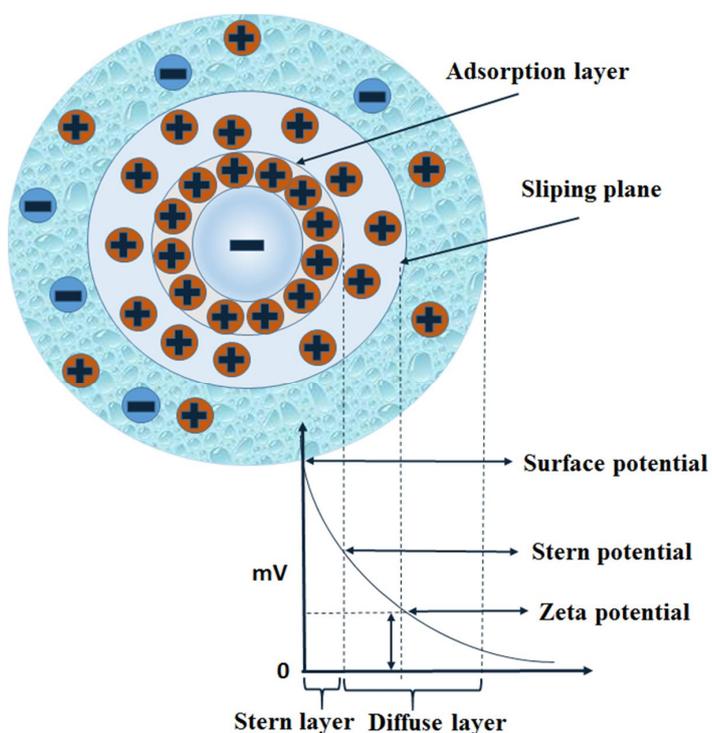


Figure 8. Zeta potential diagram of the charged surface of a particle (modified from reference [141]).

### 2.3.5 Effect of pH

Experimental data show that the adsorption of many elements depends on the solution pH [37-44, 142-146]. The adsorption efficiency of cations increases with pH, while for the anions, adsorption efficiency increases as pH decreases. The surface charge changes as pH changes. The charge of transition metals can be changed also depending on pH [147]. For example, the oxidation state of arsenic directly depends on pH and the redox potential of the solution. Species of arsenic include arsenites (As (III)), arsenates (As (V)), arsenious acid ( $\text{H}_3\text{AsO}_3$ ,  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HAsO}_3^{2-}$ ), arsenic acid ( $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ), as well as their methyl and dimethyl derivatives. As(III) is a more toxic form of arsenic and it does not adsorb effectively compared with As(V), the conversion of one form into another by pH adjustment allows more efficient arsenic removal.

The effect of pH on the ion adsorption is complicated by the fact that in addition to changes in the surface charge on the adsorbent, the magnitude and charge sign of the ion

may change. This leads to a significant change in the adsorption capacity. For example, the transformation of each of the following forms can be observed as pH increases:



During the selection of the best conditions for the removal of each contaminant it is important to find the optimum pH.

### 2.3.6 Adsorbent amount

The amount of adsorbent also determines the effective removal of pollutants by adsorption [148-162]. The efficiency of pollutant removal increases with the amount of adsorbent, but the excessive amount of adsorbent is not cost-effective. The amount of adsorbent needs to be optimized. The percentage of pollutant removal increases with the increase of adsorbent dose. Thus, the smaller the amount of adsorbent needed for complete removal of adsorbate, the higher the efficiency of the adsorbent. The main parameters affecting the removal efficiency are the surface area of the adsorbent, the number and size of the pores, the zeta potential of the material and the presence of functional groups. Various methods of surface modification of adsorbents can be used to improve their properties.

### 2.3.7 Desorption

The reverse adsorption process is the exudation of sorbate to the liquid phase from the sorbent, and is called desorption. Reversible adsorption means that the process takes place at the expense of physical intermolecular forces and that desorption has a very low activation energy. These include adsorbates which form hydrogen bonds with the surface of the adsorbent. The weakening of the binders between the adsorbent and adsorbate causes desorption. Desorption typically occurs more slowly than adsorption and is directly dependent on the retention value of the removed compounds in the adsorbent surface [163-166].

The study of desorption is essential in understanding the adsorbent efficiency, the competition between adsorbates, and the possibility of reusing the adsorbent. It is also very important to check whether any impurities of the adsorbents' surface are desorbed into the treated solution [163-166].

## 2.4 Low-cost sorbents and their modification methods

This study is concerned with the neutralization of AMD, the removal of metal ions, chloride and sulphate anions, cyanides, and arsenite and arsenate from synthetic and real mine and process waters with low-cost adsorbents.

Activated carbon and alumina are commercial advanced adsorbents for the removal of various pollutants from different types of water [167]. They have a high adsorption capacity and yield good regeneration that makes it possible to reuse them several times. After activation these materials have a high surface area and developed porosity. The sorption capacity of these adsorbents may approach  $\approx 1000 \text{ g m}^{-3}$ . The application of both adsorbents is limited by the high cost, which greatly increases after the activation of their surface. Classic methods of carbon and alumina activation have been described below.

Activated carbon can be obtained by chemical or physical activation. Raising the temperature in the range of 450 – 1200 °C in an inert argon or nitrogen atmosphere is necessary in all methods [168]. The use of aggressive chemicals (strong basis and acids) is necessary during activation at a low temperature (450 °C). The cost of the final product is 500 – 1,800 USD per metric ton [170].

The main method of alumina activation is thermochemical. This involves decomposition of  $\text{Al}(\text{OH})_3$  under 300 °C and then rapid cooling. This approach to the preparation of active alumina has been known since the mid 20<sup>th</sup> century. The cost of the final product is 700 – 800 USD per metric ton [171]. Activated alumina is used basically for dewatering. However, its application as a sorbent for removal of fluoride, selenium, and arsenic from water is known.

In recent years increasing attempts have been made to produce a commercial analogue of sorbents from cheaper raw materials and by-products. Brown coal, waste from the pulp and paper industry, and waste from the food industry are raw materials for producing low-cost sorbents [172–178]. Currently, numerous scientific papers have been related to the subject of activated carbon from low-cost materials, their characterisation, application, and modification, and activation methods [149, 152, 167, 169, 171, 179, 180]. Hence, special attention will be given in this work to the sorbents from low-cost precursors suitable for the removal of arsenic, cyanide, sulfate, chloride, metal ions and dyes.



Table 2. Literature data of sorption properties and capacity of different sorbents for wastewater treatment

AC from neem bark	AC from walnut wood	Soy bran	AC from Rice polish	AC	AC	Activated bio-carbon	Sorbent
Zn(II)	MB	Zn(II)	As(III)	NaCN	CN <sup>-</sup>	Cu	Pollutant
50 and 100	120	100	1	50	76	0.0005	Pollutant
	27	100				0.004	Concentration, mg L <sup>-1</sup>
	2-7	5	7	9	12	2	pH
8	120	1	24	42	80		Contact
	120	1					Time, h
	4	0.03	20	20	5	10	Sorbent
	4	0.03					Dosage,
21.4	10.0	74.0	14·10 <sup>3</sup>		3.5-16.4	720	Adsorption
23.4	42.0	53.8	15·10 <sup>3</sup>				Capacity, Removal,
			95	67			%
			97	84			
[183]	[182]	[181]	[139]		[127]	[178]	Reference

Chitosan	Chitosan	Chitosan with 3,4-DHBA	Chitosan U	Chitosan Fe	Zeolite from coal fly ash	MnO <sub>2</sub> coated zeolite	Zeolite Cu	AC from waste potato	AC from potato residue	AC from <i>Phragmites australis</i>
As		U				U	Zeolite	Co(II)	Cu(II)	Ni(II)
10	112	0.01			1000	100		200	50	
3.5	66				1000				50	
96	2.6	3				4		6	5	
	24	By column 0.5l by 4 min			48	3		3	10	48
0.5	0.5	20			1	5		1	1	0.3
14.2	1.24	330				15.1		≈400	45.0	34.0
	99	98.5			99.4	99.9			27.0	7.0
					50					
[190]	[189]	[188]	[187]	[186]	[185]	[184]	[185]	[185]	[185]	[184]

EDTA and DTPA-modified	Co	Silica	Chitosan from squid pens	Magnetic chitosan	Chitosan from fish scale	EDTA-modified chitosan	Chitosan	DTPA-modified chitosan	Chitin complex	Chitosan
Co			Cu(II)	Cu(II)	As(III)	Co	Hg	Co	Al	As
10			80	10	0.2-1	100	50	100	1000	11
3.5			3.6	5	4	2	4	2	3-6	5
4			5	4	20	24	2		72	48
2			0.4	0.4	20	2	5	2	4	0.5
20.0			134	156	0.25	63.0	110	49		2.5
21.6			80		0.27	71.0	78.0			
							98		99.9	
							98		93	
[132]			[204]	[203]	[202]	[201]	[200]	[16]	[192]	[191]

	Bacterium	Dairy manure compost	<i>Bacillus</i>	<i>Lacto-bacillus</i>	<i>Arthro-bacter</i>	Bio-sorbents	Cu(II)	Silica-alumina oxide	Natural clinoptilolite
Industrial wastes	As(V)	Pb	U	U	U			Acid orange 7	Zn
	202	104	20	20	20		100	10	14.4
	318	32					100		
	7.2	3.5	5.8	5.8	5.8				3
	456	4	1	1	1		1	360	
	4.5	15	1.5	1.5	1.5		1	0.5	10
								0.5	
	0.48	0.46	0.025	0.024	2.6 $\mu\text{mol g}^{-1}$		54.1	2.7	440
	1.21	0.43					73.2		
		96.3							
	86.8								
[158]	[157]	[156]	[156]	[156]	[156]	[100]	[161]		

Bauxsol coated sand	Fly ash	Iron ore slime	Pyrite	Fly ash	Red mud	Vanadium mine tailing	Steel slag	Steel slag	Steel slag	Iron slag
As	Pb	Pb	As	As	As(III)	Pb	Ni	Cu	Cu	Cu
1	50	50	10	10	10	200	56.6	200	200	200
1	50	50			10					
8.5	7	7	5	7.5	9.5	5.2		3.2	4.8	
4	5	2				3	24	24	24	
20	80	40	5	2	20	20	5	2	2	2
	34			50	0.32	3.82	15.9	16.2	88.5	
100	17	95	99		0.38	3.87		32.3	95.2	
99		93			90	95.3		92.4	99.4	
[205]	[150]	[147]	[164]	[163]	[162]	[161]	[160]	[159]	[159]	[159]

### 2.4.1 Activated carbon

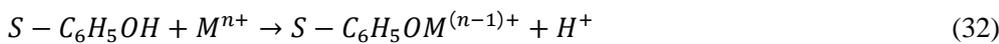
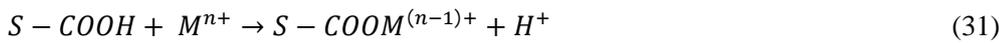
Commonly bio-wastes and various pitches are used as low-cost materials for preparation of activated carbon.

For example, a number of studies have reported the efficient removal of cyanide from water with activated bio-carbon such as lignite, nutshells, and rice hulls. The cost of sorbent from lignite is two times lower compared to commercial activated carbon and their sorption capacity was the same for the removal of cyanides from drinking water [153], [198]. To improve the adsorption properties of nutshells and rice hulls impregnation with copper and silver was applied. Sorbents from nutshells and rice hulls were also used for AMD treatment and show good capacity for metal ion removal [170]. Demiral & Güngör (2016) [199] reported good repeated removal of copper (II) by activated carbon synthesized from grape bagasee and modified using phosphoric acid under 500 °C. They assumed that this process is consistent with the chemical sorption process, because the pseudo-second order is better to describe it. Brown coal, or lignite, as an industrial solid waste is an alternative to commercial activated carbon. Lakhdhar et al. [178] have conducted a comparative analysis of the adsorption properties of the two types of unmodified lignite with commercial AC and a coconut shell-based AC. The adsorption capacity of unmodified lignite for cyanide removal was 370 mg g<sup>-1</sup>, which is two times higher than for AC from coconut shell [127].

Similar results were obtained during the removal of cobalt ions with AC synthesized from waste potato peels [185]. In this work, AC was prepared by chemical activation with phosphoric acid and heated up at various temperatures (400, 600, and 800 °C). The optimal amount of pH was found to be 6, contact time 3h, amount of AC 1 g L<sup>-1</sup>. It was also found that the temperature effect on the adsorption capacity is insignificant. The removal percentage was increased to approximately 10% with the temperature increasing from 25 to 45 °C. Maheshwari & Gupta, 2016 [181] reported results of lead and methylene blue removal by AC synthesized from walnut wood by chemical activated method. The maximum adsorption capacity for both pollutants from a multi-element solution is seen in Table 2. It was observed that adsorption capacity for MB increases about two times from a single element solution; however, the sorption capacity of lead was similar for both cases. This phenomenon can be explained by competition between Pb and MB ions during the adsorption process and the higher affinity of lead for this adsorbent as compared to MB [181]. Luo et al., 2015 [183] studied the removal of copper, nickel and acid blue 80 from single and binary solutions. The positive effect of dye ions in the removal of metal ions was observed. The maximum adsorption capacities were found for all pollutants in binary systems (Table 2). It could be explained by the synergetic effect of dye and metal ions in binary systems.

Interesting results were obtained by Humelnicu et al. for the removal of Zn(II) and Cu(II) ions with unmodified agricultural by-products from diluted wastewater. The maximum

adsorption capacity for zinc and copper ions was reached to 74.0 and 53.8 mg g<sup>-1</sup>, respectively (Table 2) [181]. Since the maximum anions removal was observed at pH values between 5 and 6, the authors suggested that the exchange mechanism between metal and hydroxide ions took place during the removal process (Eqs. 31, 32). Whereas there are reasonably good results compared to discussed above, the sorption properties of those sorbents were significantly reduced after increasing the concentration of the removed components above 100 mg L<sup>-1</sup>.



where, S is sorbent surface.

Although, all observed ACs were prepared from low-cost materials, their chemical and/or thermal activation has been necessary to increase adsorption capacities. Despite the low cost and the improvement of adsorption properties by modification, the use of these adsorbents is limited to the purification of drinking water. If the concentration of polluting substances is increased, the capacity of the adsorbents is significantly reduced. Further research studies aiming at increasing the adsorption capacity while decreasing the cost of production of activated carbon are necessary for the widespread application of those adsorbents.

#### 2.4.2 Zeolites and silica

The two main adsorbents based on silicon oxides can be selected. These are zeolites and silica.

Zeolites are natural minerals composed of silicon and aluminum oxides. Their surface is negligible but plentiful. Zeolites are widespread sorbents due to their lower cost compared to activated alumina and carbon. They have a high affinity to metal ions, such as Cd, Zn, Fe, Cu, Mn, UO<sub>2</sub> as well as arsenic. Interest in using zeolites is increasing due to selectivity. It is worth mentioning that unmodified zeolites have poorer adsorption capacity than modified zeolites [186, 200-203]. The final cost of zeolites is about 400 – 500 USD per metric ton.

A large amount of research work has been accomplished related to the use of zeolites for AMD treatment. The main objective of these studies has been to examine the competitive impact of metal ions in a complex solution. Itskos et al. [186] and Sabarudin et al. [187] found independently of each other that adsorption of certain metal ions, such as Al, Fe, Mn, Zn, Cu, Ni is not subjected to competition. They applied the different methods of surface modification, such as calcination, microwaves, and synthesis of zeolite-p from coal fly ash, respectively. Motsi et al., 2009, 2011 [200, 201] observed that the adsorption capacity of modified zeolite is 30% effectively compared to unmodified.

Silica gels were used for the adsorption of contaminants in the gas phase, firstly. A large silica surface area (from 100 to 750 m<sup>2</sup> g<sup>-1</sup>) and a high polarity ensured excellent characteristics of those adsorbents in the liquid phase [197, 198]. In liquid adsorption silica gels were used to remove various metal ions, such as Co, Ni, Cd, Cr. Immobilization of ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) is the most common method of surface modification of silica [133, 140, 180, 192]. However, the use of modified silica for water treatment from metal ions is not as extensive, since they are not biodegradable [133, 180, 192].

Wawrzkiwicz et al. studied silica-alumina oxide application for the removal of dyes and metal ions from wastewater. The authors assumed that different sorption processes can take place in complex solutions, such as wastewater for example, the formation of anion complexes between metal ions and opposite charge of sorbent surface through coulombic attraction. In the case of the interaction of metal and chloride ions, negatively charged intraspheric complexes are formed. They are interacted with hydroxyl surface groups through ion-exchange mechanism with new complexes formation [100-104].

#### 2.4.3 Chitosan

The use of chitosan as an adsorbent is the most advantageous method from an economic point of view because it is the cheapest material of those mentioned above. The cost of raw chitosan is 0.2– 0.6 USD per metric ton [191]. Modified forms of chitosan were studied for the removal of a wide range of metal ions and for both forms of arsenic [191– 195]. It was shown that chitosan has a better affinity for the As(V) than As(III). However, the removal of As(III) can be effected by the control of pH when arsenite is converted into arsenate [193]. AMD treatment with modified chitosan was conducted by some researchers [192]. It was established that AMD neutralization and the simultaneous removal of some metal ions occurs within 70 hours.

Benavente et al., 2011 [16] studied goldmine water treatment of Hg, Cu, Pb and Zn with chitosan produced from shrimp shell. The dependence of the pH was established. The maximum adsorption capacity was observed at neutral pH, and besides, mercury has the highest affinity for a given adsorbent. Chitosan is an effective adsorbent for the removal of metal ions. The possible competitive impact of cyanide on the removal of metal ions was suggested. However, this has not been proven experimentally. Abou El-Reash, 2016 [194] researched the effect of various ions on the removal of copper. These results demonstrated that modified chitosan has similar efficiency in removing copper ions from both single and complex solution.

The ability of chitosan to neutralize acid solution has been demonstrated in many studies. For example, neutralization of decantation pool (DP) and AMD and removal of Fe, Al and Cu from coal mining wastewater with chitosan were reported by Laus et al., 2007 [17].

The adsorbents from chitosan have shown high adsorption capacity and an ability for metal ion removal. This adsorbent can be regenerated, reused and dissolved in soil without impairing the environment. The use of chitosan for acidic mine water treatment is limited due to the lengthy contact time needed for effective removal of pollutants [16, 17].

#### 2.4.4 Agricultural residues

Agricultural residues, such as peat, lignite, coconut shell, tea and coffee wastes and hardwoods are frequently subjected to thermal treatment before being used as adsorbents. Some agricultural by-products can be used as bio-sorbents for bio-oxidation [196] or forming a complex with surface functional groups, such as amino, phenolic, carbonyl, alcoholic, carbonyl, and sulfhydryl groups [19]. Adsorbents from agricultural residues can be used for AMD neutralization, arsenic [132] and metal ions removal [201–205], to a greater extent for radioactive elements [158–159]. According to previous studies, all these materials need modification of the surface area to become effective adsorbents.

Compared to other agricultural wastes, coffee grounds have been less investigated in the removal of metal ions and dyes from water. Only a few studies have been published about on coffee waste as an adsorbent for water treatment [145, 161]. This material can contribute to water purification from various pollutants, because it contains a huge amount of functional groups that can be involved in the ion-exchange process.

#### 2.4.5 Municipal sewage sludge

Municipal sewage sludge has a high surface area as well as high carbon concentration in its composition. These two basic characteristics are responsible for the fact that these wastes have been of increasing interest as a low-cost material for the production of adsorbents for wastewater treatment [12, 150, 197, 203]. These materials were studied for the removal of various pollutants, such as organic compounds, metal ions, and salt from synthetic and real mine waters [204–207]. All studies conducted have shown that agro-industrial and municipal wastes have a high capacity for the removal of metal ions from acidic wastewaters. However, they need pretreatment by modification or/and activation of their surface. The requirement for complicated and expensive pretreatment of sorbents limits the widespread application of these materials [12, 150, 203]. It was also noted that the presence of  $\text{NaNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{NaOH}$  in metal solution in concentrations of 0.01, 0.01 and 0.50 M might impair removal efficiency [208]. This limits the ability of these materials in the treatment of many types of mine waters because many types of them have a high concentration of salts in their composition [203].

#### 2.4.6 Limestone

Limestone is a sedimentary rock, the foundation of which is various crystal forms of calcium carbonate [89]. Limestone is widely applied in various fields, such as building as a framework for construction materials, in agriculture to neutralize acidic soils, and for glass manufacture [209–211]. Calcium oxides obtained from limestone are used in steel production to remove phosphate and sulphate impurities. Limestone is used in the chemical extraction of gold as a regulator of pH to prevent the production of hydrogen cyanide gas [89, 212, 213]. Limestone is also an effective agent for neutralizing acid water and removing metal ions, sulphates, and chlorides from mine water [214, 215]. The price of limestone is 20–30 USD per metric ton, which is hundreds of times lower than the price of a commercial activated carbon [209]. The universality of this material is also a reason to study and use it as a low-cost sorbent for complicated mine water treatment in passive and active methods [216, 217–219]. The number of studies on limestone as a sorbent is large, but some of these are more interesting than others – for example, the use of limestone for real AMD treatment with large amounts of cationic and anionic contaminants. Masindi et al, 2015 [89] studied AMD treatment and obtained the following sequence of adsorption affinity:  $\text{SO}_4^{2-}$  ( $221.8 \text{ mg g}^{-1}$ ) > Mn ( $30.7 \text{ mg g}^{-1}$ ) > Al ( $30.5 \text{ mg g}^{-1}$ ) > Fe ( $30.2 \text{ mg g}^{-1}$ ). The neutralization of the adsorbing material was reached when the solution pH varied between 3 and 6. Limestone was able to neutralize mine water and reduce the conductivity simultaneously [125]. A removal efficiency of 80% has been achieved for several metal ions (Cu, Cd, Ni, Mn, and Zn). Labastida et al., 2013 [17] studied the potential of limestone for AMD treatment in a passive system. The pH of the solution was increased from 2 to 7. The removal of various pollutants was observed from a complex solution and respective rates achieved for As, Fe and Al of 100% and 88 and 90% for Zn and Cd. More detailed study of competitive adsorption of metal ions from waste water with a complex composition could be beneficial for the use of limestone for real industrial wastewater.

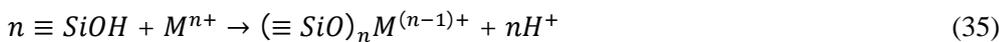
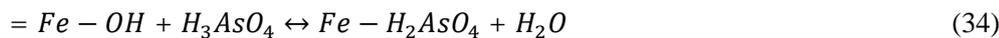
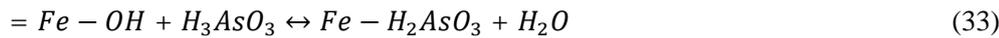
Though limestone shows good capacity for the removal of various pollutants, only a few limestone-based articles have been published relating to sulphate and chloride removal from alkaline water [209, 220]. It can have a good ability to remove anionic contaminants by ion-exchange reactions between oxides/hydroxides groups located on the surface of limestone and anions.

The use of limestone for mine water treatment can solve several objectives. These are neutralization of AMD and the removal of metal ions, sulphates and chlorides from acidic and process water.

#### 2.4.7 Industrial solid wastes

Waste-free production has been a widely discussed topic in recent years [221–227]. All solid industrial wastes can be classified by their composition. These are used for water treatment as alternative adsorbents for activated carbon. Another most promising section is metallurgical solid wastes, such as ore slimes, slag, mud, and mine tailings [160, 228–

230]. A definite pattern can be seen if the composition of these wastes is considered. They all contain oxides and/or hydroxides of various metals, such as iron and aluminum, as well as silicon oxides. Oxides and hydroxides of Al, Fe and Si are used as commercial adsorbents, such as activated alumina, iron oxide/hydroxide and silica gel, respectively. The adsorption of pollutants takes place through the formation of complexes or ion exchange by the following reactions (Eqs. 33-35):



Equations 33 and 34 are iron hydroxide complexation with As(III) and As(V), respectively. Equation 35 describes complexation between silicate and metal ions. However, the removal of arsenic and cyanide compounds with iron-content solid waste has been poorly studied. The solid waste from the iron and steel industries can be potential alternative materials for the treatment of wastewater contaminated with arsenic and cyanides.

Ion-exchange, sorption, and redox capacity properties allow for the extensive use of low-cost substitutes of these commercial adsorbents for metal ions, arsenic, and cyanide removal from waste waters. Thus, Feng et al., (2004) [156] studied the adsorption properties of iron and steel slag for Cu(II) and Pb(II). It was shown that iron slag removes metal ions more effectively than steel slag due to its greater surface area and porosity. Other researchers have studied solid wastes as adsorbents from various industries, such as iron ore slimes, metallurgical by-product, muds from the mine industry, sulphate tailings for metal ion removal [156, 225, 227]. Greater affinity (about 99%) of these adsorbents for Pb(II) compared with Cu(II), Cd(II), Zn(II) and Ni(II) was observed. Other metal ions were removed from 60% to 80%.

Masindi (2016), [14] studied the by-products of magnesite mining, such as magnesite tailings for the neutralization of goldmine AMD and the removal of iron, alumina, calcium, and sulphate. It was found that after 30 minutes the pH increased from 2 to 10 and pollutants up to about 99% were removed, except for sulphate (80%).

Ouakibi et al. (2014), [97] used phosphate carbonated wastes from a phosphate mine for the removal of Fe, Mn, Al, Ca, Zn and Cu from synthetic AMD. The experimental results showed that phosphate carbonated wastes can be used for the neutralization of AMD from acid to neutral and removal of Fe up to 80%, Al and Cu to about 100%. Genç-Fuhrman et al. (2016), [231] researched metal ions removal with sorbents from industrial materials with the presence of humic acid. Removal of many metal ions was suppressed except for Cr. This phenomena can suggest that the formation of dissolved complexes of metals and humic acid has a place in preventing effective metal sorption.

## 2.5 Granules production

Adsorption materials must be resistant to water and not stick together during and after contact with liquids by active or passive methods of wastewater treatment. The granulation of powders for other or the same materials can help to solve this problem.

Granulation is the process of fine powder particle enlargement to dust-free granules [242]. The granulation process can be divided into wet and dry granulation [242–244]. The main aim of the granulation process is to preserve the physico-chemical properties of the initial materials, such as porosity, surface area, and availability of functional groups. Granules must have a high stability upon contact with liquids and remain the same size and strength for reuse [244–247]. The method of dry granulation is often used in the pharmaceuticals industry for tablet formation, where the raw materials may be sensitive to moisture [244–247]. With wet granulation, granules with a high wettability and strength can be obtained [246, 247]. Granulation of industrial solid wastes for use of these materials as sorbents for water treatment has not been presented previously. Only a few studies have been published on the production of co-granules from bio-wastes and limestone. Here in this work, wet granulation was studied in detail.

### 3 Objectives of the study

The main objective of this research was to find a new approach for reusing industrial solid wastes and economically effective water treatment methodology to reduce the cost of water treatment, reusing of solid wastes and, consequently, more efficient use of non-renewable resources. Low-cost materials, such as limestone and solid industrial wastes, were investigated as potential sorbents to solve these problems, and particularly were applied to extract organic and inorganic compounds from various types of water. There were three commercial limestones, coffee waste, and four iron-based solid wastes from metallurgical industries (two sulphate tailings, iron sand and by-product from the pulp and paper industry). In order to understand the potential capacity of adsorbents for water treatment, the chemical composition and physicochemical properties of unmodified materials were studied in Papers I-VI. Since all materials, except limestone, were wastes, they were tested with desorption experiments to avoid secondary pollution (Papers I-VI). The adsorption capacities of all sorbents were studied with batch experiments. In addition to adsorption, the ions competition was also studied (Papers I-IV and VI). The idea for all the experiments was generic and included the following principles:

- Experiments were carried out at ambient temperature.
- The optimal amount of solution pH, contact time, dosage of adsorbents and pollutants, and ions competitions was investigated.
- The adsorption process was characterized with adsorption isotherms and kinetics.
- The desorption process and possible recycling of adsorbents were studied.

Various modification methods (mainly cost-effective ones) were applied

Based on the aim of this study, the following specific objectives and research questions were formulated:

Can the unmodified limestone, bio- and industrial wastes be used as efficient sorbents?  
Can the chosen materials be used as multifunctional and selective sorbents according to their chemical composition and surface properties?

How can the efficiency of materials, at the least the cost and development of sorbents comparable to commercial materials with the similar structure and composition, be increased?

How can liquid and solid wastes be commercially profitable products?

According to the questions posed, the specific objectives were:

1. To investigate unmodified limestone as a potential material for the removal of sulphate and chloride ions by adsorption. Two different types of unmodified limestone were applied for sulphate and chloride removal from synthetic and real alkaline process water in Paper **I**. The optimal sorption properties were estimated with a synthetic alkaline solution in order to simultaneous removal of sulfate and chloride ions from real process water.
2. To compare unmodified and modified limestone for AMD neutralization and metal ions removal.  
Low-cost modification methods were applied to increase limestone adsorption capacities. Real process water with a high concentration of chloride salts was used as a novel and previously unpublished method for limestone surface modification (Paper **II**). This modification method was compared to low-cost and environmental friendly surface modification with NaCl that was also not published before (Paper **II**).
3. To prepare a multifunctional combined sorbent from bio-waste and limestone for the removal of various pollutants from water.  
Coffee waste and limestone were granulated and tested for removal of acidic and alkaline dyes in (Paper **IV**). Ion competition for different charges of dyes was researched. The optimal properties of the granulation process were chosen, and a suitable binder was found.
4. To investigate raw industrial wastes as potential sorbents for the removal of chloride and sulphate ions from mine water.  
Unmodified iron sand and waste from the pulp and paper industry were used for this challenge in Paper **I**. Their removal capacities were compared to unmodified limestone (Paper **I**). Unmodified and modified with ALD sulphate tailings were applied as selective sorbents for selective and rapid removal of a high concentration of cyanide from process water (Paper **V**). To our knowledge, the removal of a high concentration of cyanide from process water without their dilution has not been investigated in previous studies.
5. To apply iron-based solid wastes for the removal of various pollutants.  
Modified and unmodified iron sand and sulphate tailings were studied for direct removal of As(III) and As(V) from mine water (Paper **III**). One innovative method, such as coating metal oxides with ALD, was first used for iron containing solid wastes in order to improve their adsorption properties (Papers **III**, **V** and **VI**). The modification of sorbents with ALD was compared to the economic method of surface activation with NaOH (Paper **III**). Modified iron sand with ALD was studied for simultaneous removal of sulphate and metal ions removal from real AMDs (**VI**).





## 4 Materials and methods

### 4.1 Raw materials

Coffee waste, two types of limestone and four other solid wastes were tested as adsorbents for various synthetic and real mine waters treatment. Several of these were used without modification, some materials were exposed to modification, or combined with each other. The chemical composition of the raw materials is shown in Table 3. XRD analysis was also conducted for some materials (Table 4).

Table 3. Chemical composition of raw materials. Data were collected with XRF and organic elemental analysis.

Element %w	FS	FF	RH	DI-60	L	CW	SuFe	CaFe- Cake
Al	0.2	0.8			1.5	1		0.025
As	0.002	0.007		0.003			0.18	0.01
C					3.3	60		
Ca	37.2	21.3	14.4	12	21.3	1	0.16	11.9
Co							0.026	0.001
Cr	0.004	0.003		0.001			0.063	0.004
Cu	0.002	0.002		0.004			0.054	0.355
Fe	0.43	1.1	7.2	0.46			10.3	38.9
H					0.25	6		5.2
K	0.24	0.25	0.3	0.329		1	0.026	0.025
Mn	0.01	0.02	0.27	0.004			0.004	0.012
N						3		
Ni	0.01	0.01		0.001			0.92	0.97
O					52.7	25		20.8
Rb	0.001	0.001		0.002			0.038	0.001

S	0.1	0.1	17.6	0.039	0.1	1	15.8	12.9
Si	10.3	42	0.2	4.4	42	5	3	2
Sr	0.074	0.026	0.021	0.016			0.002	0.002
Ti	0.042	0.052	2.3	0.059			0.012	0.009
Zn				0.002			0.037	0.002

Table 4. Chemical structure of raw materials. Data were collected with XRD analysis.

Material	FS	FF	RH	DI-60
Compound formula	CaMgSi <sub>2</sub> O <sub>6</sub> CaCO <sub>3</sub>	(KH <sub>3</sub> O)Al <sub>2</sub> Si <sub>3</sub> X AlO <sub>10</sub> (OH) <sub>2</sub> CaSiO <sub>3</sub>	Ca(SO <sub>4</sub> )(H <sub>2</sub> O) Ca(CO <sub>3</sub> )	Ca(CO <sub>3</sub> ) Al <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> )(OH) <sub>4</sub>
Commercial name of compound	Diopside Calcite	Illite Parawollastonite	Calcium hydrosulphate Calcite	Calcite Kaolinite

#### 4.1.1 Limestones

Two types of limestone from the Finnish metallurgical company Nordkalk were applied as adsorbents (**I**, **II**). The limestone for producing co-granules was provided by Killwaughter Chemical Ltd UK (**IV**). Limestone products are basically used for soil improvement in order to neutralize acidity (from 1.5 to 9 pH) in the production of construction and composite materials.

Before use, the limestone from Nordkalk was crushed, ground, and classified according to size. Limestone with a particle size less than 0.3 mm was used for the batch adsorption tests. The limestone from Killwaughter Chemical Ltd was obtained in powder form with a particle size of approximately 0.5 mm and less. The limestone was washed with water and oven dried for 12 h at 80 °C.

#### 4.1.2 Iron-based solid wastes

The by-products originated from Ekokem, Norilsk Nickel Harjavalta and Metsä Tissue Corporation, in Finland (**I**, **III**, **V**, **VI**). These materials were chosen because of their easy

availability and high production volumes. These are iron sand (RH), sulphate tailings (CaFe-Cake and SuFe) and pulp and paper waste, as a green sludge (DI-60).

The solid wastes consisted of various elements, including toxic ones, depending on many factors, such as industry, ore, processing methods etc. (Tables 3, 4). As a result, it can be assumed that a certain amount of pollutants can be desorbed into the solution during the adsorption process. Therefore, all solid wastes were tested by desorption and washed and dried as necessary before use (I, III, V, VI).

#### 4.1.3 Coffee wastes

The coffee wastes (CW) were collected from the cafeteria at Queen's University Belfast, Northern Ireland, and the Laboratory of Green Chemistry, Lappeenranta University of Technology, Finland.

## 4.2 Characterisation of solid materials

The chemical composition of the materials was collected with X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques. XRD data was received with a PANalytical Empyrean powder diffractometer using Cu K $\alpha$  radiation. X-ray fluorescent analyzer X-Art by Joint Stock Company Comita, St. Petersburg, Russia was used to determine of the chemical composition of the materials (Tables 3 and 4).

The particle size distribution and zeta potential of the samples were determined using a dispersion analyzer LUMiSizer 610/611 (GmbH) and ZetaSizer Nano ZS, Malvern, UK, respectively (Table 5). The zeta potential was calculated from electrophoretic mobility measurements using the Schmalukowski equation. A 1.5 g solid sample was conditioned in 50 mL of 0.001 M NaCl solutions at various final pHs for 24 h in a shaking bath. Each reported point value was an average of approximately 20 measurements. The pH of the suspension was adjusted using 0.01-1.0 M HCl.

The samples were characterized with nitrogen sorption at 196 °C using TriStar 3000 (Micromeritics Inc., USA). The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) theory.

Fourier transform infrared spectroscopy (FTIR) spectra of adsorbents were recorded with a Bruker Vertex 70v spectrometer. Spectra were collected in the mid infrared region (4000–400 cm<sup>-1</sup>) averaging 124 scans with 4 cm<sup>-1</sup> resolution. Samples were prepared according to standard KBr pellets methods (Table A2).

A scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company) and (Hitachi S-4800) with attached chemical analysis of specimen in microareas with energy dispersive X-ray spectroscopy (EDX, EDAX) was used to examine the microstructure of the materials. The experiment was carried out in a low vacuum condition in secondary electron mode and for the analyses samples were covered with a layer of gold.

The data from Spectroscopic Ellipsometry (J.A.Woollam Co, Inc, USA) from silicon wafers were used for control of the film thickness of both metal oxide coatings.

Table 5. Particle size distribution, zeta potential and BET analysis of unmodified and modified sorbents.

	The particle size distribution, $\mu\text{m}$					Specific surface area, $\text{m}^2 \text{g}^{-1}$	Pore size, nm	Zeta-potential, mV
	$\leq 90$ %	$\leq 75$ %	$\leq 50$ %	$\leq 25$ %	$\leq 10$ %			
FS	451	420	318	228	156	1.35	-	0
FS_NaCl	589	568	450	282	270	1.46	-	-15
FS_ww	273	134	131	91	90	1.29	-	-6
FF	599	567	354	185	177	1.82	-	-25
FF_NaCl	872	798	535	494	487	1.63	-	-20
FF_ww	492	421	188	87	88	1.58	-	-16
DI-60	1390	1265	1200	1020	990	3.3	3	-14
SuFe	1200	900	650	570	320	12.3	900	0
SuFe_ $\text{Al}_2\text{O}_3$	1000	850	520	470	250	63	5	20
CaFe	1450	1620	1420	1100	950	6.5	550	-4
CaFe_NaOH	1510	1730	1550	1400	1380	4.7	20	-25
CaFe_ $\text{Al}_2\text{O}_3$	1500	1650	1620	1520	1400	48	2-3	-9
CaFe_ $\text{TiO}_2$	1480	1670	1630	1500	1450	15	10	-5
RH	180	165	154	130	98	62.5	180	-7
RH_NaOH	315	450	310	285	250	8.4	30	-20
RH_ $\text{Al}_2\text{O}_3$	190	165	158	124	115	65/115	20	-20
RH_ $\text{TiO}_2$	181	168	150	127	110	74/125	3	-20

### 4.3 Real and synthetic waters

Milli-Q ultrapure water was used to prepare the stock and dilute solution. The composition of the real and synthetic waters is shown in Table 6.

#### 4.3.1 Real and synthetic process waters

Real process water was obtained from the nickel and copper metallurgical industry Norilsk Nickel Harjavalta. Process water was treated with metal ions with diluted sodium sulphate after mineral extraction (Paper I).

Synthetic process water was obtained by dissolving sodium sulphate (Merck) and sodium chloride (Sigma-Aldrich) in distilled water. 0.1 M NaOH and HCl (Merck) were used for solution pH adjustment (Paper I).

#### 4.3.2 Real mine water

Real AMD solutions were studied for neutralization and removal of Ni(II), Cu(II), Zn(II), Fe(II), As(III) and As(V) (**II, III, VI**). AMD was obtained from three depths (270, 500, and 720 m) of a sulphide mine in Finland.

The elemental composition of real process and mine water is shown in Table 6.

Table 6. Chemical composition of real process and mine waters. Data were collected with ICP and HPLC analysis. RSDs at 3 times the detection limit were less than 3%.

	pH	Cu(II), mg L <sup>-1</sup>	Ni(II), mg L <sup>-1</sup>	Zn(II), mg L <sup>-1</sup>	Fe(III), mg L <sup>-1</sup>	Cl, mg L <sup>-1</sup>	Na <sup>+</sup> , mg L <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup> , mg L <sup>-1</sup>
Process water	12	0.11	2.13	0.18	0.6	954	11570	25077
Level 270	2.6	108	13	2080	911	-	-	20120
Level 500	2.3	76	1.7	5900	3400	-	-	61600
Level 720	3.2	4.4	0.3	242	52	-	-	3470

#### 4.3.3 Synthetic solutions

A synthetic AMD solution was prepared using analytical grade sulphate metals (Ni(II), Cu(II), Zn(II), Fe(II)) (Merck) (**II, V and VI**). The concentration of stock metal solutions was 1000 mg L<sup>-1</sup> with pH 1.5.

Synthetic stock solutions of arsenite and arsenate were prepared from  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$  with 25% NaOH and 37% HCl by dissolving in distilled water (III), respectively.

MB and OII (Merck) stock solutions were prepared in distilled water with an initial concentration of  $100 \text{ mg L}^{-1}$  (IV).

A synthetic solution of cyanide ions was prepared from potassium cyanide by dissolving in distilled water with an initial concentration of  $\text{CN}^- 300 \text{ mg L}^{-1}$  (V).

#### 4.4 Instruments for solutions characterisation

##### 4.4.1 Metal ions determination

The concentration of initial and final concentration of metal ions in solutions was determined with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) iCAP 6000 Series, Thermo (UK). Detection limits and wavelength were 0.4 ppb and 324.7 nm; 0.2 ppb and 202.5 nm; 0.5 ppb and 259.9 nm; 0.1 ppb and 231.6 nm for Cu(II), Zn(II), Ni(II), Fe(III), respectively. Arsenic concentration was determined at a wavelength of 188.9 nm. The hydride generation accessory (Thermo Fisher Scientific, UK) was used for increased sensitivity to arsenic. The quantification limit of arsenic determination with the hydride generation accessory was  $0.23 \mu\text{g L}^{-1}$ .

##### 4.4.2 Ions determination with HPLC

High-performance liquid chromatography (HPLC) (Shimadzu) was used for determining sulphate, chloride, cyanide, arsenate and arsenite ions. The various columns were used, such as column for sulphate and chloride ions determination with the following parameters: 4.0 mm IDx250mmL Shodex IC SI-50 4E; mobile phase: solution of 3.2 mM  $\text{Na}_2\text{CO}_3$  and 1 mM  $\text{NaHCO}_3$  in ultrapure water; flow rate: 0.7 ml/min; temperature: ambient.

The cyanide concentration in initial and treated solutions was determined by high-performance liquid chromatography (HPLC). A Shimadzu HPLC equipped with a conductivity detector (Shimadzu Model CDD-10A) was used (column: 6.0 mm IDx250 mm Shodex RSpak KC-811; eluent: solution of 1 mM  $\text{H}_2\text{SO}_4$  in ultrapure water; flow rate: 1.0 mL/min; temperature: 40 °C; reagent 1: 0.1% Chloramin T in 0.1M phosphate buffer (pH 7.5); reagent 1 flow rate: 0.5 mL/min; reagent 2: 1-Phenyl-3-methyl-5-pyrazolone + 4-pyridinecarboxylate (Na); reagent 2 flow rate: 0.5 mL/min; reaction temperature: 80 °C; wavelength: 638 nm).

Arsenate and arsenite were determined by ion exchange chromatography using RSpak KC-811 column (Shodex) for HPLC equipment. A solution of 12mM  $\text{H}_3\text{PO}_4$  as eluent; flow rate was 1.0 mL/min; column temperature 40 °C and UV detector (195 nm) were used.

#### 4.4.3 pH and redox potential

pH and redox potential were controlled using 0.1 and 1M NaOH and HCl solutions. The initial and final pH and Eh were determined by a multi-parameter portable meter HQ40d (Hach, USA).

### 4.5 Modification of adsorbents

The main objective of this research was to develop adsorbents from low-cost materials, and to improve the adsorption properties by modification of their surface. The first one was the modification of a limestone surface with 2M NaCl solution (II). A novel and innovative method of modification of limestone was also applied in the research (II). This was the use of process water from Norilsk Nickel Harjavalta for the limestone surface modification, since its basic composition is sodium chloride. 100 g FS and FF were dissolved in 1 L of 2 M NaCl solution and 1 L alkaline wastewater and then stirred at an ambient temperature for 12 h. Prepared sorbents were washed from the reactant with distilled water and oven-dried for 12 h at 80 °C. (II).

The iron compound material surface (RH and CaFe-Cake) was modified with atomic layer deposition technology (ALD) (III, V and VI) and a low-cost method using NaOH (III).

Using NaOH allows the activation of iron compounds as well as the generation of new hydroxide reactive functional groups on the surface. The adsorbents were activated with NaOH (Sigma-Aldrich, Germany, assay  $\geq 98\%$ ) and H<sub>2</sub>O<sub>2</sub> (Sigma Aldrich, Germany, 30wt.% in H<sub>2</sub>O) to improve their adsorption capacities. Typically, 100 g RH and CaFe-Cake were suspended in 25% NaOH (Sigma-Aldrich, Germany, assay  $\geq 97\%$ ) solution and then stirred at 100 °C for 6 h with the addition of 10 mL H<sub>2</sub>O<sub>2</sub> as a catalyst. After preparation, the reaction mixture was filtered and the adsorbents were washed with distilled water and oven-dried for 12 h at 120 °C. The dried adsorbents were stored in plastic flasks. (III)

ALD technology for increasing the adsorption properties of materials does not belong to the low-cost category. However, this is a prospective and innovative method that was applied for the purposes of comparison with cheaper methods.

TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> thin films were deposited on the surface of the adsorbents using a TFS500 ALD reactor (Beneq Oy, Finland) to increase adsorption capacity for As(III) and As(V) removal. The surfaces of the SuFe, CaFe-Cake and RH adsorbents were modified with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in order to obtain Ti-OH and Al-OH groups on the surface. For the TiO<sub>2</sub> ALD process the adsorbent surface was exposed to TiCl<sub>4</sub> and H<sub>2</sub>O vapors intermittent with inert gas (N<sub>2</sub>) pulses in order to purge the reactor. The pulse time of TiCl<sub>4</sub> and H<sub>2</sub>O was 0.6 and 0.25 seconds respectively. In turn, an Al<sub>2</sub>O<sub>3</sub> film was synthesized by sequential pulses of trimethylaluminium (TMA) and H<sub>2</sub>O into the reactor with a pulse

time of 1 and 2 seconds, respectively. The ALD process was carried out at 350 °C for TiO<sub>2</sub> and 200 °C for Al<sub>2</sub>O<sub>3</sub> under pressure of 1 mbar. 300 ALD cycles were used for those materials. The silicon substrates <100> (Si-Mat, Germany) were used to control the film thickness of both metal oxides (**III**, **V** and **VI**).

Deposition of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZnO was applied for modification of granulated sulphate tailings. New sorbents were applied for synthetic and real AMDs treatment from nickel, copper, zinc, and sulfate ions (Paper **VI**). For deposition of ZnO diethyl zinc (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn was used as a precursor. The number of cycles was increased from 300 to 500 for both deposition processes (TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>), compared with the previous study (Paper **III**). The pulse time was doubled for each cycle, which made it possible to significantly reduce the temperature of the process from 350 °C to 220 °C and from 200 °C to 150 °C for TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> deposition, respectively. Deposition of ZnO was carried out at 100 °C.

Optimal parameters for oxides deposition were obtained with due account for sustaining efficient adsorption properties (Table 7).

ALD is based on a chemical interaction between gaseous reactants and active sites on the substrate surfaces (Figure 9). A process of metal oxides deposition on the sorbent surface consists of three steps. First, a precursor containing the element to be deposited is added. In this case, it is an aluminum or titanium compound, namely, trimethylaluminium (TMA) and titanium chloride (TiCl<sub>4</sub>), respectively. The monolayer of those compounds is deposited on the sorbent surface due to chemisorption. The second step is a reaction between the deposited first and second precursor, which is pulsed to the reactor. Water was used as a second precursor for both cases. Water reacts with the coated first precursor and forms a thin film of metal oxide on the sorbent surface. The method has a fine control on the film thickness and coating uniformly for the flat surfaces [237–242]. Deposition of metal oxides on the surface of adsorbents will increase the strength of granules and improve sorption capacities due to additional functional groups. ALD has several significant advantages when compared to other thin film deposition techniques, such as electrodeposition, electron beam evaporation, thermal evaporation, and sol-gel. The ability to control the thickness of the coated films using a certain number of deposited cycles making ALD one of the advance methods. Deposition of metal oxides on the

surface of iron-based solid wastes was carried out in this study as a novel method for the production of the sorbents.

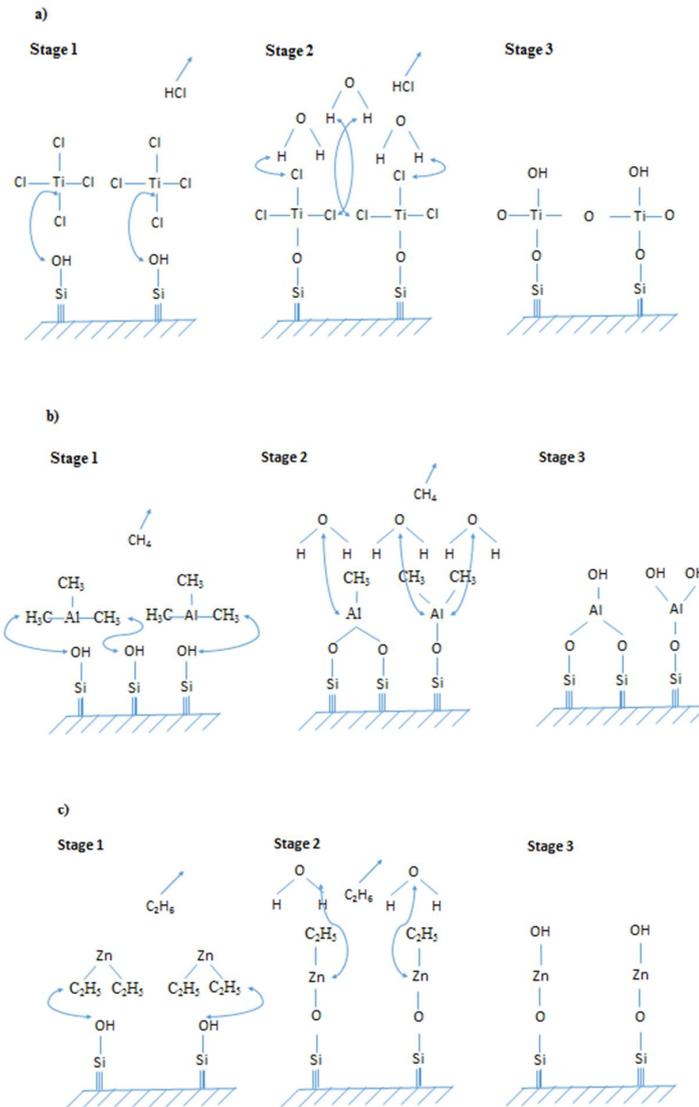


Figure 9. Schematic of deposition of Al<sub>2</sub>O<sub>3</sub>, (a) TiO<sub>2</sub> (b) and ZnO (c) into the granulated RH (VI). Conditions of the process are presented in Table 7.

Table 7. The basic conditions of ALD of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> on the surface of RH powder. Data for TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> deposition are for two processes that are described in Paper III and VI. Data for ZnO deposition was described in Paper VI only.

Precursors	TiO <sub>2</sub> deposition		Al <sub>2</sub> O <sub>3</sub> deposition		ZnO deposition	
	TiCl <sub>4</sub>	H <sub>2</sub> O	TMA	H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Zn	H <sub>2</sub> O
Pulse time, sec	0.6/1.2	0.25/0.5	1.2/2	2/4	1.8	2
t °C	350/220		220/150		100	
Pressure, mbar	6.5	6.5	6.5	6.5		
Cycles amount	250/500		250/500		500	

#### 4.6 Granules production

The wet-granulation of materials was provided with a high shear granulator Kenwood KM070 (Japan). The wet-granulation process is presented in detail in Figure 10.

Granules are formed by the addition of binders with a known concentration into powder with constant stirring in a granulator (Fig. 10) during the selected time. The combination of a known amount of polyvinyl acetate (PVAc) and acetone (Merck, UK) was used as a binder. The concentration of the binder, its volume, powder mass ration, and granulation time affect the quality of granules, namely the granule size, strength, and resistance to liquids.

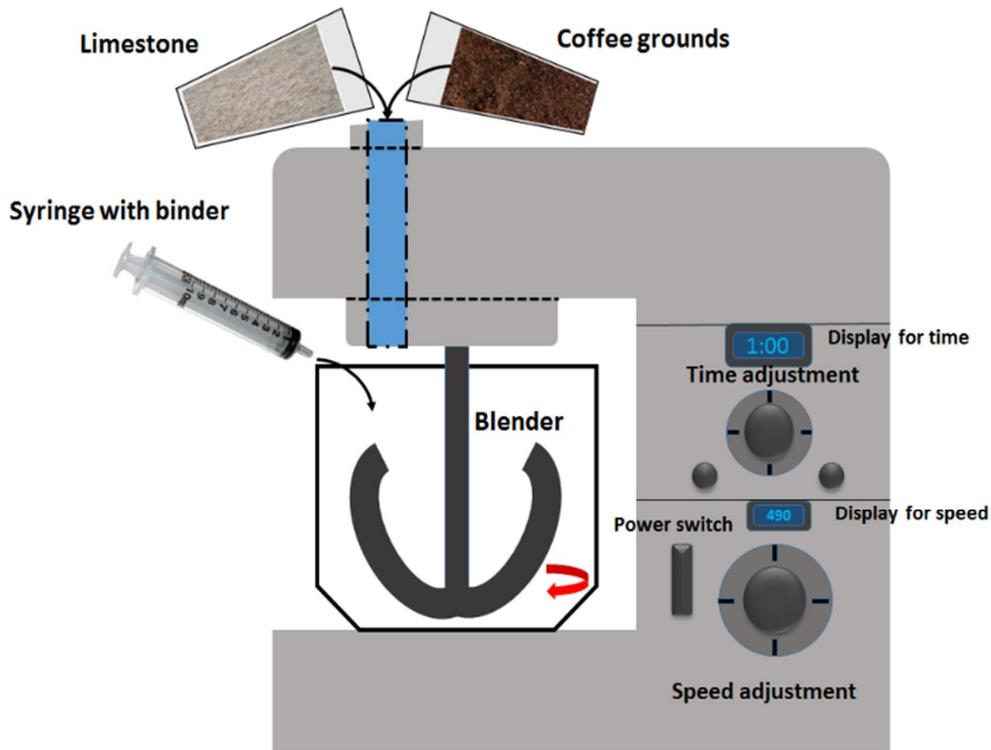


Figure 10. Scheme for a wet-granulation process of powders.

#### 4.6.1 Co-granulation of CW and limestone

The known mass of limestone powder and coffee waste was added to the mixer and mixed without binder for 60 s. The known value of the binder was added to the powder during the next 30 s without stopping the rotator. The mixing of the powder was performed at an impeller speed of 490 rpm and binding occurred within 60 s until the formation of granules (IV).

#### 4.6.2 Granulation of sulfate tailings

All experiments were carried out at room temperature (22 °C) with a mixing time and speed of 2 min and 490 rpm, respectively.

The known amount of sulphate tailing powders was added to the mixer and mixed without the binder for 60 s. The known value of the binder was added to the powder during the next 60 s without stopping the rotator. The mixing of powder and binder occurred within 120 s until the formation of granules; the impeller speed was 490 rpm (V).

The optimal concentration of binder was chosen by the addition of PVAc at different concentrations (from 10w% to 40w%) during the granulation process and amounted to 30w%. The viscosities of the binder solutions were determined by the Haake Viscotester C. The binder concentration selected made it possible to produce granules with the largest particle size from 1 to 2 mm. These granules have a better stability upon contact with water and remain approximately the same size and strength (Paper V). These granules should be used for waste water treatment during the long testing time. Granule strength was measured from diametric compression of the single granules using the method previously described [246] (Eq. 24).

$$\sigma = 2.8 \frac{f_i}{\pi d^2} \quad (24)$$

where  $f$  (N) is the compressive force during testing of granule strength,  $i$  is the number of tests, and  $d$  (mm) is the granule diameter.

Granule wettability was tested by mixing a known amount of granules with water at ambient temperature for 72 h. The strength and size of the granules were determined before and after the wettability tests. After testing, all granules were oven dried for 12 h at 80 °C.

#### 4.7 Batch adsorption and desorption experiments

All sorption tests were conducted at least three times by mixing a known weight of sorbents with a known volume of synthetic solutions or real mine waters. The experimental solutions with sorbents were shaken with a shaker ST5 (IKA KS 4000i Control). A known volume of solution was taken from the flasks at known time intervals and filtered using a 0.20 µm diameter polypropylene syringe filter. Optimal contact time, pH, and concentration of sorbents were selected during the sorption tests.

The percentage of adsorption (A) and desorption (D) was calculated as:

$$A\% = \frac{(c_i - c_{ad})}{c_i} 100\% \quad (25)$$

$$D\% = \frac{c_d}{c_{ad}} 100\% \quad (26)$$

The average value of the results was calculated to estimate the characteristics of the random component of the error of three parallel measurements:

$$X = \frac{\sum_{l=1}^n X_l}{l} \quad (27)$$

where,  $X_l$  is the result of a single measurement;  $l$  is the number of measurements.

The standard deviation of the analysis results was calculated by:

$$SD = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{l-1}} \quad (28)$$

The systematic error of the experimental data was evaluated using the addition of determined elements.

$$C_{exp} = C_{exp+add} - C_{add} \quad (29)$$

where,  $C_{exp}$  is element concentration without additives;  $C_{exp+add}$  is element concentration with concentration of additives;  $C_{add}$  is additive concentration. The standard deviation for the method of addition was calculated by Eq. 28.



## 5 Results and discussion

The chemical compositions of the raw materials are presented in Tables 3 and 4. As can be seen, calcium was included in all material compositions. Iron composed 10% of the total weight of RH and CaFe-Cake and 40% of SuFe. Silicon is one of the components of each material. The limestone contained up to 10% silicon.

However, except for the elements responsible for the sorption properties, the solid wastes (RH, DI-60, SuFe and CaFe-Cake) consisted of various elements related to toxicity, such as S, As, Cd, Ni, Mo. Assuming that some amount of pollutants may become an obstacle to using them for AMD treatment and metal ion removal due to the desorption from structure of sorbents, raw materials were tested for desorption of elements into acidic and alkaline water. The results are shown in Figure 11. Desorption of iron was observed from both sulphate tailings, SuFe and CaFe-Cake, RH and DI-60. Desorbed concentration of iron amounted to 40%, 10%, 7% and 3% from total weight of sorbents. No other element desorption was observed or was below the detection limits of the analytical instruments used. Materials were washed with distilled water and oven-dried for 12 h at 80 °C before use.

The materials can be divided into three groups, namely limestone (FF and FS), iron-based materials (RH, DI-60, SuFe and CaFe-Cake) and bio-sorbent (coffee waste). Each group is presented below in the relevant sections.

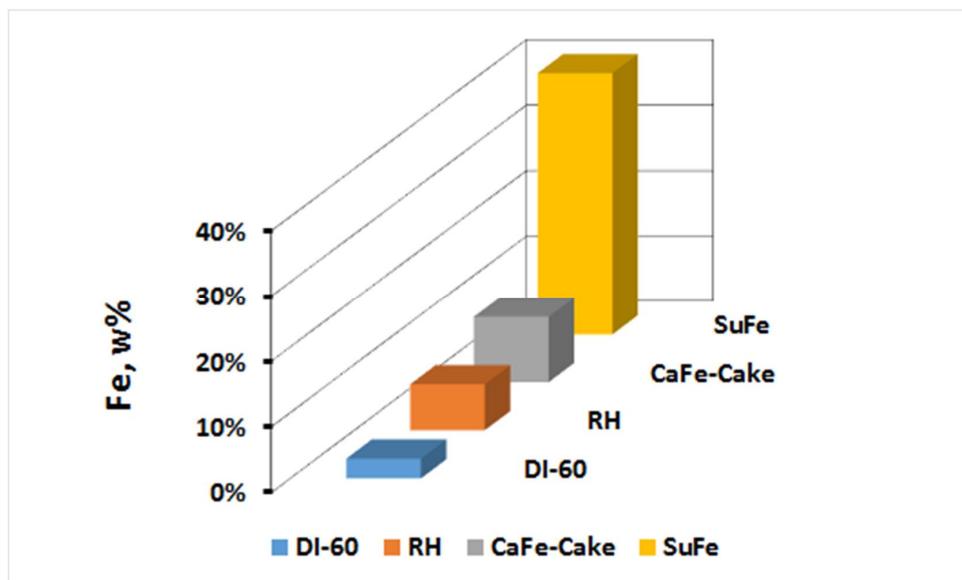


Figure 11. Data of preliminary tests of iron desorption from structure of raw materials. Known amounts of raw materials were mixed with 10% suprapure  $\text{HNO}_3$ .

## 5.1 Limestone

### 5.1.1 Characterization of limestone

Based on the results obtained with XRF and XRD, all three types of limestone have similar structures, according to expectations, corresponding to wollastonite, calcite, illite, kaolite, jarosite, diopside, illite, and gypsum (Tables 3-5) [157-159]. Calcite and silicate compounds are the main components of those materials. Their size of particles was uniform and amounted to approximately  $500\ \mu\text{m}$ , since they were initially ground at the factory. The particle size distribution and the specific surface areas of the original materials are presented in Table A 2.

Spectroscopic studies with FTIR confirmed the results of XRF studies (Table 3, 4 and A 2). Compounds of calcium, silicone and various OH groups were found. The new hydroxide groups appeared on the surface of the modified limestones, which may be a result of the introduction of sodium onto the surface of the limestones (Table A 2).

SEM pictures of initial and modified limestones are given in Figure 12. As can be seen, the surface structure of the original sorbents consists of different particle sizes of approximately  $200\ \mu\text{m}$  and less. However, the surface of the FS modified with process water is more uniform (Fig. 12c). For those modified sorbents with NaOH and for FF, the surfaces were almost unchanged.

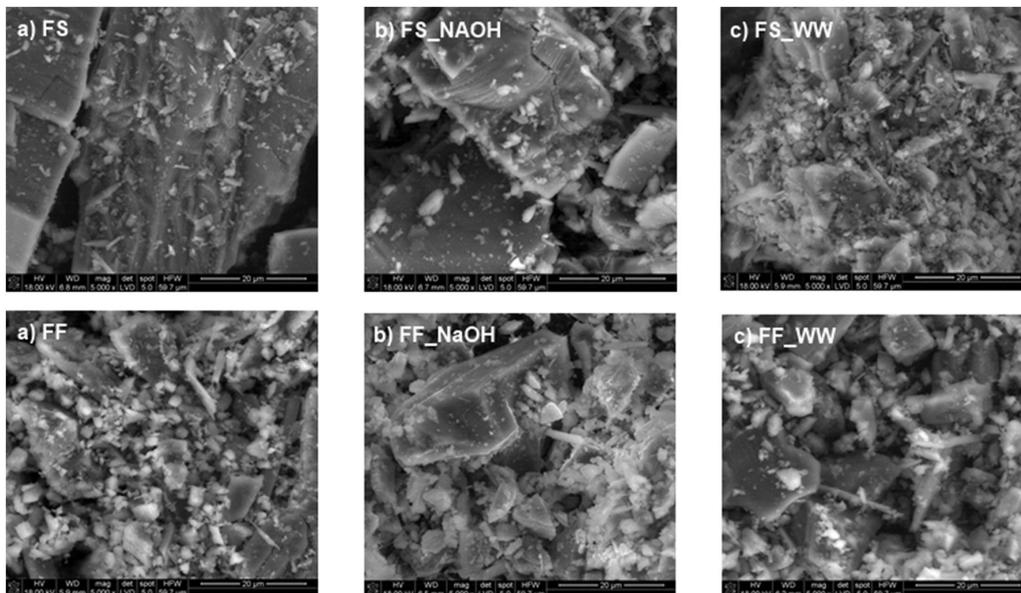


Figure 12. SEM images of unmodified FS, FF and modified with NaOH FS\_NaOH, FF\_NaOH and modified with real process water FS\_WW and FF\_WW limestone surface at 1000x magnification and scale bar 100 $\mu$ m (Paper II).

The zeta potential of FF is -25 mV, as opposed to FS with 0 mV. The zeta potential of modified FS\_NaCl increased to value -15 mV; however, it was not hardly changed for FF\_NaCl. The experiments showed that during the first hour of contact with FF with AMD, active effervescence was observed. The chemical reaction between FS and AMD was accompanied by a slight effervescence. It may be suggested that FF is a more capable sorbent to coagulate or flocculate the process, which was confirmed theoretically also in other studies [71, 104, 246].

More detailed characteristics of limestone surfaces are given in Papers I, II and IV.

### 5.1.2 Modification of limestones

In addition to the application of unmodified limestone for sulphate and chloride removal (Paper I), their modified forms were used for AMD treatment (Paper II). Two modification methods for the limestone surface were used in this research (Paper II).

The modification with sodium chloride is environmentally friendly and low-cost. Limestone covering with a salt layer makes it possible to increase the surface area of sorbents and the number of functional groups for exchange process with pollutant ions. As far as we know, this method has not been used previously.

Using alkaline process water with a high concentration of chloride salt as a modifier for limestone surface is an innovative proposal for the recovery of process water. This method was first described and applied successfully in this work. The conditions of both modification methods are outlined in Paper I.

### 5.1.3 Application of limestone

Following the estimate that all chemical compounds are structurally similar, calcite should have high adsorptive properties for sulphate and chloride ions [7, 104, 246], unmodified limestones were studied for alkaline process water treatment (Paper I). Since limestone is used in the neutralization of acidic content in water and soil [156-158], it was also applied to AMD neutralization. Its capacity to remove iron, zinc, copper, and nickel ions was also studied (Paper II). According to previous studies and chemical composition results of limestone, it can be stated that both types of limestone have elements with higher solubility than calcium, as magnesium and potassium. Those components can be related to the neutralization of AMD and the removal of pollutants by sorption mechanism. As can be discussed in paragraph 2 of this research, the silica, which are contained in both types of limestone (see Table A2) can be reacted with metal ions through the adsorption mechanism. Many researchers use the term "silica" to describe the adsorption process of metal ions. However, the silanol groups are functional surface

groups that are related to this process, as was suggested by [100-104]. The presence of silanol groups on the surface of unmodified and modified FF is confirmed by FTIR analysis (Table A 2).

The removal of sulphate and chloride ions from industrial water is a difficult and expensive challenge [110, 227]. Removal of their ions with solid wastes has not always been successful as has been reported previously [209, 220, 229]. Unmodified limestones were applied for the removal of a high concentration of sulphate and chloride removal, and showed a good ability to remove of salt ions, as was demonstrated in Paper I.

The optimal amount and contact time for both unmodified limestones (FF and FS) for removal of chloride and sulphate ions were found and amounted to  $40 \text{ mg L}^{-1}$  and 480h, respectively. Optimal parameters and sorbent characterisation were carried out with the initial concentration of chloride and sulphate ions  $20 \text{ g L}^{-1}$  in synthetic process water. The concentration of chloride and sulphate ions in real water was  $2.5$  and  $30 \text{ g L}^{-1}$ , respectively. The equilibrium of the system during the adsorption process was described with Langmuir, Toth and BiLangmuir adsorption isotherms (Paper I). Despite the greater size of the molecules, sulphate ions were better adsorbed from a synthetic solution with chlorides with FS than with FF. In the case of FF the adsorption of both ions was approximately equal (Table 7, Fig. 13). From real process water, sulphates were also better removed, but only slightly more than half of the chloride ions were removed, which may be related to competition during the adsorption process (Paper I).

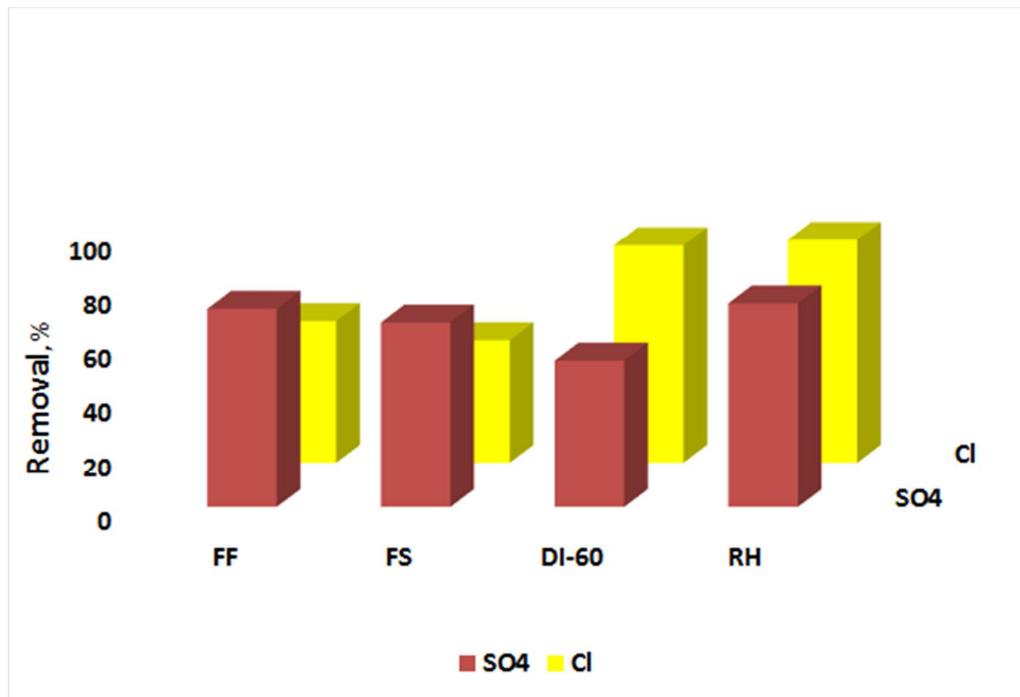
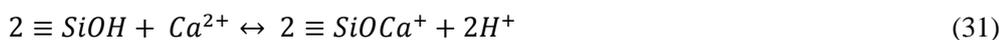


Figure 13. Removal of chloride and sulphate ions from real process water with unmodified limestones (FF and FS) and iron-containing materials (DI-60 and RH). Initial concentration of  $SO_4^{2-}$  and  $Cl^-$  was 30 and 2.5 g L<sup>-1</sup>, respectively. Amount of sorbents was 40 g L<sup>-1</sup>.

In the case of the removal of sulphate and chloride ions, the ion exchange mechanism between hydroxyl groups and pollutants should occur. Sulphates were removed better than chloride ions with both limestone that are in agreement with results from other studies [229, 243]. According to results obtained during this research, it can be assumed that limestone has a better affinity for sulphate than chloride ions and can be used for alkaline water treatment with a high concentration of both anions.

In case of metal ion removal (Paper II), the sorption mechanism may be governed by an ion-exchange reaction between active sites of silica and metal ions (Eq. 30-32):



The neutralization of synthetic (pH 1.5) and real AMD (pH 2.3-3.2) was studied with modified and unmodified FF and FS by batch method. An increase of pH to 6.5-6.8 after 6 h was registered (Fig. 14). As can be seen, FF shows superior neutralization qualities

compared to FS. The pH increased from 1.5 to 6 after 300 min with an initial dose of FF 20 g L<sup>-1</sup>. Whereas to achieve a pH of 6 with FS, a dose of equal 50 g L<sup>-1</sup> is required.

During the neutralization process, metal ions were removed with a different capacity for various limestones. The competition between metal ions in the complex solution with modified limestone was studied (Paper II). It was observed that up to about 90% of nickel and zinc ions were removed in 1 h and 6 h with FS\_NaCl and FF\_NaCl, respectively. After this time, desorption for both ions was observed. The main reason for this phenomenon may be strong competition between the ions. Therefore, copper and iron are the ions with the highest affinity for both adsorbents. They tend to form stronger bonds on the surface sites, compared to zinc and nickel. Stronger complexation of copper and iron ions than with zinc and nickel has been reported elsewhere [123, 214, 244]. It was suggested that the ion-exchange mechanism was much more likely than precipitation because the maximum removal of metal ions was reached at a pH value less than 6, while the precipitation of metal salts occurs at a higher pH. However, it was reported that during the removal of metal ions from multicomponent solutions, the removal of zinc and nickel increased to approximately 10% in comparison with a single component solution. It could be because some iron precipitated and secondary metal removal could be observed. The major mechanism of secondary metal removal is adsorption and co-precipitation with newly formed iron compound particulates. After the treatment of the multicomponent system, the colour of adsorbents was changed from white to dirty yellow, which could also indicate a certain level of iron precipitation as hydroxide. Precipitation of Fe(OH)<sub>3</sub> on the limestone particles was also observed by Wang et al. (2013) [64].

The study of desorption of removed pollutants from the surface of unmodified and modified sorbents has also been carried out to understand the possible removal mechanisms and recycling of sorbents. It was found that the sorbents used to remove single ion, released this ion into the solution almost completely. However, the sorbents used for multi-elements removal have been more difficult to regenerate. The data of the desorption study for sorbents reuse is presented in Table 8. It can be seen that modified sorbents can be used for ADM treatment three times without an apparent reduction in their adsorption capacities. Data for unmodified and modified limestone reuse has not been presented in the published paper.

After batch experiments aiming to find the optimal conditions for AMD treatment with unmodified and modified limestone, it was found that the optimal dosage and contact time for both types of limestone was 40 g L<sup>-1</sup> and 12 h, respectively. The initial concentration of each metal ion was 200 ppm. The adsorption process was described better with the pseudo-second-order model and Langmuir, Sips, and Toth adsorption isotherms (Paper II). It was found that modified limestones have better adsorption capacity for all four metal ions, in contrast to unmodified limestones, which only adsorb iron and copper ions well. Both adsorbents showed an affinity for the metal ions studied as follows:

FS: Ni(II) < Zn(II) < Cu(II) < Fe(III)

FF: Ni(II) < Zn(II) < Fe(III) < Cu(II)

The removal of iron, copper, zinc, and nickel ions from real AMD from three different depths (270 m, 500 m and 720 m) was also studied (Figure 15). Unmodified and modified FF showed better adsorption capacity than FS, as was the case with synthetic AMD. The removal capacity for modified FF reached about 100% for all metal ions (Table 7). Notwithstanding the fact that many authors have observed the affinity for researched metal ions [63, 69, 121, 232, 235, 245], the complete removal of metal ions from real AMD with modified limestone, which has been achieved in this work, was a success, especially for zinc and nickel ions.

Based on the results of earlier co-authors' research [133], limestone was used for the production of co-granules with CW for the removal of dyes (Paper IV).

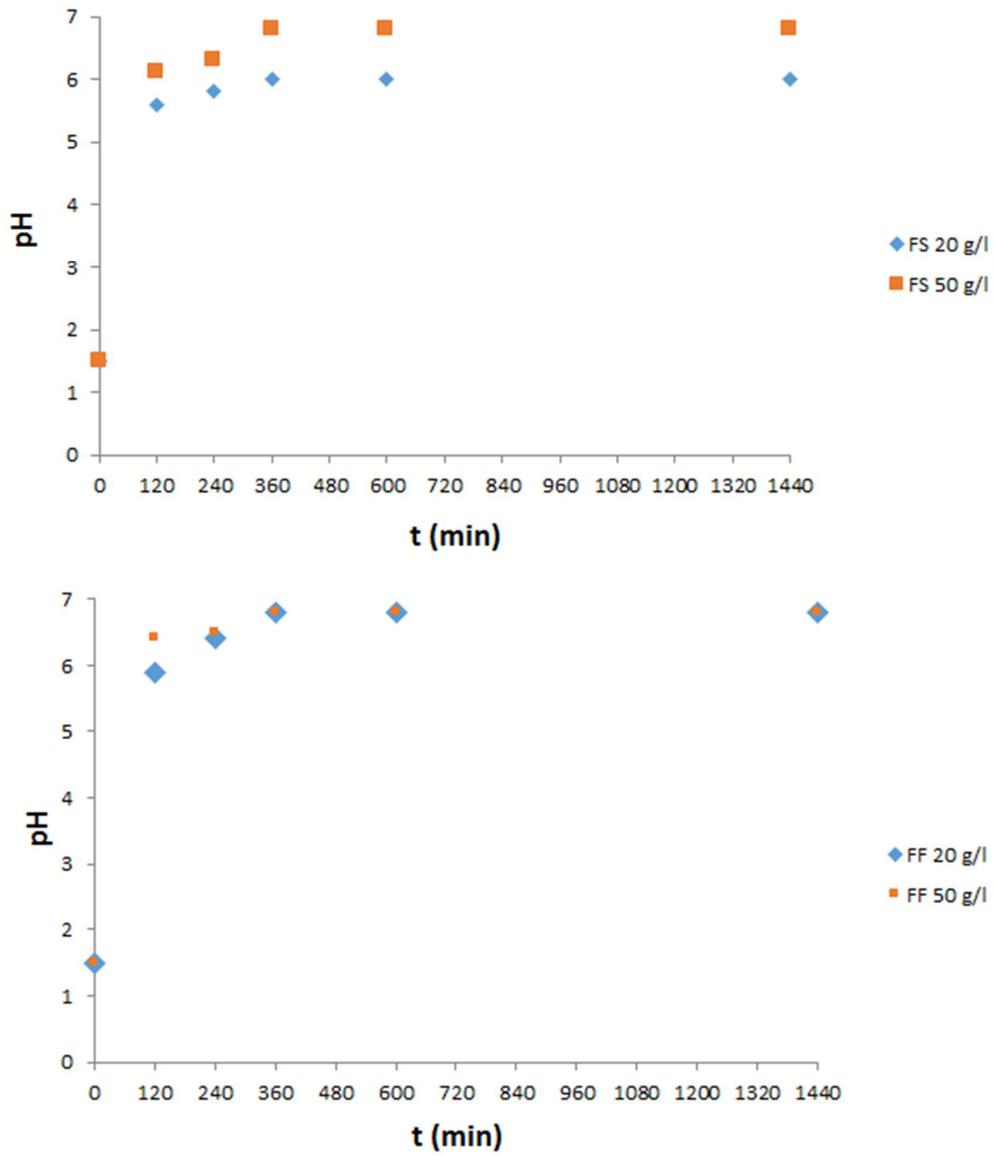


Figure 14. Neutralization of AMD by FS and FF with concentration of 20 and 50 g L<sup>-1</sup> in 24 h.

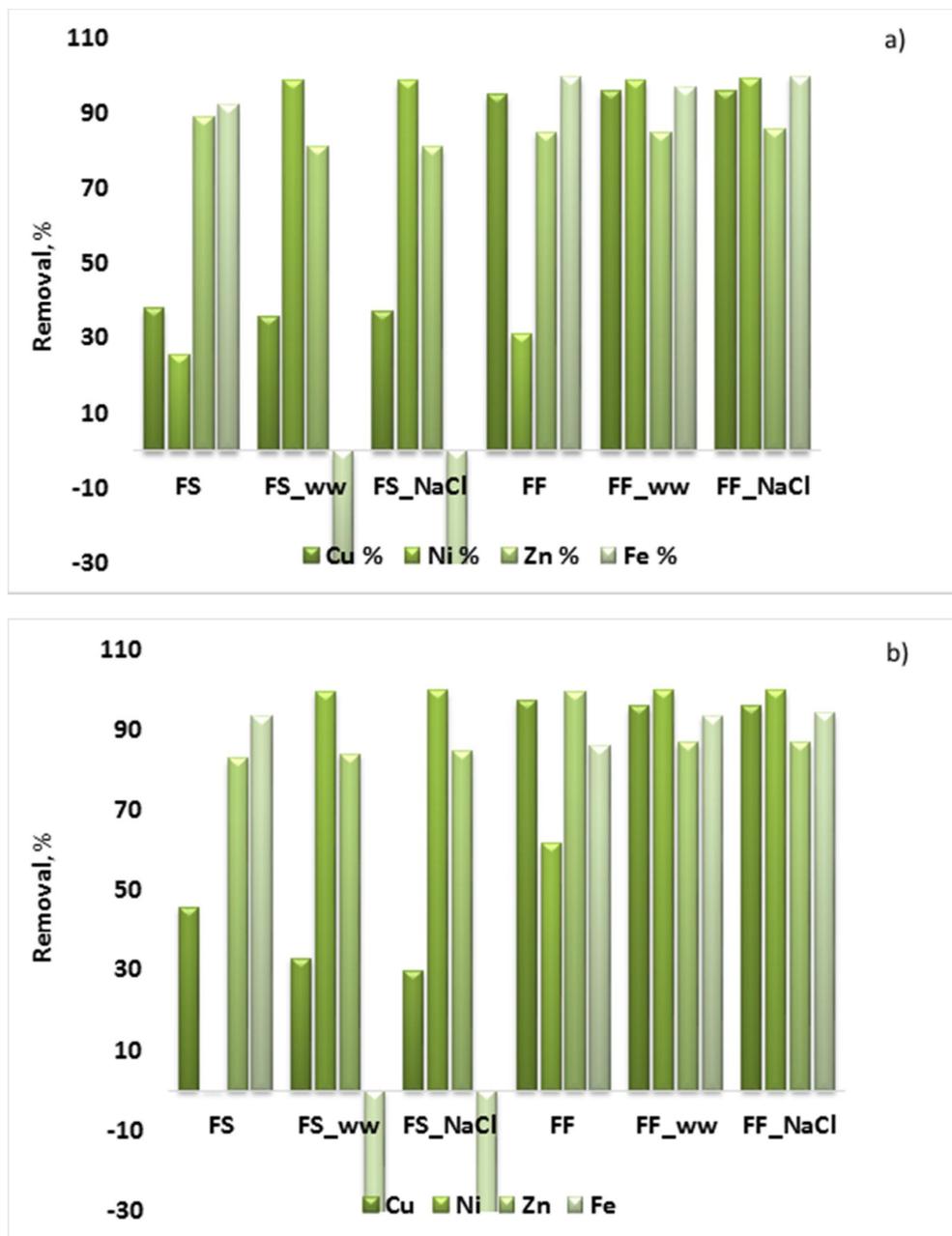


Figure 15. The removal of metal ions from real AMD with unmodified and modified FS\_NaCl (a) and FF\_NaCl (b). The initial concentration of copper, zinc, nickel and iron ions was  $0.3125 \text{ mmol L}^{-1}$ ,  $0.3058 \text{ mmol L}^{-1}$ ,  $0.3389 \text{ mmol L}^{-1}$  and  $0.3571 \text{ mmol L}^{-1}$ , respectively.

## 5.2 Sorbents from bio-products

Coffee waste was used for the production of co-granules with limestones and considered in accordance with this application.

### 5.2.1 Characterization of adsorbent

Coffee waste contains many different organic components, as was confirmed by organic elemental analysis and determination of functional groups on the surface by FTIR (Tables 3 and A 2). Besides organic and hydrocsilic groups, CW also has in its structure silicon and sulphur compounds (Table 2). The particle size distribution analysis showed that CW has a heterogeneous structure and the diameter of particles ranges from 100 to 1000  $\mu\text{m}$  (Fig. 16). Although the BET method shows that the specific surface area of CW is very low and amounted to less than unity, it has a complex surface structure (Fig. 17a). However, the co-granules inherited the surface structure of limestone rather than that of coffee (Fig 17c).

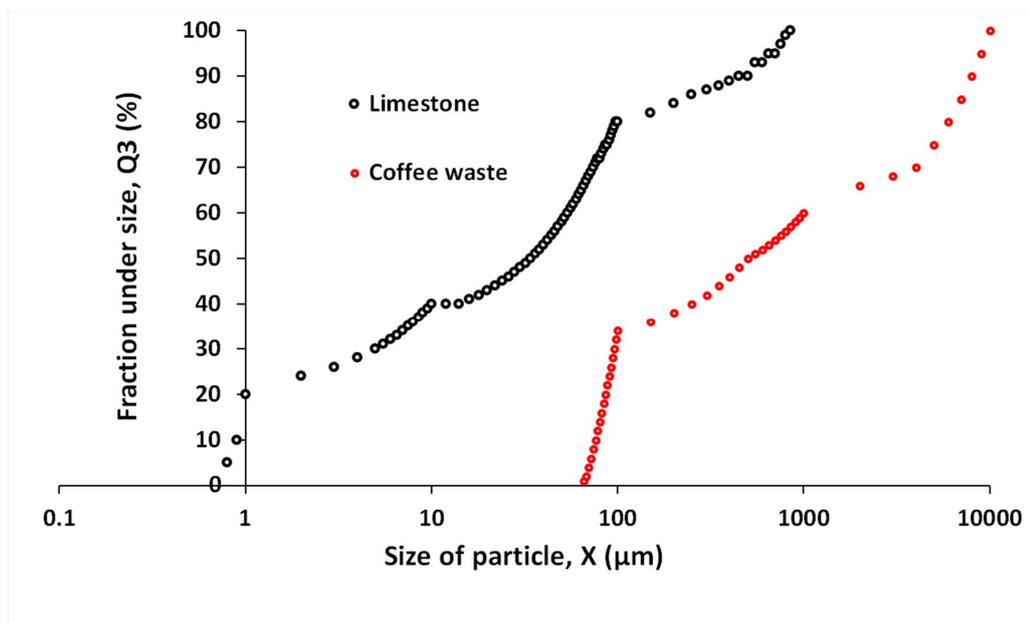


Figure 16. Particle size distribution of limestone and coffee waste (Paper IV).

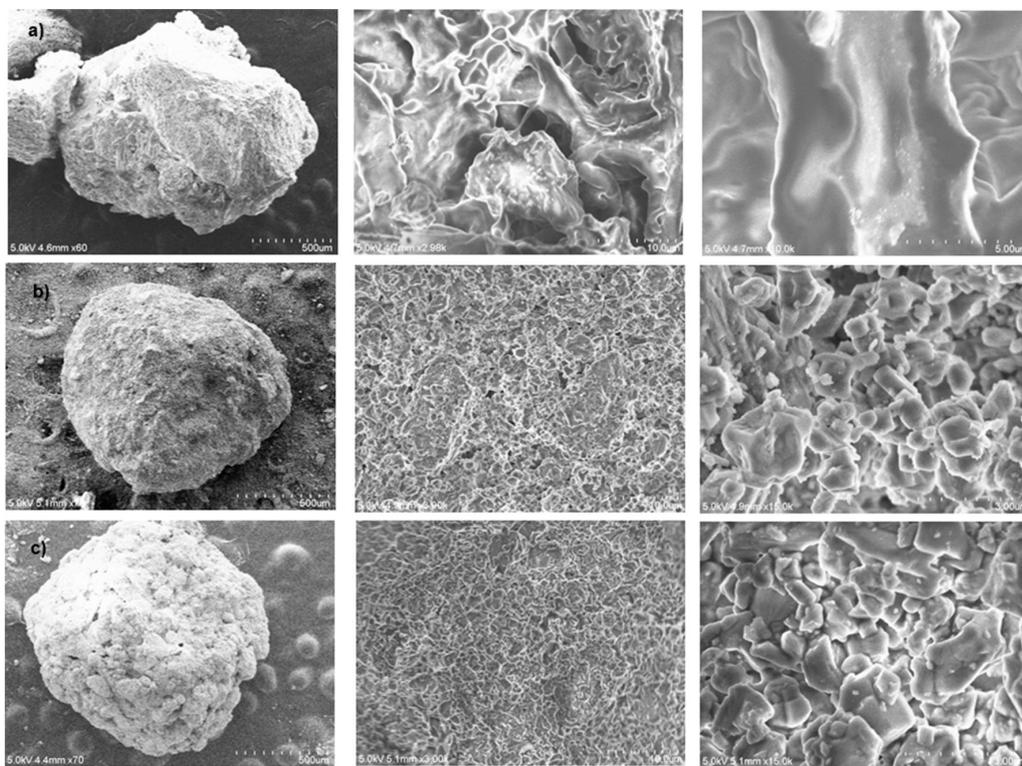


Figure 17. SEM pictures of the granule surface of coffee waste (a), limestone (b) and co-granules (c) with different resolution (500, 10 and 5  $\mu\text{m}$  for each material).

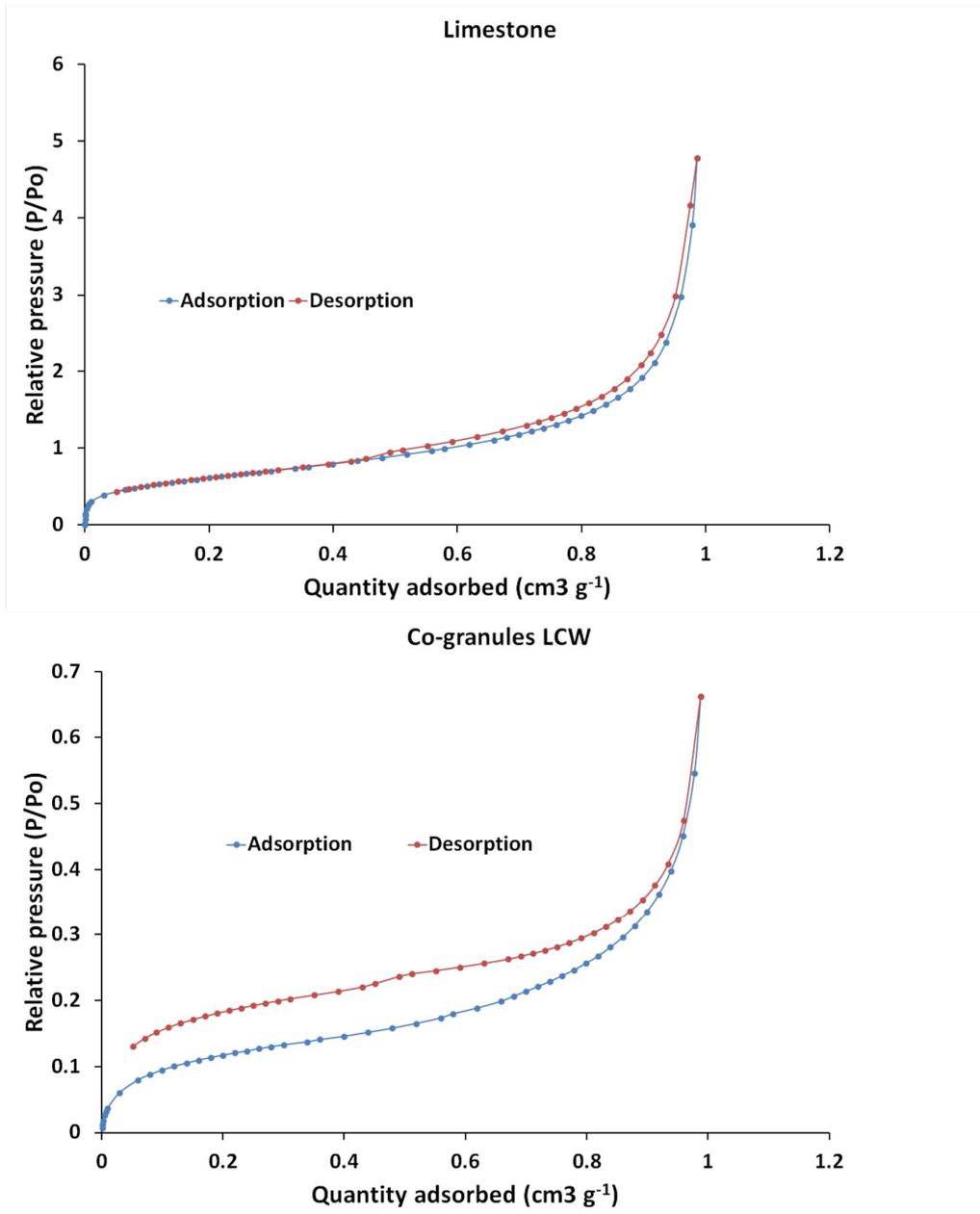


Figure 18. BET analysis of limestone powder and co-granulated sorbent from coffee waste and limestone.

Figure 18 shows that the hysteresis in the limestone is occurred between 0.5-1.0 relative pressures that can be point to the presence of pore. However, the difference between two plots is so significant that it can be assumed that the surface of limestone is monolayer and nonporous. The surface area, pore size, and distribution are incised on the granulated combined sorbent, as can be seen from the data of the BET analysis (Figure 18 and Table 6).

### 5.2.2 Application of co-granules

As has been shown elsewhere, coffee grounds have been applied successfully in the removal of some dyes and metal ions from wastewaters [163, 147, 254–260]. This may be due to the fact that a sufficient amount of nitrogen and carboxylic groups were present in their composition [261] (Table A1). The complex chemical composition of CW may be the reason for the effective removal of different pollutants. For example, amino, hydroxyl, carboxyl, sulphates, and silicate groups can participate in the removal process for both anionic and cationic pollutants. Based on the previous results of co-authors [133], CW was selected to increase the adsorption efficiency by ion-exchange reactions for limestone. Methylene Blue (MB) and Orange II (OR) were used as acidic and basic pollutants for research on the adsorption properties of combined sorbent (Paper IV).

### 5.2.3 Combined sorbent production

Data on the use of polyvinyl acetate as a binder for limestone and bio-waste has not been published before. PVAc was chosen as the binder because other studied binders have low adhesive properties for granulation of powders with different particle size, which are limestone and coffee waste (Figure 14).

Particular attention was paid to the choice of optimal concentration of binder because it was important in order to produce strong granules with sufficient surface area. After the preliminary test, the concentration of binder was chosen and amounted to 30%. The largest granules (1-2 mm) with high wettability were produced with a 3/7 combination ratio of CW and L. This ratio was used for the production of the granules studied. The use of PVAc as the binder allows the formation of granules with high strength and size more than 1-2 mm compared to previous studies [133, 233].

The results of the FTIR analysis show that all functional groups from both materials are present on the surface of the granules (Table A 2). The production of the granules and their properties are described in Paper IV.

### 5.2.4 Adsorption properties of granules

The adsorption capacities of the granules were examined with cationic (MB) and anionic (OR) dyes in single and mixed synthetic solutions. The optimal conditions were selected during the sorption process from single solutions of dyes and presented in Figure 19. The competition of pollutant removal was researched by a mixture of both pollutants with

CW, L, and LCW adsorbents. The initial concentration of the dyes was  $5 \text{ mg L}^{-1}$  for each. Equilibrium in the systems was achieved with the concentration of each adsorbent at  $2 \text{ g L}^{-1}$ . The maximum removal of MB and OR was 100% after 6 h and 85% after 8 h, respectively (Paper IV) (Table 7). The effect of pH on the removal of both dyes showed that more effective removal of MB and OR can be achieved at pH of 8 and 2, respectively (Fig. 20). The competition analysis showed that the percentage of MB removal remained the same; however, removal of OR decreased to 60% and did not change after 720 h (Paper IV).

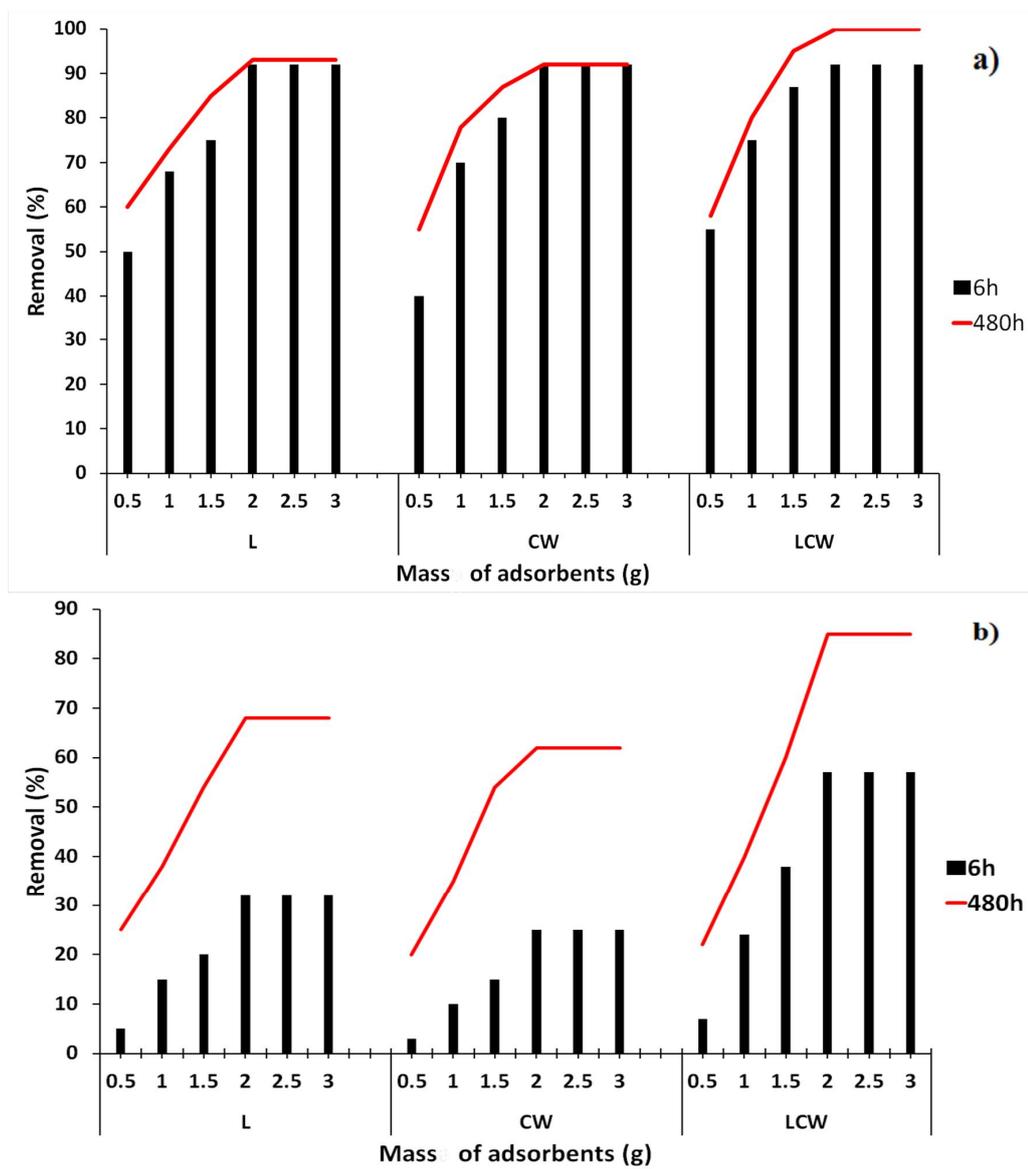


Figure 19. Optimal adsorbents amount and contact time for the removal of MB (a) and OR (b) with limestone, coffee waste and their co-granules. Initial concentration of dyes was  $2 \text{ mg L}^{-1}$ .

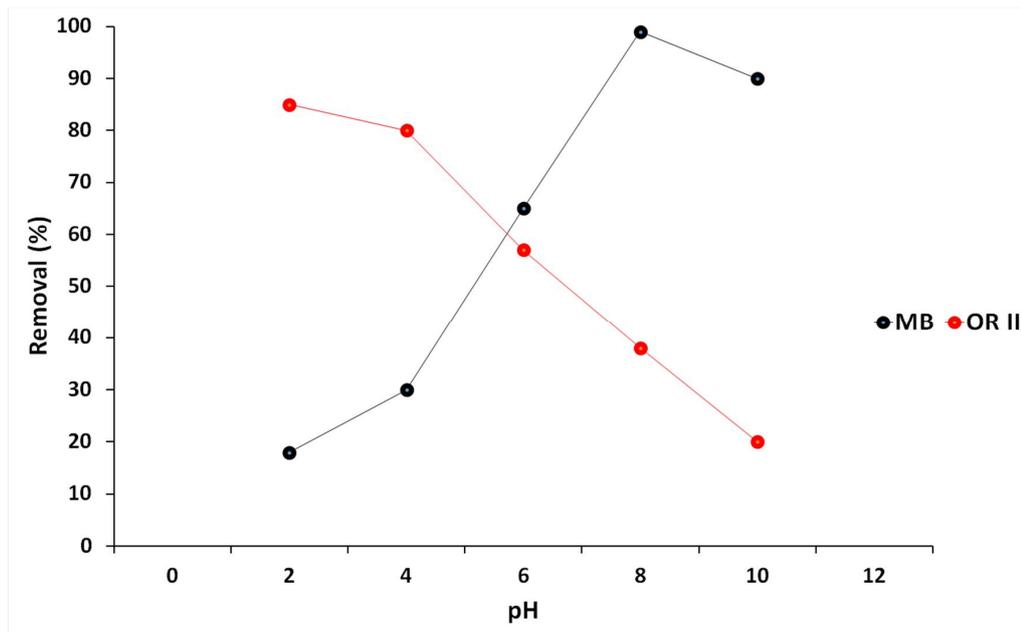


Figure 20. Effect of pH on the removal of MB and OR with an initial concentration of dyes, temperature, co-granules dosage, and contact time were kept constant at  $5 \text{ mg L}^{-1}$ ,  $25 \pm 2 \text{ }^\circ\text{C}$ ,  $2 \text{ g L}^{-1}$ , respectively (Paper IV).

It can be concluded that the co-granules produced had a greater affinity with acidic than with basic pollutants. However, they can be used for complex wastewater treatment involving more pollutants with a positive charge in solution and capable of entering into the exchange reaction with the surface of the sorbents.

### 5.3 Iron-based materials

RH, DI-60, and two sulphate tailings CaFe-Cake and SuFe were identified as iron containing materials because they have about 10w% and more of iron in composition (Papers I, III, V, VI). It can be assumed that there are iron oxides and hydroxides, since the elemental analysis and FTIR method show great amounts of oxide/hydroxide groups on the surface of those adsorbents [209-214].

### 5.3.1 Characterisation of sorbents

The chemical composition of adsorbents and their specific surface areas are presented in Tables 3, 4 and 5. The particle size of RH was about ten times smaller than DI-60, and as a consequence, the surface area of RH is significantly larger (Table 5 and see SEM images in Papers **I** and **III**). FTIR analysis showed about 17% of sulphur in the RH structure. The presence of sulphur may constitute a competitor to the removal of some pollutants by exchange reactions, such as sulphates and arsenic. However, as the desorption method shows, no compounds have not been released into solution from sorbents structure. More details on the RH and DI-60 structure are described in Papers (**I** and **III**). Two sulphate tailings were selected for one group in accordance with their chemical composition and origin. These are by-products of the nickel ore extraction process and contain large amounts of sulphates and iron compounds (Table 2). Particle size distribution and specific surface area of unmodified and modified adsorbents are presented in Table (5). SEM analysis of unmodified sulphate tailings shows that the surface areas of both sorbents are developed and non-uniform (see SEM pictures in Papers **III** and **V**).

### 5.3.2 Application of iron-based adsorbents

According to the literature and the chemical composition of RH and DI-60, they were used for the removal of sulphates and chlorides and RH for the removal of As(III) and As(V), sulphate and metal ions (Papers **I**, **III**, **VI**) [38, 111, 149, 247, 248-250]. It was assumed also that iron silicone compounds of both materials can support the removal of sulphates and chlorides by ion-exchange reactions (Paper **I**).

The optimal conditions for the removal of chlorides and sulphates from synthetic and real process water were found during the batch adsorption experiments. The optimal amount of adsorbents was 40 g L<sup>-1</sup> for both adsorbents (Fig. 21). The optimal contact time was 480 h. The initial concentration of sulphate and chloride ions was 20 mg L<sup>-1</sup> in synthetic solution and in real process water it was 30 and 2.5 g L<sup>-1</sup>. The affinity to sulphate ions was higher than to chloride ions for both adsorbents and amounted to about 90% (Paper **I**).

Tolonen et al. (2015) [220] observed the opposite interaction between an adsorbent with similar composition and sulphate and chloride ions. The competition between ions was observed during the real process water treatment. Chloride ions were better for removal. This may be due to the smaller size of chloride molecules in comparison with sulphate molecules. Another possible reason may concern the larger surface area of RH and the presence of large pores (Paper **I**).

Unmodified and modified RH and CaFe-Cake were used for the removal of As(III) and As(V) (Paper **III**). Two methods of surface modification were applied to increase the removal capacities of this sorbent. One of them is simple and low-cost. This method is the activation of the surface with NaOH and H<sub>2</sub>O<sub>2</sub>. This method activated iron compounds and generated new hydroxide functional groups on the surface (Table A1) (Paper **III**).

The other method is  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  thin films deposition on the surface of the adsorbent using a TFS500 ALD reactor (Paper **III**).

The presence of new active groups on the surface of RH was confirmed with FTIR analysis (Table A 1). As can be seen, new hydroxyls and aluminium oxides attributed to  $\text{TiO}_2$  nanoparticles appeared in the spectrum of modified RH. SEM pictures of unmodified and modified RH are presented in Paper **III**. The modified adsorbent surface with NaOH was completely covered by sodium hydroxide molecules. Particles of  $\text{TiO}_2$  form the stick and unequal structure on the RH, while  $\text{Al}_2\text{O}_3$  is synthesized into a compact and fine-pore layer (see SEM images in Paper **III**). The availability of new active functional groups on the modified surface of CaFe-Cake was confirmed by FTIR and SEM techniques (Table A1). The porosity of modified CaFe-Cake by ALD technology decreased from 10-20 to 2-3 nm. However, the crystalline nanoparticles of  $\text{TiO}_2$  could be observed in the SEM picture (Paper **III**). The thin film of oxides may be the cause of the decreasing pore size. It was also suggested by other researchers [24, 252].

All adsorption experiments were conducted with initial concentrations of both arsenic forms of  $20 \text{ mg L}^{-1}$  in synthetic solution and  $10 \text{ mg L}^{-1}$  in real AMD. The optimal amount of unmodified RH was  $40 \text{ g L}^{-1}$  for the removal of As(III) and  $20 \text{ g L}^{-1}$  for As(V). However, modification with the ALD method allows decreased dosage of adsorbents in four and two times for CaFe-Cake and RH, respectively (Fig. 21).

The removal efficacy achieved for both forms of arsenic was more than 90%. It was shown that the modification of RH is useful only for As(III) because for As(V) the percentage removal was 99% for all types of RH. The removal capacities for unmodified and modified forms were examined with synthetic solution of As(III) and As(V) with an initial concentration of  $20 \text{ mg L}^{-1}$  each (Table 8). Maximum sorption for both forms of arsenic was found with concentrations of unmodified adsorbent  $40 \text{ g L}^{-1}$ . The modification of the surface with the ALD method makes it possible to reduce the concentration of adsorbent to  $10 \text{ g L}^{-1}$  (Fig. 21). Unmodified CaFe-Cake has less capacity for the removal of arsenic. The modification with two methods increased the adsorption capacity of As(V) and As(III) in the following order: CaFe-Cake (90 and 40%), CaFe-Cake\_NaOH (99 and 70%), CaFe-Cake\_  $\text{Al}_2\text{O}_3$  (99 and 92%), CaFe-Cake\_  $\text{TiO}_2$  (99 and 95%) (Table 8).

Removal of both arsenite and arsenates from a single solution is complex and depended on an oxidation environment. The effect of pH and Eh solution was researched and presented in more detail in Paper (**III**). The peroxidation of arsenite with various oxidants is usually used for increasing kinetic activity [60]. An efficient method for removal of both arsenic forms is a successful solution of the peroxidation that has been excluded by using modified RH and CaFe\_Cake. Coated RH with  $\text{TiO}_2$  shows more effective removal of both arsenic forms and reached about 100% (Table 8).

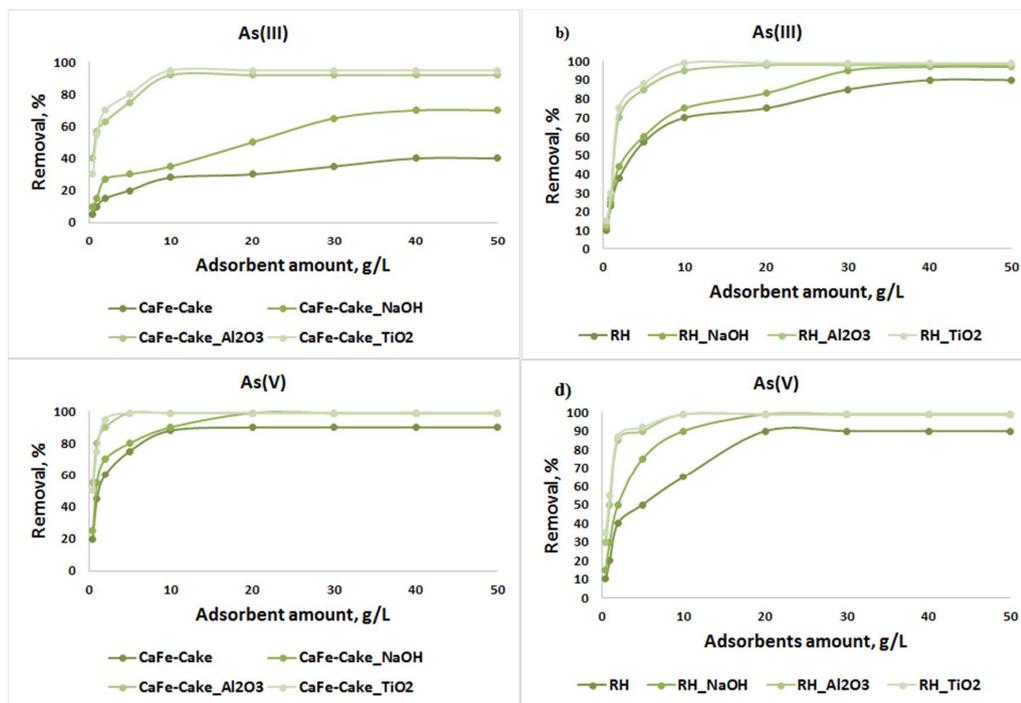


Figure 21. Effect of dosage of unmodified and modified adsorbents for the removal of As(III) and As(V) with initial concentrations of both arsenic forms of  $20 \text{ mg L}^{-1}$ .

Two unmodified and modified with atomic layer deposition of  $\text{Al}_2\text{O}_3$  sulphate tailings (CaFe-Cake and Sufe) were used for the removal of cyanide ions (Paper V). Both adsorbents were granulated before use. The procedure of granulation is described in detail in Paper V and section 4.6.2. PVAc was chosen as the binder according to preliminary results (see Paper IV and paragraph 5.2.3). The results of granule strength after wettability tests are shown in Figure 22. As can be seen, the granules with the size range of 1-2 mm have more stability properties for liquids.

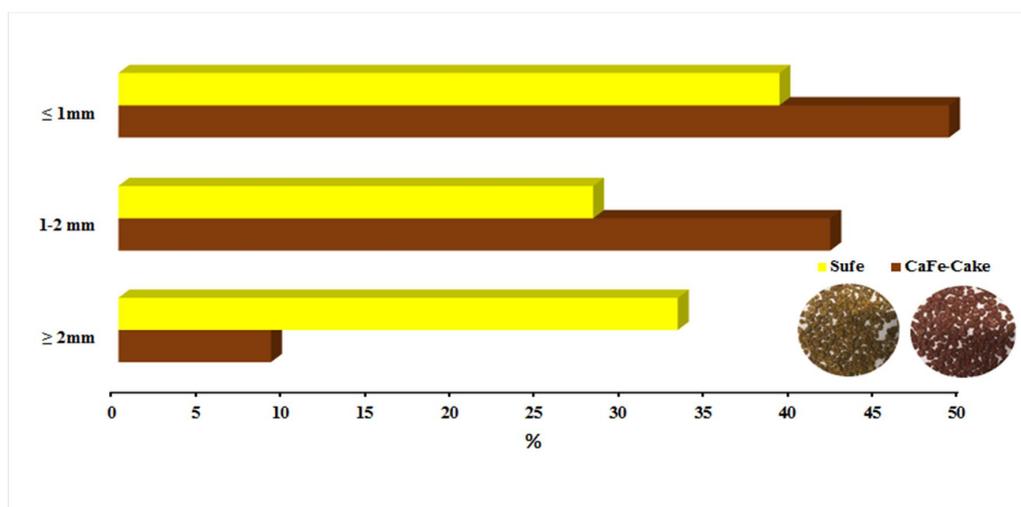


Figure 22. Size of granulated Sufe and CaFe-Cake before wettability test (Paper V).

The specific surface area of modified CaFe-Cake and Sufe were increased to seven and five times according to unmodified sorbents, respectively (Table 5) (Paper V).

The batch sorption experiments were carried out in ambient conditions. The optimal amount of both adsorbents was  $10 \text{ g L}^{-1}$  with a maximum initial concentration of cyanide ions of  $300 \text{ mg L}^{-1}$ . The maximum removal of cyanides was found to be 97% for both adsorbents (Table 8). The optimal pH for the removal of the maximum amount of cyanides was 3-4 (Paper V). The equilibrium of the system was described with Langmuir and Freundlich adsorption isotherms (Paper V).

Cyanide desorption from sorbents has been almost zero. It confirms that these sorbents can be used effectively once. The formation of a strong complex between cyanide ions and sorbent surface can be the result of the lack of desorption. The formation of the sustainable non-toxic ferrocyanide complex has been most likely according to one of two reaction mechanisms:



The obtained results have been more efficient for water treatment with a high concentration of cyanides, which is typical for gold mine process water, as compared to other research works [16, 251-253]. The modification did not increase the percent removal of cyanide ions; however, it allowed a decrease in the amount of sorbent dosage twice and reduced the adsorption time by about 60%. It can be concluded that both sulphate tailings can be effectively used for the removal of cyanide ions from wastewater. Removal of cyanides with modified sulphate tailings followed two different mechanisms.

The first is the formation of a ferrocyanide complex from iron and cyanide ions while the second is sorption of a ferrocyanide with aluminium oxide coated to the sorbent surface during modification with ALD. The double retention of cyanide ions on the modified sorbent surface is enabled to form a stable and non-toxic cyanide complex in the solution, which can be reused as the complexing agent in the metallurgical industries.

Sorption capacities for the removal of sulphate and metal ions with unmodified and modified RH were researched in Paper (VI). RH was modified with ALD of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  by increasing the amount of cycles from 300 to 500, compared with the previous study (Paper III) and at a lower temperature (Table 7). Subsequent to decreasing the temperature of the processes, it was necessary to increase the pulse time for each cycle. Although the process time was increased, a significant reduction in temperature makes it possible to achieve savings in energy costs (Table 7). The new bending vibrations corresponding to aluminum oxide at the peak between  $980\text{--}1000$  and  $610\text{--}611\text{ cm}^{-1}$ , and titanium oxides with the peak in between  $450\text{--}800\text{ cm}^{-1}$  were observed after modification of original RH with TMA,  $\text{TiCl}_4$ , respectively. Peaks between  $420$  and  $500\text{ cm}^{-1}$  are due to  $\text{ZnO}$  on the RH surface after modification with  $(\text{C}_2\text{H}_5)_2\text{Zn}$ . The peaks observed between  $2850$  and  $3000\text{ cm}^{-1}$  on the initial material can correspond to the stretching  $201$  vibration of hydroxyl groups. Those peaks disappear in the modified sorbents, indicating that the possible chemical reaction between  $\text{--OH}$  groups of raw materials and precursors (TMA,  $\text{TiCl}_4$  and  $(\text{C}_2\text{H}_5)_2\text{Zn}$ ) during the deposition of metal oxides by ALD (Table A 2 and Fig 19). SEM images also showed changes in the surface structure of modified RH. This was discussed in more detail in Paper VI.

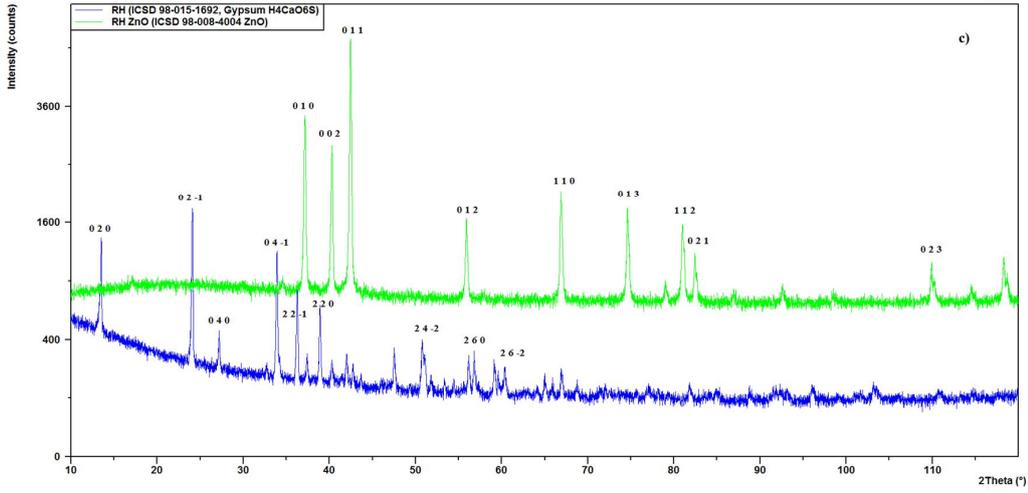
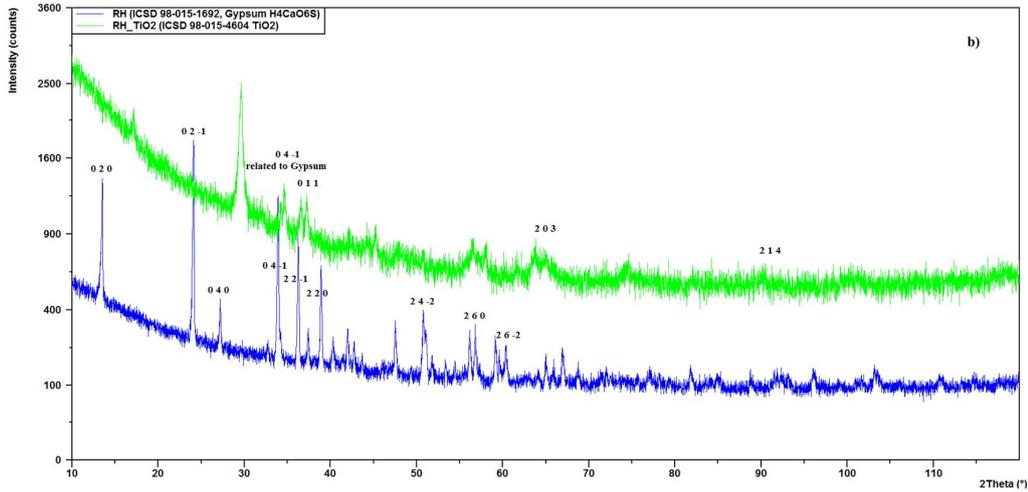
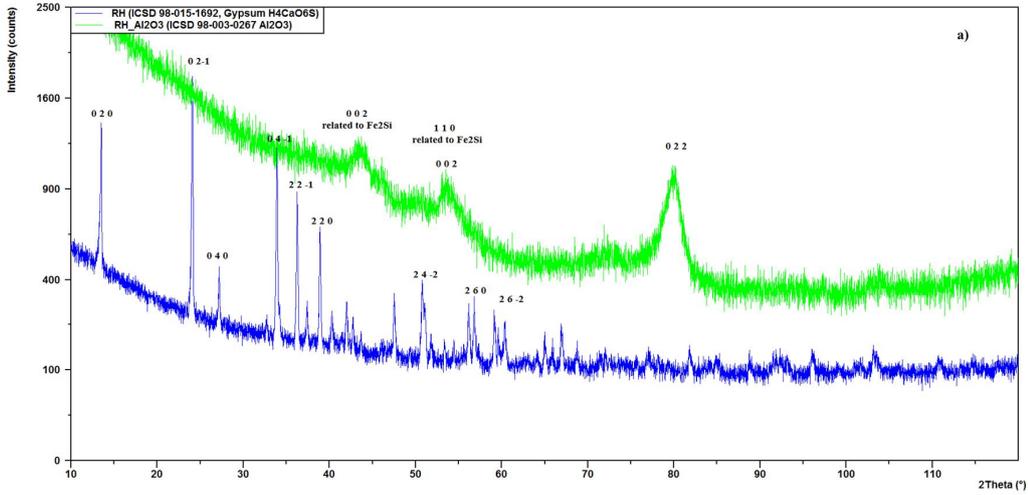


Figure 23. XRD profiles for unmodified and modified RH (Paper VI).

Sorption capacities of both modified sorbents were studied with the initial concentration of 3420 mg L<sup>-1</sup> for SO<sub>4</sub><sup>2-</sup>; 100 mg L<sup>-1</sup> for Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup> and 1000 mg L<sup>-1</sup> for Fe<sup>3+</sup>, in synthetic and real AMDs. The pollutants removal capacities for both modified sorbents increased as follows: SO<sub>4</sub><sup>2-</sup> < Ni<sup>2+</sup> < Zn<sup>2+</sup> < Cu<sup>2+</sup> < Fe<sup>3+</sup>

The similar correlation was observed in other research [215, 255, 256].

Although the percent removal of sulphate ions decreased with ALD modified RH (Paper VI) compared with previous results (Paper I), the time of removal and dosage of sorbents decreased by ten and twenty times, respectively (Table 8). The ions competition in complex synthesis and real AMD can be a case of sulphate ions removal. However, similar results were obtained for metal ions removal with limestone (Paper II) (Table 8). The amount of possible reuse cycles is presented in Table 8. It can be assumed that unmodified sorbents can be used only once. Modification of the surface makes it possible to reuse sorbents for 2-4 times. It was observed that preliminary sorbents granulation also increased the cycles of reuse.

Table 8. Summary table of removal of pollutants from synthetic solutions with unmodified and modified sorbents, and possible amount of adsorption cycles.

Sorbent name	Pollutants removal, %										cycles	
	Fe <sup>3+</sup>	Cu (II)	Zn (II)	Ni (II)	As (III)	As (V)	CN <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	MB		OR
<b>FF</b>	98	99	80	35				92	65			1-2
<b>FF_NaCl</b>	99	99	98	97								3-4
<b>FF_WW</b>	99	99	98	97								3-4
<b>FS</b>	87	98	78	20				54	90			1-2
<b>FS_NaCl</b>	98	98	97	96								2
<b>FS_WW</b>	98	99	97	97								2
<b>DI-60</b>								99	96			1-2
<b>RH</b>					90	99		89	95			1-2
<b>RH_NaOH</b>					97	99						3-4
<b>RH_Al<sub>2</sub>O<sub>3</sub></b>	99	90	80	75	98	99		50				3-4

<b>RH_TiO<sub>2</sub></b>	99	90	80	75	99	99	50	3-4
<b>RH_ZnO</b>	99	85	60	75			70	3-4
<b>SuFe</b>						97		1
<b>SuFe_Al<sub>2</sub>O<sub>3</sub></b>						97		2
<b>CaFe-Cake</b>					40	90	97	1
<b>CaFe_NaOH</b>					70	99		2
<b>CaFe_Al<sub>2</sub>O<sub>3</sub></b>					92	99	97	3
<b>CaFe_TiO<sub>2</sub></b>					95	99		3
<b>L</b>								93 68 1
<b>CW</b>								92 62 1
<b>LCW</b>								100 85 1

#### 5.4 Economic feasibility analysis of novel sorbents

Estimating the cost of water purification methods is an important criteria in the water treatment plants design. Adsorption is one of the cheapest and most effective water treatment techniques. In general, the operational cost is mainly related to the production cost of the adsorbent. The most common commercial adsorbents are activated carbons (500-1000 €/per kg), iron oxide (more than 1000 €/per ton) and activated alumina (300-500 €/per ton), which are relatively expensive. Taking into account the above mentioned aspects, manufacturing alternative highly effective adsorbents in a cost-effective manner is a relevant objective.

The adsorption properties of these materials should be compared with commercial sorbents. The local availability of those materials is an important feature especially in developing countries aiming at ensuring quality water treatment at the lowest cost. Developed countries are also interested in such materials to promote sustainable development. The total cost of the preparation of 1 kg of adsorbents, developed and researched in this work, are presented in Table 9. The price of each sorbent was calculated in accordance with the pretreatment of raw materials and all modification stages.

Electricity consumption was calculated based on the Finnish price, which was 0.5 €kW<sup>-1</sup>. It should be taken into account that during the analysis of the price of the adsorbents developed in this work, the electricity cost in developed countries is much lower. Nonetheless, in the preset case, these sorbents are aimed to be manufactured and applied locally which will reduce transportation costs and thus the final price of adsorbents. A comparative analysis of prices of adsorbents shows that the developed adsorbents are ten times cheaper than commercial ones. The modification with ALD increased the price of 1 kg modified sorbents from 0.5 to 20 times, however the price remains less than that of the commercial sorbents. As can be seen from Table 9, the changes of the parameters of ALD modification, that were implemented in Paper **VI**, allowed the reduction of the cost of the sorbents by several times, compared to the data obtained in Paper **IV**.

Table 9. Cost for preparing 1 kg novel sorbents from limestone, bio- and industrial by-products for mine and process water treatment.

Price, € per kg	FF	FS	CW	RH	DI-60	CaFe-Cake	SuFe
Prewashing and drying,	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Price of raw material	0.56	0.56	0	0	0	0	0
Granulation and drying (IV and V Papers)			1	1		1	1
Total price, €per kg	2.06	2.06	2.50	2.50	1.50	2.50	2.50
Modification with NaCl (II Paper)	0.60	0.60					

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Drying		
	0.50	0.50

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Total price, €per kg	1.66	1.66
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Modification with process water (II Paper)	0	0
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Drying		
	0.50	0.50

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Total price, €per kg	2.56	2.56
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Modification with NaOH and H <sub>2</sub> O <sub>2</sub> (III Paper)	2	2
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Drying		
	0.50	0.50

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Total price, €per kg	4.00	4.00
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Modification with ALD (III Paper)		
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TiO <sub>2</sub>		
Al <sub>2</sub> O <sub>3</sub>	53.20	53.20
	9.50	9.50
Total price, €per kg	55.70	55.70
	11.50	11.50

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Modification  
with ALD  
(VI Paper)

TiO <sub>2</sub>		
Al <sub>2</sub> O <sub>3</sub>	8.80	
ZnO	1.60	
	1.50	
Total price, €per kg	10.30	
	3.10	
	3.00	

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## 6 Conclusions and further research

In this research, various types of low-cost materials were applied for AMD, process water treatment, and the removal of dyes. Three types of limestone, four industrial by-products, and coffee waste as municipal bio-waste were characterized in terms of their chemical compositions and surface properties. The results of these analyses permitted the assumption of the possible physical and chemical capacities of these materials for the sorption of various contaminants under different reaction conditions. For example, it was found that industrial by-products have a certain number of impurities in their composition. Preliminary desorption tests were therefore conducted in acidic solution for several days. The results of these tests showed that a large amount of iron was desorbed into the solution from the surface of iron sand and both sulphate tailings. This led to the conclusion that these materials should be used with caution in the neutralization of AMD and the removal of metal ions from acid solutions. The availability of sulphates on the structure of sulphate tailings permits the conclusion that these by-products can remove arsenic and cyanides with ion-exchange reactions between sulphate and pollutant ions.

After a preliminary sorption test, the detailed study of each sorbent by batch method was conducted.

Two unmodified types of limestone were studied for sulphate and chloride ions removal. It was shown that one of these was more efficient with sulphate and the other for chloride ions. One type of limestone (FF) had a greater number of sites, which participate in the adsorption of chloride during the competition between chloride and sulphate ions, which can be related to the presence of silanolic groups in its composition. Another limestone (FS) and two industrial by-products, such as DI-60 and RH, removed sulphate better than chloride ions. It was suggested that limestone FF can be used for process water treatment with a high capacity for chloride and sulphate ions.

It was shown that even unmodified limestone provides efficient neutralization of AMD from pH 1.5 to neutral after about 6 hours. Limestone showed a good affinity for metal ions, such as Fe(III), Cu(II), Zn(II), besides Ni(II). However, both types of limestone modified with NaCl and alkaline process water showed good adsorption capacity for nickel ions. Modification of limestone with alkaline process water was presented as a novel and efficient method. This method has many advantages over the traditional modification method. In addition to increasing the adsorption capacities of adsorbents, this method makes it possible to reduce the amount of alkaline wastewater by reuse.

Combined sorbents, as co-granules, were formed from limestone and coffee wastes. PVAc was found as an appropriate binder for preparation of co-granules with higher strength that was not reported before. The adsorption capacity of co-granules of coffee wastes and limestone was investigated with acidic (MB) and alkali (OR) dyes. The competing reaction was observed during the removal of both dyes from a complex solution. Meanwhile, future experiments are required to improve the adsorption capacity of co-granules from a complex solution because the chemical composition of the constituents gives hope of producing efficient combined sorbents for both cation and anion removal from mine water. An increase in mine water treatment efficiency, as well as solid waste management and water reuse, provides numerous opportunities for further study.

Based on the theoretical and experimental study, As(III) is more toxic and removed from water solutions with less efficiency than As(V). However, unmodified iron-containing material (RH) showed a great affinity for both forms of arsenic. Sulphate tailing CaFe-Cake showed good properties only after modification with Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> deposited onto the surface of adsorbents with ALD technology. Developed sorbents make it possible to remove directly, with an average pH value of 6–8, both forms of arsenic at an ambient temperature, and consequently those new sorbents can be used for the direct removal of both forms of arsenic, as more environmentally friendly and with lower economic costs, compared to other current methods.

Novel iron-containing sorbents from an industrial solid waste were produced with ALD technology for TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO coating. The optimal sorption parameters were estimated with synthetic AMD. The optimal time (48 h for TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and 10h for RH\_ZnO) and sorbent concentration (2 g L<sup>-1</sup>) were determined by a batch method. The maximum sorption capacities of RH\_Al<sub>2</sub>O<sub>3</sub>, RH\_TiO<sub>2</sub> and RH\_ZnO were around 650, 200, 200, 150 and 100 mmol g<sup>-1</sup> for removal of SO<sub>4</sub><sup>2-</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup>, respectively. The sorption process was carried out using complexation and an ion-exchange mechanism. The deposition of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO on the surface of granulated sorbents sufficiently increased the sorption capacities of raw material for real AMD treatment. The modified sorbents could be used for real AMD treatment with a high capacity for some pollutants. RH\_ZnO show higher adsorption capacities for real AMD treatment and equilibrium was observed even after 10 h, which is about five times faster compared with other modified sorbents. Considering that the lower temperatures were used for deposition of metal oxides in this work and modified with ZnO and Al<sub>2</sub>O<sub>3</sub> sorbents showed perfect capacities for removal of ions from real mine water, with the ALD modification cost lower compared with previously published results.

Modified with ALD granulated sulphate tailings were applied for cyanide removal with a high concentration from synthetic process water. Surface modification with ALD increased the granules strength and sorption capacities of sulphate tailings about three and five times, respectively. Modification of the adsorbent reduced the adsorption time of cyanide ions by 40% and also a smaller adsorbent dose of modified adsorbent is needed for cyanide removal in comparison to unmodified adsorbent. The adsorption capacity was

reached at  $3.5 \text{ mmol g}^{-1}$ , which is several times higher compared to other published data. Developed sorbents with high adsorption capacities for cyanide removal are an efficient opportunity for not only economically underdeveloped countries, but for environmental management on the whole. It was observed that strong nontoxic ferrocyanide complex formed between the sorbents' surface and cyanide ions during the synthetic process water treatment. The second mechanism removal of cyanide was carried out by sorption of ferrocyanide with aluminum oxide coated on the sorbent surface during modification with ALD. This new nontoxic material can be suggested as a complexing agent for removal of trace amounts of radioactive elements, such as caesium and uranium.

The desorption study and reuse of unmodified and modified sorbents shows that ALD modification makes it possible to increase the reuse of sorbents to 3-4 times. Other modification methods also make it possible to use sorbents repeatedly, but the number of repetitions is only 2-3 times.

Overall, according to the comparative analysis of prices for commercial sorbents and the ones developed during this work, it can be confirmed that the novel new sorbents are more cost effective than the commercial ones. According to the obtained results in this work, the developed sorbents can be recommended for further experiments for real AMD and process water treatment by columns. Column experiments make it possible to select better parameters for simultaneous removal of sulphate and metal ions from AMD and sulphate and chloride ions from process water.



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## Appendix A: Additional tables

Table A 1. Data of solid wastes amount, their reusing, water consumption and use of chemical dangerous for the environment was collected from Finnish Network for Sustainable Mining official site.

Dragon Mining Oy	Boliden Kevitsa	Company Name
Au	Boliden Kevitsa	Agnico Eagle Finland Oy
	Cu, Au, Zn	Au
	Ni, Cu, Au, Pt, Pl	Specialisation
0.53	1	37
	0.42 (100% wt, tailings), 50%taili	30.3
	0.99	1.8
	0.99	0.99
	19.6% is reused as backfill in underground mines	Volume of solid wastes, Mt
Not reported	100% reused	Reusing of solid wastes, %
1.2	2.3	5
	51	28
	26.4	Water consumption M <sup>3</sup>
	3.6	Raw water, %
0	CuSO <sub>4</sub> 269t, ZnSO <sub>4</sub> 272t, fuels 2539 t	Toxic chemicals
	Sodium ethyl xanthate 270t, Sodium isopropyl xanthate 22t, potassium ethyl xanthate 135 t	CN <sup>-</sup> , 186t

Yara		Endomines			
Suomi Oy	Terrafame Oy	Pyhäsalmi Mine Oy	Outokumpu Chrome Oy	Nordkalk	
apatite, lime	Ni, Zn	Cu, Fe, Zn	Cr	limestone	Au
30.8 Mt	8.5 Mt	1.4	3.04	2.6	1.3
27.5 (gangue 63.2%, 29% of gangue is reused)	4,676,300 tonnes	0.46 (tailings 100%)	1.0 (tailings 83.4%, shear rock 16.6%)	0.17 tailings	1.2 (73% wr, tailings 26.5%, topsoil 0.5%)
Not reported	Not reported	Not reported	100% is reused	Not reported	53.0% of waste rock is utilized
11	1	5.5	2.7	1.6	1.1
20		68	6.25		5.9
Flotation chemical s 1363 t	H <sub>2</sub> SO <sub>4</sub> 53000 t; liquid N <sub>2</sub> 829.6 t;	CuSO <sub>4</sub> 388 t; Zn SO <sub>4</sub> 549 t; CN <sup>-</sup> 8.4 t	light fuel oil 1658 t; heavy fuel oil 238 t; diesel 150 t	0	Danafloat 507 6.3t; potassium amyl xanthate (PAX) 1-percent solution 5.6t; copper sulphate, 1-percent solution 2.5t



Al-O2	Al-O	Ti-O2	N-H	Si-O-H	R-O-H	Ca-O	R=C=O	R=C=O
-	-	-	-	3200-	-	2512	-	-
-	-	-	3294	2923	2853	-	1743	1654
-	-	-	+	+	2853	2512	1743	-
-	-	-	-	2874-	3329	-	1798	-
-	-	-	-	2876-	3457	2513	1797	1627
-	-	-	-	2984	3468	2513	1797	-
-	-	-	-	2880	-	2514	1797	-
-	-	-	-	-	3455	2516	1800	1637
-	-	-	-	-	3480	2513	1797	1633

Ca-O	Ca-C≡O <sub>3</sub>	C-O	S=O <sub>2</sub>	Si-O-Si	Si-O	Ca-C≡O <sub>3</sub>	C-H	C≡O <sub>3</sub>	Compound
-	-	-	430-538	-	830-1100	875	-	712	DI-60
-	1430	1120-1160	458-466	660	-	876	-	-	RH
-	1430	1120-1160	466-473	600-661	-	876	-	-	RH_NaOH
-	1430	1120-1160	466-473	600-661	-	876	-	-	RH_Al2O3
-	1430	1120-1160	466-473	600-661	-	876	-	-	RH_TiO2
-	-	-	473-466	661-600	-	-	-	-	CaFe-Cake
-	-	-	466-473	600-661	-	-	-	-	CaFe- Cake_NaOH
-	-	-	466-473	600-661	-	-	-	-	CaFe- Cake_Al2O3
-	-	-	466-473	600-661	-	-	-	-	CaFe- Cake_TiO2
-	-	-	473-466	661-600	-	-	-	-	SuFe

Al-O2	Al-O	Ti-O2	N-H	Si-O-H	R-O-H	Ca-O	R-C=O	R-C=O
-	-	-	-	3620-	3410	2515	-	-
-	-	-	-	3200-	3450-	-	-	-
-	-	-	-	3700	3480	-	-	-
-	-	-	-	-	1690	-	-	-
610-611	980-1000	-	-	-	1620	-	-	-
-	-	450-800	-	-	1620-	-	-	-
-	-	-	-	-	1690	-	-	-
-	-	-	-	-	1620-	-	-	-
-	-	-	-	-	1690	-	-	-
610-611	980-1000	-	-	-	1620-	-	-	-
-	-	450-800	-	-	1690	-	-	-
-	-	-	-	-	1620-	-	-	-
-	-	-	-	-	1690	-	-	-

## **Publication I**

Iakovleva, E., Mäkilä, E., Salonen, J., Sitarz, M., Sillanpää, M.

**Industrial products and wastes as adsorbents for sulphate and chloride removal from synthetic alkaline solution and mine process water**

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## Industrial products and wastes as adsorbents for sulphate and chloride removal from synthetic alkaline solution and mine process water



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### HIGHLIGHTS

- The solid wastes and limestone were tested to removal of sulphates and chlorides.
- Their alkaline mine process water treatment capacity were compare.
- Tests were conducted with synthetic and real mining process water.

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### ABSTRACT

Two limestones and two solid wastes were tested as adsorbents for chloride and sulphate ion removal from synthetic and real alkaline process mining water. The composition and surface structure of the adsorbents were analysed by ED-XRF, XRD, SEM and MIR spectroscopy and the nitrogen adsorption method. The optimal adsorption time and amount of adsorbent were determined by batch analysis with an anion concentration of 20 mg/L. In synthetic solution adsorbents removed 99% of  $\text{SO}_4^{2-}$  and 96% of  $\text{Cl}^-$  and in real process water the removal rate was 85% and 74% for  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , respectively. It was found that equilibrium could successfully be fitted to the Langmuir, Toth and BiLangmuir adsorption isotherms.

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### 1. Introduction

Water is a vital factor in many industrial processes, including mining. Water is much more than a medium for cooling, creating steam, transport or cleaning; it is often an essential component of the process or product [1,2].

As water shortages increase, so does the need to use unconventional supplies such as seawater or wastewater for industrial processes. The water deficit may also be met by energy intensive water recovery systems such as cooling water systems for industrial processes. With the right treatment technologies, water can be reused over several cycles which helps to bridge the gap between water supply and demand [1,3].

Process water treatment problems can be solved using a variety of treatment technologies, such as the electro-chemical method

[4–7], biological degradation [8], membrane filtration [9,10], coagulation [11–13], adsorption or ion exchange [10,14–17]. Low-cost process water recovery is one of the most significant issues facing industry today. Ion exchange is considered to be one of the best and most efficient methods for removing anions from water due to its high efficiency, simplicity and low cost.

Process water content depends on the type of industrial process. Alkaline mining process waters require special treatment mainly due to the combination of a high concentration of anions, such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , and a low concentration of metal ions [1].

The removal of anions from highly alkaline process water is expensive and quite challenging. Sulphate and chloride removal is often accomplished thorough an ion exchange mechanism with limestone [10,18,19]. This process involves ion exchange between  $\text{OH}^-$  on the adsorbent surface and removed anions. Natural lime is often used for process and wastewater treatment [20–24]. Sulphate removal from water by adsorption has not always been successful, for example, in A. Darbi et al.'s research on sulphate removal from drinking and groundwater by bentonite [10]. Solid waste, however, is similar in composition to limestone and has a demonstrably high capacity to adsorb anions from wastewaters,

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yet it has received the least amount of research attention [25,26]. This work took a novel approach to the removal of sulphate and chloride ions from alkaline process water. Two limestone products and two solid wastes from various industries were used as adsorbents. Two challenges were faced; real mining process water treatment forms  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , and it is difficult to reuse solid wastes. The adsorption capacities of unmodified solid wastes were studied and the effect of both competing ions on the adsorption process was also investigated.

## 2. Materials and methods

### 2.1. Materials

Two solid wastes, iron sand (RH) and pulp and paper waste (DI-60), were used. RH and DI-60 were obtained from Ekokem Company and Metsä Tissue Corporation (Finland), respectively. Two limestone products, filter sand (FS) and flotation fines (FF), obtained from Nordkalk Corporation (Finland) were applied as adsorbents. Before use all the adsorbents were milled, washed with distilled water, and oven dried for 12 h at 80 °C. The dried adsorbents were stored in glass flasks. Sodium sulphate (Merck) and sodium chloride (Sigma–Aldrich) were used for the preparation of sulphate and chloride solutions. Solution pH adjustment was carried out with 0.1 M NaOH and HCl (Merck). Milli-Q ultrapure water was used to prepare the stock and dilute solutions.

### 2.2. Characterisation of adsorbents

The particle size distribution and zeta potential of the samples were determined using dispersion analyser LUMISizer 610/611 (LUM GmbH) and ZetaSizer Nano ZS (Malvern Instruments Ltd., UK), respectively. 1.5 g of solid sample was conditioned in 50 ml of 0.001 M NaCl solutions at various final pH for 24 h in a shaking bath. Zeta potential was calculated from electrophoretic mobility measurements using the Smoluchowski equation; each value was an average of approximately 20 measurements. The pH of the suspension was adjusted using 0.01–1.0 M HCl. All solutions were prepared using ultrapure water and solution pH was determined with a pH Electrode SenTix 81.

The physical structure of the samples was analysed with  $\text{N}_2$  adsorption at  $-196$  °C with TriStar 3000 (Micromeritics Inc.). The specific surface area was calculated from the adsorption isotherm using Brunauer–Emmett–Teller (BET) theory [27].

Infrared spectroscopic measurements in middle infrared (MIR) spectra of adsorbents were recorded with a Bruker Vertex 70v spectrometer. MIR: transmission technique, samples were prepared by the standard KBr pellets method. Spectra were collected in the mid infrared region ( $4000$ – $400$   $\text{cm}^{-1}$ ) averaging 124 scans with  $4$   $\text{cm}^{-1}$  resolution. Samples were prepared according to the standard KBr pellets method.

The microstructure of the materials were examined using scanning electron microscopes (SEM, Nova Nano SEM 200, FEI Company and Hitachi S-4800), with energy dispersive X-ray spectroscopy (EDX, EDAX) for micro-area analysis. The experiment was carried out at low vacuum conditions in secondary electron mode and samples were covered with a layer of gold.

X-ray diffraction (XRD) data were collected with a PANalytical Empyrean powder diffractometer using  $\text{Cu K}\alpha$  radiation. The configuration was a standard Bragg–Brentano ( $\theta/\theta$ ) reflection setup with a Ni-filter placed in front of the detector. The measurements were performed in a  $\theta$  scanning range of  $3$ – $90^\circ$  with a  $0.007^\circ$  step size and 69 s of measurement time for each step at ambient temperature and pressure.

The chemical composition of materials was determined by an energy dispersive X-ray fluorescent (ED XRF) analyser X-Art (Joint Stock Company Comita, St. Petersburg, Russia) [28].

### 2.3. Batch adsorption experiments

Ion exchange tests were conducted by mixing a known weight of FF, FS, RH and DI-60 with 15 ml of synthetic sulphate and chloride ions in alkaline solution. The ion concentrations of the synthetic solution ranged from 20 to 2000 mg/l. The solutions were shaken in a mechanical shaker ST5 (CAT M.Zipper GmbH, Staufen, Germany) from 1 to 720 h. 2 ml samples of the solution were taken from flasks at known time intervals and then filtered using a  $0.20$   $\mu\text{m}$  diameter polypropylene syringe filter. All tests were performed at ambient temperature ( $22 \pm 2$  °C) and pressure. The final concentrations of sulphate and chloride anions in the solutions were determined with high-performance liquid chromatography (HPLC). A Shimadzu HPLC equipped with a conductivity detector (Shimadzu Model CDD-10A) was used (column:  $4.0$  mm ID  $\times$   $250$  mL Shodex IC SI-50 4E; mobile phase: solution of  $3.2$  mM  $\text{Na}_2\text{CO}_3$  and  $1$  mM  $\text{NaHCO}_3$  in ultrapure water; flow rate:  $0.7$  ml/min; temperature: ambient). Adsorption was calculated as:

$$A = \frac{C_i - C_t}{C_i} * 100, \quad (1)$$

where A is adsorption (%),  $C_i$  and  $C_t$  (mg/l) are the ion concentrations in the initial and post treatment solutions, respectively.

#### 2.3.1. Sorbent optimisation

The optimum amount of sorbent was determined by mixing 15 ml of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  synthetic solutions with different amounts of sorbent (2, 5, 10, 20, 30, 40, and 50 g/l). Each result is the average of three samples.

#### 2.3.2. Contact time optimisation

The optimum contact time was determined by mixing 40 g/l of FF, FS DI-60, and RH in 15 ml flasks tumbled at 100 rpm from 1 to 720 h with an initial concentration of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  of 20 mg/L. Samples were taken after 1, 2, 4, 8, 24, 48, 96, 120, 240, 480, and 720 h.

## 3. Results and discussion

### 3.1. Adsorbent characterisation

The chemical compositions of the studied materials are shown in Table 1. These results were obtained by ED-XRF and XRD. Each material contains calcium (12–37%). RH contains more than 17% sulphur. Such a high sulphur concentration could affect the removal of sulphate ions, because sulphur on the adsorbent surface can initiate competition in the ion exchange process [13]. All chemical compounds structurally similar to calcite should have high adsorptive properties for sulphate and chloride ions.

The particle size distribution and specific surface area of the original materials are shown in Table 2. The particle size of FS and FF adsorbents are approximately the same (approximately 500  $\mu\text{m}$ ). The particle size for DI-60 is about three times larger ( $\approx 1500$   $\mu\text{m}$ ), and for RH it is four times smaller ( $\approx 125$   $\mu\text{m}$ ). Unexpectedly, the active surface area of RH is significantly larger than that of other adsorbents, which may be explained by its relatively high porosity. The results of spectroscopic analysis of the adsorbent are shown in Fig. 1. Each image presents two spectra, before (1) and after (2) washing and drying the adsorbents. As can be seen, pretreatment does not change the distribution and location

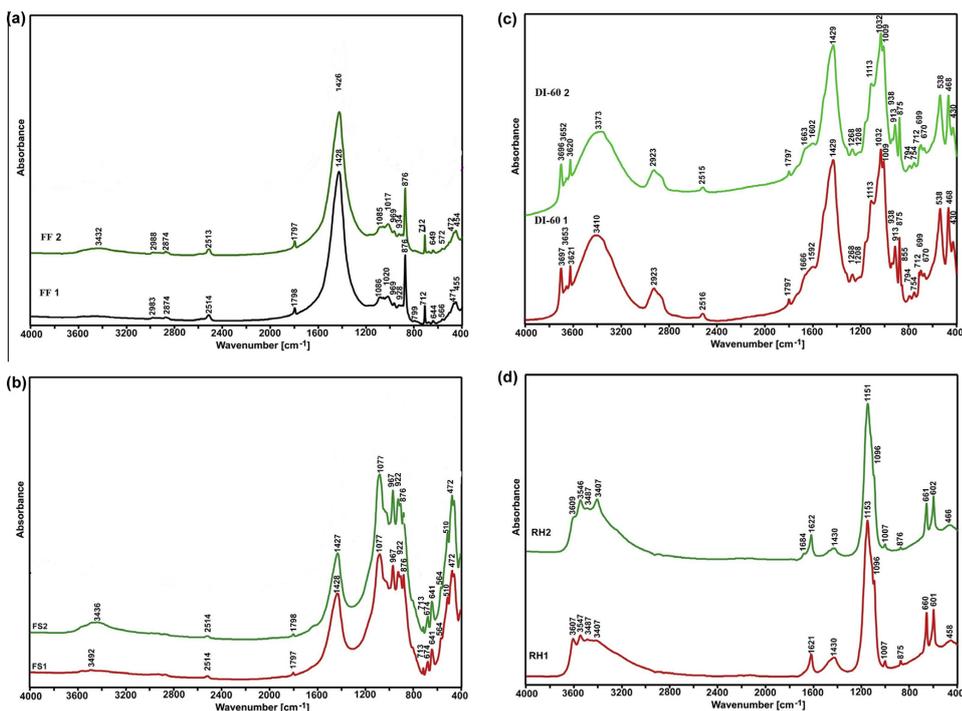
**Table 1**  
Chemical composition of adsorbents (XRF and XRD analysis).

Element (%)	FS	FF	RH	DI-60
Ca	21.3	37.2	14.4	12.0
Fe	1.07	0.43	7.2	0.46
K	0.254	0.241	0.3	0.329
Mn	0.0216	0.0100	0.27	0.0043
S	0.100	0.105	17.6	0.039
Si	42	10.3	0.2	4.4
Sr	0.026	0.074	0.021	0.016
Ti	0.052	0.042	2.3	0.059
Rb	0.0013	0.0005	0.001	0.0020
Compounds formula	CaMgSi <sub>2</sub> O <sub>6</sub> CaCO <sub>3</sub> (K,H <sub>3</sub> O)Al <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub>	(K,H <sub>3</sub> O)Al <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub> CaSiO <sub>3</sub>	Ca(SO <sub>4</sub> )x(H <sub>2</sub> O) Ca(CO <sub>3</sub> )	Ca(CO <sub>3</sub> ) Al <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> )(OH) <sub>4</sub>
Compounds name	Diopside Calcite	Illite Parawollastonite	Calcium sulphate hydrate Calcite	Calcite Kaolinite

**Table 2**  
Characteristic of the surface of adsorbents.

Name of adsorbent	Particle size (μm)	Specific surface area (m <sup>2</sup> /g)	Zeta-potential (mV) pH = 11
FF	599	1.35	0
FS	451	1.82	-25
RH	180	62.5	-7
DI-60	1390	3.29	-14

of functional groups on the adsorbent surface. Spectroscopic studies in the mid-infrared (MIR) region confirm the results of the XRD studies. The spectra of each adsorbent show two additional bands characteristic of water molecules, at about 1620–1640 and 3450–3480 cm<sup>-1</sup> (Fig. 1). The OH<sup>-</sup> stretch vibrations of the SiOH group adsorb at 3200–3700 cm<sup>-1</sup>, and strong Si–O bands at 830–1100 cm<sup>-1</sup> are observed in the spectra of DI-60 (Fig. 1c). The spectra of sulphones show strong adsorption bands at 1120–1160 cm<sup>-1</sup> for RH (Fig. 1d). These bands arise from symmetric SO<sub>2</sub> [29]. Adsorbent



**Fig. 1.** MID spectrums of FF (a), FS (b), DI-60 (c) and RH (d).

surfaces were studied by XRD (Table 1) and MRI (Table 2). Both methods showed the presence of sulphur on the RH surface and silicone on the FF, FS, and DI-60 surfaces.

SEM images are presented in Fig. 2. The structure of RH is the finest, which is partly due to its highly specific surface area. This is confirmed by data on the active surface of adsorbents obtained by the BET method (Table 2); RH has the largest active surface area.

### 3.2. Optimisation of adsorbent amount and ion competition

The optimal amount of adsorbent for chloride and sulphate removal with an initial concentration of 20 mg/l is shown in Fig. 3. This indicates that initially  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  removal increased with increasing amounts of adsorbent, with equilibrium reached at an adsorbent concentration of 40 g/l. The highest removal percentage of sulphate (99%) was achieved with DI-60; sulphate removal was 88.5%, 90%, and 92% with RH, FS, and FF, respectively. Kolics et al. described the competition between sulphates and chlorides during the adsorption on aluminium [30]. They found that chlorides were adsorbed better than sulphates. Our experiments show that in case of adsorption with DI-60 and RH, ion competition was not observed:  $\text{Cl}^-$  ion removal reached approximately 96% with DI-60 and RH. With limestone-like adsorbents (FF and FS), however, this was not the case. Chloride removal was substantially lower than that of sulphates; only 66% and 54% were removed with FF

and FS, respectively. Chloride was adsorbed better than sulphate with RH, which had the highest adsorption capacity. This phenomenon can be considered as one of the factors influencing for better adsorption of  $\text{Cl}^-$  ions than  $\text{SO}_4^{2-}$  ions, because chloride ions are smaller than sulphate [12]. Since RH has a porous surface structure it was better able to adsorb chloride.

### 3.3. Contact time optimisation

It was found that the removal percentage increases with time, reaching the maximum at 480 h (Fig. 4). The maximum amount of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  adsorbed to FF, FS, DI-60, and RH was 65% and 92%; 90% and 54%; 96% and 99%; 95% and 89%, respectively. It was observed that the ion exchange process does not change the initial pH of the solution [12,13].

### 3.4. Adsorption isotherms

Equilibrium of the adsorbate sorption on the adsorbent surface at a constant temperature is described with empirical models known as adsorption isotherms. Mathematical modelling of adsorption isotherms gives us information about the adsorption mechanism. A rigorous theory of adsorption isotherms was proposed by Langmuir for monolayer adsorption on specific homogeneous sites without attractive forces between the adsorbate

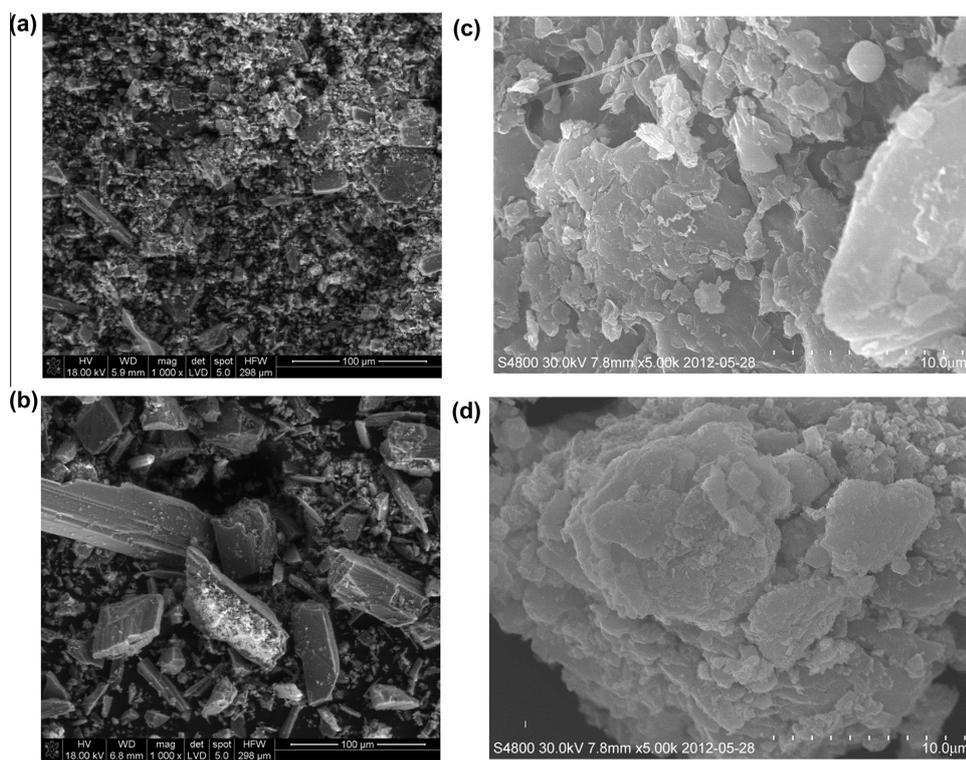


Fig. 2. SEM images of FF (a), FS (b), DI-60 (c) and RH (d).

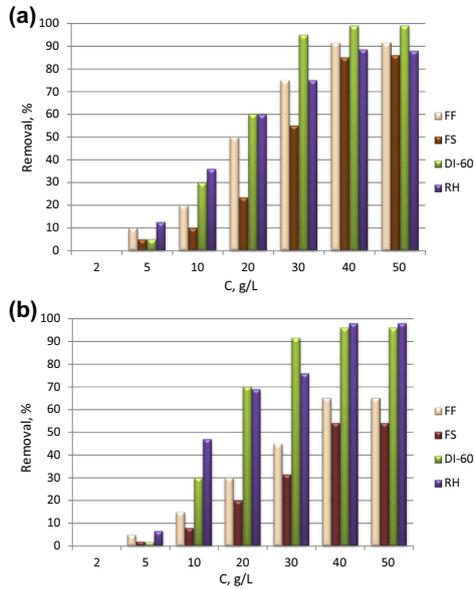


Fig. 3. Effect of dosage of FF, FS, DI-60 and RH for removal of  $\text{SO}_4^{2-}$  (a) and  $\text{Cl}^-$  (b) with initial concentration of ions 20 mg/L.

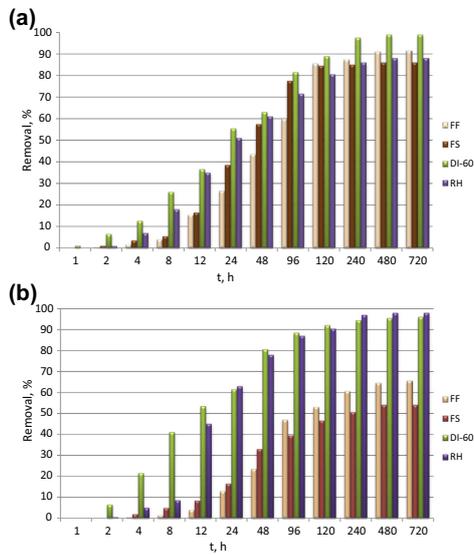


Fig. 4. Kinetics of  $\text{SO}_4^{2-}$  (a) and  $\text{Cl}^-$  (b) ions removal with FF, FS, DI-60 and RH, at pH 12. Initial ions concentration is 20 mg/L.

molecules and their mobility along the surface [31]. Further development of the theory eliminates assumptions made by Langmuir. Since the adsorbents have a complex structure, homogeneous as well as heterogeneous adsorption mechanisms are possible. Two-parameter Langmuir isotherm (Eq. (2)) was used to describe a classic case of adsorption in a homogeneous system. Three-parameter (Toth Eq. (3)) and four-parameter (BiLangmuir Eq. (4)) models were selected to describe adsorption process in the case of a heterogeneous system:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = \frac{q_m C_e}{(a_T + C_e^{m_T})^{1/m_T}} \quad (3)$$

$$q_e = \frac{q_{m1} K_{L1} C_e}{1 + K_{L1} C_e} + \frac{q_{m2} K_{L2} C_e}{1 + K_{L2} C_e} \quad (4)$$

where  $q_e$  and  $C_e$  are anion-exchange capacity (mmol/g) and concentration of anions in the solution (mmol/L) at equilibrium, respectively;  $q_m$  is the maximum uptake capacity;  $K_L$  is Langmuir,  $K_{L1}$  and  $K_{L2}$  are the BiLangmuir constants related to the energy of anion-exchange;  $a_T$  is the adsorptive potential constant (mmol/L) and  $m_T$  the heterogeneity factor of the Toth isotherm.

Isotherm parameters were calculated with minimisation of the error distribution between experimental and predicted data by Marquardt's percent standard deviation (MPSD):

$$\sum_{i=1}^n \left( \frac{q_{e, \text{exp}} - q_{e, \text{calc}}}{q_{e, \text{exp}}} \right)^2 \quad (5)$$

The Langmuir isotherm is the most frequently used theory [32]. A basic assumption is that one molecule occupies a site and no further adsorption can take place at that site. In the other words, at equilibrium, saturation point is reached where no further adsorption can occur. Parameter  $q_m$  shows the number of adsorbent sites that actively interact with anions of the sorbate. The  $K$  coefficient is the affinity between sorbate and adsorbent. According to Langmuir theory the affinity between the studied adsorbents and adsorbates is:

$$\text{RH; FS; DI-60: } \text{SO}_4^{2-} > \text{Cl}^-$$

$$\text{FF: } \text{Cl}^- \geq \text{SO}_4^{2-}$$

The number of sites ( $q_m$ ) which participate in the adsorption of  $\text{Cl}^-$  is much greater than in the adsorption of  $\text{SO}_4^{2-}$ . This could be because chloride molecules are smaller than sulphate molecules; Langmuir theory implies that the amount of adsorbed chloride will be much greater [33]. Yet since the affinity ( $K$ ) of adsorbents to sulphate ions is higher, better removal of sulphate could be observed with FF, FS and DI-60. Chloride was more effectively removed with RH, since its pores are significantly larger than those of other sorbents (Table 2). The combination of large RH pores and small chloride ions allows for near complete chloride removal (Fig. 3b). Comparison with published data was difficult, because very few studies of the concurrent removal of chloride and sulphate ions exist; however, Hendricks found the same relationship between sulphate and chloride ions [34].

The Toth isotherm (three-parameter equation) is an adaptation of Langmuir theory to allow for a heterogeneous system. The Toth equation is obtained by adding two parameters, ( $a_T$ ) and ( $m_T$ ), to the Langmuir equation [35]. Those two parameters allow for heterogeneity of system. The Toth isotherm fits adsorption of both anions with DI-60 slightly better than the Langmuir one (Fig. 5), apparently because DI-60 is more heterogeneous.

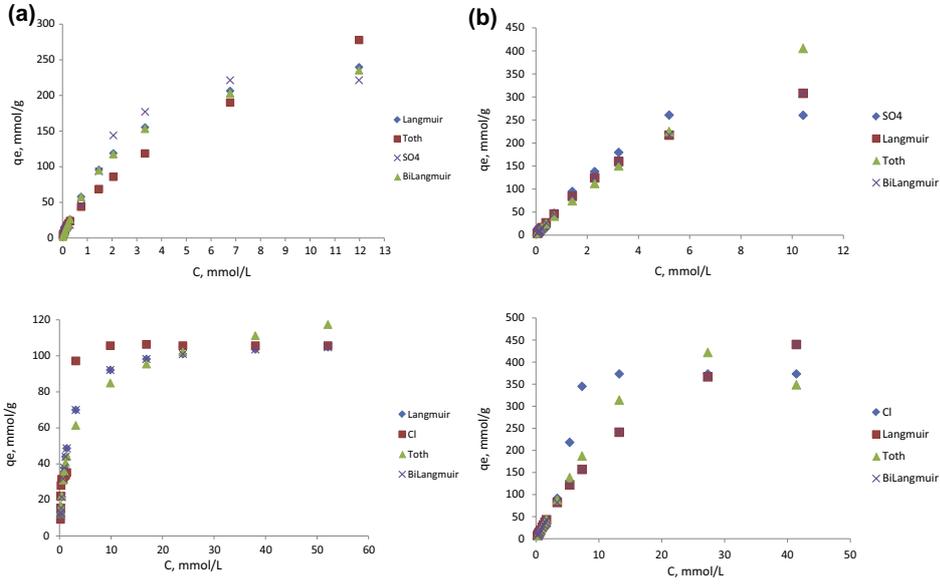


Fig. 5. Adsorption isotherms for  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  with FF (a), FS (b), DI-60 (c) and RH (d) (40 g/L). Contact time is 480 h, initial ions concentration is 20 mg/L.

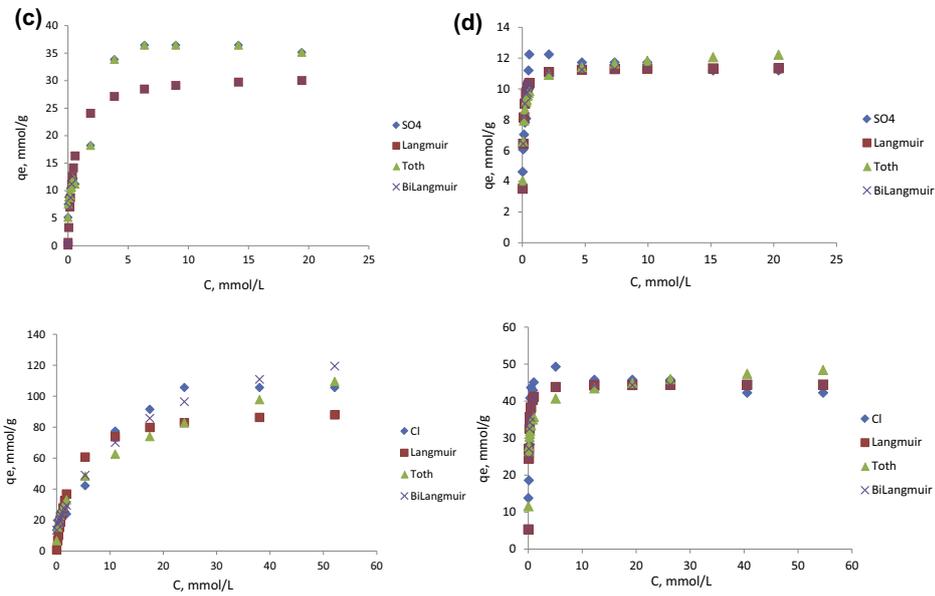
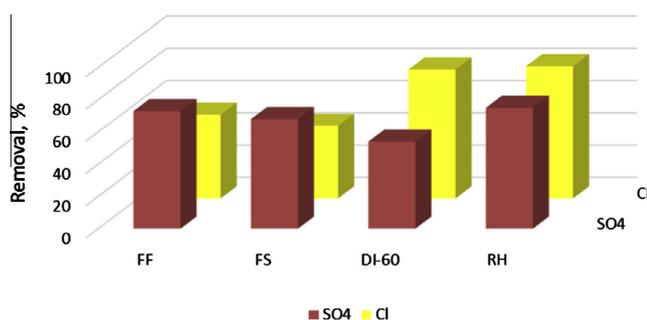


Fig. 5 (continued)

**Table 3**  
Isotherm parameters for FS, FF, DI-60 and RH during adsorption process of anions from synthetic solution.

		$C_e$ (mmol/L)	$q_{e, exp}$ (mmol/g)	$q_{e, model}$ (mmol/g)	$q_m$ (mmol/g)	$K_L$ (L/mmol)	$R^2$		
<i>Langmuir</i>									
FF	$SO_4^{2-}$	6.77	221	215	285	0.453	0.998		
	$Cl^-$	16.9	106	104	115	0.583	0.984		
FS	$SO_4^{2-}$	5.2	261	217	526	0.135	0.998		
	$Cl^-$	13.2	373	241	718	0.038	0.997		
DI-60	$SO_4^{2-}$	8.96	29.13	36.46	30.85	1.895	0.928		
	$Cl^-$	23.94	105	83	93	0.355	0.928		
RH	$SO_4^{2-}$	4.74	11.72	11.24	11.37	18.68	0.728		
	$Cl^-$	5.07	49.3	43.8	44.5	12.06	0.757		
		$C_e$ (mmol/L)	$q_{e, exp}$ (mmol/g)	$q_{e, model}$ (mmol/g)	$K$ (L/mmol)	$a_T$ (mmol/L)	$m_T$	$R^2$	
<i>Toth</i>									
FF	$SO_4^{2-}$	6.8	221.4	190.2	10,936	0.019	0.338	0.995	
	$Cl^-$	16.9	106.3	102.2	141.5	0.821	0.854	0.997	
FS	$SO_4^{2-}$	5.2	260.7	225	114.5	0.207	0.177	0.999	
	$Cl^-$	13.2	373.3	314.1	35.8	10,149	2.67	0.997	
DI-60	$SO_4^{2-}$	6.4	36.5	25.9	29.2	14.3	0.941	0.985	
	$Cl^-$	23.9	105.6	82.8	60,389	0.001	0.641	0.981	
RH	$SO_4^{2-}$	0.55	12.2	9.9	616	0.035	0.957	0.897	
	$Cl^-$	5.07	49.3	40.7	3810	0.019	0.929	0.961	
		$C_e$ (mmol/L)	$q_{e, exp}$ (mmol/g)	$q_{e, model}$ (mmol/g)	$q_{m1}$ (mmol/g)	$q_{m2}$ (mmol/g)	$K_1$ (L/mmol)	$K_2$ (L/mmol)	$R^2$
<i>BiLangmuir</i>									
FF	$SO_4^{2-}$	6.8	221.4	218	118.5	166.4	0.162	0.101	0.995
	$Cl^-$	16.9	106.3	98.2	95	32.9	0.133	16.7	0.989
FS	$SO_4^{2-}$	5.2	260.7	217.2	139.8	123.5	0.089	0.033	0.998
	$Cl^-$	13.2	373.3	241.2	271.4	120.5	0.038	0.213	0.997
DI-60	$SO_4^{2-}$	6.4	36.5	28.5	37.7	8.03	0.257	78.9	0.991
	$Cl^-$	23.9	105.6	96.4	17.6	132.1	140.9	0.154	0.991
RH	$SO_4^{2-}$	0.55	12.2	10.4	11.0	0.106	20.7	0.107	0.775
	$Cl^-$	5.07	49.3	43.8	3.7	42.3	1.7	14.1	0.825



**Fig. 6.** Removal of  $SO_4^{2-}$  and  $Cl^-$  with FF, FS, DI-60 and RH from real process water. Initial concentration of  $SO_4^{2-}$  and  $Cl^-$  was 30 and 2.5 g/L, respectively. Amount of adsorbents is 40 g/L.

The BiLangmuir isotherm assumes that the surface contains two divergent active sites having different affinities towards the target compound [36]. BiLangmuir isotherms for both anions fit better to the FF, FS, and DI-60 adsorbents (Fig. 5), possibly because these adsorbents have at least two anion adsorption sites. The BiLangmuir model was rather efficient in reflecting the adsorption process.

### 3.5. Anion removal from real process water

Chloride and sulphate ion concentrations in real mining process water were 2.5 and 30 g/L, respectively. The chemical composition of the process water is presented in Table 3. The removal of anions was conducted by batch method at ambient temperature for 480 h with 40 g/L of each adsorbent. The experiment was carried out in three steps, using fresh adsorbent at each stage, and the total pro-

cess took 60 days. Chloride removal with FF, FS, DI-60, and RH was 52%, 45%, 80%, and 82%, respectively; sulphate removal with the same adsorbents was 73%, 68%, 54%, and 75%, respectively (Fig. 6). Increasing adsorbent concentration and time did not increase anion removal, as might be expected. Equilibrium occurred at the optimal adsorption time (480 h) and adsorbent concentration (40 g/L). The lower removal of anions from the real process water could be due to its complex composition. It contains other ions beside  $Cl^-$  and  $SO_4^{2-}$  which can act as competitors during the adsorption process.

## 4. Conclusions

The efficiency of four solid wastes used as anion exchangers to remove chloride and sulphate ions from alkaline mining process water was investigated. The optimal adsorption parameters were

estimated with synthetic solution. The optimal time (480 h) and adsorbent concentration (40 g/L) were determined by batch method. The maximum adsorption capacities of FF, FS, DI-60 and RH ranged from 221, 261, 29 and 12 mmol/g for  $\text{SO}_4^{2-}$  removal, to 106, 373, 105 and 49 mmol/g for  $\text{Cl}^-$  removal, respectively. All three isotherms (Langmuir; Toth; BiLangmuir) described both anion exchange processes well. The FF and FS removed more than 50% of both anions and RH removed approximately 80% of sulphate ions. The DI-60 removed more than 80% of both sulphate and chloride ions. All adsorbents could be used industrially for alkaline process water treatment: although the removal process is long (around 2 months), the treatment requires a minimum amount of energy and is low in cost due to the use of solid wastes as adsorbents.

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## **Publication II**

Iakovleva, E., Mäkilä, E., Salonen, J., Sitarz, M., Wang, S., Sillanpää, M.  
**Acid mine drainage (AMD) treatment: Neutralization and toxic elements removal with  
unmodified and modified limestone**

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## Acid mine drainage (AMD) treatment: Neutralization and toxic elements removal with unmodified and modified limestone



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### ABSTRACT

Limestones and their modifications from Nordkalk Corporation (Finland) flotation fines (FF) and filter sand (FS) as potential adsorbents for AMD treatment and wastewater purification from Cu, Fe, Zn and Ni ions were studied. Limestones were capable of binding significant amounts of Cu and Fe from synthetic AMD solutions and wastewater, while unmodified limestones were not good for Zn and Ni removal. Two methods of surface area modification were suggested. The first one with 2 M solution of NaCl and the second one with wastewater from Norilsk Nickel Harjavalta. The structure of materials and their surface area were characterized by SEM, EDX, MIR spectroscopy and nitrogen adsorption methods. Optimal amount of adsorbents for different model and real solutions was found. Adsorption kinetics showed that the adsorption equilibrium was reached within approximately 8 h. The kinetic data fits to a pseudo second order model with correlation coefficients greater than 0.999. The adsorption capacity was the highest at solution pH range of 6–7. Langmuir, Toth and Sips models were used to fit the adsorption isotherms. Based on the parameters calculated from models, the adsorption capacity decreased in the order of Cu > Fe > Zn > Ni for FF and Fe > Cu > Zn > Ni for FS. The research showed that the proposed modified limestones can be successfully used for AMD neutralization and removal of Cu(II), Fe(III), Zn(II) and Ni(II).

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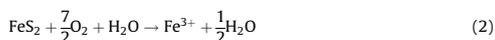
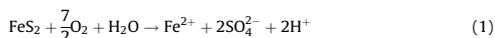
### 1. Introduction

Each year global mining industry produces several billion tonnes of solid inorganic wastes or by-products, including liquid wastes through its mineral processing and metal production operations (Charbonier, 2001; Akcil and Koldas, 2006).

Composition of solid and liquid wastes in mining varies greatly depending on the process, methods of enrichments and treatments of ores. Mine waters can be categorized into three groups according to their acid–base properties: acid mine drainage (AMD) with pH 6 and below, neutral mine drainage with pH 6 and above, and saline mine drainage with pH above 6 containing more than 1000 mg L<sup>-1</sup> of carbonates (Wolkersdorfer, 2008). AMD is formed by the

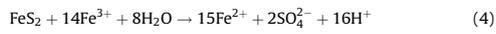
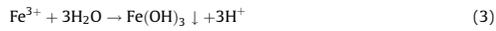
decomposition of pyrites (Wolkersdorfer, 2008). After hydrothermal deposits of copper, lead, zinc, tin, and other nonferrous/colored metals into pyrites, substantial amounts of them are sent to landfill as they are economically inefficient to treat further.

Process of pyrites decomposition is hazardous because of mining water acidification and also because a large number of various toxic trace elements are released during the process, these are Ag, As, Bi, Cd, Co, Cu, Hg, Mo, Ni, Pb, Ru, Sb, Se, Sn, Te, and Zn (Abraitis et al., 2004; Chandra and Gerson, 2010; Deditius et al., 2011). The pyrite oxidation process has been extensively studied and can be summarized by the following reactions:



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First, the oxidation of sulfide to sulfate is observed by the action of water and oxygen leaving Fe (II) unoxidized (Eq. (1)). Then the oxidation of Fe (II) to Fe (III) occurs (Eq. (2)) and part of Fe (III) is precipitated as ferric hydroxide (III) (Eq. (3)) while the other part

reacts with pyrite oxidizing sulfide to sulfate in the presence of water reducing Fe (III) to Fe (II) (Eq. (4)). All four reactions above are parallel processes, which occur and last as long as there is access to water and oxygen. Rios et al. (2008), described in detail the process of pyrite decomposition.

There are three main problems attributed to mining, such as AMD treatment, utilization of solid wastes and reusing of process water. Various adsorbents for mining wastewater purification have been recently reviewed (Iakovleva and Sillanpää, 2013). Recently interest has arisen to use solid wastes as adsorbents for waste water purification (Bhatnagar et al., 2014; Ahmaruzzaman, 2011;

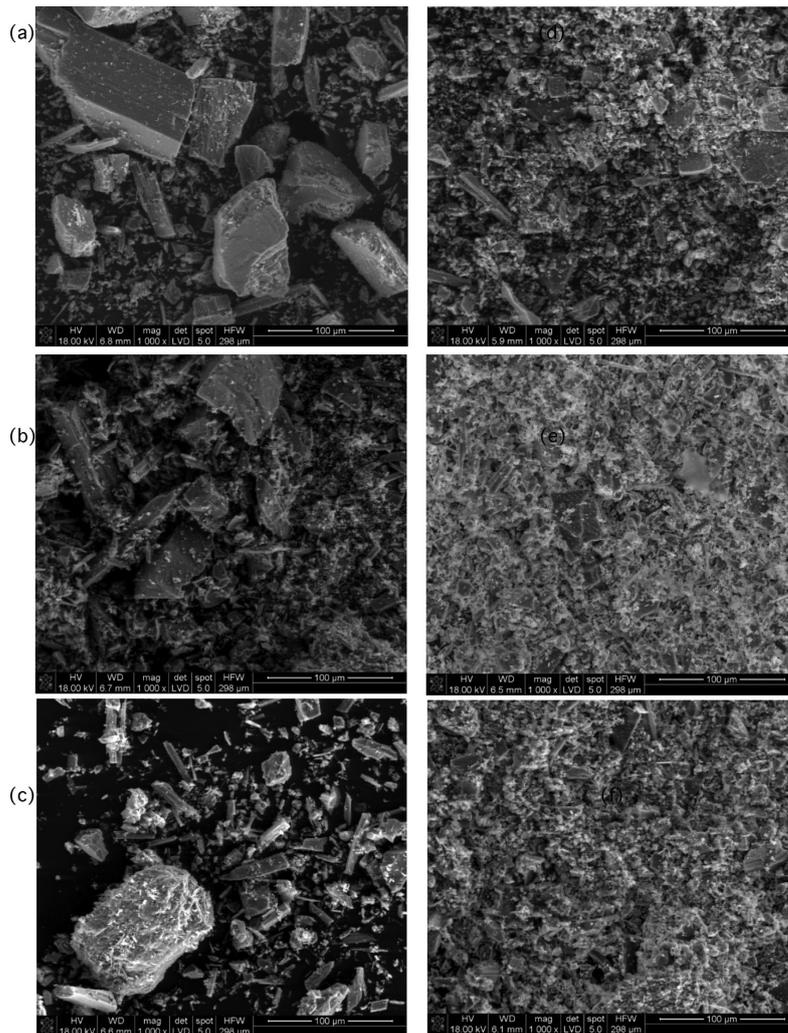


Fig. 1. SEM pictures of initial FS (a), modified FS with NaCl (b) and modified FS with MPW (c), initial FF (d), modified FF with NaCl (e) and modified FF with MPW (f).

Gupta et al., 2011; Oliveira et al., 2007; Wan Ngah et al., 2011; Zhang and Itoh, 2003). A number of AMD techniques of neutralization and recovery of toxic metal ions have been used, primarily including solid materials such as lime (Silveira et al., 2009) and limestone sand (Watten et al., 2005), fly ash (Gitari et al., 2008), natural clinker (Rios et al., 2008), alkaline paper mill (Castillo et al., 2010) and lignite (Mohan and Chander, 2006). The above studies have shown good potential for the use of solid wastes as adsorbents for wastewater treatment. Some investigations (Repo et al., 2011; Yögurtcuoğlu and Uçurum, 2011; Argun and Dursun, 2008; Zhao et al., 2013) showed that solid wastes are more efficient as adsorbents if pre-modified. For example, aminopolycarboxylic acids have been immobilized on solids to enhance their adsorption capacity (Repo et al., 2013). Modification method should be simple and inexpensive.

Limestones have been studied extensively as neutralizers for AMD and they are used mainly in passive wastewater treatment (Watten et al., 2005; Sibrell et al., 2006; Aziz et al., 2008; Strosnider and Nairn, 2010; Silva et al., 2012). In previous study, two limestones, FS and FF were investigated for purification of sulphates and chlorides from mining process water (MPW) (Iakovleva et al., 2015). In this study, MPW was used as a reagent for modifying of FS and FF the surface area. Three challenges were addressed; (1) AMD neutralization, (2) metal ions removal and (3) reuse of solid wastes using two solid wastes from limestone industry of Nordkalk Corporation (Finland).<sup>1</sup> Nordkalk produces limestone products, which are used, for example, for soil improvement in order to neutralize acidity. The products are used mainly in the paper, steel and building materials industries as well as in environmental care and agriculture (Nordkalk.com). Toxic metals, such as iron, copper, zinc and nickel, were chosen as targets metals since they can be found in mine wastewaters in large quantities. These metals are commonly present in substantial amounts in AMD and pose a serious threat to the environment and human health (Kemp et al., 2010). Moreover, if iron and copper ions can be removed from solution by precipitation, removal of nickel is much more complex task (Aziz et al., 2008; Sdiri et al., 2012; Alcolea et al., 2012). Electrochemical methods are most frequently used for the removal of nickel from solutions (Curteanu et al., 2011; Gao et al., 2007). The objective of this work was to find the least expensive way to purify water from metal ions specified above. The aim of this study was to investigate the performance of limestones for simultaneously AMD neutralization and the removal of Zn (II), Fe (III), Cu (II), Ni (II). Effect of competing ions on the adsorption process was studied. Removal of Cu (II), Zn (II), Fe (III), Ni (II) from real mine water was tested as well.

## 2. Materials and methods

### 2.1. Characterization of adsorbents

The particle size distribution and zeta potential of the samples were determined using dispersion analyzer LUMiSizer 610/611 (GmbH) and ZetaSizer Nano ZS, Malvern, UK, respectively. The zeta potential was calculated from electrophoretic mobility measurements using the Schmalukowski equation. A 1.5 g solid sample was conditioned in 50 mL of 0.001 M NaCl solutions at various final pHs for 24 h in a shaking bath. Each reported point value was an average of approximately 20 measurements. The pH of the suspension was adjusted using 0.01–1.0 M HCl. All solutions were prepared using ultrapure water. The pH of solutions was determined with a pH Electrode SenTix 81.

**Table 1**

Chemical composition of adsorbents (XRF and XRD analysis), RSDs at 3 times the detection limit were less than 10%.

Chemical composition, %	Commercial names of materials	
	FF	FS
Al	0.8	0.2
As	0.002	0.007
Ca	37.2	21.3
Cr	0.004	0.003
Cu	0.002	0.002
Fe	0.43	1.07
K	0.24	0.25
Mn	0.01	0.022
Ni	0.01	0.01
S	0.10	0.10
Si	10.3	42
Zn	0.002	0.006
Compounds formula	(K,H <sub>2</sub> O)	CaMgSi <sub>2</sub> O <sub>6</sub>
	Al <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub>	CaCO <sub>3</sub>
	CaSiO <sub>3</sub>	(K,H <sub>2</sub> O)
Compounds name	Illite	Al <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub>
	Parawollastonite	Diopside Calcite

The samples were characterized with nitrogen sorption at 196 °C using TriStar 3000 (Micromeritics Inc. USA). The specific surface area of samples was calculated using the Brunauer–Emmett–Teller (BET) theory.

FTIR spectra of adsorbents were recorded with a Bruker Vertex 70v spectrometer. Spectra were collected in the mid infrared region (4000–400 cm<sup>-1</sup>) averaging 124 scans with 4 cm<sup>-1</sup> resolution. Samples were prepared by the standard KBr pellets methods.

Microstructure of the produced materials was examined using of scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company) with attached chemical analysis of specimen in microareas with energy dispersive X-ray spectroscopy (EDX, EDAX). The experiment was carried out at low vacuum condition in secondary electron mode. For the analysis samples were covered with a gold layer.

XRD data was collected with a PANalytical Empyrean powder diffractometer using Cu K $\alpha$  radiation. The configuration was a standard Bragg–Brentano ( $\theta/\theta$ ) reflection setup with a Ni-filter placed prior to the detector. The measurements were performed between  $\theta$  scanning range of 3–90° with a 0.007° step size and the 69 s of measurement time for each step under ambient temperature and pressure.

### 2.2. Materials

Two limestones, FS and FF used in this study, were obtained from Nordkalk Corporation (Finland). Both materials are commercially used for pH increasing (from 1.5 to 9). Synthetic AMD solutions of Fe (II), Cu (II), Zn (II) and Ni (II) were prepared from analytical grade Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, ZnSO<sub>4</sub>·H<sub>2</sub>O and NiSO<sub>4</sub>·6H<sub>2</sub>O, respectively (obtained from Merck). The required metal concentration was 100 mg L<sup>-1</sup>. Real AMD were obtained from a sulfide mine in Finland from three depths (270, 500 and 720 m). Their compositions were tested with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) spectrometer iCAP 6000 Series, Thermo (UK), with the detection limits for copper, zinc, iron and nickel at 0.4 ppb, 0.2 ppb, 0.1 ppb and 0.5 ppb, respectively. Cu was analyzed at 324.7 nm, Zn at 202.5 nm, Ni at 231.6 nm and Fe at 259.9 nm. MPW for surface area modification of adsorbents was obtained from Norilsk Nickel Harjavalta. MPW is process water from nickel chemical production after raw purification with diluted sodium sulfate solution. Then metal ions were precipitated using soda ash and caustic soda (Na<sub>2</sub>CO<sub>3</sub> and NaOH).

<sup>1</sup> Nordkalk.com, <http://www.nordkalk.com/mine>.

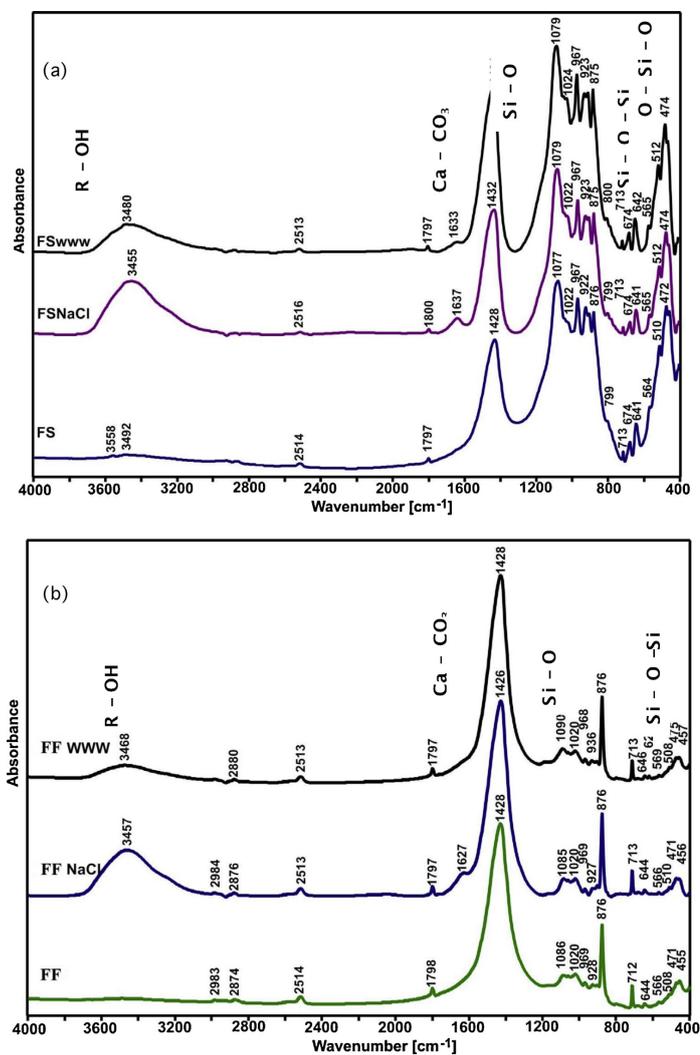


Fig. 2. MIR analysis of unmodified and modified FS (a) and FF (b).

### 2.3. Modification of adsorbents

To improve adsorption properties of the limestones, two modification methods were suggested. The first one with 2 M solution of NaCl and the second one with MPW from Norilsk Nickel Harjavalta. New modified adsorbents are (FS\_NaCl, FS\_ww, FF\_NaCl and FF\_ww). 100 g FS and FF were placed in 1 L of 2 M NaCl solution or 1 L alkaline MPW and then stirred at ambient temperature for 12 h. After preparation, the reaction mixtures were filtered and washed

with distilled water and the modified adsorbents were oven-dried for 12 h at 80 °C. The dried adsorbents were stored in glass flasks.

### 2.4. Batch sorption

Batch adsorption tests were conducted by mixing known weight of FS and FF with 50 mL of synthetic and real AMD solution of known metal ions concentration. Metal ions concentrations in model solution were in range of 10–300 mg L<sup>-1</sup>. The mixture was

**Table 2**

The particle size distribution, specific surface area and zeta-potential results of adsorbents.

	The particle size distribution, $\eta\text{m}$					Specific surface area, $\text{m}^2 \text{g}^{-1}$	zeta-potential, mV pH 11
	<90%	<75%	<50%	<25%	<10%		
FS	451	420	318	228	156	1.35	0
FS_NaCl	589	568	450	282	270	1.46	-15
FS_ww	273	134	131	91	90	1.29	-6
FF	599	567	354	185	177	1.82	-25
FF_NaCl	872	798	535	494	487	1.63	-20
FF_ww	492	421	188	87	88	1.58	-6

**Table 3**

Elemental composition of mining water from copper mine of Finland and process water (MPW) from Norilsc Nickel Harjavalta, RSDs at 3 times the detection limit were less than 3%.

	pH	Cu(II), ppm	Ni(II), ppm	Zn(II), ppm	Fe(III), ppm	Cl <sup>-</sup> , ppm	Na <sup>+</sup> , ppm
Level 270	2.6	108	13	2080	911	-	-
Level 500	2.3	76	1.7	5900	3400	-	-
Level 720	3.2	4.4	0.3	242	52	-	-
NorNikel	12	0.11	2.13	0.18	0.60	954	11570

shaked in a mechanical shaker ST5 (CAT M.Zipper GmbH, Staufen, Germany) from 30 min to 72 h, and 10 mL samples of the solution were taken from the flasks at known time intervals and then filtered, using 0.20  $\mu\text{m}$  diameter polypropylene syringe filter. The temporal evolution of the solution pH was monitored.

The experiments were conducted to observe the effect of competitive metal ions by mixing model solutions containing Cu (II), Zn (II), Ni (II) and Fe (III). The final concentration of the pollutant ions in the aqueous phase then was determined by ICP-OES. The percentage adsorption (%) was calculated as

$$\% \text{Adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (5)$$

where  $C_i$  and  $C_f$  are the concentrations of the metal ions in the initial and after treatment solutions, respectively.

#### 2.4.1. Kinetic study

Amount of adsorbents was  $40 \text{ g L}^{-1}$  in a constant volume (50 mL) of synthetic solutions containing the different metal ions (Cu(II), Fe(III), Ni(II) and Zn(II)) with concentration of 20 ppm and 200 ppm. The agitation time was varied from 1 to 72 h. The sorption experiments were carried out in triplicate in order to observe the reproducibility of the results, and the mean value was used. In each case the standard deviation between the triplicate experiments was about  $\pm 5\%$ .

#### 2.4.2. Effect of solution pH

Effect of initial solution pH on adsorption was determined by mixing 0.8 g of adsorbent with 20 mL of Zn (II), Cu (II), Ni (II) and Fe (III) solutions with the concentration of  $200 \text{ mg L}^{-1}$  and multi element solution of  $20 \text{ mg L}^{-1}$  for each component at various pH values ranging from 1.5 to 9. Solution pH was adjusted with 1 M, NaOH and HCl solutions. The mixture was shaken for 48 h then the solution was filtered and analysed.

#### 2.4.3. Neutralization of AMD

pH was monitored during the adsorption process (50 mL of solution was contacted with 2.5 g of all materials for 72 h).

### 3. Results and discussion

#### 3.1. Adsorbents composition and characterization

The Fig. 1 shows the SEM pictures of original and modified adsorbents. Original surface has sufficiently pronounced

crystalline structure of the adsorbents with different particle sizes. Surface modified adsorbents are more smooth and porous.

Chemical composition of studied materials is shown in Table 1. These results were obtained by XRF and XRD. Materials under investigation were found to have similar structure. The predominant exchangeable cations were found to be Ca and Si for both potential adsorbents. All chemical compounds similar in structure to calcite, jarosite, kaolite, diopside, illite, wollastonite and gypsum should have high adsorptive properties.

Spectroscopic studies in the Mid-infrared (MIR) (Fig. 2) confirm the results of XRD studies. The system of bands in each sample is characteristic for calcite (bands  $1428 \text{ cm}^{-1}$ ,  $875 \text{ cm}^{-1}$ , and  $713 \text{ cm}^{-1}$ ) and diopside ( $1077\text{--}1079 \text{ cm}^{-1}$ ,  $1022\text{--}1024 \text{ cm}^{-1}$ ,  $967 \text{ cm}^{-1}$ ,  $922 \text{ cm}^{-1}$ ,  $641\text{--}646 \text{ cm}^{-1}$ , and  $474\text{--}475 \text{ cm}^{-1}$ ). The difference is only in the proportions of these bands. Spectrum of

**Table 4**

Comparison of the adsorption efficiencies on unmodified and modified adsorbents at room temperature.

Adsorbent	Metal	Contact time	pH	$q_m$ ( $\text{mmol g}^{-1}$ )	Removal, %
FF	Fe	5	4.5	3.4	98
	Cu	12	8	3.0	99
	Zn	12	8	2.5	80
	Ni	8	6	1.2	35
FF_NaCl	Fe	4	4	3.5	99
	Cu	8	6	3.1	99
	Zn	8	6	3.0	98
	Ni	12	8	3.3	97
FF_ww	Fe	4	4	3.5	99
	Cu	8	6	3.1	99
	Zn	8	6	3.0	98
	Ni	12	8	3.3	97
FS	Fe	8	6	3.1	87
	Cu	12	7	3.0	98
	Zn	24	7.5	2.4	78
	Ni	12	7	0.7	20
FS_NaCl	Fe	8	6	3.5	98
	Cu	12	7	3.0	98
	Zn	12	7	3.0	97
	Ni	8	6	3.2	96
FS_ww	Fe	8	6	3.5	98
	Cu	12	7	3.1	99
	Zn	12	7	3.1	97
	Ni	8	6	3.3	97

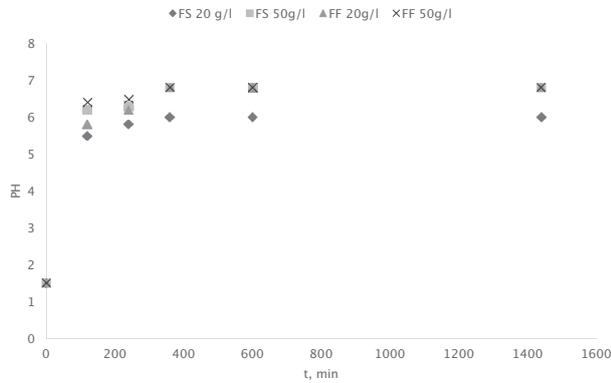


Fig. 3. Neutralization of AMD by FS and FF with concentration of 20 and 50 g/L in 24 h.

modified limestones indicate the presence of small amounts of hydroxyl groups (bands at  $3558$  and  $3492\text{ cm}^{-1}$ ), possibly a layered silicate or other silicate containing hydroxyl group (Yang et al., 2008). The comparison between initial and modified adsorbents shows that a new adsorption band around  $3480\text{--}3455\text{ cm}^{-1}$  appears as a result of new hydroxide groups. It may be due to the introduction of sodium cation onto the structure of adsorbents surface in the form of sodium hydroxide.

The particle size distribution and specific surface area results of the original and modified materials are shown in Table 2. The surface areas of both adsorbents and their modified forms are approximately the same.

Modification of FF and FS with 2 M NaCl solution resulting in increase and homogenization of the adsorbent particle size (Table 2). Despite the fact that the particle size increased, the surface area had not grown most probably due to the crystal structure of sodium chloride. Modification of FS and FF with MPW decreases and homogenizes the particle size of adsorbents. This may be due to the fact that MPW has a corrosive environment and during the modifications process, the expansion of the adsorbent surface may occur, which also leads to particle size reducing. The results for surface area of unmodified and modified adsorbents also confirm the change of the surface structure.

Zeta potential of each adsorbent does not exceed the value  $\pm 30$  and was approximately  $-15\text{ mV}$  for FS, and  $-25\text{ mV}$  for FF. The zeta potential of the adsorbents tested in water is shown in Table 2. Furthermore, FF particles show slightly more negative zeta potential value compared to FS particles. If the zeta potential is low, attraction exceeds repulsion and the dispersion stability is violated. Thus, the colloids with high zeta potential are electrically stable, while colloids having low zeta potential tend to coagulate or flocculate (Viallis-Terrisse et al., 2001).

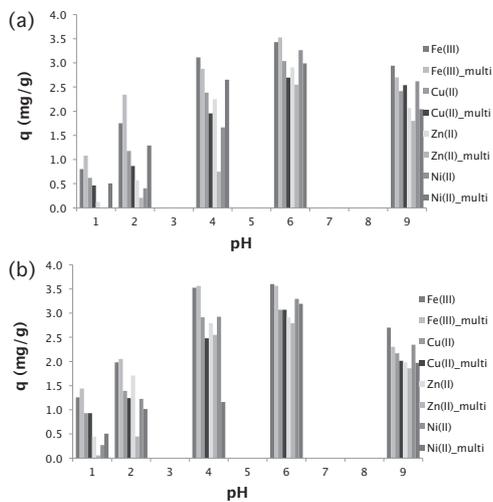


Fig. 4. Effect of pH on removal efficiency of Fe(III), Cu(II), Zn(II) and Ni(II) from single and multi ions solutions with FS\_NaCl (a) and FF\_NaCl (b). Initial concentration of metal ions in single and multi component solution is  $20\text{ ppm}$ , dose of sorbent is  $40\text{ g L}^{-1}$ .

### 3.2. Sorbents modification

The contents of calcium and silicates in adsorbents were 20–35%. Thus, one can assume that suitable modification techniques should be similar to those used for calcite and silicates modification. Widely used, calcite and silicate modification techniques are not simple and cheap (Yogurtcuoglu and Uçurum, 2011; Gomari et al., 2006; Yuan et al., 2008). Based on the analysis of the surface area of the adsorbents the original calcite surface was smooth. To increase the surface area we tried to cover the adsorbent with a salt layer. This increases the surface area, as well as the number of functional groups to participate in ion exchange process. As an affordable modification method, sodium chloride treatment was chosen. Modification of materials with NaCl markedly improved the removal of nickel and zinc from the modeling solution. As alkaline matrix and high chloride ion content seem to be promising as the second approach for adsorbents modification, we decided to study MPW from Norilsk Nickel Harjavalta. Elemental composition of MPW and their pH are shown in Table 3. The concentration of chloride ions in this water is sufficient for the surface modification of calcite. The experimental

**Table 5**  
Pseudo-first- and pseudo-second-order kinetic parameters for metal ions adsorption on FS and FF modified with NaCl.

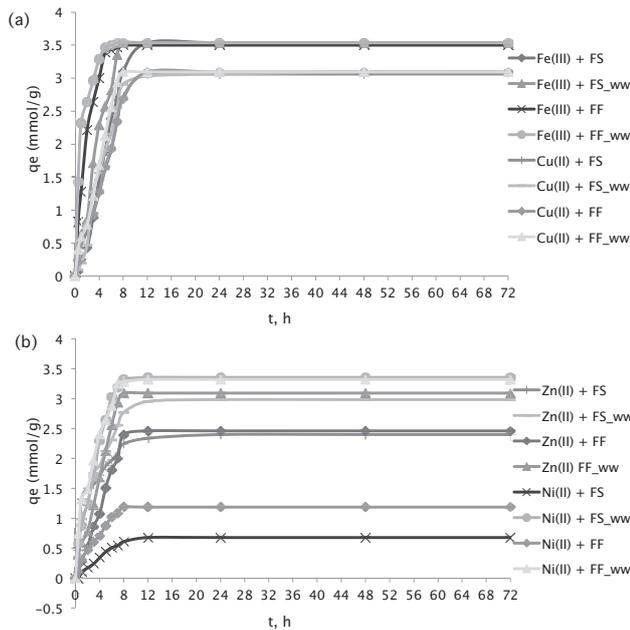
	$C_0$ (mmol L <sup>-1</sup> )	$q_e \text{ exp (mmol g}^{-1}\text{)}$		$q_e \text{ (mmol g}^{-1}\text{)}$		$K_2 \text{ (g mmol/min)}$		$R^2$		
		Pseudo-first-order	Pseudo-second-order	Pseudo-first-order	Pseudo-second-order	Pseudo-first-order	Pseudo-second-order	Pseudo-first-order	Pseudo-second-order	
FS_NaCl	Cu (II)	0.22	0.058	0.057	0.049	0.064	1	0.28	0.23	0.97
	Zn (II)	0.99	0.039	0.042	0.039	0.044	1	1.15	0.74	0.98
	Ni (II)	0.71	0.048	0.054	0.048	0.06	1	0.37	0.68	0.92
	Fe (III)	0.053	0.075	0.086	0.075	0.096	1	0.19	0.6	0.98
FF_NaCl	Cu (II)	0.61	0.035	0.035	0.044	0.091	1	0.025	0.1	0.98
	Zn (II)	0.84	0.035	0.041	0.035	0.048	1	0.245	0.1	0.94
	Ni (II)	0.13	0.052	0.052	0.061	0.069	1	0.216	0.28	0.97
	Fe (III)	0.004	0.067	0.082	0.067	0.104	1	0.077	0.32	0.98

data showed that the best result was observed with adsorbent modified with NaCl, however, materials modified with MPW showed good adsorption capacity as well (Tab. 4). Removal of Ni(II) increase from 20 and 35% to 97% with modified FF and FS adsorbents, respectively. Use of such adsorbents modified with process water would solve several problems at the same time – modifications of adsorbents, purification of process water from the alkaline chlorides, as well as subsequent use of adsorbents with

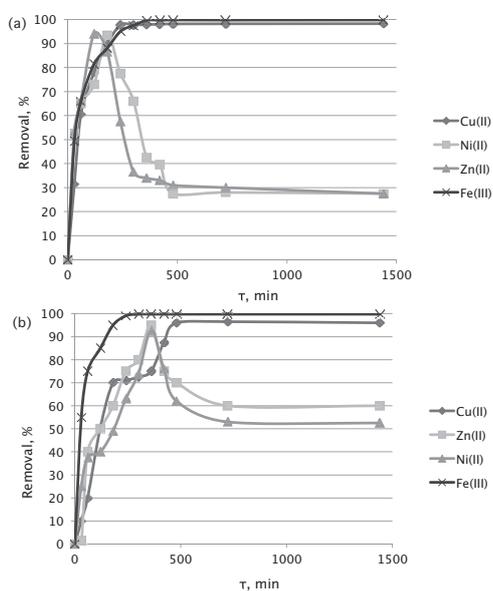
improved properties for metals removal and neutralization of AMD.

3.3. Selection of optimal conditions for AMD treatment

Neutralization of AMD and metal ions removal were studied by varying contact time of solution with adsorbents, adsorbents dosage and metal ion concentration.



**Fig. 5.** Kinetic of Fe(III) and Cu(II) (a), Zn(II) and Ni(II) (b) adsorption with unmodified and modified FS and FF.



**Fig. 6.** Removal of copper, zinc, nickel and iron by modified FS with NaCl (a) and modified FF with NaCl (b) from multielement model solution with concentration of ions  $0.3125 \text{ mmol L}^{-1}$ ,  $0.3058 \text{ mmol L}^{-1}$ ,  $0.3389 \text{ mmol L}^{-1}$  and  $0.3571 \text{ mmol L}^{-1}$ , respectively.

### 3.3.1. Neutralization of AMD

Neutralization of AMD is generally the first step in mine water treatment. The acidity reduction properties of FS and FF were tested by batch method showing solution pH increased from 1.5 to 6.8 within 72 h. The results are presented in Fig. 3. FF and FS reduce the acidity of AMD fast. The increase of the initial pH (1.5) of the AMD occurred on contact with FS ( $20$  and  $50 \text{ g L}^{-1}$ ) and FF ( $20$  and  $50 \text{ g L}^{-1}$ ). After 2 h of shaking by the batch method, the pH reached 5.0–6.5. The reaction rates decrease as equilibrium was reached. The pH increase is the result of the progressive dissolution of the sorbent during the shaking process. The pH was stabilized after 6 h whereas the same time (6 h) was required using the modified materials as adsorbents for the metal ions removal. The final pH was 6.8, indicating that effective neutralization of AMD took place.

### 3.3.2. Effect of pH

pH is an important parameter in the sorption process optimization, since it affects not only the surface charge of adsorbents, but also the degree of ionization of the metal ions in solution. The effect of the initial pH of Cu (II), Ni (II), Fe (III) and Zn (II) solutions on the amount adsorbed was studied by varying the initial pH from 1.5 to 9, under constant temperature (Fig. 4). Maximum adsorption efficiency was achieved at pH 5–6 for each metal. At higher pHs the sorption capacity values decrease due to precipitation of hydroxide complexes especially for Zn (II) and Fe (III), and reduction in  $q_e$  value was observed at higher pHs (Sdiri et al., 2012). Initial pH of solution significantly affected adsorption characteristics of FF\_NaCl and FS\_NaCl, and removal of Cu (II), Ni (II), Fe (III) and Zn (II) was at maximum level in neutral solution. For example, in case of Cu (II) and Ni (II) sorption by FS the desorption of metal ions increased at the pH above 6. In multi ions solutions

similar pattern was observed for FS\_NaCl and FF\_NaCl adsorbent (Fig. 4).

It seems that ion desorption takes place due to supersaturation of the solution. While as the part of ions precipitated and other of ions remain in solution. Ions partially precipitate and partially remain in the solution. Various researchers have also reported that the mechanism of sorption and precipitation depends on characteristic reactions of metals with calcite. Adsorption is occurring at metals concentrations lower than  $2 \text{ mg L}^{-1}$ , while at higher concentrations precipitation is dominating (Aziz et al., 2008; Sdiri et al., 2012; Alcolea et al., 2012; Macias et al., 2012).

### 3.3.3. Kinetic studies

The optimum dosage of the adsorbents for the best removal of most metals from model solutions was  $40 \text{ g L}^{-1}$ . The equilibrium occurs at 8 h at the concentration of 200 ppm. The results of the kinetic experiments of metals adsorption from synthetic solutions onto different adsorbents are shown in Table 5 and Fig. 5. Kinetics was studied using pseudo-first- (Eq. (6)) and second-order models (Eq. (7)).

The pseudo-first-order model is associated with the kinetics of one-site adsorption governed by the rate of the surface reaction. The equation is given as:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (6)$$

The pseudo-second-order model, which assumes that the adsorption process is governed by the surface reaction, has the form:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (7)$$

where  $q_t$  and  $q_e$  ( $\text{mmol g}^{-1}$ ) represent the amount of metals adsorbed at time  $t$  (min) and at equilibrium, respectively, and  $k_2$  is the pseudo-second-order rate constant.

The adsorption process of metals from liquids was described best with the pseudo-second-order model. This model suggests that the system includes the formation of at least two compounds, or is a multi-component system with a complex compound of adsorbent with adsorbate.

### 3.3.4. Equilibrium study with adsorption isotherms

Removing metals from single metal solutions and the mixture was also conducted. Fig. 5 and Table 4 show that the modified adsorbents, FF\_ww, FF\_NaCl, FS\_ww and FS\_NaCl, have better adsorption properties for metals. Nickel and zinc are hardly removed with unmodified adsorbents. Apparently, this is due to the fact that the surface of unmodified adsorbent has a low affinity to these ions.

Study of multiple metal solution (Figs. 4 and 6) also shows that the best degree of removal takes place on modified materials, than on unmodified adsorbents. During the first six hours removal of all four metal ions is observed. Then desorption of Ni (II) and Zn (II) into the solution takes place. After approximately 12 h the equilibrium is observed in the system. Both adsorbents have exhibited greater affinities to iron and copper ions. While strong bonds are formed on the surface area of the adsorbents due to iron and copper ions, bonds of zinc and nickel ions with the adsorbent surface are weakened, and Zn (II) and Ni (II) desorb into solution. The desorption of zinc and nickel ions might be associated with supersaturation of solution, as is observed above. Apparently, iron and copper ions formed more stable complexes, than zinc and nickel ions. The same pattern was observed by other researchers (Aziz et al., 2008; Sdiri et al., 2012; Alcolea et al., 2012).

Adsorption capacity, equilibrium concentration of the adsorbate and affinity of adsorbates to adsorbents were fitted with the Langmuir (Eq. (8)), Sips (Eq. (9)) and Toth (Eq. (10)) adsorption

**Table 6**  
Isotherm parameters for FS\_NaCl and FF\_NaCl during adsorption process of metal ions from model solution.

		$C_0$ (mmol L <sup>-1</sup> )	$q_m \text{ exp}$ (mmol g <sup>-1</sup> )	$q$ (mmol g <sup>-1</sup> )	$K_L$ (L/mmol)	$R^2$	
Langmuir model							
FS_NaCl	Cu (II)	0.068	0.391	0.066	472	0.895	
	Zn (II)	0.068	0.391	0.076	19	0.905	
	Ni (II)	0.038	1.864	0.043	8.26	0.968	
	Fe (III)	0.089	$8.9 \times 10^{-4}$	0.13	3010	0.969	
FF_NaCl	Cu (II)	0.071	0.004	0.083	745	0.977	
	Zn (II)	0.119	0.033	0.247	15	0.931	
	Ni (II)	0.075	0.366	0.107	3.52	0.985	
	Fe (III)	0.006	0.089	0.17	203	0.944	
Sips model							
FS_NaCl	Cu (II)	0.068	0.391	0.129	0.246	1.972	0.988
	Zn (II)	0.068	0.391	0.073	1.062	21	0.907
	Ni (II)	0.038	1.864	0.06	0.52	1.744	0.988
	Fe (III)	0.089	$8.9 \times 10^{-4}$	0.131	1.01	3052	0.969
FF_NaCl	Cu (II)	0.071	0.004	0.078	1.217	886	0.937
	Zn (II)	0.119	0.033	0.129	4.298	44	0.846
	Ni (II)	0.075	0.366	0.089	1.874	5.313	0.951
	Fe (III)	0.006	0.089	0.183	0.913	164	0.940
Toth model							
FS_NaCl	Cu (II)	0.068	0.391	0.066	0.002	0.985	0.914
	Zn (II)	0.068	0.391	0.076	0.052	1.028	0.903
	Ni (II)	0.038	1.864	0.067	0.242	1.264	0.845
	Fe (III)	0.089	$8.9 \times 10^{-4}$	0.506	$0.03 \times 10^{-2}$	3.766	0.372
FF_NaCl	Cu (II)	0.071	0.004	0.055	0.001	1.136	0.953
	Zn (II)	0.119	0.033	$0.03 \times 10^{-2}$	$2.7 \times 10^{-5}$	4.189	0.967
	Ni (II)	0.075	0.366	0.548	1.005	2.419	0.92
	Fe (III)	0.006	0.089	-	-	-	-

isotherms for modified adsorbents (FS\_NaCl and FF\_NaCl). Coefficients of sorption isotherms equations and graphs of the adsorption isotherms are showed in Table 6.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

$$q_e = \frac{q_m (K_S C_e)^{n_s}}{1 + (K_S C_e)^{n_s}} \quad (9)$$

$$q_e = \frac{q_m C_e}{(a_T + C_e^{m_T})^{1/m_T}} \quad (10)$$

where  $q_e$  and  $C_e$  are sorption capacity (mmol g<sup>-1</sup>) and concentration of metal ions in the solution (mmol L<sup>-1</sup>) at equilibrium, respectively;  $q_m$  is the maximum uptake capacity;  $K_L$  and  $K_S$  are Langmuir and Sips constants related to the energy of sorption, respectively;  $n_s$  is coefficient of Sips isotherm describes the surface heterogeneity;  $a_T$  is the adsorptive potential constant (mmol L<sup>-1</sup>) and  $m_T$  the heterogeneity factor of the Toth isotherm.

The parameters were calculated with minimisation of the error distribution between experimental and predicted data by Marquardt's percent standard deviation (MPSD).

Langmuir adsorption model allows us to describe the sorption of substances in a single homogeneous layer of sorbent with finite number of active binding sites. The coefficient  $q_m$ , that reflects the amount of sorption sites in the sorbent molecule that actively interact with sorbate, and the coefficient  $K$ , which indicates the degree of affinity between the sorbate and sorbent, can be

calculated with Langmuir model. Affinity shows the increasing degrees for metal ions to the surface of the adsorbent on the basis of coefficient  $K$  values as follows:

$$\text{FS: Ni(II)} < \text{Zn(II)} < \text{Cu(II)} < \text{Fe(III)}$$

$$\text{FF: Ni(II)} < \text{Zn(II)} < \text{Fe(III)} < \text{Cu(II)}$$

Both adsorbents show less affinity for nickel and zinc ions. It was difficult to find a suitable model of adsorption isotherm for adsorption process description. Apparently, this is due to the heterogeneous structure of adsorbents, alongside with their complex structure. Some of the isotherms fit the description of the rare cases of adsorption system presented in literature (Erkey, 2011).

The Toth isotherm is an empirical equation, which was derived to improve the Langmuir model fittings at both low and high concentrations. The Toth model assumes an asymmetrical quasi-Gaussian energy distribution and is useful in the cases of heterogeneous adsorption. These models were used to describe the adsorption on FF and FS. It was found that Toth model was inappropriate to describe iron adsorption process on FF. The Sips isotherm is a combination of the Langmuir and Freundlich isotherms and can be derived using either equilibrium or thermodynamic approach and was used to describe of FF and FS adsorbents.

Correlation coefficients ( $R^2$ ) were calculated to estimate the relevant patterns and are given in Table 6. The  $R^2$  values of the isotherms described by Langmuir, Sips and Toth models are relatively close. However, it can be concluded that Toth model is better for FS and Sips model for FF, both involving the sorption on a

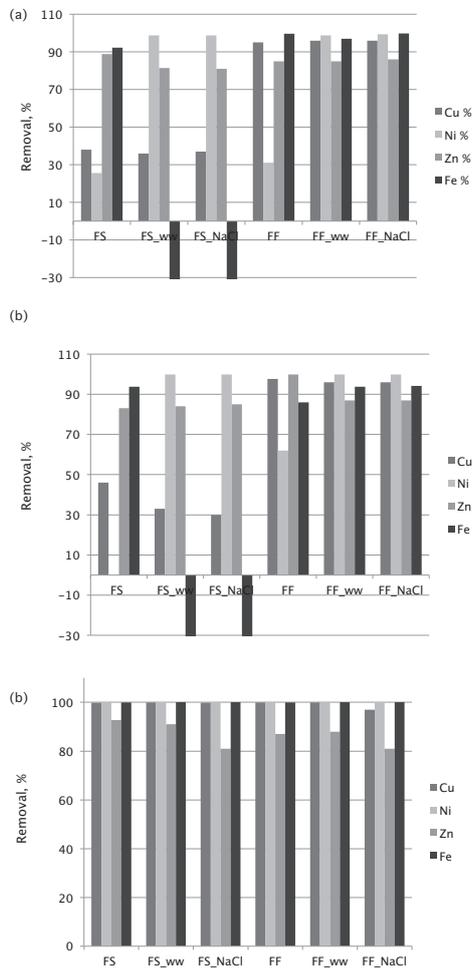


Fig. 7. Mining water treatment with unmodified and modified FS and FF from different mining depths: (a) 270 m, (b) 500 m, (c) 720 m. Contact time is 24 h, agitation speed is 50 rpm.

heterogeneous surface. When the first active positions with lower energy are filled, a continuous variation of sorption energy occurs.

### 3.4. Mine water treatment

Mine water treatment is a very complex process and depends on several factors, such as waters matrices, composition and pH. In this study, waters from different mining depths were investigated. pH was 2.3–3.2 and the chemical composition is presented in Table 3. AMD neutralization and metal ions removal were studied. The experiments were carried out at ambient temperature for 12 h with  $40 \text{ g L}^{-1}$  unmodified and modified FS and FF. After 8 h pH increase to 6.5–6.8. Both unmodified and modified FFs shows

better adsorption properties in mine waters treatment compared to FSs (Fig. 7). Unmodified FF showed good affinity for Zn and Fe in all waters and better affinity than FS for Cu in waters from 1st and 2nd depths. Desorption of Fe (III) for levels 1 and 2 on unmodified and modified FS was observed. Modified FF adsorbed nearly 100% of all metal ions (Zn (II), Fe (III), Cu (II) and Ni (II)).

### 3.5. Removal mechanism of metal ions

There are two mechanisms of metal ions removal from acidic solutions. These mechanisms are sorption, include complexation and ion-exchange mechanism (Aziz et al., 2008; Yuan et al., 2008; Aziz et al., 2004; Christensen et al., 2001; Martin et al., 2005; Miller et al., 2011) and precipitation (Watten et al., 2005; Wang et al., 2013; Allende et al., 2012; Miller et al., 2013). In these experiments, ion-exchange is much more likely than precipitation. Since, like most silicates, unmodified and modified FS and FF shows a negative surface charge at high pH (as given in Eqs. (11–13)) and it will be changed due to the adsorption of ions on to the surface. Dissociation equilibrium of silicate sites due to the pH increase is given in (Eq. (11)). Calcium ion should be exchanged with hydrogen ion and attached to the surface of the adsorbent to form a complex compound (Eq. (12)). Further interaction in solution leads to an ion exchange between calcium and metal ion, while pH of the solution increased (Eq. (13)).



Iron compounds, such as oxides and hydroxides are known to be effective sorbents for various ion metals (Iakovleva and Sillanpää, 2013), including nickel and zinc. Since iron is a component of FF and FS materials, nickel and zinc could be removed by complexation of these ions with iron compounds onto surface area of sorbents.

During removal of ion metals from multicomponent solutions, the removal of zinc and nickel increased to approximately 10% in comparison to single component solution. It could be because some of iron precipitated and secondary metal removal could be observed. Major mechanism of secondary metal removal is adsorption and co-precipitation with newly formed iron compound particulates. After treatment of multicomponent system, the color of adsorbents was changed from white to dirty yellow, that also could indicate a certain level of iron precipitation as hydroxide. Precipitation of  $\text{Fe}(\text{OH})_3$  on the limestone particles was also observed by Wang et al. (2013).

Modified adsorbents removed nickel and zinc ions approximately four times more effective than unmodified ones (Fig. 5, Table 3). Possible explanation of these results is that the metal ions could create a surface complex, and the ternary complexation of nickel and zinc with carbonate or chloride were formed. For example complexation of nickel and zinc with carbonate was observed by Miller et al. (2011). However, in the next study, the same authors suggested the benefit of co-precipitation of these metals under the same conditions (Miller et al., 2013). Batch experiments show that the removal effectivity of nickel and zinc ions is heavily affected by presences the carbonates and chlorides on the surface area of modified adsorbents and somewhat by the iron content in solution. Therefore, besides an adsorption mechanism, co-precipitation of iron, zinc and nickel ions could

be have place during the removal process of metals from acidic solutions.

#### 4. Conclusions

Modification of limestones surface area by sodium chloride and process water with high content of chlorides, sodium hydroxide and sodium carbonate seems effective and inexpensive methods of modification.

It was found that unmodified and modified materials exhibit good adsorption properties for Zn (II), Fe (III), Cu (II). Both unmodified adsorbents were better to copper and iron, however FF can be used for removal of zinc and nickel as well. These adsorbents neutralized the solution acidic and changed pH from 1.5 to 6. Both limestones can be effectively used after modification as adsorbents for AMD treatment and removal of iron, copper, zinc, and nickel as well. For industrial application of these adsorbents, further experiments in their selectivity to different kinds of pollutants, such as cations and anions are required. Preliminary experiments using the pilot plant are required.

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## **Publication III**

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**Modified and unmodified low-cost iron-coating solid wastes as adsorbents for efficient removal of As(III) and As(V) from mine water**

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## Modified and unmodified low-cost iron-containing solid wastes as adsorbents for efficient removal of As(III) and As(V) from mine water



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### ABSTRACT

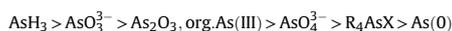
Sulphate tailings and iron sand – industrial solid wastes containing iron oxide/hydroxides – were investigated as potential adsorbents for arsenic removal from water. Two effective methods of surface modification by NaOH treatment and atomic layer deposition of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> thin films were used for increasing As(III) and As(V) removal capacities of both adsorbents. The structure and surface area of the materials were characterised by scanning electron microscopy, middle infrared region spectroscopy, energy dispersive X-ray spectroscopy, and nitrogen adsorption. The iron sand waste was capable of binding significant amounts of As(III) and As(V) from synthetic solutions and wastewater. The sulphate tailings also showed a high adsorption capacity. Adsorption kinetics showed that equilibrium was reached within 240 min and fit to a pseudo second-order model with correlation coefficients greater than 0.99. Adsorption capacity was at the highest value at a solution pH range of 6–8. The Langmuir and Toth models can be used to fit the adsorption isotherms. The research showed that the proposed solid wastes can be successfully used for the adsorption of As(III) and As(V).

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### 1. Introduction

Arsenic is one of the most dangerous elements to human health and the environment (Mandal and Suzuki, 2002). In some areas (Mukherjee et al., 2006), such as Bangladesh (Asadullah and Chaudhury, 2011), India (Roychowdhury, 2010) the Tibetan Plateau (Huang et al., 2009), Chile (Gidhagen et al., 2002), the USA (Camacho et al., 2011), and Cambodia (O'Neill et al., 2013), Panonian reftion (northern part of Serbia, southern Hungary and part of Romania) (Lekic et al., 2013) arsenic is a natural component of ground waters, which has caused the mass poisoning to the people for drinking water. Arsenic is also a by-product of certain industries, including copper, gold and silver mining. In many countries, arsenic

has caused cancers by entering natural waters with mining sewage (Iakovleva et al., 2015). The impact on human health depends on the oxidation forms of the arsenic in the following order according to their toxicity index:



It is believed that the higher toxicity of As(III) compared to As(V) is attributed to the capability of reacting with sulphur-containing fragments of protein molecules, leading to a loss of functional properties of certain enzymes in the human body (Doull's, 2001).

The acidity and redox potential (Eh) of an arsenic solution are the most important factors determining the predominant oxidation form of arsenic (Iakovleva et al., 2015). The redox potential ranges for different arsenic forms are as follows: oxidation (Eh > 100–150 mV), transition (Eh 0–100 mV) and reduction (Eh < 0). Oxidative waters usually contain sufficient amounts of dissolved oxygen, for examples some natural waters and closed mining water. All forms of As are

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Notation	
ALD	Atomic layer deposition
AMD	Acid mine drainage
BET	Brunauer–Emmett–Teller theory
CaFe-Cake	sulphate tailings
CaFe-Cake <sub>Al<sub>2</sub>O<sub>3</sub></sub>	modified sulphate tailings with Al <sub>2</sub> O <sub>3</sub>
CaFe-Cake <sub>NaOH</sub>	modified sulphate tailings with NaOH
CaFe-Cake <sub>TiO<sub>2</sub></sub>	modified sulphate tailings with TiO <sub>2</sub>
FT-IR	Fourier Transform Infrared Reference Spectra
RH	iron sand
RH <sub>Al<sub>2</sub>O<sub>3</sub></sub>	modified iron sand with Al <sub>2</sub> O <sub>3</sub>
RH <sub>NaOH</sub>	modified iron sand with NaOH
RH <sub>TiO<sub>2</sub></sub>	modified iron sand with TiO <sub>2</sub>
SEM	scanning electron microscopy
TMA	trimethylaluminium
XRD	X-ray diffraction
ED-XRF	energy dispersive X-ray fluorescence

rapidly oxidised to As(V) in these waters. The transition media are usually unstable geochemical solutions with variable oxygen and sulphide contents. Slow processes of oxidation and reduction take place under these conditions. The reducing media are waters containing metal ions in reduced forms. They are typically anaerobic ground waters. Under these conditions As is predominantly in the form of As(III) (Mohan and Pittman, 2007). The low value of Eh is observed also in alkaline solutions with rich amount of sulphates and chlorides (DeLaune and Reddy, 2005).

There are various methods of removing As from water including coagulation and filtration (Wickramasinghe et al., 2004; Cui et al., 2014), lime softening (Nguyen et al., 2008); photo-oxidation (Nguyen et al., 2009); membrane processes (micro, ultra, and nanofiltration) (Pal et al., 2014; Chan and Dudeney, 2008; Ning, 2002; Lakshmanan et al., 2010); electro dialysis reversal (Lakshmanan et al., 2010) and adsorption with various adsorbents activated carbon (Wu et al., 2013), alumina (Ruiping et al., 2009), iron oxides and hydroxides (Tresintsi et al., 2012; Maji et al., 2011; Meng et al., 2002; Ghosh and Gupta, 2012). Adsorption is one of the most affordable, cheap and effective methods. Different adsorbents have been used for As removal from different media. Recently, several research groups have attempted to find an effective and low cost adsorbent for arsenic removal. The candidates were activated alumina and activated carbons (Han et al., 2013a, 2013b; Chuang et al., 2005; Doušová et al., 2011). Activated alumina was found to be very efficient and it could be regenerated in situ to extend the adsorbent lifetime. Yet its sorption efficiency is high only at low pH and arsenites must be pre-oxidised to arsenates before adsorption (Han et al., 2013a; Lunge et al., 2014). It was found that activated carbon was able to remove only a few mg g<sup>-1</sup> of As. Besides low capacity, regeneration problems also existed and the high price was not conducive to widespread utilisation. Several researchers studied activated carbon produced from industrial by-product with iron oxide/hydroxides to improve its adsorption properties (Chuang et al., 2005; Doušová et al., 2011). Numerous attempts were also made to activate cheap sorbents such as clays, silica and sand with iron oxides/hydroxides. Such activation drastically improves their adsorption capacity (Zuo et al., 2012; Rahman et al., 2013; Aredes et al., 2013; Wu et al., 2013). Industrial iron or iron compound by-products (iron oxides, oxyhydroxides and hydroxides, including ferric oxide (FeO-OH), goethite (-FeO-OH) and hematite (-Fe<sub>2</sub>O<sub>3</sub>), etc.) are the most widely used adsorbents, due to their high

removal efficiency and low cost (Tresintsi et al., 2012; Maji et al., 2011; Meng et al., 2002; Ghosh and Gupta, 2012; Banerjee et al., 2008; Wang and Tsang, 2013). Yet they are efficient only at low pH and cannot be regenerated. More details of these adsorbents and their application in arsenic removal can be found in the review (Iakovleva et al., 2015). It seemed promising to use iron containing wastes as adsorbents for As removal in order to satisfy the following criteria: low cost pre-treatment, sorption efficiency in a wide range of acidity and inexpensive regeneration. Therefore, this work investigates the behaviour of two industrial by-products as adsorbents for As(III) and As(V) removal from synthetic and real mining wastewater. The by-products are originated from Ekokem and Norilsk Nickel Harjavalta factories in Finland. These materials were chosen because of their availability and high production volumes.

The objectives of this study were to evaluate and compare the performance of the adsorbents in raw and modified states with two different methods. One of the economic and effective method is surface activation with NaOH in liquid phase (Wickramasinghe et al., 2004). This method activates iron oxide/hydroxide compounds and generates new hydroxide reactive functional groups on the surface, which provide to increase of ion exchange process. The other efficient method of adsorbent activation is functionalization of the surface with additional chemical groups. In this study we used an atomic layer deposition technique (ALD) based on chemical interaction between gaseous reagents and active sites on the adsorbent surface. The ALD process was carried out in sequential steps which consists of gaseous precursor pulses in order to deliver the reagent inside the reactor. This sequence is usually referred as ALD cycle and repeat of required amount of times in order to obtain certain coating thickness on the surface. Detailed information on ALD process can be found elsewhere (Ahmadzade et al., 2015; George, 2010).

## 2. Materials and methods

### 2.1. Materials

Two solid wastes, with commercial names of RH (industrial sand) and CaFe-Cake (sulphate tailings) were milled, washed with distilled water and dried for 12 h at 80 °C. The dried adsorbents were stored in glass flasks. Milli-Q ultrapure water was used for the preparation of the stock and diluted solutions. AMD was obtained from a sulphide Finnish mine from depth 270 m. The composition of real AMD is shown in Table 1. The initial concentration of As(III) and As(V) was added to AMD and amounted 10 mg L<sup>-1</sup> for both for of arsenic.

### 2.2. Adsorbent modification

#### 2.2.1. Activating the surface area by NaOH

Since the main objective of this work was to create low-cost adsorbents for water purification from arsenic, one of the cheapest methods of activating the surface of the iron compounds (oxides and hydroxides) is a two-stage method using NaOH. This method activates both iron compounds and generates new hydroxide reactive functional groups on the surface. The adsorbents were activated with NaOH (Sigma-Aldrich, Germany, assay ≥98%) and H<sub>2</sub>O<sub>2</sub> (Sigma-Aldrich, Germany, 30wt.% in H<sub>2</sub>O) to improve their adsorption capacities. Typically, 100 g RH and CaFe-Cake were suspended in 25% NaOH (Sigma-Aldrich, Germany, assay ≥97%) solution and then stirred at 100 °C for 6 h with the addition of 10 mL H<sub>2</sub>O<sub>2</sub> as a catalyst. After preparation, the reaction mixture was filtered and the adsorbents were washed with distilled water and oven-dried for 12 h at 120 °C. The dried adsorbents were stored in plastic flasks.

**Table 1**  
Chemical composition of AMD.

AMD from depth 270 m	Cu, mg L <sup>-1</sup>	Zn, mg L <sup>-1</sup>	Fe, mg L <sup>-1</sup>	Mn, mg L <sup>-1</sup>	As(III), mg L <sup>-1</sup>	As(V), mg L <sup>-1</sup>	Redox, Eh	pH
	108	2080	911	80	10	10	444	3.2

### 2.2.2. ALD of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> on sulphate tailings

TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> thin films were deposited on the surface of adsorbents by using TFS500 ALD reactor (Beneq Oy, Finland) for increasing adsorption capacity for As(III) removal. The surface of the CaFe-Cake and RH adsorbents were modified with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in order to obtain Ti–OH and Al–OH groups on the surface, respectively. For TiO<sub>2</sub> ALD process, adsorbent surface was exposed to TiCl<sub>4</sub> and H<sub>2</sub>O vapours intermittent with inert gas (N<sub>2</sub>) pulses in order to purge the reactor. The pulse time of TiCl<sub>4</sub> and H<sub>2</sub>O was 0.6 and 0.25 s, respectively. In turn, Al<sub>2</sub>O<sub>3</sub> film was synthesized by sequential pulses of trimethylaluminium (TMA) and H<sub>2</sub>O into the reactor with the pulse time of 1 and 2 s, respectively. ALD process was carried out at 350 °C for TiO<sub>2</sub> and 200 °C for Al<sub>2</sub>O<sub>3</sub> under pressure of 1 mbar. 300 ALD cycles were deposited for both materials. The silicon substrates <100> (Si-Mat, Germany) was used to control of the film thickness of both metal oxides.

### 2.3. Adsorbent characterisation

FT-IR spectra were recorded with a Bruker Optik Vertex 70 spectrometer. The spectrometer is equipped with a DLATGS detector which covers a spectral range from 12000 to 250 cm<sup>-1</sup>, operating at room temperature with a sensitivity of  $D^* > 2 \times 10^8 \text{ cm Hz}^{1/2} \text{ W}^{-1}$ .

The morphology and surface of adsorbents were examined using a SEM, Zeiss Supra 40VP with field emission cathode, GEMINI electron-optics column, oil-free vacuum system, and variable pressure operating mode.

XRD data were collected with a PANalytical Empyrean powder diffractometer using Cu K $\alpha$  radiation. The configuration was a standard Bragg–Brentano ( $\theta/\theta$ ) reflection setup with a Ni-filter placed prior to the detector. The measurements were performed at a  $\theta$  scanning range of 3–90° with a 0.007° step size and 69 s of measurement time for each step at ambient temperature and pressure.

The chemical composition of materials was determined by an ED XRF analyser X-Art (Joint Stock Company Comita, St. Petersburg, Russia) (Serebryakov et al., 2004).

The samples were characterised with nitrogen sorption at 196 °C using a TriStar 3000 (Micromeritics Inc., USA). The specific surface area of samples was calculated using the BET theory (Brunauer et al., 1938).

TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> film thicknesses were measured on silicon substrates by J.A. Woollam M-2000UI spectroscopic ellipsometer (J.A. Woollam Co., Lincoln, United States). A Cauchy model was used to fit the experimental data.

### 2.4. Batch adsorption experiments

Batch adsorption tests were conducted by mixing a known weight of adsorbents with 50 mL of synthetic solution and wastewater at a known arsenic ion concentration. As(III) and As(V) concentrations of the solutions were in the range of 5–300 mg L<sup>-1</sup>. The mixture was shaken in a mechanical shaker ST5 (CAT M.Zipper GmbH, Staufen, Germany) from 30 min to 72 h, and 10 mL of the solution were taken from the flasks at known time intervals and then filtered, using a 0.20  $\mu\text{m}$  diameter polypropylene syringe filter. The temporal evolution of the solution pH and Eh were monitored

using a pH meter WTW Inolab pH 730 and glass electrode SenTix 81 (Germany), respectively.

All solutions were prepared with ultrapure water. Stock solutions of As(III) and As(V) were prepared from As<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>5</sub>, with 25% NaOH and 37% HCl, respectively. Arsenic concentration was determined using an Inductively Coupled Plasma/Optical Emission Spectrometry (ICP-OES) iCAP 6000 Series, Thermo (UK), at a wavelength of 188.98 nm. The hydride generation accessory (Thermo Fisher Scientific, UK) was used for increased sensitivity to arsenic. The quantification limit of arsenic determination with the hydride generation accessory was 0.23  $\mu\text{g L}^{-1}$ .

The percentage of adsorption (%) was calculated (Eq. (2)) as

$$\% \text{Adsorption} = (C_i - C_f) * 100 / C_i, \quad (2)$$

where, C<sub>i</sub> and C<sub>f</sub> are the concentrations of the metal ions in the initial and post-treatment solutions, respectively.

Arsenate and arsenite concentrations were determined by ion exchange chromatography using RSpak KC-811 column (Shodex, Japan) for HPLC equipment (Shimadzu, Japan). Solution of 12 mM H<sub>3</sub>PO<sub>4</sub> as eluent; flow rate was 1.0 mL/min; column temperature 40 °C and UV detector (195nm) were used.

#### 2.4.1. Sorbent amount optimisation

The optimum sorbent amount was determined by contacting 15 mL of As(III) and As(V) synthetic solutions with different amounts of sorbent (0.5, 1, 2, 5, 10, 20, 30, 40, and 50 g L<sup>-1</sup>). Each result is the average of three samples.

#### 2.4.2. Kinetic study

The optimum time was determined by contacting 40 g L<sup>-1</sup> of unmodified and modified RH and CaFe-Cake in 50 mL flasks tumbled at 100 rpm from 1 to 60 h. Samples were taken at 0.5, 1, 2, 3, 4, 5, 9, 13, 17, 21 and 24 h.

#### 2.4.3. Effects of solution pH and Eh

The effects of initial solution pH and Eh on adsorption were determined by mixing 40 g of CaFe and RH with 20 mL of As(III) and As(V) solutions with the concentration of 20 mg L<sup>-1</sup> for each component at various pH and Eh values ranging from 2 to 9 and 120–730 mV. Solution pH was adjusted with 1 M NaOH and HCl solutions. The mixture was shaken for 48 h and the solution was filtered and analysed. pH solutions was adjusted with 1 M NaOH and HCl. Redox potential varied depending on pH changes and it was recorded in each case. The start and finite pH and Eh were determined by a multi-parameter portable meter HQ40d (Hach, USA).

## 3. Results and discussion

### 3.1. Adsorbent characterisation

The chemical composition data of the studied materials were obtained by XRF and XRD analyse (Table 2). According to the results, CaFe-Cake and RH contains about 8% of iron. A large amount of sulphur can affect water purification, either positively or negatively. If the sulphur is in sulphate form it could improve the removal of arsenic (Tresintsi et al., 2014). On the other hand, the sulphur could be desorbed from the surface of the adsorbent in the

**Table 2**  
Chemical composition of adsorbents (XRF and XRD analysis).

Element	CaFe, wt%	RH, wt%
Si	<2	0.2
S	2.9	17.6
K	0.025	0.3
Ca	11.9	14.4
Ti	<0.01	2.3
Cr	0.005	0.031
Mn	0.013	0.27
Fe	7.8	7.2
Ni	0.28	+
Cu	0.024	0.002
Zn	0.037	0.018
As	0.001	+
Rb	0.001	0.001
Sr	0.0016	0.021
Compounds formula	CaSO <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub>	Ca(SO <sub>4</sub> )(H <sub>2</sub> O)
Compounds name	Gypsum	Ca(CO <sub>3</sub> )

solution as a polluting by-product. A relatively high level of sulphur was found on the surface of the unmodified adsorbents; 2.94 and 17.6% for CaFe-Cake and RH, respectively. After modification with NaOH the obvious appearance of sodium and a decrease in sulphur level was observed, corresponding to the introduction of NaOH onto the adsorbent surface. Spectroscopic study showed the bending vibration of Si–O–Si at about 661–600 cm<sup>-1</sup> and bending vibration of O–Si–O at about 473–466 cm<sup>-1</sup> (Sitarz, 2008). In the spectra of each adsorbent, there were two additional bands at about 1620–1690 and 3407–3610 cm<sup>-1</sup>, which are the characteristic peaks for adsorbed water (Table 3). The new bending vibration of H–O–H at 3406–3407 was observed in modified adsorbents by NaOH, and can be attributed to bonders of additional hydroxyl group. The FT-IR spectra of modified RH and CaFe-Cake with Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are given in Table 2. The peak between 800 and 450 cm<sup>-1</sup> was observed for both adsorbents modified with TiO<sub>2</sub> and attributed to TiO<sub>2</sub> nanoparticles. Two new peaks were appeared in the spectrum of both adsorbents modified with Al<sub>2</sub>O<sub>3</sub>. The peak at about 980–1000 cm<sup>-1</sup> was assigned to the Al–O stretching bands, and other peak about 611 cm<sup>-1</sup> is Al–O<sub>2</sub> bending vibration.

The particle size distribution and specific area of the unmodified and modified adsorbents are shown in Table 3. The specific surface area of RH is approximately ten times greater than that of CaFe-Cake. The SEM images of unmodified and modified adsorbents are shown in Figs. 1 and 2. The modification of CaFe-Cake and RH with NaOH shows that the surface of the modified material is completely covered by NaOH layer, partly causing the observed reduction in specific surface area through increased mass and partial filling of the porosity. Despite the apparent aggregation of the particles in the images, they still appeared to be microparticles, indicating that the size of the material surface area is largely due to their fine structure and macroporous nature.

**Table 3**  
Band assignments of the FTIR spectra of adsorbents.

Adsorbent	Wave number (cm <sup>-1</sup> )						
	Si–O–Si 600–661	O–Si–O 466–473	H–O–H 1620–1690	H–O–H 3470–3610	Ti–O <sub>2</sub> 450–800	Al–O 980–1000	Al–O <sub>2</sub> 610–611
CaFe-Cake	+	+	+				
CaFe-Cake_NaOH	+	+	+	+			
CaFe-Cake_Al2O3	+	+	+			+	+
CaFe-Cake_TiO2	+	+	+		+		
RH	+	+	+				
RH_NaOH	+	+	+	+			
RH_Al2O3	+	+	+			+	+
RH_TiO2	+	+	+		+		

The film thickness of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> was controlled on silicon substrates. Five silicon samples were placed in the reactor around sorbents for each of process. The measurements of film thickness showed uniform deposition of thin films. The growth rate was 1.3 Å/cycle and 0.6 Å for Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, respectively and correlated with previous publication (George, 2010).

The specific surface area for modified RH with Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> remained unchanged compared to the unmodified material (Table 4). However, for CaFe-Cake it increased by about two times. According with the porosimeter data, the pore size is considerably decreased and became 10–20 and 2–3 nm for both adsorbents modified with TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively. The distinctive crystalline nanoparticles of TiO<sub>2</sub> can be observed on Fig. 1d. TiO<sub>2</sub> lay down on the surface of sulphate tailing by the sufficiently uniform layer. However, TiO<sub>2</sub> form the more thick and unequal structure on the RH surface (Fig. 2d). Aluminium oxide is produced in a compact and fine-pored layer on the both adsorbents (Figs. 1c and 2c).

### 3.2. Adsorption performance

#### 3.2.1. Effect of adsorbent dosage

The optimal amount of unmodified and modified CaFe-Cake and RH for As(III) and As(V) removal with initial concentration of 20 mg L<sup>-1</sup> was found. It can be seen (Fig. 3) that initially the percentage of As(III) and As(V) removal increased with increasing amounts of adsorbent and depended on the modification. For example, ALD method decreases adsorbent amount in four and two times for CaFe-Cake and RH, respectively. Equilibrium for As(III) and As(V) removal was reached at both unmodified adsorbents with concentration of 40 g L<sup>-1</sup> and 20 g L<sup>-1</sup>, respectively. The highest removal percentage of As(V) and As(III) (99 and 90%) was achieved with RH, while removal percentages with CaFe-Cake were 90 and 40%, respectively (Fig. 4).

As can be seen, the removal percentage of As(III) increased significantly from 40% with modified CaFe-Cake and amounted at 70, 92 and 95% for CaFe-Cake\_NaOH, CaFe-Cake\_Al<sub>2</sub>O<sub>3</sub>, CaFe-Cake\_TiO<sub>2</sub>, respectively (Fig. 3). The removal percentage of As(III) with RH\_NaOH, RH\_Al<sub>2</sub>O<sub>3</sub>, RH\_TiO<sub>2</sub> increased from 90 to 97, 98 and 99%, respectively. The removal percentage of As(V) with all of modified adsorbents changed only slightly at about 99%.

#### 3.2.2. Effects of solution pH and redox potential

The effects of solution pH and redox potential were investigated with unmodified and modified adsorbents. The oxidation state of arsenic directly depends on pH and redox potential of the solution. Arsenic species are include arsenites (As (III)), arsenates (As (V)), arsenious acid (H<sub>3</sub>AsO<sub>3</sub>, H<sub>2</sub>AsO<sub>3</sub>·, HAsO<sub>3</sub><sup>2-</sup>), arsenic acid (H<sub>3</sub>AsO<sub>4</sub>, H<sub>2</sub>AsO<sub>4</sub>·, HAsO<sub>4</sub><sup>2-</sup>), as well as their methyl- and dimethyl derivatives. Therefore, the degree of arsenic oxidation state in the solution can be controlled by

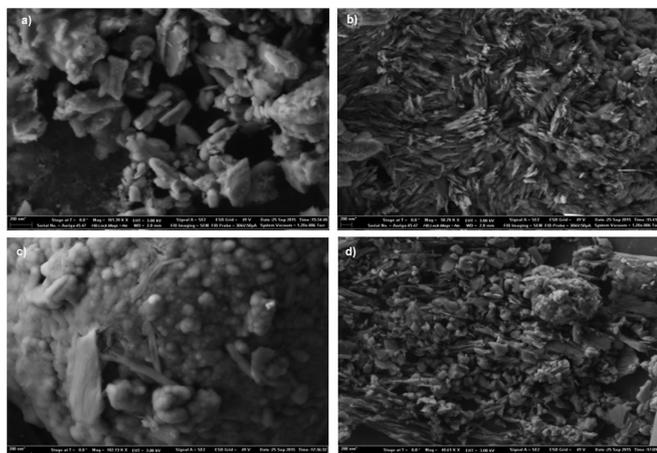


Fig. 1. SEM images of a) unmodified CaFe-Cake, b) CaFe-Cake\_NaOH, c) CaFe-Cake\_Al<sub>2</sub>O<sub>3</sub> d) CaFe-Cake\_TiO<sub>2</sub>.

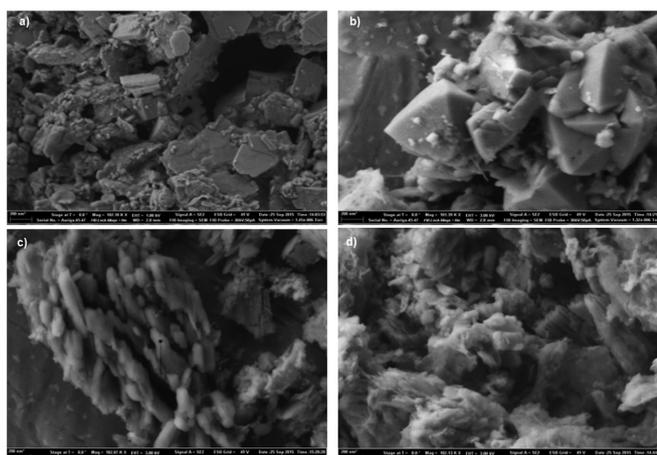


Fig. 2. SEM images of a) unmodified RH, b) RH\_NaOH, c) RH\_Al<sub>2</sub>O<sub>3</sub> d) RH\_TiO<sub>2</sub>.

Table 4

The particle size distribution and specific surface area of adsorbents.

Adsorbent	Specific surface area, m <sup>2</sup> g <sup>-1</sup>	Pore size, nm
CaFe-Cake	6.5	550
CaFe-Cake_NaOH	4.7	20
CaFe-Cake_Al <sub>2</sub> O <sub>3</sub>	10.2	2–3
CaFe-Cake_TiO <sub>2</sub>	15	10
RH	62	180
RH_NaOH	8.4	30
RH_Al <sub>2</sub> O <sub>3</sub>	65	20
RH_TiO <sub>2</sub>	74	3

varying pH. The removal efficiency of As(III) and As(V) with modified CaFe-Cake increases significantly from 40 to 95% and from 90 to 99%, respectively, as pH increases from 6 to 8, in compare with unmodified CaFe-Cake. In case with modified RH in compare with unmodified, the removal efficiencies of both forms of arsenic increase smoothly from 95 to 98% for As(III) and from 78% to 98% for As(V), respectively, as pH increases from 6 to 8. In addition to the above, equilibrium was observed for both sorbents only at pH 8. In case that the removal percent for both form of arsenic did not change or increased slightly. Equilibrium in the system from pH 6–8 has been observed by some researchers (Banerjee et al., 2008; Wang and Tsang, 2013;

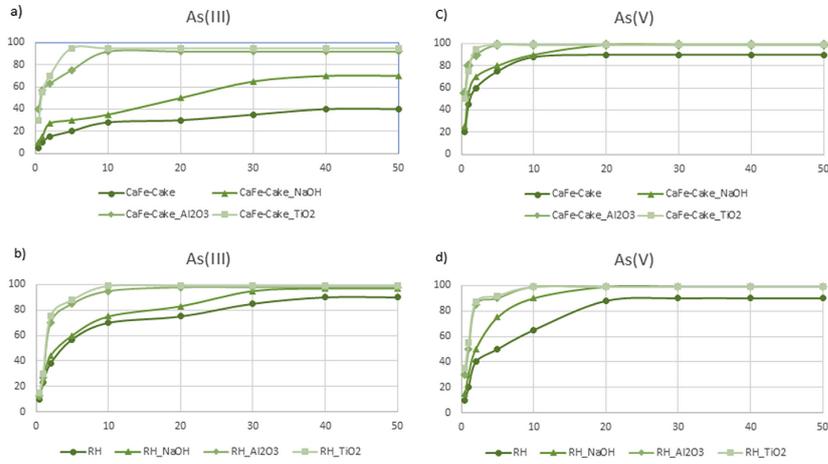


Fig. 3. Removal of As(III) (a,b) and As(V) (c,d) with different amount of adsorbents. Initial concentration of arsenic is 20 mg L<sup>-1</sup>.

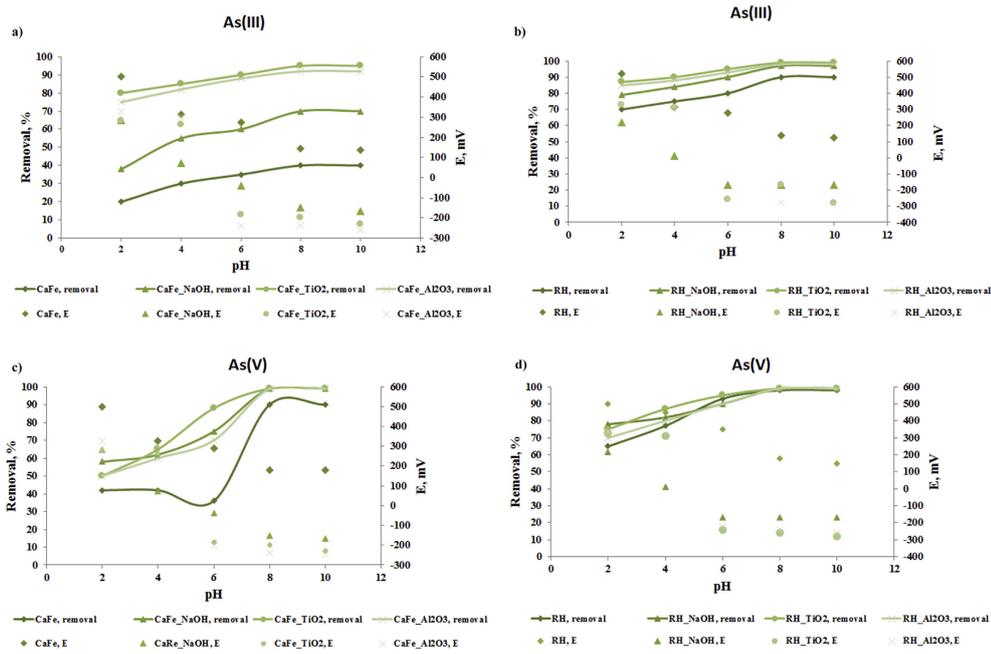
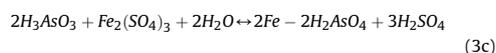
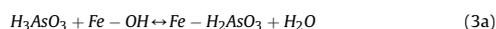


Fig. 4. Effect of solution pH (should be read in the left) and redox potential (should be read on the right) for removal of (a, b) As(III) with CaFe-Cake and RH, respectively; (c, d) As(V) with CaFe-Cake and RH, respectively.

Wang et al., 2014). The coagulation and complex formation of arsenic with iron sulphate or hydroxide is controlled by pH and occurred better at pH range from 6 to 8 (Wang et al., 2014). The value of Eh decreased during adsorption process in compare with initial value. It happens because of reaction which occurs between arsenic compounds and adsorbent and may form complex compound. In turn, this process results in decrease of Eh which can be explained by release of sulphate from adsorbents surface (Wang et al., 2014). In both cases a sustained decrease in Eh from 550 to about –280 could be seen (Fig. 4). This is confirmed by the fact that in the more reactive systems Eh is less than 100 mV (Doull's, 2001). Since one of the objectives of this research was to study the behaviour of adsorbents for arsenic removal from acid mine wastewaters, it could be supposed that RH is more effective for As(III) and As(V) removal than CaFe-Cake at a pH less than 6. The better removal of arsenic with RH can be explain by the fact, that CaFe-Cake has sulphur compounds in their composition, which may negatively affect to arsenic removal, as was estimated above. The surface area of RH is greater than surface area of CaFe-Cake by an order (Table 4). It also can be the cause of the better capacity of RH for arsenic removal compared to CaFe-Cake. For both adsorbents, it could be better to increase pH above 6 first before carrying out the adsorption process, which will then be more effective. According to this experiment, pH 6 was selected as the optimum value for batch adsorption experiments.

### 3.2.3. Kinetic study

Kinetic models describe the process of chelation on the adsorbent surface, depending on adsorbent and adsorbate contact time. The mechanism of the complex formation of As(III) and As(V) with ferric hydroxide or sulphate is shown below (Eqs. (3a), (3b) and (3c)).



Adsorption kinetics was studied using pseudo second-order models under pH 6. The pseudo second-order model, which assumes that the adsorption process is limited by the surface reaction, takes this form (Eqs. (4) and (5)):

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (4)$$

$$\frac{d[As]}{dt} = k_2(q_{As} - q_{Fe-OH/SO_4})^2 \quad (5)$$

where  $q_{As}$  and  $q_{Fe-OH/SO_4}$  ( $\text{mmol g}^{-1}$ ) represent the amount of ion adsorbed at time  $t$  (min) and at equilibrium, respectively, and  $k_2$  is the pseudo second-order rate constant.

The estimated parameters of the pseudo second-order equation are listed in Table 5. The process of arsenic adsorption from liquids is well described by the pseudo second-order model. This model suggests that the system includes the formation of at least two compounds, or it is a multi-component system with a complex compound of adsorbent and adsorbate. Equilibrium was observed in the system after 750 and 1200 min for As(III) and As(V), respectively with CaFe-Cake and CaFe-Cake\_NaOH (at pH 10) and after 750 min for both forms of arsenic with RH and RH\_NaOH (at pH 6). Considering that As(III) and As(V) are the neutral and

**Table 5**

Estimated parameters of the pseudo-second-order equation for (a) CaFe and (b) RH. Agitation speed is 50 rpm, concentration of As(III) and As(V) is 0.266 mmol/l.

Adsorbent	Adsorbate	pH 6		
		$q_e$ ( $\text{mmol g}^{-1}$ )	$k$ ( $\text{L mmol}^{-1}$ )	$R^2$
CaFe	As(III)	0.004	3.05	0.97
	As(V)	0.012	0.99	0.97
CaFe_NaOH	As(III)	0.006	1.79	0.94
	As(V)	0.013	1.41	0.94
CaFe_Al <sub>2</sub> O <sub>3</sub>	As(III)	0.026	0.66	0.95
	As(V)	0.052	0.63	0.96
CaFe_TiO <sub>2</sub>	As(III)	0.049	0.20	0.98
	As(V)	0.053	0.34	0.99
RH	As(III)	0.007	4.04	0.93
	As(V)	0.007	6.51	0.88
RH_NaOH	As(III)	0.007	0.88	0.98
	As(V)	0.014	1.38	0.98
RH_Al <sub>2</sub> O <sub>3</sub>	As(III)	0.014	0.93	0.99
	As(V)	0.027	4.51	0.98
RH_TiO <sub>2</sub>	As(III)	0.028	0.23	0.99
	As(V)	0.029	0.47	0.99

charged ions, respectively, the effect of pH on  $k$  was more signified for As(V), than for As(III). Other researchers (Banerjee et al., 2008) reported an analogue effect of pH on As(V) and As(III) adsorption with iron hydroxides and oxides. For modified adsorbents with ALD, equilibrium was observed a little early and at about 480 min for both adsorbent.

### 3.2.4. Adsorption isotherms

As it is crucial to understand the interaction between adsorbate and adsorbent, the Langmuir (Eq. (6)) and Toth (Eq. (7)) isotherm models were used:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

$$q_e = \frac{q_m C_e}{(a_T + C_e^{m_T})^{1/m_T}} \quad (7)$$

where  $q_e$  and  $C_e$  are arsenic adsorption capacity ( $\text{mmol g}^{-1}$ ) and concentration of arsenic in the solution ( $\text{mmol L}^{-1}$ ) at equilibrium, respectively;  $q_m$  is the maximum uptake capacity;  $K_L$  is Langmuir constant;  $a_T$  is adsorptive potential constant ( $\text{mmol L}^{-1}$ ),  $m_T$  is the heterogeneity factors of the Toth isotherm.

The Langmuir isotherm produced the monolayer coverage from the adsorption model, and the fitted  $q_m$  values of As(III) and As(V) by CaFe-Cake and RH were calculated to be 26.7 and 36.7; 215 and 248  $\text{mmol g}^{-1}$  at  $T = 25$  °C, respectively. The maximum uptake capacity for both forms of arsenic was ten times higher for RH than for CaFe-Cake. The maximum adsorption capacity was also higher for As(V) for both adsorbents, as was also observed by Wang and Tsang (2013), under the same experimental conditions. The comparison of  $R^2$  indicated that the Toth and Langmuir models well describe the adsorption of As(III) onto CaFe-Cake and RH (Table 6) for lower adsorbate concentrations. These phenomena could be due to the fact that the system is homogenous at low concentrations of adsorbate. With increasing concentrations of adsorbate, however, competitive sites appeared and the process proceeded in a heterogeneous phase. The Toth model well describes the adsorption process throughout the range of concentrations. This is in agreement with the finding of Lakshmanan et al. (2010), who stated that the Toth isotherm model can be better applied to adsorption processes on heterogeneous surfaces than the Langmuir model.

**Table 6**  
Isotherm parameters for CaFe-Cake and RH during adsorption process of As(III) and As(V) from model solution.

Langmuir model		$C_i$ (mmol/l)	$q_{m \text{ exp}}$ (mmol/g)	$q_m$ (mmol/g)	$K_L$ (L/mmol)	$R^2$	
CaFe-Cake	As(III)	0.933	26.66	93.8	0.004	0.99	
	As(V)	2.533	36.66	92.5	0.722	0.99	
RH	As(III)	34.12	215	45.2	0.82	0.99	
	As(V)	2.50	248	21.1	0.79	0.99	
Toth		$C_i$ (mmol/l)	$q_{m \text{ exp}}$ (mmol/g)	$q_m$ (mmol/g)	$a$ (mmol/l)	$m$	$R^2$
CaFe-Cake_NaOH	As(III)	2.66	31.4	32.2	1.16	3.38	0.99
	As(V)	1.02	2	2.21	6.37	1.28	0.99
CaFe-Cake_Al <sub>2</sub> O <sub>3</sub>	As(III)	2.0	31	32.7	0.59	4.87	0.98
	As(V)	0.49	8	7.9	139	2.74	0.99
CaFe-Cake_TiO <sub>2</sub>	As(III)	1.13	40	42.4	2.97	2.74	0.99
	As(V)	0.63	8	7.8	122	2.68	0.99
RH_NaOH	As(III)	2	1	1.99	2.2	0.95	0.99
	As(V)	9.33	94	9.77	0.03	9.77	0.99
RH_Al <sub>2</sub> O <sub>3</sub>	As(III)	1.33	2	1.5	1	0.58	0.99
	As(V)	2.66	33.3	158	8287	158	0.99
RH_TiO <sub>2</sub>	As(III)	0.66	2	1.52	0.9	0.47	0.98
	As(V)	2	33	13.3	40	13.3	0.99

### 3.3. Desorption process

Study of the desorption process showed that the greatest desorption (from 98% to 50%) of As(V) occurred at pH 10 with CaFe-Cake. At pH 7, desorption of both As(III) and As(V) took place with CaFe-Cake (Fig. 5). The same phenomenon has been obtained previously (Sun et al., 2013). With RH, desorption occurred only for As(V) at pH 4 after 240 min (Fig. 6). The increasing desorption of As(V) at pH 10 with respect to pH 7 from CaFe-Cake and lack desorption of As(III) from RH can be associated with the onset of the reverse reaction (3c) with increasing pH. The large amount of sulphates in composed of CaFe-Cake is potential reason to counter reaction and desorption of As(V).

### 3.4. Removal of arsenic from wastewater

Mining wastewater treatment is a very complex process and depends on several factors, such as wastewater matrices and pH. A mining wastewater from a 270 m depth with a pH of 3.2 was investigated in this research. The experiments were carried out at ambient temperature for 12 h with 40 g L<sup>-1</sup> and 20 g L<sup>-1</sup> unmodified CaFe-Cake and RH, respectively. The pH of 3.2 was increased to 6.8 and the Eh decreased from 700 to 500 after 8 h. Removal of As(III) and As(V) from the real wastewater was more effective with RH (nearly 100%), than with CaFe-Cake (Fig. 7). Unmodified RH

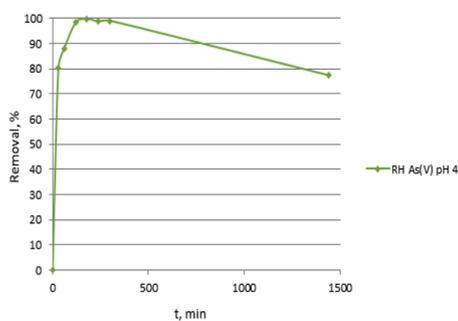


Fig. 6. Desorption process of As(V) with RH.

showed a good affinity for As(III) and As(V) in wastewaters. The affinity for As(III) was greater than for As(V) with CaFe-Cake. The percent removal of arsenic by modified and unmodified CaFe-Cake from real AMD is lower, than from synthetic solution. This may be due the fact that the real AMD has in composition a significant concentration of metal ions, which may be the cause of competitive reactions with adsorbent surface.

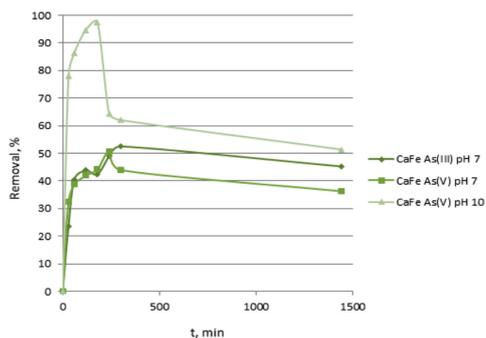


Fig. 5. Desorption process of As(III) and As(V) with CaFe-Cake.

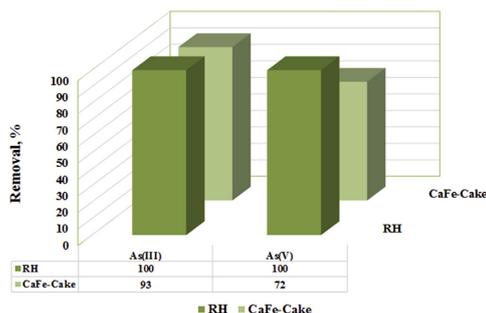


Fig. 7. Removal of As(III) and As(V) from real AMD with unmodified RH and CaFe-Cake.

#### 4. Conclusions

The structural and compositional properties of two solid wastes were studied. The thin TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> layers on the solid wastes by ALD increase the removal efficiency of the both adsorbents about two times as high as that modified with NaOH. However, ALD is expensive and complicate method for industrial production of adsorbents, for the time being. Since, modification with sodium hydroxides could be used as an effective and inexpensive method of improving the properties of both adsorbents. The adsorption behaviour of unmodified and modified adsorbents was investigated for the removal of arsenic (III) and (V) from synthetic solutions and acidic wastewaters from a mining site. It was found that these materials exhibit effective adsorption properties for arsenic. Both adsorbents were more efficient with As(V) than As(III), however RH can be used to remove both forms of arsenic. Therefore, CaFe-Cake and RH solid wastes can be used effectively after modification as adsorbents for As removal.

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## **Publication IV**

Iakovleva, E., Sillanpää, M. Maydannik, P., Sillanpää, M., Liu, J.T., Allen, S., Albadarin, A.B.,  
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**Manufacturing of novel low-cost adsorbents: co-granulation of limestone and coffee waste.**

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Research article

## Manufacturing of novel low-cost adsorbent: Co-granulation of limestone and coffee waste



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### ABSTRACT

Limestone and coffee waste were used during the wet co-granulation process for the production of efficient adsorbents to be used in the removal of anionic and cationic dyes. The adsorbents were characterized using different analytical techniques such as XRD, SEM, FTIR, organic elemental analysis, the nitrogen adsorption method, with wettability, strength and adsorption tests. The adsorption capacity of granules was determined by removal of methylene blue (MB) and orange II (OR) from single and mixed solutions. In the mixed solution, co-granules removed 100% of MB and 85% of OR. The equilibria were established after 6 and 480 h for MB and OR, respectively.

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### 1. Introduction

During recent decades, researchers considered solid wastes as sources of biofuels (Schröder, 2015), fertilizers (Nishio and Nakashimada, 2013), composite materials (Pavla, 2011) and low-cost adsorbents for water treatment (Kaushik et al., 2009; Bhatnagar et al., 2015; Iakovleva and Sillanpää, 2013). The main problems regarding water treatment are the minimization and reuse of processed water, and cost saving including a reduction in energy consumption. Despite a quarter century of studies, these problems of solid and liquid wastes management are as relevant today as 25 years ago, when the term “industrial ecology” was introduced (Smith et al., 2015).

For example, Finland is first in the world for coffee consumption and has about 50M kg coffee wastes per year (Ojaniemi, 2010). Coffee wastes are mostly used as a source for bio-energy and fertilizers (Cruz et al., 2015; Adi and Noor, 2009). In some research papers, coffee waste has been used as biosorbents for the removal

of acid dye (Gupta and Suhas, 2009; Rafatullah et al., 2010; Lafi et al., 2014; Roh et al., 2012; Kyzas et al., 2012), organics (Al-Zaben and Mekhamer, 2013; Lafi and Hafiane, 2015; Rossmann et al., 2012) and metal ions from aqueous solutions (Azouaou et al., 2010; Boonamnuayvitaya et al., 2004; Ching et al., 2011; Kaikake et al., 2007; Oliveira et al., 2008; Pujol et al., 2013). Coffee waste has a high C/N ratio, and contains carboxylic group (Cruz et al., 2015) ensuring high efficiency for metal ions removal due to chelates formation (Adi and Noor, 2009; Lafi et al., 2014). Therefore, the coffee waste could be used as potentially effective sorbent for various pollutants, including metal ions. In order to test properties of new adsorbent Methylene Blue (MB) and Orange II (OR) were used as model acidic and basic pollutants, respectively. Various functional groups such as amino, hydroxyl, carboxyl and sulfate on the bio-waste surface, which can act as binding sites for acidic and basic dyes, help to increase the adsorption effect (Adegoke and Bello, 2015; Kyzas et al., 2012). Clay and siliceous materials show high affinity for pollutants in acidic solution as a scavenger through an ion-exchange process (Iakovleva et al., 2015).

A combination of limestone and coffee waste might improve the removal efficiency of pollutants and ensure neutralization of the acidic water, based on the ion-exchange reactions on the surface of combined sorbent.

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Adsorbents must have certain properties to be suitable for industrial use. The combined sorbents must be resistant to water, must not stick together, and should retain the properties of the original materials (Albadarin et al., 2014; Mangwandi et al., 2014). Granulation of two different materials was chosen as a way to produce a uniform dual adsorbent. There are some requirements of the material to be produced, including segregation of the powder particles, uniform granules, their wettability, strength and stability in the solutions. The adsorbent should be stable to the transportation as well. The main parameters of the granulation process are process variables such as processing time, impeller speed and formulation variables such as particles size and choice of binder. Homogeneous materials are granulated uniformly, and produce pellets of the similar size and composition. Our choice of binder was made taking into account results of previous studies (Mangwandi et al., 2014). The widely used carboxymethylcellulose binder was not suitable in this research as it is water soluble; the resultant granules would disintegrate when coming into contact with the waste water. It seems that polyvinyl acetate (PVAc) might give better results in the granulation of dissimilar materials and it is water insoluble.

The main aim of this research was to develop a low-cost and effective sorbent for water treatment of both anionic and cationic pollutants, as well as neutralization of acidic water. Limestone seemed to be one of the most suitable candidates for acidic water neutralization as well as for removal of a number of pollutants. Limestone is a commercial material for acidic neutralization of water and agriculture's grounds (Iakovleva et al., 2015; Mangwandi et al., 2014). This work proposes the novel approach to the treatment of waste water from cationic and anionic dyes using the same sorbent. In order to improve the adsorption properties of the limestone, a combination of limestone and coffee wastes will be used in this research. In this study, coffee waste and limestone were co-granulated using PVAc as binder. The strength and wettability of granules, as well as their reuse and resistance to liquid solutions were determined. Adsorption properties of new adsorbents were tested for their ability to remove MB and OR. The competition of removal of both cationic and basic dyes from complex liquid was examined.

## 2. Raw materials

Limestone was provided by Killwaughter Chemical Ltd UK. The CW was collected from the cafeteria at Queen's University Belfast, Rami cafeteria of Mikkeli and Green Chemistry Laboratory of Lappeenranta University of Technology. Before use, CW was washed with distilled water, and oven dried for 12 h at 60 °C.

Polyvinyl acetate (PVAc) and acetone by MERCK UK were used as a binder in the granulation process. Solution of PVA was prepared by dissolving a known mass of the PVAc (from 10 to 40%) in acetone. The mixture was stirred for about 20 min at 60 °C to obtain a homogenous solution. The viscosities of the binder solutions were determined by the Haake Viscotester C.

## 3. Co-granules production

A small bench scale high shear granulator (KENWOOD KM070 (Japan) was used for the granulation of materials. The known mass of limestone powder and coffee waste were added to the mixer and mixed without binder for 60 s. The known value of binder was added to the powder during the next 30 s without stopping the rotator. The mixing of powder was performed at an impeller speed of 490 rpm and binding occurred within 60 s until the formation of granules.

## 4. Characterization of raw materials and co-granules

### 4.1. Spectral and physics characterization

The particle size distribution was determined using dispersion analyzer LUMiSizer 610/611 (GmbH). The measurements were performed thrice.

The chemical composition and organic elemental analysis of raw materials were determined with an energy dispersive X-ray fluorescent (ED XRF) analyzer X-Art (Joint Stosk Company Comita, St. Petersburg, Russia) and CHNS-O analyzer (Flash 2000 Elemental Analyzer, Thermo Fisher Scientific, UK), respectively.

FTIR spectra of raw materials and granules were recorded with a Bruker Vertex 70v spectrometer. Spectra were collected in the mid infrared region (4000–400 cm<sup>-1</sup>) averaging 124 scans with 4 cm<sup>-1</sup> resolution. Samples were prepared by the standard KBr pellet methods.

The samples were characterized with nitrogen sorption at 196 °C using TriStar 3000 (Micromeritics Inc., USA). The specific surface area of samples was calculated using the Brunauer-Emmett-Teller (BET) theory.

Microstructure of the raw and produced materials was examined using a scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company). The experiment was carried out at low vacuum condition in secondary electron mode. For the analysis, samples were covered with a gold layer.

In order to study the effect of binder viscosity on the co-granulation process, different granulation experiments were carried out using binder solution of different concentrations whilst maintaining the other processing conditions constant. All experiments were carried out at room temperature (24 °C) with mixing time and speed of 2 min and 490 rpm, respectively.

The effect of the L and CW ratio on the granulation process was studied using different amounts of each material. The granules were dried for 12 h at 80 °C. The dried granules were separated according to size by sieving. The percentage of co-granules in each size range was calculated by following equation:

$$n = \left( \frac{m_i}{m_t} \right) \times 100\% \quad (1)$$

where  $m_i$  and  $m_t$  are initial and total the measure range mass of co-granules, respectively.

Granules strength was measured from diametric compression of the single granules using previously described method using Eq. (2).

$$\sigma = 2.8 \times \left( \frac{F_i}{\pi D^2} \right) \quad (2)$$

where  $F_i$  (Newton) is compressive force during testing of granules strength,  $i$  is number of tests,  $D$  (mm) is granules diameter.

Granules wettability was tested by mixing a known mass of granules with water at ambient temperature for 72 h. After testing, all granules were oven dried for 12 h at 80 °C. The strength and size of granules were determined before and after wettability tests.

### 4.2. Batch adsorption experiments

Sorption tests of pollutants were conducted by mixing a known weight (from 0.5 to 40 g L<sup>-1</sup>) of L, CW, PVAc and LCW with 15 ml of synthetic solution of MB and OR. The concentration of dyes on the synthetic solution ranged from 5 to 20 mg L<sup>-1</sup>. The experimental solutions were shaken by a shaker ST5 (IKA KS 4000i Control) from 1 to 720 h. 10 mL solutions were taken from flasks at known time

**Table 1**  
Chemical composition of raw materials (XRF and organic elemental analysis).

Element	L (w%)	CW (w%)
Al	1.5	<1
C	3.3	60
Ca	21.3	<1
H	–	6
K	0.25	<1
N	–	3
O	52.7	25
S	0.1	<1
Si	42	5

intervals and filtered using a 0.20  $\mu\text{m}$  diameter polypropylene syringe filter. For determination of final concentration of dyes, 2 mL of solution was taken and determined by UV/Vis spectrometer (Lambda 45 PerkinElmer Instrument) at wavelength 664 and 486 for MB and OII, respectively.

The percentage adsorption was calculated as:

$$\% \text{Adsorption} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (3)$$

where A is adsorption,  $C_i$  and  $C_t$  ( $\text{mg L}^{-1}$ ) are the pollutants concentrations in the initial and treated solutions, respectively.

## 5. Results and discussion

### 5.1. The chemical composition of materials

The chemical compositions of the raw materials are presented in Table 1. These results were collected with ED-XRF and organic elemental analysis. The limestone contains about 20% calcium and 40% silicon. The coffee waste consists mainly of organic components, such as lignin, nitrogenous compounds, fibers, etc. (Narita and Inouye, 2014).

### 5.2. The particle size distribution

The average value of particle size distribution has been reported in Fig. 1. The coffee waste particles are approximately ten times

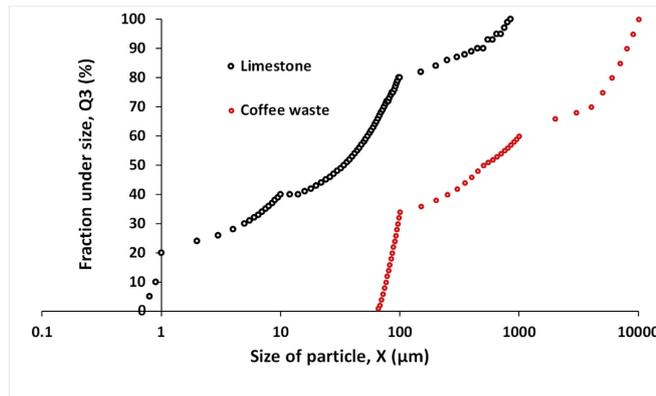
larger than the limestone particles. Their diameters range from 100 to 1000  $\mu\text{m}$  and are less uniform than limestone powder. More than ten times difference in particle size of the two materials might cause problems during the binding process. Also, great difference in particles size might complicate uniform granulation. Therefore, the selection of the ratio of the two raw materials presents three challenges. The first is to choose the concentration of binders for sufficient strength at which the granules will withstand long exposure to water. The second is to choose the appropriate ratio of the two materials with different particle size. And the last is to produce granules with sufficient surface area of sorbents for efficient pollutant removal.

### 5.3. Co-granules production

The optimal concentration of binder was chosen by granulation of limestone and coffee waste separately. The data of binder solution viscosity and matrix of granulation test are presented in Tables 2 and 3. After preliminary tests the optimal binder concentration of 30% was chosen. The preliminary co-granules tests demonstrated that, for the preparation of the largest granules ( $>1000 \mu\text{m}$ ) with high wettability, the best combination was 7 parts limestone to 3 parts coffee waste. This ratio was used for further experiments. The chosen materials ratio and binder concentration produced the greatest number of granules with particle size from 1 to 2 mm. These granules have better stability upon contact with water and remain approximately the same size and strength (Table 2). These co-granules should be used for waste water treatment over an extended testing time.

**Table 2**  
Viscosity of binder solutions with various concentration of PVA.

$C_{\text{PVA}}$ (%)	$\mu$ (mPa·c)
10	1.4
15	13
20	37
25	52
30	72
35	111
40	157



**Fig. 1.** Particle size distribution of limestone and coffee waste.

**Table 3**

Mass fraction of raw materials, size and strength of granules before and after wettability test.

Mass fraction of limestone	Mass fraction of coffee waste	Size of granules, before wettability test (%)			Strength of granules before wettability test (MPa)	Strength of granules after wettability test (MPa)
		1–2 mm	0.5–1 mm	≤0.5 mm		
1.0	0.0	28	49	23	28	21
0.75	0.25	25	27	48	28	10
0.70	0.30	60	30	10	35	14
0.60	0.40	49	47	4	12	2
0.50	0.50	40	53	7	10	3
0.40	0.60	36	45	19	11	3
0.30	0.70	30	46	24	9	2
0.25	0.75	28	48	24	27	39
0.0	1.0	40	53	7	28	42

**Table 4**

FTIR spectrum data for raw materials and granules.

Compound	WN <sub>L</sub> (cm <sup>-1</sup> )	WN <sub>CW</sub> (cm <sup>-1</sup> )	WN <sub>LCW</sub> (cm <sup>-1</sup> )
C=O <sub>2</sub>	719	+	+
C-H	–	808	–
Ca-C≡O <sub>3</sub>	871	–	+
Si-O	1100	1029	+
S=O <sub>2</sub>	–	1158	–
C-O	–	1239	+
Ca-C≡O <sub>3</sub>	1377	–	+
Ca-O	–	1518	+
R=C=O	–	1654	–
R=C=O	–	1743	+
Ca-O	2512	–	+
R-O-H	–	2853	+
Si-O-H	3200–3700	2923	+
N-H	–	3294	+
R-O-H	–	3329	+

#### 5.4. Spectral characteristics

Spectroscopic studies of limestone in the mid-infrared region with FTIR analysis confirms the results of XRD studies. The compounds of calcium, carbonate, and silicone were detected with both analyses (Tables 1 and 4). Various organic compounds remained in coffee waste even after extraction, as confirmed by XRF, FTIR and organic elemental analysis. The results of spectroscopic analysis show that co-granules were composed of nearly all functional groups from the two raw materials. This indicates that the pre-

mixing of raw materials was uniform and the binder did not block the functional groups which are involved in the adsorption process.

The coffee waste has very low specific surface area and therefore is not presented. Specific surface area of the limestone and co-granules is about 2.2 m<sup>2</sup> g<sup>-1</sup> and only 0.4 m<sup>2</sup> g<sup>-1</sup>, respectively (Figs. 2 and 3). The low surface area of coffee waste and coating of the coffee waste particles with PVAc could cause sharp decrease of co-granules specific area. However, the spectroscopic analysis shows complex structure of materials. SEM images are presented in Fig. 4.

The surface structure of coffee waste is underdeveloped and almost flat, as was confirmed by BET method data (Fig. 4a). The structure of limestone is highly developed (Fig. 4b). The size of most particles is less than a micrometer. The surface of co-granules inherited a complex structure of limestone (Fig. 4c). Most likely, this is due to the fact that the fine particles of limestone are distributed on the flat surface area of coffee waste and set up agglomerations. For the purpose of this study, it is important that the functional groups of CW were available for pollutants during the removal process. The presence of functional groups on the surface area of co-granules was confirmed with FTIR (Table 4).

#### 5.5. Synthetic dye solution treatment

The removal of MB and OR with novel combinative granulated sorbents from single synthetic solution and mixture was

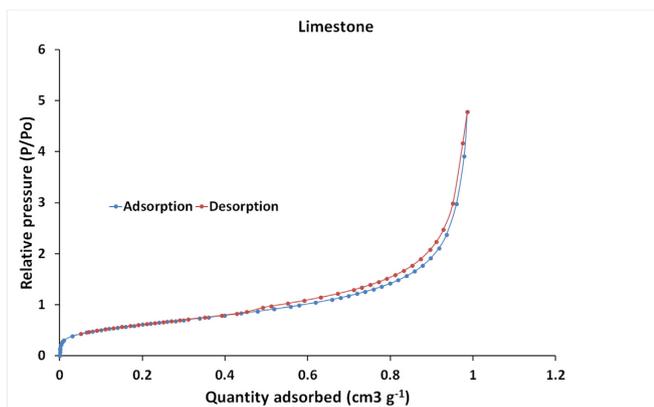


Fig. 2. Adsorption-desorption analysis of limestone with N<sub>2</sub>.

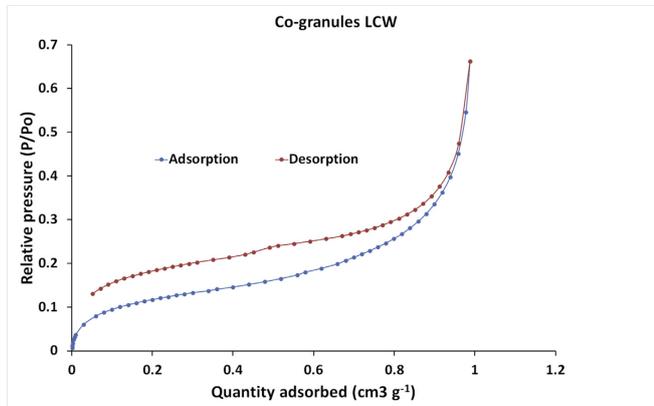


Fig. 3. Adsorption-desorption analysis of co-granules with N<sub>2</sub>.

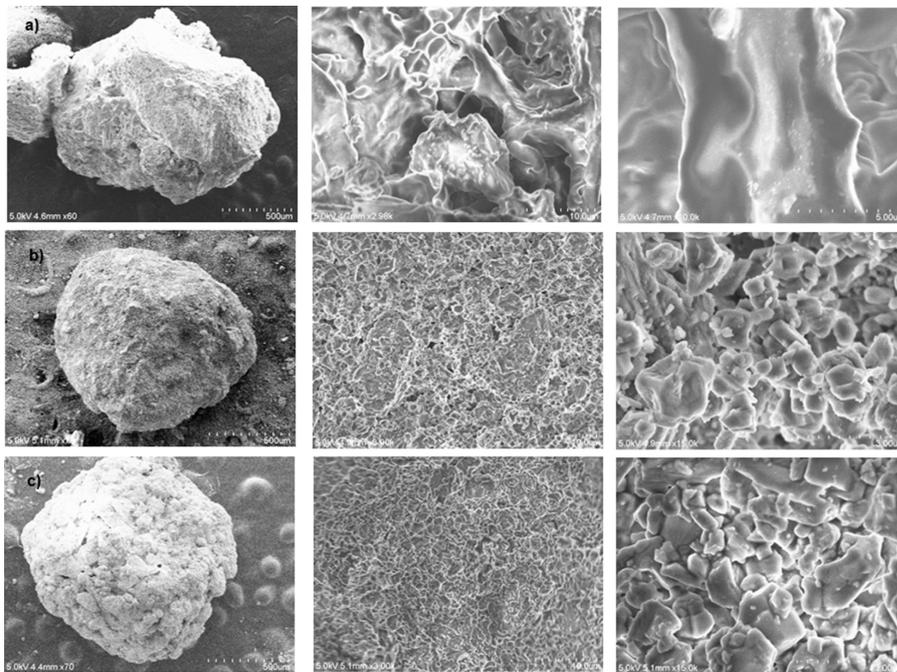


Fig. 4. SEM image of CW (a), L (b) and LCW (c).

researched in this work. The adsorption properties of co-granules and their materials were studied separately to understand possible removal mechanisms. The possible effect of binder on the removal of pollutants has been eliminated by the adsorption test

using PVAc for treatment of solution from both dyes.

#### 5.5.1. Optimization of adsorbent amount and contact time

The optimal amount of adsorbents and efficient contact time

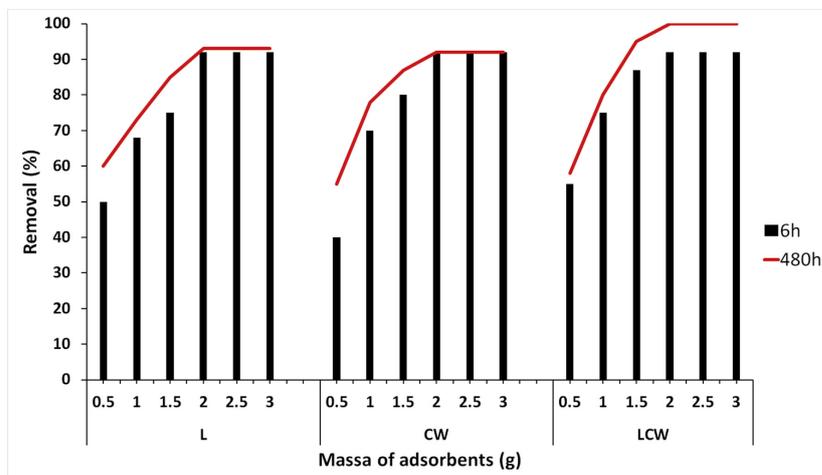


Fig. 5. Optimal conditions for the removal of MB with limestone, coffee waste and their co-granules.

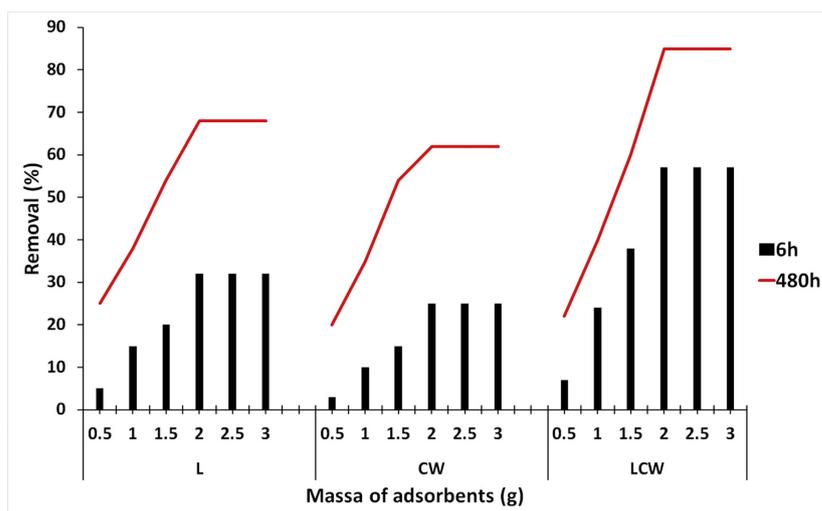


Fig. 6. Optimal conditions for the removal of OR with limestone, coffee waste and their co-granules.

with an initial concentration of dyes  $2 \text{ mg L}^{-1}$  are shown in Figs. 5 and 6.

The equilibrium of the systems was reached with the concentration of each adsorbents at  $2 \text{ g L}^{-1}$  for both dyes. The maximum removal of MB, 100%, and OR, 85% removal, was found after 6 and 480 h, respectively. Removal of both dyes was relatively higher with co-granules, as compared to each material individually. This could be explained by a smaller number of functional groups on the

surface area of the co-granules capable of removing anions, compared with cations.

#### 5.5.2. Effect of pH and possible removal mechanism

The impact of solution pH on the dyes adsorption process has been investigated by increasing the initial pH from 2 to 10, while the initial dyes concentration, temperature, co-granules dosage and contact time were kept constant at  $5 \text{ mg L}^{-1}$ ,  $25 \pm 2 \text{ }^\circ\text{C}$ ,  $2 \text{ g L}^{-1}$  and

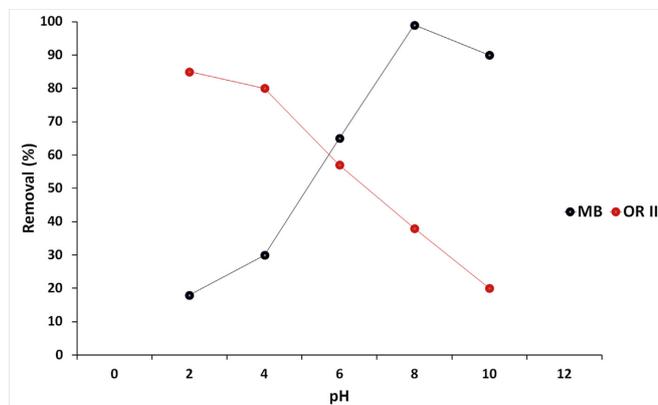


Fig. 7. Effect of pH on the adsorption amount of MB and OR with co-granules.

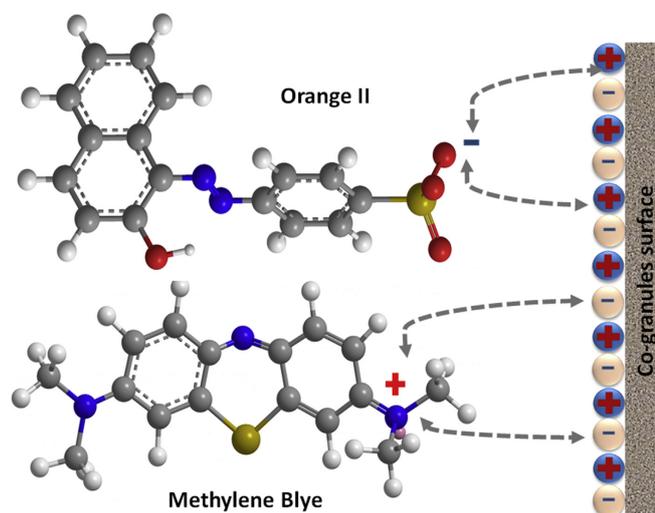


Fig. 8. Ion-exchange mechanism of MB and OR removal.

60 min, respectively (Fig. 7).

The study of the effect of pH on the removal of cationic and anionic dyes confirms the results of previous researchers (Albadarin et al., 2011; Ramesh et al., 2005; Kyzas et al., 2012; Lafi and Hafiane, 2015; Lafi et al., 2014). MB was removed from the solution more efficiently at high pH as the adsorption mechanisms associated with the formation of a complex between the positively charged ions and negatively charged dye ion on the adsorbent surface. While the adsorption capacity of OR increases in basic medium by electrostatic interaction between negatively charged dye ions and positively charged cell of co-granules surface (Lafi and Hafiane, 2015).

The possible removal mechanism of cationic and anionic dyes is ion-exchange between co-granules surface and pollutants. In case of OR there might be two mechanisms: ion-exchange between the positively charged ions on the surface of the co-granules and anionic dyes and physisorption between OR and carbon which is part of the coffee waste. For the removal of OR by ion-exchange mechanism the ionic strength of the solution should provide an exchange between the similar sodium cations, or between calcium and sodium (Fig. 8).

The process of adsorption of dyes is reversible. This was confirmed by desorption studies performed using solutions at different pH; the dyes were easily desorbed from the adsorbent

surfaces. Concentrated hydrochloric acid and sodium hydroxide, were used for the desorption of MB and OR, respectively. Experiments showed that desorption process of MB was 100%, while desorption efficiency of OR was only 50%. The reusing experiments showed that the developed co-granules can be used only once.

### 5.5.3. MB and OR ions competition

Competition between MB and OR during the adsorption on co-granules was observed. The presence of MB reduced the removal of OR from 85% to 60%. During experiments it was found that the amount of removed MB remained at 100% and equilibrium was reached after 24 h. However, the removal of OR was 60% and did not increase even after 720 h. By contrast, desorption process of OR into solution was observed and measured to be about 20%. It could be explained by the fact that the limestone increased pH of initial solution to pH 8 during the removal process. Decreasing concentration of OH<sup>-</sup> could change the positive charge surface of co-granules to negative, thereby reducing the sorption capacity of dye anions (Kyzas et al., 2012).

## 6. Conclusion

The novel efficient co-granules from CW and L for purifying acidic wastewater containing dyes were produced. The co-granules showed more affinity to acidic than to basic pollutants, and percentage removal from complex solution was 100 and 60, respectively. However, decreasing of pH solution to 2, allowed to increase to 85% removal of basic pollutants. The strength and resistance to wettability of co-granules makes them suitable for various types of water treatment, including passive and column methods. Use of these novel materials would reduce not only bio-waste amount, but would also benefit the water treatment with efficient and low-cost adsorbents.

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## **Publication V**

Iakovleva, E., Sillanpää, M., Mangwandi, C., Albadarin, A.B., Maydannik, P., Khan, S.,  
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**Application of Al<sub>2</sub>O<sub>3</sub> modified sulfate tailings (CaFe-Cake and SuFe) for efficient removal  
of cyanide ions from mine process water.**

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**Application of Al<sub>2</sub>O<sub>3</sub> modified sulfate tailings (CaFe-Cake and SuFe) for efficient removal of cyanide ions from mine process water**

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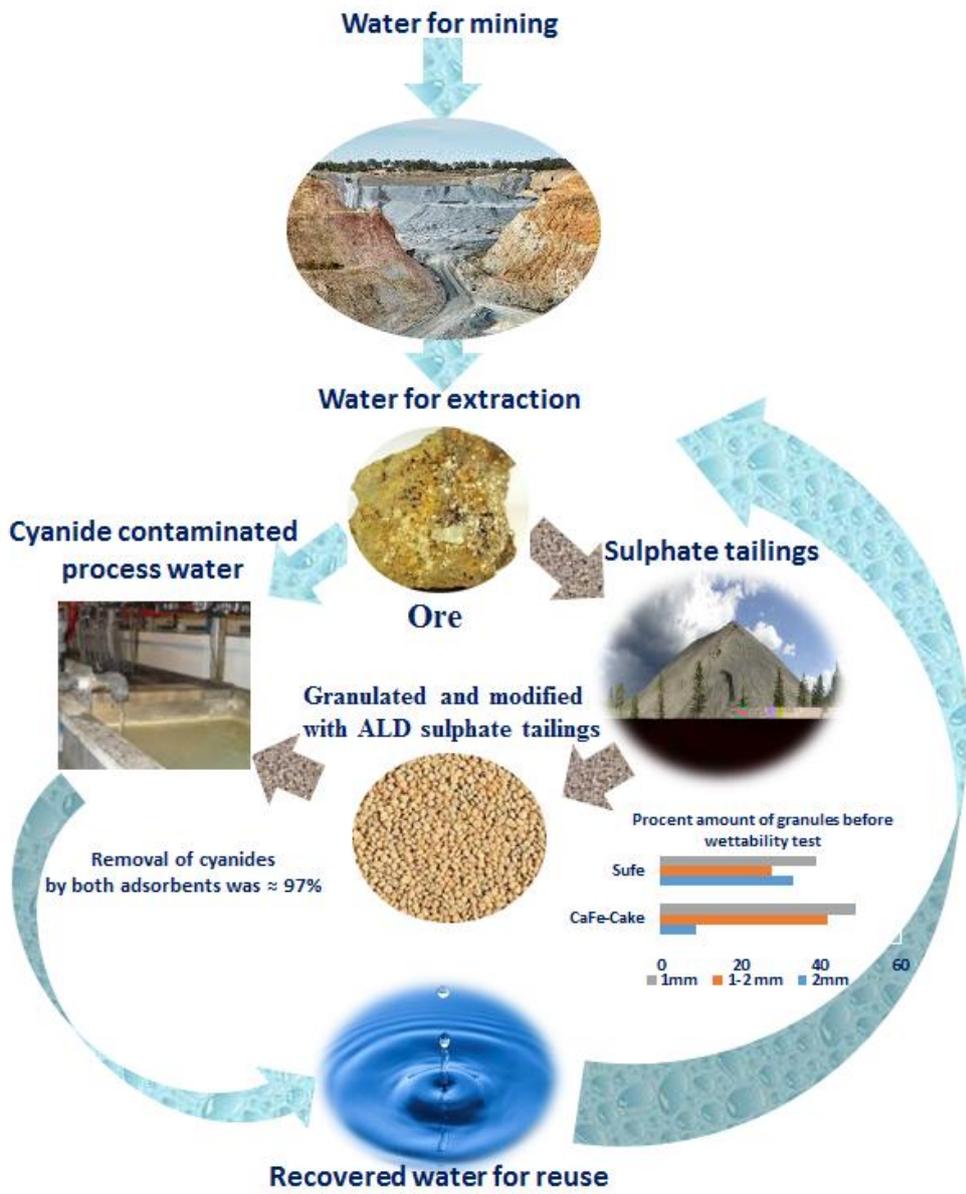
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## **ABSTRACT**

A novel approach for the management of solid and liquid wastes of mining was implemented in this work. Unmodified and modified metallurgical solid wastes, sulfate tailings, were used as adsorbents for the removal of cyanide ions from synthetic mine process water. Energy dispersive X-ray fluorescence (ED-XRF), scanning electron microscopy (SEM) and nitrogen adsorption methods, based on Brunauer-Emmett-Teller (BET) theory, were used for analysis of composition, structure and surface area of the adsorbents. A wet-granulation method was used for preparation of granules from sorbent powders with polyvinyl acetate as a binder and the further modification of the sorbent surface was carried out by atomic layer deposition (ALD) of  $\text{Al}_2\text{O}_3$ . The granules were used for the removal of cyanide ions from synthetic solutions by batch adsorption method. ALD-modified sorbent showed approximately  $3.5 \text{ mmol g}^{-1}$  adsorption capacity for cyanide ions. The adsorption isotherm was fitted with Langmuir and Freundlich adsorption models. The cyanide ions on the modified sorbent surface is enabled to form a stable and non-toxic cyanide complex in the solution, which can be reused as the complexing agent in the metallurgical industries.

## **Keywords**

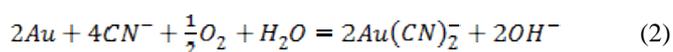
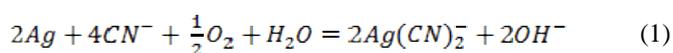
Solid wastes; rapid cyanide removal; mine water treatment; sulfate tailing reusing.



## 1. Introduction

Cyanides are inexpensive and efficient reagents, which are used in various industrial processes, such as mining and exploration, pharmaceutical industry, agriculture (Kuyucak and Akcil, 2013).

The cyanide ion has a high affinity for gold and silver, which allows to be used effectively for metal extraction (Iakovleva and Sillanpää, 2013), according to the reaction, known as Elsner's Eqs. 1 and 2:

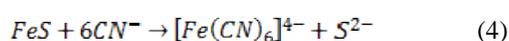
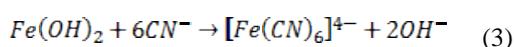


On the other hand, cyanide and its compounds are very toxic to living organisms and able to replace copper and sulphur-containing compounds, thereby disrupting oxygen transport processes in the cells (Aggrawal, 2013). The facts of accidental cyanide leakage in the world were recorded, in Romania, Japan, Argentina and China (Johnson, 2015). Although the effect of cyanide on aquatic flora and fauna is not long-term, because it is rapidly destroyed by natural processes, the severe consequences can take place, which caused large-scale pollution, the death of fish, plankton and plants. Searching for efficient method for rapid removal of a high concentration of cyanide from aqua solutions could be a solution for the problem of large-scale pollution.

Many studies have been reported for cyanide removal during the last decade: viz. photoelectrocatalytic (Zhao et al., 2015), UV degradation (Hanela et al., 2015), ozone oxidation (Cui, et al., 2014), electro dialysis (Scarazzato et al., 2014), and biodegradation (Yu et al, 2016),

based on the ability of cyanide to be oxidized and complexation with various metals, forming a non-reactive compounds. The most cost-effective method is the complexation of cyanide with various metal ions (Kuyucak and Akcil, 2013; Zhao et al., 2015; Dash et al., 2009; Seung-Mok and Diwakar, 2009; Xu et al., 2015).

In particular, potassium cyanide is neutralized with iron sulfide or iron hydroxide to form a non-toxic and insoluble ferrocyanide complex:



Due to the selectivity and affinity of iron sulphide for cyanides, FeS-containing materials are used as a complexing agent to remove cyanides from solutions, and in particular from industrial water (Kuyucak and Akcil, 2013; Yu et al., 2016).

The mining and processing of mineral extraction generate a billion metric tons of solid waste annually. The majority of the waste are sulphate tailings. For some minerals, the amount of tailings might reach from 20 to 98%. Basic treatment procedure for tailings is storage in lakes until dewatered (Wills, et al., 2016; Iakovleva et al., 2015). Disposal, recycling and/or reuse of tailings are very important and require innovative solutions. Whereas, sulfate tailings contain iron and sulfate compounds, they can be efficient material for cyanide removal by complexation (Iakovleva et al., 2015; Silva et al., 2012). Due to increased environmental requirements and control, the desire to reuse solid waste and water in the industry, the use of solid waste containing iron-sulfur compounds has become an alternative option for cyanide removal. Several techniques have been applied for the modification of adsorbent materials to enhance their removal efficiency, such as magnetic sedimentation (Bakhteeva et al., 2017; Cao et al., 2017),

addition of various functional groups (Liu et al., 2017) and development of iron-bio-combined sorbents (Tiwari et al., 2017). The deposition of metal oxides on the surface of powders and granules for the modification of adsorbent materials has been studied by several authors (Orak, 2016; Sampath et al., 2016; Tiznado et al., 2014). Deposition of metal oxide by atomic layer deposition (ALD) has been using often for depositing thin metal oxide layers on the surface of solar cells and semiconductors (Chang et al., 2015; Frijters et al., 2016; George, 2010; Iakovleva et al., 2016; Jõgiaas et al., 2015; Kilbury et al., 2012; Kukli et al., 2016). ALD is a self-terminating cyclic process providing sequential layering of metal oxides on the surface and helpful to get the ultrafine film with controlled thickness. ALD mechanism leads to several unique properties of layers, viz ALD films grow without pinholes and discontinuities (Leskelä et al., 1999). The main objective of present study is the utilization of solid wastes as potential adsorbents for the removal of cyanide ions. For this purpose, two unmodified tailings from different mineral processing were selected as potential sorbents for selective removal of cyanide compounds from synthetic wastewater. Since the sulphate tailings are fine powder and using these materials without pre-treatment is complicated, raw materials were granulated before using. Granulation of tailings provides a suitable adsorbent for both passive and column methods in wastewater treatment. The resistance to wettability, preserving porosity and surface properties of raw materials were also tested. Further, granulated sorbent was modified by using atomic layer deposition technique for the enhancement of stability and efficiency of adsorbent material. As application of ALD treatment for enhancement is an innovative solution for development of sorbents from industrial solid wastes. In this study, the raw materials, unmodified and modified granules were characterized by Fourier-transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) analyzer, zetasizer and scanning electron microscopy (SEM). In adsorption

studies, the effects of contact time, pH, initial cyanide concentration, and regeneration of adsorbent were investigated.

## **2. Materials and methods**

### **2.1. Granules production**

Two sulfate tailings (CaFe-Cake and SuFe) were provided by Norilsk Nickel Harjavalta, Finland. Both materials were wastes from the metal extraction process. Before use, the sulfate tailings were dried at 60 °C for 12 h in hot air oven (9000 Series, Termaks, Norway). After drying, agglomeration of tailings particles was observed, so both materials were ground to increase homogeneity. A wet-granulation with polyvinyl acetate as a binder was chosen (Mangwandi et al., 2014; Mangwandi et al., 2010; Mangwandi et al, 2011). Polyvinyl acetate (PVAc) was used for the granulation of both sulfate tailings. Acetone by Merck (UK) was used as a solvent for binder preparation during the dissolving process with a known mass of PVAc. The mixture was stirred for 20 min at 60 °C to obtain a homogenous solution.

A high shear granulator (Kenwood KM070, Japan) was used for the granulation of materials. Sulfate tailing powders (150 g) were added to the mixer. The binder was added with the powders without stopping the rotator. The mixing of powder and binder occurred within 120 s to form granules; the impeller speed was 220 rpm. The optimal concentration of binder was selected by the addition of PVAc with different concentrations (from 10 to 40 w%) during the granulation process and it was found to be 30 wt%. The viscosities of the binder solutions were determined by the Haake Viscotester C.

## 2.2. Modification of granule surface by ALD

Trimethyl aluminum (TMA) was used as a precursor for the deposition of  $\text{Al}_2\text{O}_3$  granules by ALD method. A TFS500 ALD reactor (Beneq Ltd, Finland) was used for deposition of  $\text{Al}_2\text{O}_3$  thin films onto surface of both granulated materials. The pulse time of  $\text{Al}_2\text{O}_3$  deposition time (3.5 sec), pressure (6.5 mbar), reactor temperature (250 °C) and cycles (500) were chosen after preliminary test. Monocrystalline silicon <100> substrate (Si-Mat, Germany) was placed into the reactor together with the powder sample in order to extract information regarding film thickness deposited onto the substrate surface. Once the process was finished, film thickness was measured using spectroscopic ellipsometry (M-2000, J.A. Woollam Co.).

Since the modification of sulphate tailings is a multi-step process, which included granulation of raw material, drying and ALD coating, the average price of prepared sorbents is approximately 11.50 €kg<sup>-1</sup>, while the price of commercial activated carbon, which is known to be as efficient sorbent for cyanide removal, is ranges from 500 to 1500 €kg<sup>-1</sup> (Marsh & Rodriguex-Reinoso, 2006). This price of novel sorbents, based on sulphate tailings, includes the cost of electricity based on the Finnish price. It should be taken into account that in the developing countries that occupy the first places in gold mining in the world, the price of electricity is many times less than in northern Europe. A clear benefit of these sorbents is that they are mining solid wastes and the price of the raw products is based only on the costs of logistics. Further use of waste material from mining, will also reduce the waste disposal cost which is used for the proper treatment of waste before discharge.

### **2.3. Physical characterisation of materials**

The chemical composition of sulfate tailings was determined with an energy dispersive X-ray fluorescence (ED-XRF) analyser X-Art (Joint Stosk Company Comita, St. Petersburg, Russia).

FTIR spectra of raw, unmodified granulated and modified granulated sorbents were recorded with a Bruker Vertex 70v spectrometer.

The particle size distribution of the materials was obtained using a dispersion analyser, LUMiSizer 610/611 (LUM GmbH). Zeta-potential of raw and developed sorbents was determined with ZetaSizer Nano ZS, Malvern, UK, and calculated from electrophoretic mobility measurements using the Schmalukowski equation.

The samples were characterized with nitrogen sorption at 196 °C using a TriStar 3000 (Micromeritics Inc., USA). The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) theory.

Microstructure of the surface of raw and modified materials was examined using a scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company). All experiments were carried out at low vacuum conditions in a secondary electron mode.

Granules wettability was tested by mixing a known amount of granules with water at ambient temperature for 72 h. The strength and size of granules were determined before and after the wettability tests. After testing, all granules were dried in an oven at 80°C for 12 h. All experiments were carried out at room temperature (22 °C) with mixing time and speed of 2 min and 490 rpm, respectively. The granule strength was measured from diametric compression of the single granules using previously described methods (Mangwandi et al, 2013) (Eq. 5).

$$\sigma = 2.8 \times \left( \frac{F_i}{\pi D^2} \right) \quad (5)$$

where  $F$  (N) is compressive force during testing of granule strength,  $i$  is amount of tests,  $D$  (mm) is granule diameter.

#### 2.4. Batch adsorption experiments

Sorption tests of cyanide were conducted by mixing a known dose (from 0.5 to 40 g L<sup>-1</sup>) of granulated CaFe-Cake and SuFe with 15 mL of synthetic solution of potassium cyanide (obtained from Merck, German). The concentration of cyanide in the solution ranged from 10 to 300 mg L<sup>-1</sup>. The experimental solutions were shaken by a shaker ST5 (IKA KS 4000i Control) from 1 to 720 h and 1.5 mL sample was taken from flasks at known time interval and filtered using a 0.20 µm polypropylene syringe filter. Optimum time was determined by contacting 40 g L<sup>-1</sup> of CaFe-Cake and SuFe in 15 mL flasks tumbled at 100 rpm from 1 to 720 min with initial concentration of CN<sup>-</sup> at 20 mg L<sup>-1</sup>. Samples were taken after 30, 60, 120, 240, 360, 720 min. For optimization of adsorbent dose, initial amount of both adsorbents ranged from 1 to 40 g L<sup>-1</sup> by keeping 20 mg L<sup>-1</sup> initial cyanide concentration. The test was carried out in triplicate and reported result is the average of the three tests. The effect of initial solution pH on adsorption was determined by mixing 40 g of CaFe-Cake and SuFe with 20 mL of cyanide solution at the initial concentration of 20 mg L<sup>-1</sup> and pH values ranging from 2 to 9. Solution pH was adjusted with 1 M NaOH and HCl solutions. The mixture was shaken for 48 h and the solution was filtered and analysed. Final concentration of cyanide was determined by high-performance liquid chromatography (HPLC). A Shimadzu HPLC equipped with a conductivity detector (Shimadzu Model CDD-10A) was used (column: 6.0 mm IDx250 mm L Shodex RSpak KC-811; eluent: solution of 1 mM H<sub>2</sub>SO<sub>4</sub> in ultrapure water; flow rate: 1.0 mL/min; temperature: 40 °C; reagent

1: 0.1% Chloramin T in 0.1 M phosphate buffer (pH 7.5); reagent 1 flow rate: 0.5 mL/min; reagent 2: 1-Phenyl-3-methyl-5-pyrazolone + 4-pyridinecarboxylate (Na); reaction temperature: 80 °C; wavelength: 638 nm).

The percentage adsorption was calculated as:

$$\% \text{Adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (6)$$

where  $C_i$  and  $C_f$  ( $\text{mg L}^{-1}$ ) are the initial and final concentration of cyanide ions respectively.

The zeta potential was calculated from electrophoretic mobility measurements using the Schmalukowski equation. Known amount of solid samples were conditioned in 50 mL of 0.001 M NaCl solutions at various final pHs for 24 h in a shaking bath. Each reported point value was an average of approximately 20 measurements. The pH of the suspension was adjusted using 0.01–1.0 M HCl and KOH.

### 3. Results and discussion

#### 3.1. Comparison of granules properties

The granules produced should be stable under aqueous conditions for a longer period of time to allow for the use in wastewater treatment. The binder solution viscosity and matrix of the granulation test are presented in Table 1. Granulation tests showed that both materials formed granules with the same size range from 1 to 2 mm. However, CaFe-Cake formed more homogeneous granules with a smaller fraction; 10% of total mass is biggest than 2 mm. At the same time, SuFe formed more stable granules and their strength decreased after wettability test negligibly, in comparison to CaFe-Cake granules (Figures 1b & 2b). The modified granules from both tailings with particle size from 1 to 2 mm have a better stability upon contacting with

water and remain approximately the same size and strength compare with unmodified granules (Figures 1b & 2b).

Table 1. Viscosity of binder solutions with various concentration of PVA.

$C_{PVA}, \%$	$\mu, \text{mPa}\cdot\text{c}$
10	1.4
15	13
20	37
25	52
30	72
35	111
40	157

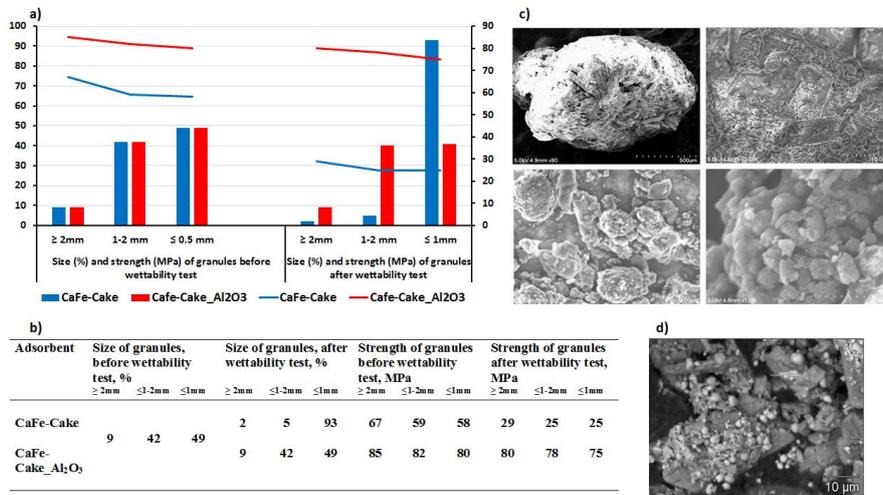


Figure 1. Comparative data of unmodified and modified CaFe-Cake granules size and strength before and after wettability test (a, b), SEM images of unmodified (c) and modified (d) CaFe-Cake granules.

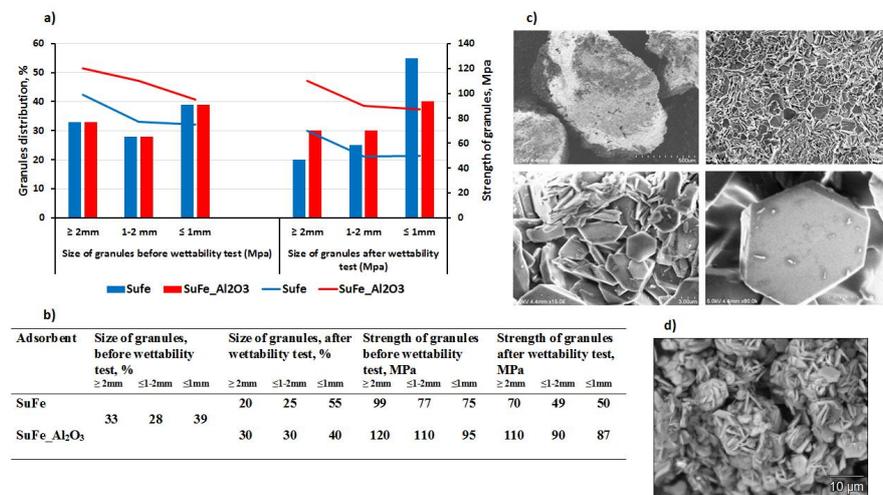
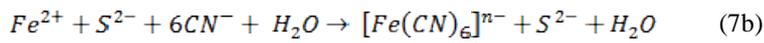
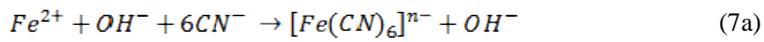


Figure 2. Comparative data of unmodified and modified SuFe granules size and strength before and after wettability test (a, b), SEM images of unmodified (c) and modified (d) SuFe granules.

### 3.2. Possible removal mechanism and sorbents characterization

According to XRF analysis, the contents of iron are 10 wt% and 39 wt% for CaFe-Cake and SuFe, respectively (Table 2). A high content of iron compounds should provide good adsorptive properties for cyanide ions by ion exchange. The possible mechanism of the complex formation of ferrocyanide can take place in two ways:



Because iron is included in the sorbent composition by iron hydroxide and iron sulphate, both mechanisms may occur as presented in Eq. 7a and 7b, respectively.

Comparative data of chemical composition, specific surface area and pore size of original and granulated unmodified and modified materials are shown in Table 2. Specific surface area of unmodified CaFe-Cake is lower than unmodified SuFe materials (Table 2). Increased surface area was observed in aluminium oxide modified granulated sorbent. For aluminum oxide modified granulated sorbents, specific surface area increase to 7 and 5 times for CaFe-Cake and SuFe, respectively (Table 2). Specific surface area excursion can be directly related to the appearance of new functional groups on the surface after modification.

Table 2. Comparative data of chemical composition, specific surface area and pore size of unmodified and modified CaFe-Cake and SuFe.

Element	CaFe-Cake, w%	gCaFe-Cake, w%	gCaFe- Cake_Al <sub>2</sub> O <sub>3</sub> , w%	SuFe, w%	gSuFe, w%	gSuFe_ Al <sub>2</sub> O <sub>3</sub> , w%
Al	0.2	0.2	1.2	0.3	0.3	1.5
Si	<2	<2	-	<3	<3	-
K	0.03	0.03	-	0.03	0.03	-
Ca	11.9	10.0	10	0.16	0.15	0.18
Fe	10.0	10.0	10	38.7	39.0	38.5
Specific surface area, m <sup>2</sup> g <sup>-1</sup>	6.5	6	48	12.3	12	63
Pore size, μm	0.6	0.7	0.65	0.9	1.0	1.0

SEM pictures (Figures 1c & 2c) show the granules surface of CaFe-Cake and SuFe at different magnifications. SEM images of CaFe-Cake showed the presence of agglomerated particles. However, SuFe has a fine polyhedrous particles which are stacked onto each other. Figures 1d and 2d show the surface of both modified sulfate tailing with ALD method. It is very clear from SEM images of modified granules that ALD treatment modified granule surface. The surface of the modified sorbents are more developed and covered with distinctive particles of aluminum oxides. The surface is uneven, however, as XRF analysis is shown, weight amount of aluminum increases five times compared to the original materials (Table 2).

It can be seen in Fig. 3 that initially the percentage of cyanide removal increased with increasing the adsorbent amount, and the maximum equilibrium reached at the adsorbent concentration of 10 g L<sup>-1</sup>. In the case of the both granulated modified sorbents, the maximum equilibrium reached at the concentration of 5 g L<sup>-1</sup>. The highest removal approximately 97% of cyanide was achieved with both unmodified and modified adsorbents.

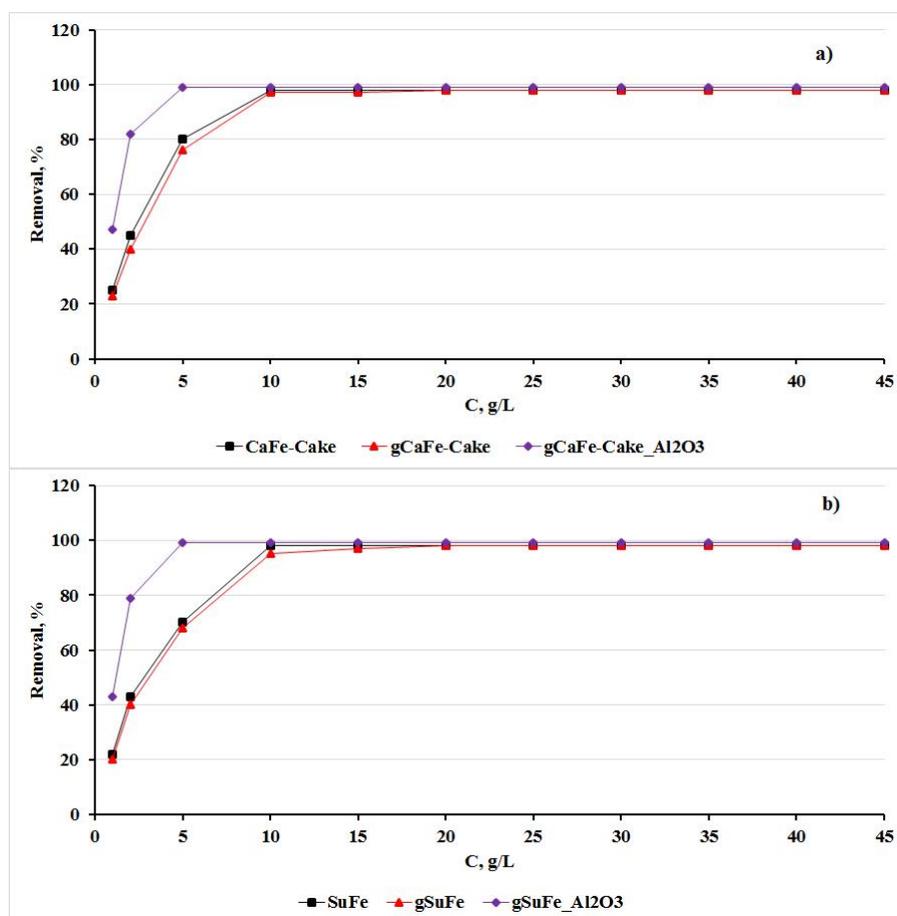


Figure 3. Selection of the optimal amount of adsorbents with range of initial concentration of both adsorbents from 1 to 45 g L<sup>-1</sup>.

However, the removal percentage increased upon increasing time and reached the maximum at 360 min for unmodified and 210 min for modified sorbents (Fig. 4). This equilibrium is stable and desorption of cyanide ions from ferrocyanide complex was not observed even after 720 min of the experiment. Adsorption kinetics was studied using the pseudo-first and pseudo-second order models.

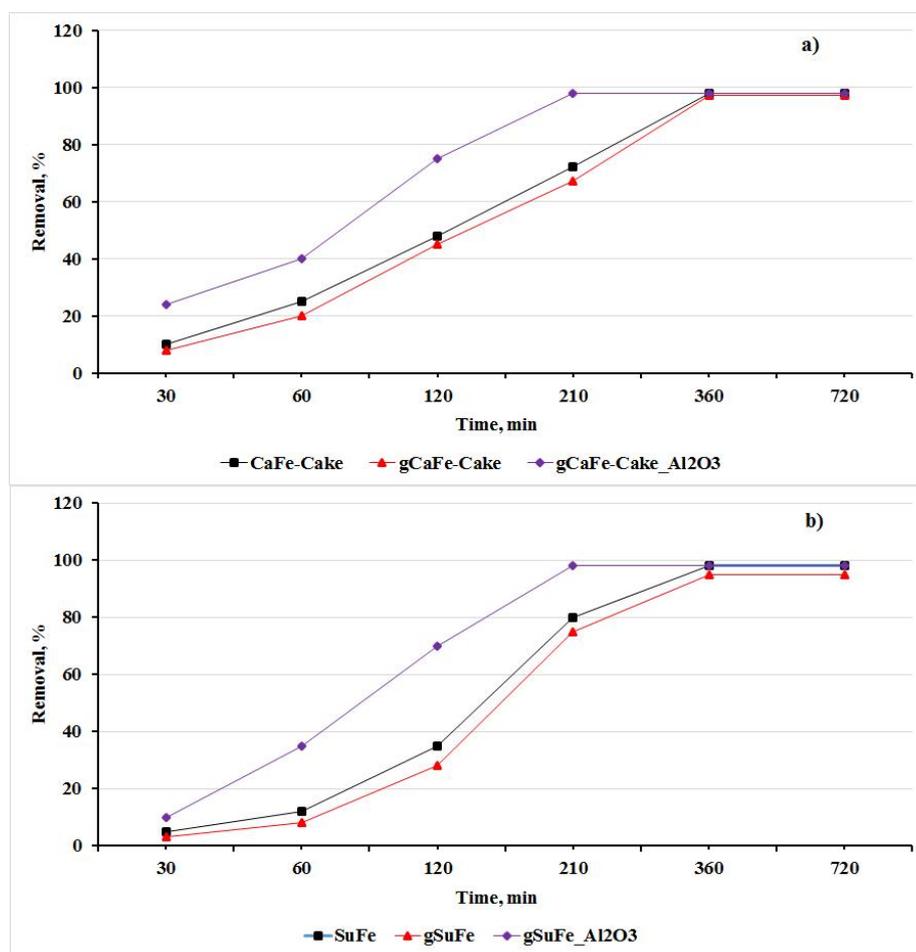


Figure 4. Optimisation of contact time with initial concentration of modified and unmodified adsorbents 40 g L<sup>-1</sup>.

The pseudo-second order model described the adsorption process of cyanides better and assumed two-site-occupancy adsorption by the rate of the surface reaction (Eq. 6, Table 3):

$$\frac{dq}{qt} = k_2(q_s - q)^2 \quad (8)$$

Where  $q$  and  $q_e$  are amount of metals adsorbed at time  $t$  (min) and at equilibrium, respectively.

The pseudo-second-order rate constant is  $k_2$ .

Table 3. Pseudo-first- (P1O) and pseudo-second (P2O) order models for unmodified and modified CaFe-Cake and SuFe with initial concentration of both adsorbents 40 g L<sup>-1</sup> and initial concentration of cyanide ions 0.769 mmol g<sup>-1</sup>.

	$q_{e\text{exp}}$ (mmol g <sup>-1</sup> )		$q_e$ (mmol g <sup>-1</sup> )		$K$ (g mmol min <sup>-1</sup> )		$R^2$	
	P1O	P2O	P1O	P2O	P1O	P2O	P1O	P2O
CaFe-Cake	1.87	1.87	1.12	2.13	1	0.36	0.85	0.99
gCaFe-Cake	1.37	1.37	0.99	1.32	1	0.35	0.85	0.99
gCaFe-Cake_Al2O3	3.52	3.52	2.15	3.33	1	0.45	0.80	0.99
SuFe	2.86	2.86	1.06	2.28	1	0.25	0.87	0.99
gSuFe	2.65	2.65	1.03	2.65	1	0.23	0.85	0.99
gSuFe_Al2O3	3.52	3.52	1.98	3.41	1	0.33	0.85	0.99

The pseudo-second-order model suggested that the system includes at least two reacting components with formation of one or two other compounds (Semiokhin et al., 1995; Ho and McKay, 1999). In this case the reaction between iron and cyanide ions takes place. The formation of a strong complex is confirmed by the lack of desorption after a long time.

The adsorption of formed ferrocyanide complex by aluminum oxide which was coated to the modified sorbents can take place as additional sorption mechanism of cyanide removal from solution. The high adsorption capacity of  $\text{Al}_2\text{O}_3$  for removal of ferrocyanide  $(\text{Fe}(\text{CN})_6)^{4-}$  has been proven by (Bushey and Dzombak, 2004). They showed that approximately 100% of ferrocyanide was adsorbed by aluminum oxides at  $\text{pH} < 7$  (Bushey and Dzombak, 2004).

Zeta potential measurements were carried out over the pH from 1 to 10 and shown in Figures 5. It can be seen that the lowest potential values have the unmodified raw materials, CaFe-Cake and SuFe at pH around 8 and 9, respectively. The zeta potential of both modified sorbents is shifted towards the positive values. However, unmodified and modified Sufe exhibit higher positive potential at all range of pH compared with CaFe-Cake. It can be due to the fact that SuFe contents highest concentration of Fe than CaFe-Cake (Table 2).

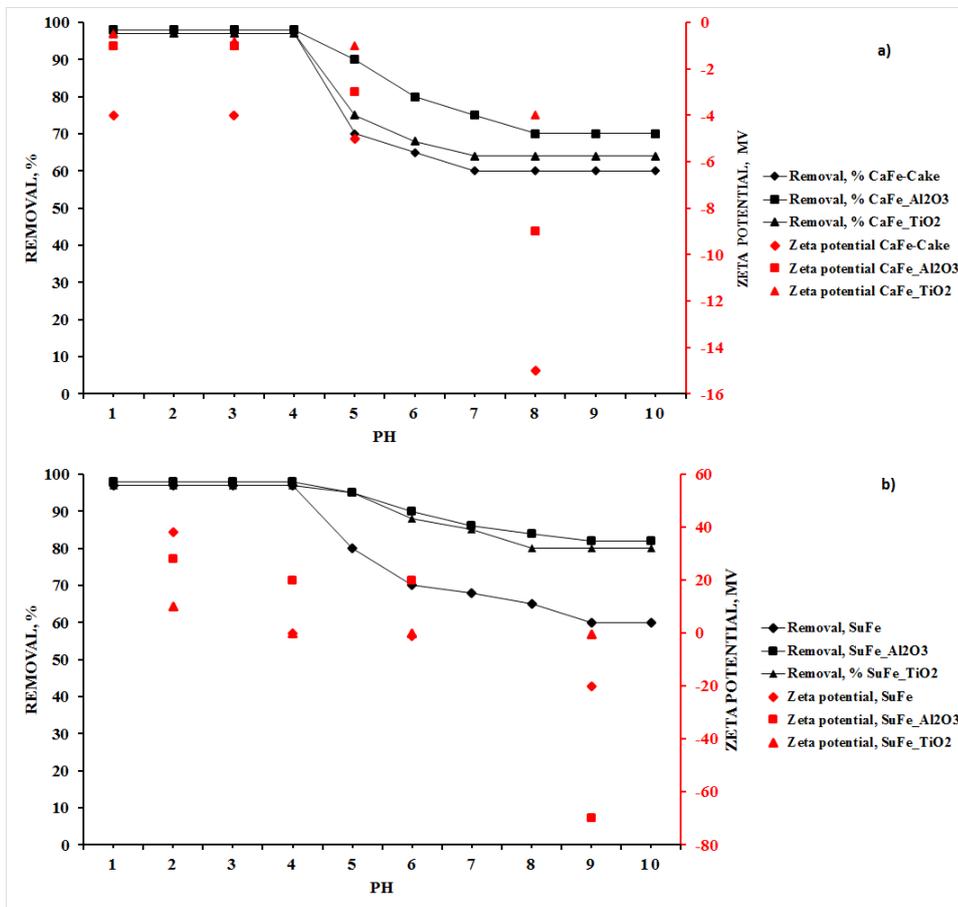


Figure 5. The study of pH influence on the removal of cyanide ions with initial concentration of both adsorbents  $40 \text{ g L}^{-1}$

Oxidation of cyanide directly depends on solution pH. The removal of cyanide with both adsorbents occurs easily at pH 3-4 and with more positive values of the surface charge. Removal efficiency decreased significantly from 97% to 60% as pH increased from 6 to 9 (Fig. 5). This could be the effect of better adsorption capacity of  $\text{Al}_2\text{O}_3$  and iron hydroxide for  $\text{pH} < 6$ . Cyanide ions formed ferrocyanide complex with sorbent surface and adsorbed completely at low pH. Similar results were observed by other researchers (Bushey and Dzombak, 2004; Golbaz et al.,

2014; Shen et al., 2014; Zheng et al., 2014). The experimental results show that cyanide ions adsorbed to modified sorbents easily and in a shorter time than to unmodified sorbents. Bushey and Dzombak also reported that cyanide adsorbs to the greatest extent on Al<sub>2</sub>O<sub>3</sub> than iron hydroxide sites (Bushey and Dzombak, 2004). According to the experiments, pH 4 was selected as the optimum value for batch adsorption.

The adsorption isotherms are used to explain the mechanism of pollutant removal. Langmuir and Freundlich isotherms were used for the description of cyanide removal mechanism in this research:

$$q_e = \frac{(q_m k_l C_e)}{(1 + k_l C_e)} \quad (9)$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad (10)$$

The equation can be linearized and 1/n was found by linear regression:

$$\ln q_e = \ln K_f - \frac{1}{n} \ln C_e \quad (11)$$

where  $K_l$  and  $K_f$  are Langmuir and Freundlich constants, respectively, which correspond to adsorption capacity.  $n$  is Freundlich constant which corresponds to adsorption intensity and unit of this constants less than unity indicates the chemical sorption process, while the unit greater than 1 can point to the physisorption process (Yang, 1998). The  $n$  value indicates the degree of nonlinearity between solution concentration and adsorption (Yang, 1998). The  $n$  value was determined to be  $< 1$ , indicating that an irreversible chemical reaction is taking place (Table 4). In this case, the formation of complexes is most probably dominating the process.

Table 4. Isotherm parameters for CaFe-Cake and SuFe during adsorption process of cyanide ions from synthetic solution. Initial concentration of CN in 20.8 mmol L<sup>-1</sup>.

	$q_m$ mmol g <sup>-1</sup>	$K$ , L mmol <sup>-1</sup>	$n$	$R^2$
Langmuir				
gCaFe-Cake	1.10	3.87		0.75
gCaFe-Cake_Al2O3	3.50	3.95		0.82
gSuFe	1.31	2.68		0.78
SuFe_Al2O3	3.80	2.72		0.80
Freundlich				
gCaFe-Cake	1.52	5.45	0.62	0.99
gCaFe-Cake_Al2O3	3.50	6.01	0.62	0.99
gSuFe	1.72	6.18	0.57	0.98
gSuFe_Al2O3	3.80	6.22	0.60	0.98

Isotherm parameters were calculated with minimization of the error distribution between experimental and predicted data by Marquardt's percent standard deviation (MPSD):

$$\sum_{i=1}^n \left( \frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right)_i^2 \quad (12)$$

The maximum uptake capacity for cyanide ions was about three times higher for both modified sorbents than for unmodified (Table 4). The additional reaction sites were introduced to the surface of both sorbents during modification, which explains the enhancement of their adsorption capacity.

Two parameters of the Freundlich isotherm that take into account the heterogeneity of sorbents surface describe the cyanide adsorption better than Langmuir. These data correlated with previous reports on cyanide removal from solutions with Freundlich isotherms (Behnamfard and Salarirad, 2009; Giraldo et al., 2010; Agarwal et al., 2013).

The comparative analysis of maximum adsorption capacity of modified adsorbents and other reported adsorbents for cyanide ions is presented in Table 5. From the table 5, it is clear that developed adsorbents showed significant adsorption capacity in comparison to other adsorbent materials. The obtained results exceed by three and more times compare with data reported in other studies. For example, Ning et al. (2013) and Uppal et al. (2017) obtained zeolite and Zn peroxide nanomaterials with adsorption capacity for cyanide of 0.07 and 0.08 mmol g<sup>-1</sup>, respectively, that are fifty times less than granulated Sufe<sub>2</sub>Al<sub>2</sub>O<sub>3</sub> (Table 5); activated carbon from coconut shell obtained by Singh & Balomajumder (2016) has 20 times and other ones approximately 2-3 times (Moussavi & Talebi, 2012; Dwivedi et al., 2016) less effective adsorption capacity than modified CaFe-Cake and SuFe (Table 5).

Table 5. Comparison of maximum adsorption capacity of cyanide ions from industrial wastewater with various novel sorbents.

	$q_{max}$ (mmol g <sup>-1</sup> )	Reference
	1)	
Zeolites	0.07	(Ning et al., 2013)
Polymeric complex	3.6	(Zheng et al., 2014)
Zn peroxide nanomaterial	0.08	(Uppal et al., 2017)
Modified pistachio hull	1.41	(Moussavi & Talebi, 2012)
<i>Prunus amygdalus</i> (Almond) shell	1.145	(Dwivedi et al., 2016)
<i>Tectona grandis</i> (Sagwan) leaves	0.658	
Activated carbon from coconut shell	0.189	(Singh & Balomajumder, 2016)
gCaFe-Cake <sub>Al2O3</sub>	3.5	This work
gSuFe <sub>Al2O3</sub>	3.8	This work

The high affinity of cyanide ions to metal cations is resulted from the strong complex formation with iron compounds. The complex of hexacyanoferrate(II) ions produced by the reaction of Fe<sup>2+</sup> and CN<sup>-</sup> is particularly resistant and non-toxic (Eqs. 7a and 7b) (Kouřim et al., 1964). This complex compound has a low dissociation, which makes the reusing of developed granules economically unviable.

## Conclusions

In this study, solid waste “sulfate tailing” were used as a potential source for the development of efficient adsorbent for the selective removal of cyanide ions from synthetic mine water. Granular materials from the solid wastes were obtained with a high strength which were used for the selective removal of cyanide ions from acidic wastewater and it was found to be very efficient even for very high concentration of cyanide ions. Approximately 97% removal was obtained for the 300 mg L<sup>-1</sup> cyanide solution.

Strong ferrocyanide complex formation prevents cyanide ions desorption into the solution. Surface modification with ALD increased granules strength and sorption capacities of sulphate tailings about three and five times, respectively. Modification of adsorbent reduced the adsorption time of cyanide ions by 40% and also less adsorbent dose of modified adsorbent is needed for cyanide removal in comparison to unmodified adsorbent. Removal of cyanides with modified sulphate tailings followed two different mechanisms. The first is the formation of ferrocyanide complex from iron and cyanide ions while the second is sorption of ferrocyanide with aluminium oxide coated to the sorbent surface during modification with ALD. The double retention of cyanide ions on the modified sorbent surface is enabled to form a stable and non-toxic cyanide complex in the solution, which can be reused as the complexing agent in the metallurgical industries. The removal of cyanide ions from water with sulphate tailings is a rapid and effective method, which allows reusing solid wastes and can be used for the treatment of cyanide polluted wastewater.

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## **Publication VI**

Iakovleva, E., Sillanpää, M., Maydannik, P., Khan, S., Doshi, B., Kamwilaisak, K., Wang, S.

**Novel sorbents from low-cost materials modified with atomic layer deposition for acid mine drainage treatment.**

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## **Novel sorbents from low-cost materials modified with atomic layer deposition for acid mine drainage treatment**

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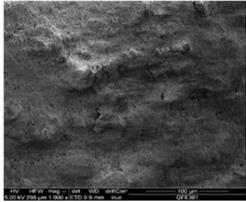
## **ABSTRACT**

Modified and unmodified iron-based industrial by-product was applied for synthetic and real mine water treatment from metal (Ni (II), Cu (II), Fe (III), Zn (II)) and sulphate ions. Atomic layer deposition of titanium dioxide, alumina and zinc oxides with low temperature was used as an innovative modification method for improving physical and chemical capacities of granulated raw material. The structural and surface properties of unmodified and modified materials were analysed by scanning electron microscopy, nitrogen adsorption-desorption, energy dispersive X-ray, and Fourier transform infrared spectroscopy. It was found that modified sorbents have better characteristics for removal of pollutant ions to compare with raw one. The maximum adsorption capacities were obtained as 645, 222, 210 and 135 mmol g<sup>-1</sup>, for modified sorbent with ZnO and amounted, sulphate ions and copper ions, respectively. For zinc and nickel ions it was reached better for RH\_Al<sub>2</sub>O<sub>3</sub> at 150 and 98 mmol g<sup>-1</sup>, respectively. The order of sorption capacity for both sorbent was Fe>Cu>SO<sub>4</sub>>Zn>Ni.

## **Keywords**

ALD for powder modification; metal ions removal; sulphate ions removal; solid wastes reusing.

Industrial by-product RH



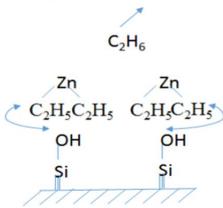
Granulation

Granulated RH

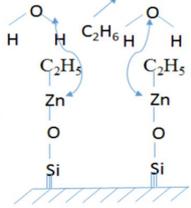


Modification with ALD

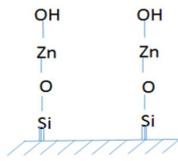
Stage 1



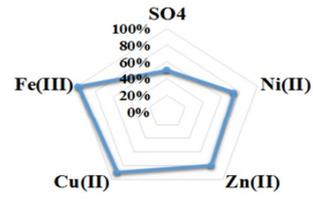
Stage 2



Stage 3



AMD treatment



## **1. Introduction**

Reusing of industrial wastes is the main challenge for the current industry, environment, and science [1-6]. Universal and selective sorbents manufactured from industrial solid wastes is one of the field for the utilising of wastes that has been researched intensively in recent years [7-16]. Reducing of water consumption by its reusing and water treatment with new methods is also an important task that is solved by a collaboration of research institutes and industry. Mine industry is one of the largest consumers of water [13-14]. Acid mine drainage (AMD) is one type of mine water and formed from underground waters that flow to the dump after exploration of ore, and this is one of the most serious threats to the environment. The chemical composition of AMD depends on the composition of the ores. Most of the contaminants of AMD are sulfates and pollutants ions, such as iron, copper, zinc, manganese, arsenic, and nickel [15-16]. Compared with existing methods of AMD treatment, such as wetland and reactive barriers [17-19], coagulation [20-21] and separation processes [22-23], sorption is one of the low-cost and efficient method for many contaminants removal from water [24-26].

Selection of sorbents for AMD treatment is a relevant objective. Acidic neutralization of mine water with the subsequent removal of polluting ions is a basic ideology for many water treatment methods. However, neutralization of AMD can lead to the precipitation of metals in the form of insoluble salts, which increase the solid wastes. A good solution to this problem can be a sorbent, which can treated mine water by complexation excluding precipitation. Iron-based sorbents fabricated from solid industrial wastes have a perfect ability to remove arsenic, metal ions and certain cations from acid liquids without precipitation [27-32]. Synthesis of sorbents from industrial solid wastes for removal of various pollutants from wastewater is research interest in recent years for recycling of solid wastes [7-16]. Solid waste from Ekokem Ltd Finland consisting

of iron compounds was chosen as a potential sorbent for AMD treatment from Fe (III), Ni (II), Cu (II), Zn (II), and sulphate ions. The raw material was granulated before testing for the further possibility of using this sorbent for industrial purposes. Famously, the problem of granulation is to obtain granules with high strength and resistance to water, while preserving the properties of the raw materials, such as porosity and high sorption capacities. According to the previous results, the granulation of powder form of sorbents carried out with a mixture of polyvinyl acetate (PVAc) and acetone [33]. This adhesive allows obtaining granules with good strength while maintaining the porosity of the material.

Granulated sorbents should be modified according to the compliance with requirements for the sorbents, such as stability to the treatment liquids, efficient capacity to remove necessary pollutants, preservation of granules strength after wettability, a large number of cycles. Deposition of metal oxides could allow to increase the strength of granules, but also should improve sorption capacities of adsorbent due to additional functional groups on the surface. Chemical deposition of metal oxides is divided to different categories according to the liquid [33-37] and vapor precursors [38]. For modification of granulated sorbent, we can use only vapor precursors, because the granulated material does not have sufficient strength after wettability tests, as previously shown results [33]. There are two methods, chemical vapor deposition (CVD) and atomic layer deposition (ALD). Although CVD is considered cheaper and easier compared to ALD, it has certain restrictions on temperature limitation and control of the layer thickness, unlike ALD. The film thickness and quality are controlled more accurately by ALD [38]. According to our previous results [32], modified RHs with deposition of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  have a good affinity towards removal of both forms of arsenic from mine water.

In this study, deposition of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZnO}$  on the surface of the granulated sorbent was applied. The temperature for the deposition of aluminum oxide and titanium dioxide was decreased compared to previous research [32]. Low temperature (LT) ( $100\text{ }^\circ\text{C}$ ) was applied for the deposition of  $\text{ZnO}$ . Development of more pure films with less thickness is occurred by high process temperature and quite a few papers reported about ALD with LT for different metal oxides deposition [38-39]. In this case, a costly methodology is more important than physical properties of deposited films. Therefore, less temperature for the deposition of chosen oxides was applied in this research work. To our knowledge there is not any study focused to metal oxides ALD with low temperature to surface of powder or/and granules, that can be applied as multifunctional sorbents for mine water treatment.

In this study, physical and chemical properties of modified granules were researched and compared with each other and with the initial material. Raw and modified sorbents were studied for the treatment of synthetic and real AMDs from nickel, copper, zinc, iron and sulphates ions. Ions competitions during synthetic and real mine water treatment were also researched.

## **2. Materials and methods**

Chemical composition of solid industrial waste (RH) is shown in Table 1. This material was essentially based on sulphur, calcium and iron compounds. RH was milled to form uniform size of 0.2 mm powder before granulation. The obtained powder was washed with distilled water and dried at  $80\text{ }^\circ\text{C}$  for 12 h.

The synthetic AMD was prepared from  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ ,  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3\cdot 5\text{H}_2\text{O}$  (Merck,  $\geq 99\%$ ) with Milli-Q ultrapure water. The real AMD was obtained from a sulphide Finnish mine from depths of 270, 500 and 720 m. The chemical composition of real

AMD and the final concentration of ions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and high-performance liquid chromatography (HPLC) for metal and sulphate ions, respectively (Table 2). ICP-OES spectrometer iCAP 6000 Series, Thermo (UK) was used for determination of Zn (II), Ni (II), Cu (II) and Fe (III) with the detection limits and spectral absorption lines at 0.2 ppm and 202.5 nm; 0.5 ppm and 231.6 nm; 0.4 ppm and 324.7 nm; 0.1 ppm and 259.9 nm; 2ppm and 188.9 nm, respectively. The concentration of sulphate ions was tested by high-performance liquid chromatography (HPLC), Shimadzu (Japan). Shodex IC column SI-50 4E (4.0 mm ID x 250 mmL), conductivity detector, solution of 3.2 mM Na<sub>2</sub>CO<sub>3</sub> and 1 mM NaHCO<sub>3</sub> as mobile phase, with flow rate 0.7 ml min<sup>-1</sup>.

Table 1. Chemical composition of raw RH (XRF results).

Element	wt %
Si	0.2
S	17.6
K	0.3
Ca	14.4
Mn	0.27
Fe	7.2

Table 2. Chemical composition of real AMD.

Level	Cu	Zn	Fe	Ni	Sulfate	Redox	pH
m	mg L <sup>-1</sup>	E					
270	110	2000	905	8.9	20120	444	2.6
500	76	5900	3400	2.8	61600	440	2.3
720	14	242	53	1.3	3470	422	3.2

### 3. Production of sorbents

The granulation of raw material was carried out using polyvinyl acetate (PVAc) and acetone (Merck UK) as a binder. The recipe for the binder preparation was used from the previous study [33]. ALD of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO thin films to granulated sorbent was carried out using a TFS500 ALD reactor (Beneq Oy, Finland). The precursors, such as trimethyl aluminium Al(CH<sub>3</sub>)<sub>3</sub> (TMA), titanium tetrachloride (TiCl<sub>4</sub>) and diethyl zinc (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn for modification of material surface with ALD, were obtained from a Finnish company, Volatec Ltd. Table 3 shows the optimal conditions of the deposition process. The number of cycles was increased from 300 to 500 for both deposition processes (TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>), compared with the previous study [32] (Iakovleva et al., 2016). The pulse time was doubled for each cycle, which allowed to significantly reduce the temperature of the process from 350 to 220 °C and from 200 to 150 °C for TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> deposition, respectively. Deposition of ZnO was carried out with 100 °C. Monocrystalline silicon <100> substrate (Si-Mat, Germany) was placed into the reactor together with the powder sample in order to extract information regarding film thickness deposited onto the substrate surface. Once

the process was finished, the film thickness was measured using spectroscopic ellipsometry (M-2000, J.A. Woollam Co.).

Table 3. The basic conditions of ALD of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO on the surface of RH powder.

Precursors	TiO <sub>2</sub> deposition		Al <sub>2</sub> O <sub>3</sub> deposition		ZnO deposition	
	TiCl <sub>4</sub>	H <sub>2</sub> O	TMA	H <sub>2</sub> O	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Zn	H <sub>2</sub> O
Pulse time, sec	1.2	0.5	2	4	1.8	2
t °C	220		150		100	
Pressure, mbar	6.5	6.5	6.5	6.5	6.5	6.5
Cycles amount	500		500		500	

#### 4. Characterization of materials

##### 4.1. Spectral and physical characterisations

Crystalline structure characterization of RHs was provide with XRD (PANalytical Empyrean powder diffractometer). The measurements were performed between  $\Theta$  scanning range of 10-120° with a 0.007° step size and 69 s of measurement time for each step under ambient temperature and pressure.

The particle size and their distribution of the material were obtained using a dispersion analyser LUMiSizer 610/611 (LUM GmbH). The unmodified and modified sorbents were also characterised by nitrogen adsorption-desorption at 77 K using a TriStar 3000 (Micromeritics Inc., USA). The specific surface area and pore size of the samples were calculated using the Brunauer-Emmett-Teller (BET) theory.

Morphology of unmodified and modified sorbents was studied with a scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company). The experiment was carried out in low vacuum condition in a secondary electron mode.

FTIR spectra of adsorbents were collected with a Bruker Vertex 70v spectrometer in the mid-infrared region (4000–400  $\text{cm}^{-1}$ ) at 124 scans with 4  $\text{cm}^{-1}$  resolution.

Granules strength was measured from diametric compression of the single granules with compressor Instron 4505 (Instron Industrial Products, UK). After measuring it was calculated using Eq. (1):

$$\sigma = 2.8 \times \left( \frac{F_i}{\pi D^2} \right) \quad (1)$$

where  $F_i$ , Newton is a compressive force of granules strength by  $i$  times;  $D$ , mm is a diameter of granules.

The film thickness of modified sorbents was controlled using the data from Spectroscopic Ellipsometry (J.A.Woollam Co, Inc, USA) from a silicon wafer.

#### 4.2. Batch adsorption experiments

Synthetic and real AMDs were used for batch adsorption tests in triplicate with the mixing of unmodified and modified RHs by a mechanical shaker ST5 (CAT M.Zipper GmbH, Staufen, Germany) 0.5 to 72 h. The initial concentration of pollutant ions varied from 5 to 3470  $\text{mg L}^{-1}$ , according to experiments. The sampling of 10 mL solution carried out according to experiments for control of ions concentrations by ICP-OES and HPLS for metal and sulphate ions, respectively. All samples were filtered with 0.20  $\mu\text{m}$  polypropylene filters. The systematic error of results did not exceed 3%.

The percentage adsorption (%) was calculated as

$$\% \text{ Adsorption} = (C_i - C_t) * 100 / C_i, \quad (2)$$

where,  $C_i$  is an initial concentration of pollutant ions and  $C_t$  is a final concentration of the ions treatment.

## 5. Results and discussion

### 5.1. Raw and modified sorbents characterization

The crystalline structure of unmodified and modified sorbents was obtained with XRD analyser. The raw RH material contains around 14% of Ca, 7% of Fe and 17% of S. Sulphur may desorb to treated water and will cause the secondary pollution. Preliminary desorption study of modified materials has shown, that the sulfur availability was not observed on the solution after 720 h for RH\_ZnO. However, a slight desorption of sulfur onto solution was observed for raw RH and modified RH\_TiO<sub>2</sub> and RH\_Al<sub>2</sub>O<sub>3</sub>. The absence of sulfur was also confirmed with FTIR on the surface of modified sorbents RH\_TiO<sub>2</sub> and RH\_Al<sub>2</sub>O<sub>3</sub>. Series of adsorption peaks from 1120 to 1160 cm<sup>-1</sup> corresponding to the sulfur compounds are detected on the surface area of modified sorbents (RH\_Al<sub>2</sub>O<sub>3</sub> and RH\_TiO<sub>2</sub>), however, with a lower intensity compared to the raw material (Table 4). It can be assumed that sulfur trioxide is formed by heating of the sorbent during the modification by the following reaction:



Solid sulfur trioxide is an unstable polymeric compound with a low melting point, which forms a sulfuric acid upon contact with water. According to obtained results, all modified sorbents were washed with water in order to avoid re-contamination of treated water with sulfuric acid.

Table 4. Band assignment of the FTIR spectra of raw and modified materials.

Adsorbent	Wave number, cm <sup>-1</sup>							
	O-S-O	Si-O-Si	O-Si-O	H-O-H	O-Ti-O	Al-O	O-Al-O	Zn=O
	1120-	600-	466-	1620-	450-	980-	610-611	437-500
	1160	661	473	1690	800	1000		
RH	+	+	+	+				
RH_TiO <sub>2</sub>	+	+	+	+	+			
RH_Al <sub>2</sub> O <sub>3</sub>	+	+	+	+		+	+	
RH_ZnO		+	+	+				+

The successful modification of the granules surface is confirmed by the analysis of the chemical composition of the surface with FTIR. New peaks that are located between 980 – 1000 and 610 – 611 cm<sup>-1</sup>; and between 450 – 800 cm<sup>-1</sup>, respectively, confirm the presence of aluminum and titanium oxides on the surface of modified sorbents. Peaks between 420 and 500 cm<sup>-1</sup> are due to ZnO on the RH surface after modification with (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn. The peaks observed between 2850 and 3000 cm<sup>-1</sup> on the initial material, can be corresponded to the stretching vibration of hydroxyl groups. Those peaks are disappearing on the modified sorbents, that indicating the possible

chemical reaction between –OH groups of raw materials and precursors for deposition of metal oxides (TMA, TiCl<sub>4</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn) by ALD.

Doubling the number of ALD cycles compared to our previous experiments, resulted in an almost doubled decrease of surface area of all modified sorbents. However, the pore diameter of modified sorbents is increased significantly (Table 5). The decreasing of the specific surface area of modified sorbents simultaneously with increasing of pore diameter can be explained by the fact that micropores were blocked during the ALD process, resulting in a decrease of specific surface area and total pore volume. The same effect was described by Onn et al. (2017) [39]. In our previous study [32], the surface area of modified RH was increased. The opposite results may be due to the fact that in this research the number of cycles was increased and the temperature of the reaction was reduced.

Table 5. The pore size and specific surface area of unmodified and modified sorbents.

Sorbent	RH	RH_TiO <sub>2</sub>	RH_Al <sub>2</sub> O <sub>3</sub>	RH_ZnO
Specific surface area, m <sup>2</sup> g <sup>-1</sup>	54	23	31	11
Total pores surface area, m <sup>2</sup> g <sup>-1</sup>	51	20	29	10
Total pores volume, cm <sup>3</sup> g <sup>-1</sup>	0.14	0.12	0.11	0.05
Pore diameter, nm	11.1	23.9	15.3	19.0

It can be seen in SEM images (Fig.1), the metal oxide films on the surface of modified sorbents cannot be called a uniform, as it should be in case of deposition to a silicone plate. However,

aluminum oxide is located most uniformly and presented as a dense film with a large number of pores with the diameter not more than 20 nm, which was confirmed by BET analysis (Fig 2 and Table 5). Some fields of modified RHs are highlighted with circles on Fig. 1b, 1c, and 1d, which are corresponded to metal oxide films.

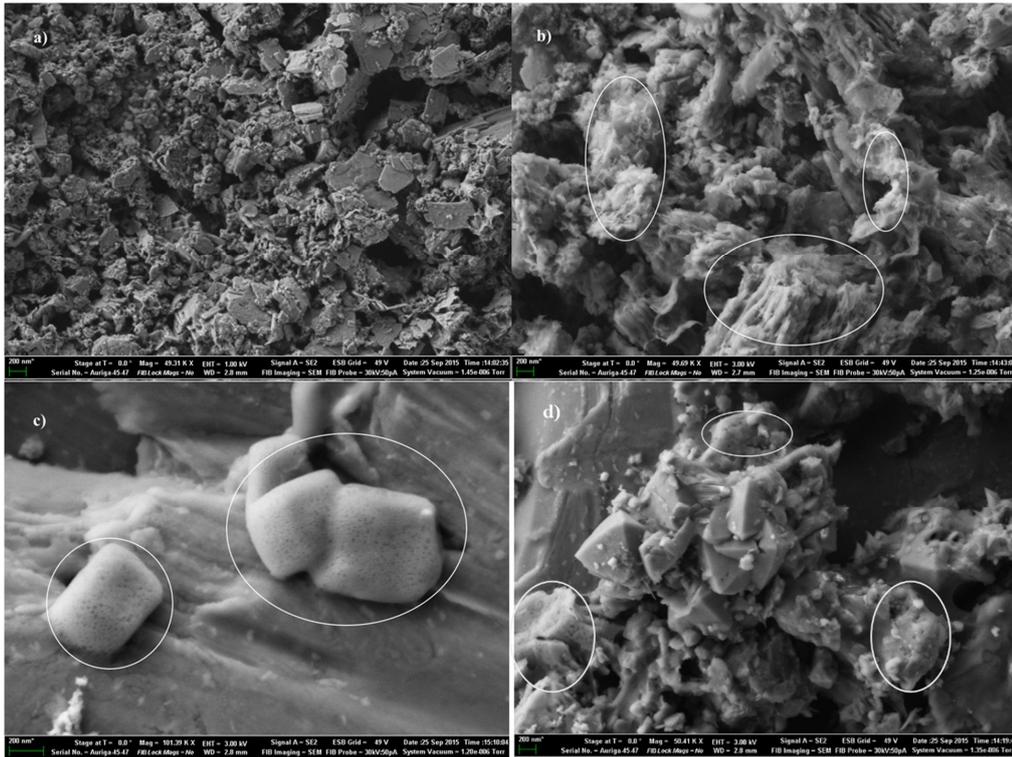


Figure 1. SEM images of a) unmodified RH, b) modified RH with TiO<sub>2</sub>, c) modified RH with Al<sub>2</sub>O<sub>3</sub>, d) modified with ZnO.

Data of reference Si wafer is confirmed the growth of film thickness to 0.19, 0.4 and 0.3 nm per cycle for Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZnO, respectively, and these results correlated with previous publications [10, 39, 41](Singh et al., 2016; Mura no et al., 2016; Cheng et al., 2017).

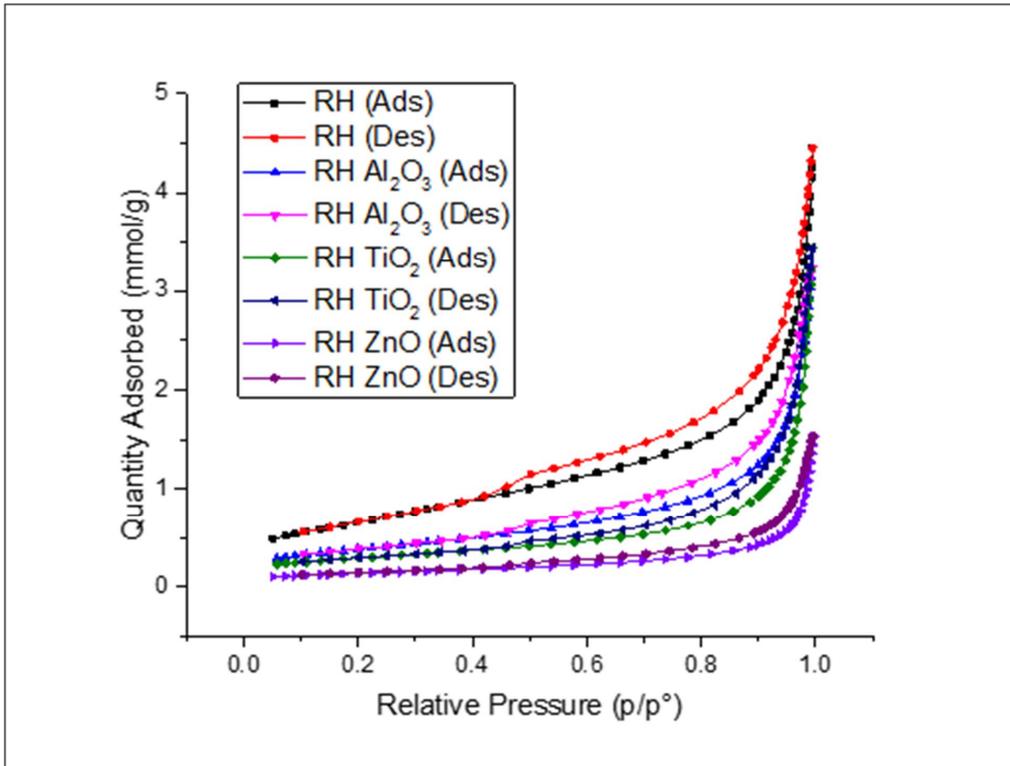


Figure 2. BET analysis of unmodified and modified RHs.

Figure 3 illustrated the X-ray diffraction patterns for the raw RH as matched with [ICSD 98-002-7221] related to gypsum compared with modified RHs with [ICSD 98-003-0267], [ICSD 98-015-4604] and [ICSD 98-008-4004] of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZnO, respectively. As can be seen from the Figure 3, the structure of initial material RH was changed after modification. All the peaks of modified RHs are assigned to Al<sub>2</sub>O<sub>3</sub> (Fig. 3a), TiO<sub>2</sub> (Fig. 3b), and ZnO (Fig. 3c), respectively. The intensity of the peaks that correspond to the crystalline structure of the raw RH is significantly increased or excused. The average crystallite sizes of indicated peaks of modified sorbents are 40.8 nm, 36.4 nm and 145 nm for RH\_ Al<sub>2</sub>O<sub>3</sub>, RH\_ TiO<sub>2</sub>, and RH\_ZnO, respectively. These values are

correlated with the data obtained by measuring of the thickness of films and they amounted 95 nm, 200 nm, and 150 nm, respectively for RH\_Al<sub>2</sub>O<sub>3</sub>, RH\_TiO<sub>2</sub>, and RH\_ZnO. It was calculated by following Equation 4:

$$r_G = l_f \times N_c \quad (4)$$

where,  $r_G$  is a growth rate of film per cycle;  $N_c$  is a number of ALD cycles.

## 5.2. Possible reaction mechanisms of ALD process

To understand ALD process, a knowledge of the surface chemistry involved is required. According to the chemical composition of this material, the mechanism of interaction between silica oxide and basic precursors, as TiCl<sub>4</sub>, TTC, and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn most likely have a place to be, as mentioned by other researchers [42-43] (Kubala et al., 2009; Ritala et al., 1993). The possible chemical reactions of the surface species at oxide bridge sites of silica are proceeded in three stages. The first one is a reaction between the hydrolytic group of surface and the functional groups of based precursor, such as Cl<sup>-</sup>, CH<sub>3</sub><sup>-</sup> and C<sub>2</sub>H<sub>5</sub><sup>-</sup> for TiCl<sub>4</sub>, TTC and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn, respectively (Fig. 4a, 4b and 4c stage 1). The second reaction corresponds to a purge by water molecules and the formation of new hydroxyl groups on the surface, which are involved in the layering of the second row of metal oxide by next cycles (Fig. 4a, 4b and 4c stages 2 and 3).

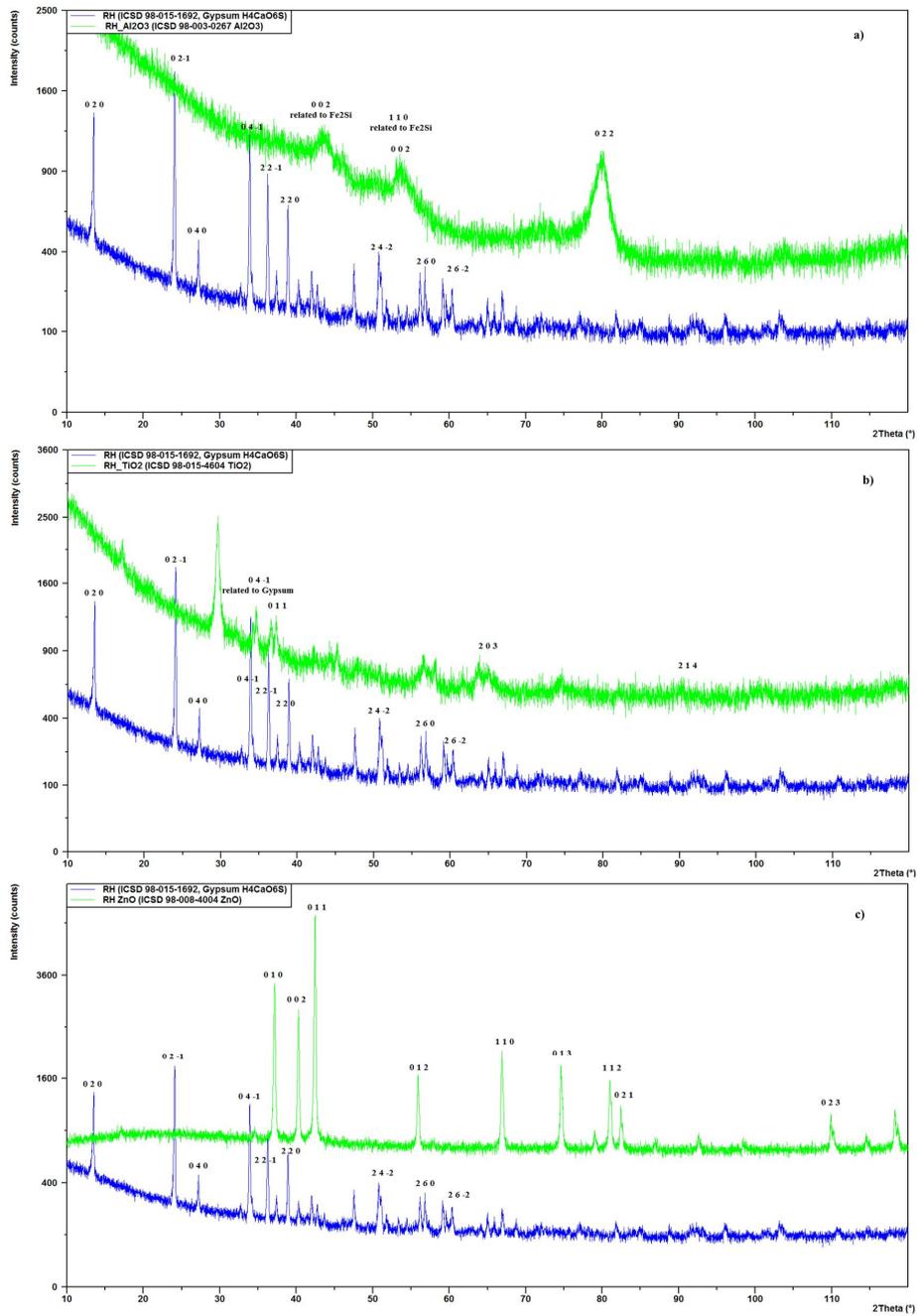


Figure 3. XRD profiles of unmodified and modified RH sorbents.

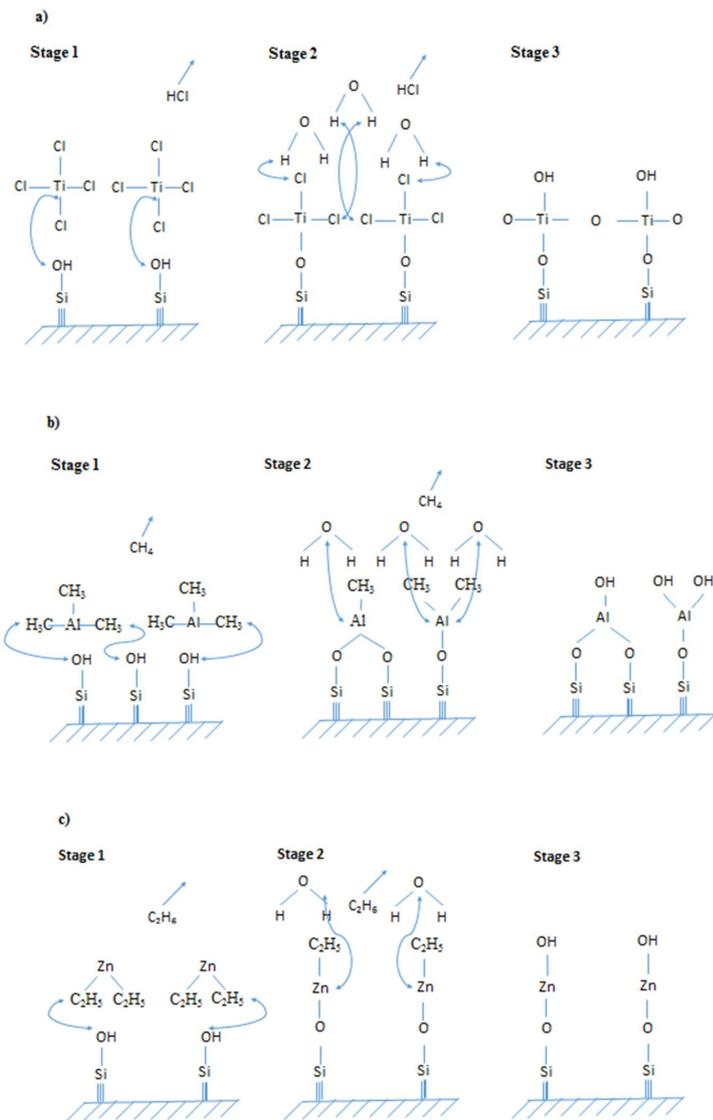


Figure 4. Reaction mechanisms of ALD coating of  $\text{Al}_2\text{O}_3$  (a),  $\text{TiO}_2$  (b) and  $\text{ZnO}$  (c) with ALD.

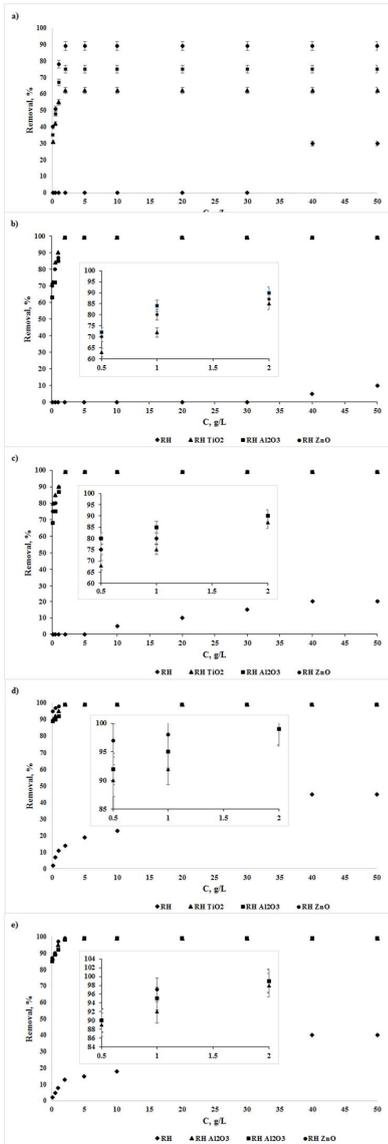


Figure 5. Effect of dosage of RH, RH\_TiO<sub>2</sub> and RH\_Al<sub>2</sub>O<sub>3</sub> for removal of SO<sub>4</sub><sup>2-</sup> (a), Ni<sup>2+</sup> (b), Zn<sup>2+</sup> (c), Fe<sup>3+</sup> (d) and Cu<sup>2+</sup> (e) from synthetic solution with initial concentration of sulphate ions at 3.5 g L<sup>-1</sup> and metal ions at 100 mg L<sup>-1</sup>.

### 5.3. Synthetic and natural AMD treatment

The adsorption of unmodified and modified materials was examined with synthetic and natural AMD solutions for removal of  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ .

#### 5.3.1. Optimisation of adsorbent amount and contact time

An equilibrium of the system for metal and sulphate ions was reached with the mass of modified adsorbent at  $2 \text{ g L}^{-1}$ . At the same time, the optimal mass of unmodified sorbent was  $40 \text{ g L}^{-1}$ , that 20 times more than for modified RH (Fig. 5).

The optimisation of contact time was researched with the initial concentration of  $\text{SO}_4^{2-}$  was  $3470 \text{ mg L}^{-1}$ ;  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cu}^{2+}$  was  $100 \text{ mg L}^{-1}$  and  $1000 \text{ mg L}^{-1}$  for  $\text{Fe}^{3+}$ . The initial amount of all adsorbents was  $10 \text{ g L}^{-1}$ . The equilibrium was reached after 48 h for RH\_ $\text{Al}_2\text{O}_3$  and RH\_ $\text{TiO}_2$  modified sorbents. The pollutants removal were similar for RH\_ $\text{Al}_2\text{O}_3$  and RH\_ $\text{TiO}_2$  sorbents and amounted around 70% for sulphate ions and 99% for metal ions (Figures 6 (a & b)). The best results were found for RH\_ $\text{ZnO}$  sorbents that treated synthetic AMD from metal and sulphate ions almost completely (Figure 6 (c)). The equilibrium for RH\_ $\text{ZnO}$  was reached after 6h. The initial pH of was 2.5 and it was changed from 2.5 to 6 during 12h [32, 44-45].

The most effective removal of metal ions has been observed with the similar pH by many researchers [12, 46-48]. Initial pH of sorbents is around 3 (Table 2), the pH of the treated solution should be higher than this value for the better removal of metal ions. The opposite is true for sulphate ions, which are present as anions in solution and remove better at less than 6 pH. However, better sorption capacity for sulphate ions was observed at 6 pH also. This could be the effect of competitions between sulphate and metal ions in complex solution.

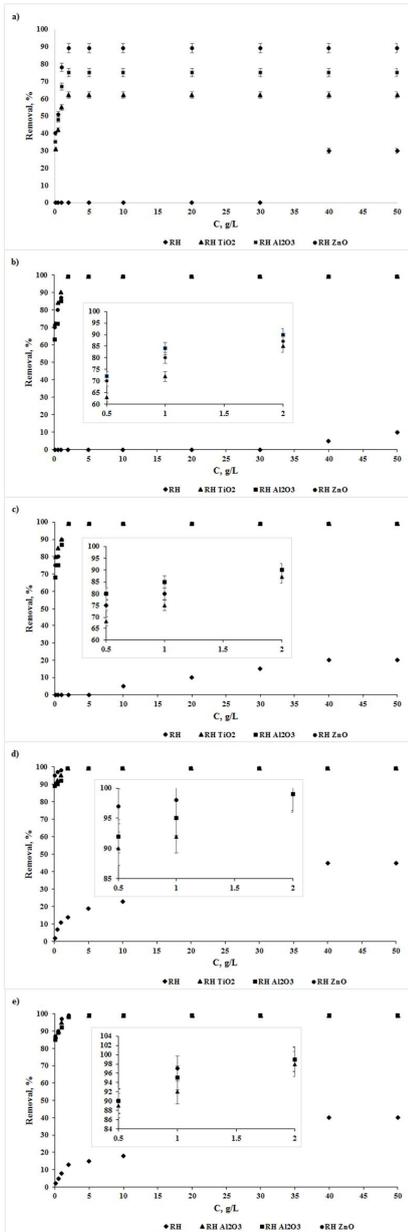


Figure 6. Removal of sulphate and metal ions with modified adsorbents (a) RH\_TiO<sub>2</sub>, (b) RH\_Al<sub>2</sub>O<sub>3</sub> (c) and RH\_ZnO.

A dependence of zeta potential on pH is shown in Figure 7. Unmodified and modified sorbents have a positive value of zeta potential in the acid range. In this case, the isoelectric point for all sorbents lies at between pH 3-4. The highest adsorption capacity for all sorbents occurs at 6 pH, when zeta potential lies out of the isoelectric point and has value around -10 mV for RH<sub>Al<sub>2</sub>O<sub>3</sub></sub> and RH<sub>TiO<sub>2</sub></sub> and -15 mV for RH<sub>ZnO</sub>. The similar pattern for relationship of pH, zeta potential, and adsorption efficiency was observed by many other researchers [49-51].

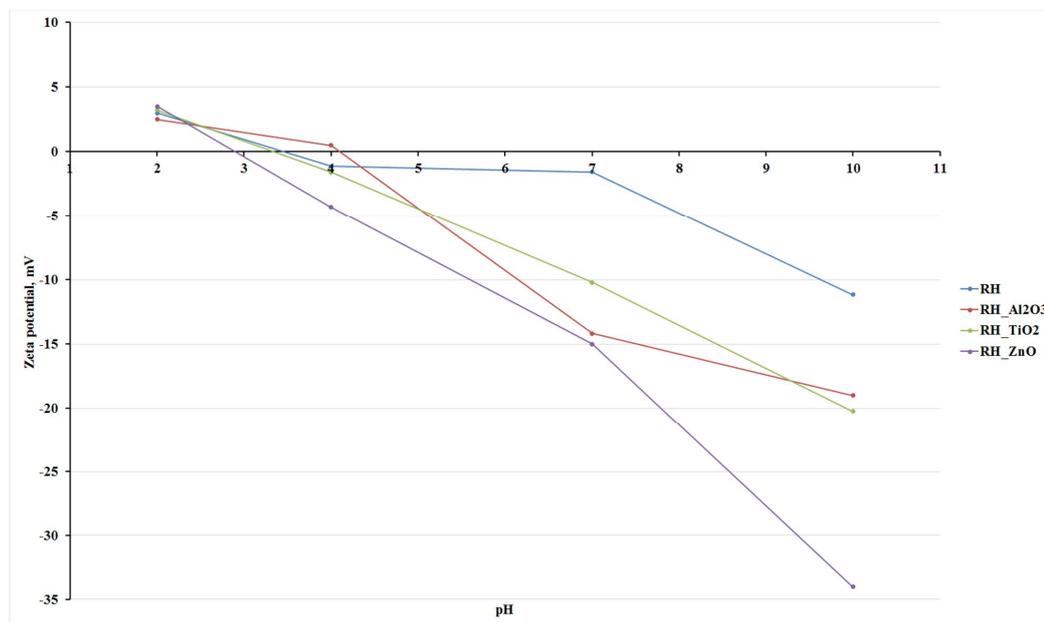


Figure 7. Dependence of zeta potential on pH during of unmodified and modified RHs.

Rates of chemical processes for removal of iron, copper, zinc, nickel and sulphate ions with both modified sorbents were studied by pseudo-first-order (PFO) (Eq. 5) and pseudo-second-order (PSO) (Eq.6) models.

$$\frac{dq}{dt} = k_1(q_e - q) \quad (5)$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (6)$$

where  $dq$  is the average concentration of adsorbed phase ( $\text{mmol g}^{-1}$ ),  $q_e$  is the concentration of adsorbed phase at equilibrium ( $\text{mmol g}^{-1}$ ),  $t$  is the experimental time,  $k$  is the kinetic constant.

The sorption process of sulphate and metal ions for modified sorbents was described better with the pseudo-second-order than with pseudo-first-order model, excepting removal of zinc, copper and iron ions by RH\_Al<sub>2</sub>O<sub>3</sub> (Table 6). Removal of these metal ions was fitted better with pseudo-first-order model. It can point to the fact, that adsorption of mentioned ions was performed by physisorption, through their entering into the pores of the sorbent or by complex formation with sorbent functional groups [31, 52]. Pseudo-second-order model indicates the more complex process between sulphate and nickel ions with RH\_Al<sub>2</sub>O<sub>3</sub> and all ions with RH\_TiO<sub>2</sub> and RH\_ZnO. The possible reaction mechanism of pollutant ions with sorbents will be described below.

### 5.3.2. Adsorption isotherms and reaction mechanisms of pollutants removal

The Langmuir adsorption isotherm (Eq. 7) was used for describing the equilibrium between the adsorption of pollutants on the sorbent surface.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where,  $q_e$  and  $q_m$  are sorption capacities ( $\text{mmol g}^{-1}$ ) at equilibrium and maximum, respectively;  $C_e$  is the concentration of pollutant ions in the solution ( $\text{mmol L}^{-1}$ ) at equilibrium;  $K_L$  is Langmuir constant related to the sorption energy.

Table 6. Pseudo-first- (PFO) and pseudo-second-order (PSO) parameters for metal ions adsorption on modified sorbents RH\_Al<sub>2</sub>O<sub>3</sub>, RH\_TiO<sub>2</sub> and RH\_ZnO.

		C <sub>i</sub>	q <sub>e exp</sub>	q <sub>e</sub> mmol g <sup>-1</sup>		K <sub>2</sub> g mmol h <sup>-1</sup>		R <sup>2</sup>	
		mmol	mmol						
		L <sup>-1</sup>	g <sup>-1</sup>						
				PFO	PSO	PFO	PSO	PFO	PSO
RH_Al <sub>2</sub> O <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	36.2	2.24	2.34	2.90	0.08	0.03	0.96	0.97
	Ni <sup>2+</sup>	1.69	0.17	0.18	0.23	0.06	0.21	0.94	0.94
	Zn <sup>2+</sup>	1.54	0.15	0.16	0.20	0.07	0.35	0.96	0.93
	Cu <sup>2+</sup>	1.56	0.16	0.16	0.19	0.09	0.46	0.97	0.94
	Fe <sup>3+</sup>	17.86	1.79	1.83	2.16	0.11	0.05	0.98	0.94
RH_TiO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	36.2	2.24	2.77	3.39	0.09	0.03	0.97	0.98
	Ni <sup>2+</sup>	1.69	0.17	0.18	0.23	0.06	0.24	0.95	0.95
	Zn <sup>2+</sup>	1.54	0.15	0.16	0.19	0.08	0.04	0.96	0.97
	Cu <sup>2+</sup>	1.56	0.16	0.16	0.19	0.11	0.60	0.97	0.99
	Fe <sup>3+</sup>	17.86	1.79	1.83	2.15	0.12	0.06	0.96	0.99
RH_ZnO	SO <sub>4</sub> <sup>2-</sup>	36.2	2.24	2.81	3.20	0.10	0.09	0.94	0.99

Ni <sup>2+</sup>	1.69	0.17	0.18	0.19	0.06	0.21	0.93	0.98
Zn <sup>2+</sup>	1.54	0.15	0.16	0.17	0.07	0.35	0.87	0.98
Cu <sup>2+</sup>	1.56	0.16	0.16	0.17	0.09	0.46	0.90	0.99
Fe <sup>3+</sup>	17.86	1.79	1.83	1.92	0.09	0.05	0.92	0.99

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The parameters were calculated with minimisation of the error distribution between experimental and predicted data by Marquardt's percent standard deviation (MPSD):

$$\sum_{i=1}^n \left( \frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right)_i^2 \quad (8)$$

Langmuir isotherm parameter  $q_m$  shows the number of adsorbent site that actively interacts with the pollutant ions [53]. This parameter increases for all pollutants after modification of raw RH with both methods. The number of sites which participate in the adsorption of ions is much higher for SO<sub>4</sub><sup>2-</sup> (645 mmol g<sup>-1</sup>). It is about 200 mmol g<sup>-1</sup> for copper and iron ions, except for nickel and zinc ions (about 100 mmol g<sup>-1</sup>) (Table 7).

The K coefficient is the affinity between sorbate and adsorbent. The following affinity was obtained between the adsorbents and adsorbates according to Langmuir theory:



This order is confirmed by many researchers [46, 55-56], and the similar correlation was observed in our previous work [9].

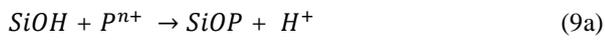
Table 7. Isotherm parameters for unmodified and modified RHs during AMD treatment process.

		$C_e$	$q_{e \text{ exp}}$	$q_{e \text{ model}}$	$K_L$	$R^2$
		(mmol L <sup>-1</sup> )	(mmol g <sup>-1</sup> )	(mmol g <sup>-1</sup> )	(L mmol <sup>-1</sup> )	
Langmuir						
RH	SO <sub>4</sub> <sup>2-</sup>	47.4	11.72	11.24	18.68	0.74
	Ni <sup>2+</sup>	1.69	0.11	0.10	9.01	0.70
	Zn <sup>2+</sup>	1.54	0.20	0.19	12.03	0.75
	Cu <sup>2+</sup>	1.56	0.39	0.40	21.09	0.82
	Fe <sup>3+</sup>	1.78	0.75	0.72	25.12	0.87
RH <sub>Al<sub>2</sub>O<sub>3</sub></sub>	SO <sub>4</sub> <sup>2-</sup>	47.4	650	622	20.15	0.82
	Ni <sup>2+</sup>	1.69	98	100	10.17	0.85
	Zn <sup>2+</sup>	1.54	150	145	12.05	0.84
	Cu <sup>2+</sup>	1.56	201	204	20.22	0.87
	Fe <sup>3+</sup>	1.78	225	215	26.30	0.90
RH <sub>TiO<sub>2</sub></sub>	SO <sub>4</sub> <sup>2-</sup>	47.4	623	620	21.30	0.95
	Ni <sup>2+</sup>	1.69	85	83	9.6	0.85
	Zn <sup>2+</sup>	1.54	137	136	12.5	0.85

	Cu <sup>2+</sup>	1.56	190	185	20.3	0.90
	Fe <sup>3+</sup>	1.78	215	210	25.7	0.93
RH_ZnO	SO <sub>4</sub> <sup>2-</sup>	47.4	645	632	20	0.97
	Ni <sup>2+</sup>	1.69	87	85	10	0.90
	Zn <sup>2+</sup>	1.54	135	137	12	0.91
	Cu <sup>2+</sup>	1.56	210	225	22	0.95
	Fe <sup>3+</sup>	1.78	222	234	28	0.98

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The complexation and ion-exchange mechanisms take place during the metal and sulphate ions removal in this experiments. The unmodified and modified RH contain silicate compounds, which can react with ions by following reactions:



The addition of aluminium, titanium and zinc oxides onto the surface of sorbent allows a significant increase of ions removal (Fig. 5). It can be due to the appearance of additional functional groups, which also participate in the removal of ions from solution. As it is known that activated alumina (Al<sub>2</sub>O<sub>3</sub>) is a highly porous commercial sorbent with a surface area more than 200 m<sup>2</sup> g<sup>-1</sup> used for the removal of various pollutants [2, 57-58]. Titanium dioxide has a lower chemical reactivity than activated alumina, however, its porosity and big surface area also

contribute to the application for the removal of various pollutants from water [59]. Zinc oxide has unique physical and chemical properties, such as high electrochemical coupling coefficient and chemical stability that have to indicate it as a potential effective material for the sorbent. Therefore, the increase of pollutant ion removal depends on the increase of the sorbent surface area and the presence of additional functional groups.

### 5.3.3. Real AMDs treatment with modified RHs

Removal of ions from real AMDs was conducted by the batch method at ambient temperature for 720 h with 2 g L<sup>-1</sup> of modified sorbents. Removal of ions from real AMD was conducted by the batch method at ambient temperature for 720 h with 2 g L<sup>-1</sup> of modified sorbents. AMD from depth 720 m was treated more efficiency than other ones (Fig 8). It can be explained by competitive ions removal from AMD with a higher concentration of all remove pollutants. Increasing adsorbents concentration and sorption time did not increase removal efficiency. Equilibrium occurred at the optimal sorption time (48 h) and sorbents concentrations of 2 g L<sup>-1</sup> for RH\_Al<sub>2</sub>O<sub>3</sub> and RH\_TiO<sub>2</sub>. The lower sorption capacity of both sorbents for real AMD compared to synthetic solutions could be due to complex composition of real AMD. Other ions can act as competitors during the adsorption process, such as chloride, ammonium and some trace amount of metal ions. However, it was found, that RH\_ZnO has equilibrium for removal of all pollutants even after 10 h. RH\_ZnO more efficiently also for removal all pollutants to compare with other modified RHs.

### 5.4. Economic feasibility analysis of novel sorbents.

Cost estimating of sorbents is a main the operational cost of water purification with adsorption. The total cost of the preparation of 1 kg of novel sorbents was calculated according to the pretreatment and modification stages of raw materials. Since these sorbents are aimed to be applied

and produced by local mine industries, the electricity consumption was calculated based on the Finnish price (0.18 €/kWh). However, it should be mentioned, that the electricity cost in developed countries is much lower, therefore, the final price can be decreased. The prices of novel sorbents were compared with the previously manufactured by ALD sorbents [32] and with the most common sorbents [60], such as iron oxide (more than 1000 €/per kg), activated carbon (500-1000 €/per kg), and alumina (300-500 €/per kg), and iron oxide (Table 8). It can be seen, the changes of the parameters of ALD modification, that were implemented in previous paper [32], allowed the reduction of the cost of the sorbents by several times, compared to the data obtained in this work. A comparative analysis of prices of adsorbents shows that the developed adsorbents are ten times cheaper than commercial ones. The modification with ALD increased the price of 1 kg modified sorbents from 0.5 to 20 times, however the price remains less than that of the commercial sorbents.

Table 8. Comparative price analysis of novel sorbents.

	Prewashing and drying, €/per kg	Granulation and drying, €/per kg	Modification with ALD, previous research (Iakovleva et al., 2016), €/per kg	Modification with ALD (this research), €/per kg	Total price, previous research, (Iakovleva et al., 2016) €/per kg	Total price (this research), €/per kg
RH_Al <sub>2</sub> O <sub>3</sub>	1.50	1.00	9.50	1.60	12.00	4.10
RH_TiO <sub>2</sub>	1.50	1.00	53.20	8.80	64.70	11.30
RH_ZnO	1.50	1.00	-	1.50	-	4.10

## 6. Conclusions

Novel iron-containing sorbents from an industrial solid waste were produced with ALD technology for TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZnO coating. The optimal sorption parameters were estimated with synthetic AMD. The optimal time (48 h for TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and 10h for RH\_ZnO) and sorbent concentration (2 g L<sup>-1</sup>) were determined with a batch method. The maximum sorption capacities of RH\_Al<sub>2</sub>O<sub>3</sub>, RH\_TiO<sub>2</sub>, and RH\_ZnO were around 650, 200, 200, 150 and 100 mmol g<sup>-1</sup> for removal of SO<sub>4</sub><sup>2-</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Ni<sup>2+</sup>, respectively. The sorption process was carried out using complexation and ion-exchange mechanism. The deposition of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZnO on the surface of granulated sorbents sufficiently increased the sorption capacities of raw material for real AMD treatment. The modified sorbents could be used for real AMD treatment with a high capacity for some pollutants. RH\_ZnO shown higher adsorption capacities for real AMD treatment and equilibrium was observed even after 10 h, that about five times faster to compare with other modified sorbents.

Considering that the lower temperatures were used for deposition of metal oxides in this work and modified with ZnO and Al<sub>2</sub>O<sub>3</sub> sorbents showed perfect capacities for removal of ions from real mine water, the ALD modification cost was lower in comparison with previously published results. According to the comparative analysis of prices for commercial sorbents and the ones developed during this work, it can be confirmed that the novel new sorbents are more cost effective than the commercial ones. Novel sorbents can be recommended for the further experiments for real AMD treatment by columns.

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