Lappeenranta-Lahti University of Technology LUT
LUT School of Engineering Science
Master's Program in Chemical and Process Engineering

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ACTIVATED CARBON FILTRATION OF ELECTROLYTE SOLUTIONS

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TIIVISTELMÄ

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Elektrolyyttiliuosten aktiivihiilisuodatus

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Tämän diplomityön tarkoituksena oli tutkia aktiivihiilisuodatusta. Kirjallisessa osassa tutkittiin aktiivihiilen ominaisuuksia sekä käyttökohteita ja aktiivihiilisuodatuksen pääperiaatteita. Aktiivihiilen ominaisuuksista tutkittiin rakenteita, valmistustapoja, adsorptiota sekä regenerointia. Aktiivihiilisuodatuksen tutkimuksessa keskityttiin suodatusprosessien perusteisiin sekä yleisiin prosessiparametreihin. Aktiivihiilen lisäksi kirjallisessa osassa tutkittiin biohiilen ominaisuuksia sekä mahdollisia käyttökohteita.

Kokeellisen osan pääpaino oli tutkia elektrolyyttiliuosten puhdistamista aktiivihiilisuodatuksella. Metallien uuttoprosesseissa prosessivirtoihin jää usein orgaanisia uuttoaineita, joita pitää suodattaa pois. Suodatuskokeiden tavoite oli tutkia kuinka tehokkaasti aktiivihiili poistaa orgaanista ainetta elektrolyyttiliuoksista. Biohiiltä kokeiltiin vaihtoehtoisena suodatusmateriaalina elektrolyyttiliuosten suodatuskokeissa. Kokeellisessa osassa tutkittiin myös kaivosteollisuuden jäteveden suodatusta, missä oli tarkoitus selvittää aktiivihiilen kykyä erottaa anioneja ja raskasmetalleja jätevedestä. Jäteveden puhdistukselle suoritettiin suodatuksen lisäksi adsorptiokoe, missä tutkittiin aktiivihiilen ja biohiilen kykyä adsorboida anioneja ja raskasmetalleja.

Aktiivihiilellä saavutettiin keskimääräisesti elektrolyyttiliuoksen suodatuskokeissa orgaanisen aineen pitoisuudeksi 5 mg/l, kun syöttövirran orgaanisen aineen pitoisuus oli noin 50 mg/l. Biohiilellä saatiin erotettua keskimääräisesti vähemmän orgaanista ainetta kuin aktiivihiilellä. Jätevesisuodatuksessa aktiivihiili poisti erittäin heikosti anioneja. Jäteveden adsorptiokokeen perusteella aktiivihiili adsorboi raskasmetalleja tehokkaammin kuin anioneja. Biohiili adsorboi kokeiden perusteella jätevedestä heikommin anioneja ja raskasmetalleja kuin aktiivihiili.

ABSTRACT

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Activated carbon filtration of electrolyte solutions

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98 pages, 41 figures, 18 tables

Examiners:

Professor Antti Häkkinen

D.Sc Maria Mamelkina

Keywords: activated carbon, activated carbon filtration, adsorption, biochar, filtration

The purpose of this thesis was to study activated carbon filtration. In the literature part, the properties and applications of activated carbon and basic principles of activated carbon filtration were studied. The study of activated carbon properties focused on the structure, preparation method, adsorption and regeneration of activated carbons. The investigation of activated carbon filtration introduced the basics of filtration processes as well as the general process parameters. In addition to activated carbon, the literature part also investigated the properties and possible applications of biochar.

The focus of the experimental part was to study the purification of electrolyte solutions by activated carbon filtration. In metal extraction processes, organic extractants often remain in the process streams and need to be removed. The aim of the filtration tests was to investigate how effectively activated carbons remove organic matter from electrolyte solutions. Biochar was tested as an alternative filtration material in the electrolyte filtration experiments. The experimental part also studied the filtration of mining wastewater, where the ability of activated carbon to separate anions and toxic metals from wastewater was investigated. In addition to filtration, the wastewater treatment was subjected to an adsorption test, where the abilities of activated carbon and biochar to adsorb anions and toxic metals were investigated.

With activated carbon, the average concentration of organic matter in the electrolyte filtration experiments was 5 mg / l, when the organic matter content of the feed stream was about 50 mg / l. Biochar removed organic matter averagely less than activated carbon. In wastewater filtration, activated carbon removed anions poorly. Based on the wastewater adsorption experiment, activated carbon adsorbs toxic metals more effectively than anions. Biochar adsorbed anions and toxic metals less effectively than activated carbon.

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Abbreviations

AC	Activated carbon
ACF	Activated carbon fibre
BET	Brunauer–Emmett–Teller theory for specific surface area
EBCT	Empty bed contact time
GAC	Granular activated carbon
MTZ	Mass transfer zone
PAC	Powdered activated carbon
TC	Total carbon content

List of Symbols

A	cross sectional area of packed bed, [m^2]
b	Langmuir free energy constant, [dm^3/g]
C_b	concentration of adsorbate in effluent at breakthrough, [mg/l]
C_e	equilibrium concentration in solution, [mg/l]
C_{op}	organic phase concentration, [mg/l]
C_{tc}	total carbon concentration, [mg/l]
C_x	effluent concentration at exhaustion point, [mg/l]
C_0	concentration in feed, [mg/l]
CUR	carbon usage rate, [kg/m^3]
$EBCT$	Empty bed contact time, [min]
ΔH	enthalpy change
K_F	Freundlich constant for adsorption capacity, [$(mg/g)/(dm^3/mg)^n$]
L_b	packed bed depth, [m]
M_c	activated carbon mass, [kg]
M_{Cr}	molar mass of carbons in extraction reagent, [g/mol]
M_{Cs}	molar mass of carbons in extraction solvent, [g/mol]
M_r	molar mass of extraction reagent, [g/mol]
M_s	molar mass of extraction solvent, [g/mol]
n	adsorption intensity constant
Q	total volume flow rate, [m^3/h]
q_e	equilibrium concentration of adsorbent, [mg/g]
q_m	maximum adsorption capacity, [mg/g]

V_B	packed bed volume, [m^3]
V_t	treated volume of water flow, [m^3]
v_f	linear flow rate, [m/h]
x	portion of extraction solvent in organic phase
y	portion of extraction reagent in organic phase

Contents

1 Introduction 1

2 Activated carbon 2

2.1 Structure 2

2.2 Carbon raw materials 5

3 Activation process of carbon 6

3.1 Physical activation 7

3.2 Chemical Activation 8

4 Activated carbon adsorption 9

4.1 Adsorption in liquid solutions 10

4.1.1 Effects of activated carbon properties in adsorption 10

4.1.2 Effects of adsorbate properties in adsorption 12

4.1.3 Effects of solution chemistry in adsorption 13

4.2 Activated carbon coalescing 14

5 Activated carbon adsorbents 15

5.1 Granular activated carbon (GAC) 15

5.2 Powdered activated carbon (PAC) 16

5.3 Other activated carbon adsorbents 16

5.4 Commercial activated carbon suppliers 17

6 Regeneration of activated carbons 18

6.1 Thermal regeneration 19

6.2 Steam regeneration 19

6.3 Chemical regeneration 21

6.4 Other regeneration methods 21

7 Activated carbon applications 21

7.1 Water treatment 22

7.2 Applications in hydrometallurgy 23

7.2.1 Gold recovery 23

7.2.2 Purification of metal electrolyte solutions 24

7.3 Other applications 24

8 Biochar 25

8.1 Biochar production and activation 26

8.2 Biochar adsorption and potential applications 28

8.2.1 Organic compound adsorption with biochar 29
8.2.2 Toxic metal adsorption with biochar 30
8.3 Biochar versus Activated carbon 31
9 Activated carbon filtration 32
9.1 Fixed bed filters 32
9.1.1 GAC filter column dimensions and operational factors 34
9.1.2 Backwash in GAC filters 36
9.1.3 Typical operational parameters for GAC wastewater filters 37
9.1.4 Commercial wastewater fixed bed filters 39
9.2 Fluidized bed filtration reactors 40
9.3 Moving-bed filtration reactors 41
9.4 Activated carbon canisters 42
9.5 Activated carbon adsorption theory in fixed bed columns 42
9.5.1 Adsorption isotherms of activated carbon 43
9.5.2 Breakthrough curve and mass transfer zone 45
9.5.3 Effects of operational parameters in fixed bed filtration 46
10 Wastewater filtration 48
10.1 Materials 48
10.2 Analysis methods 50
10.3 Filtration equipment 50
10.4 Wastewater experiment procedures 52
10.5 Wastewater results 52
10.5.1 Wastewater filtration results 53
10.5.2 Wastewater adsorption test results 57
10.6 Conclusions of wastewater experiments 60
11 Electrolyte filtration 62
11.1 Materials 62
11.2 Analysis methods 63
11.3 Equipment 64
11.3.1 Biochar particle sieving 66
11.4 Filtration procedure 67
12 Electrolyte filtration results 68
12.1 Preliminary test results 68

12.2 Activated carbon filtration results 70
12.2.1 Effects of the physical properties of activated carbon on filtration 74
12.3 Electrolyte filtration with biochar 77
12.4 Electrolyte filtration with alternative medias 81
13 Conclusions 84
References 86

1 Introduction

Activated carbon is one of world's most used adsorbents. It is estimated that activated carbon has over one thousand different applications (Dias et al., 2007). Activated carbon is known to be an effective adsorbent with extremely high surface areas (Bansal & Goyal, 2005). Activated carbons have been used for thousands of years in human history for medical uses, but the first industrial application was colour removal from sugar manufacturing process in 1794 (González-García, 2018). Nowadays, activated carbon is extremely popular in industrial water treatment and gas purification processes (Kwiatkowski, 2012). Activated carbon production is a large industry and it produced 1 962 000 tons/year in 2018 (Grand View Research, 2019).

Activated carbon can be used to remove organic matter from electrolyte solutions of metal extraction processes. It is extremely important to remove organic matter from electrolyte streams before they enter electrowinning step where the desired metals are deposited onto cathodes. The organic matter can cause impurities in metals at the cathode, drops in current efficiency and even explosion and fire risks in the electrowinning process. Target concentrations for organic matter can be as low as 2 mg/l. (Sole et al., 2007)

The purpose of this thesis was to study activated carbon filtration. In the literature part, there is covered activated carbon properties, production and regeneration procedures, applications and the basic principles of activated carbon adsorption and filtration. In addition to activated carbon, also basic properties and applications of biochar were covered in the literature part. In the experimental part, the main purpose was to investigate how effectively activated carbon filtration removes organic matter from electrolyte solutions. Activated carbon was also tried in mining wastewater filtration and adsorption experiments where the goal was to separate anions and metal ions from a synthetic mining water. Biochar was also used in the electrolyte filtration and wastewater adsorption experiments as an adsorbent and filter medium.

2 Activated carbon

Activated carbons are not found in nature by themselves and they require an activation process where carbonaceous material is turned into activated carbon. Activated carbon is a carbon-based material which is made from organic materials. Its primary element is carbon, but it also consists of small amounts of other elements such as hydrogen, oxygen, nitrogen and sulphur. Chemical composition of common activated carbons is 88% carbon, 6 to 7% oxygen, 1% sulphur, 0,5% hydrogen and 0,5% nitrogen. Activated carbon is stated to be one of worlds most used adsorbent materials and it is known for its high surface area, porosity and effective absorption. (Bansal & Goyal, 2005) Typical surface area values are in the range of 800-1500 m^2/g and pore volume values in 0,2-0,6 cm^3/g (Bansal & Goyal, 2005). The most advanced activated carbons can reach values of 3000 m^2/g and 1,2 cm^3/g (Moreno-Castilla & Rivera-Utrilla, 2001). The adsorption capacity of activated carbon is based on the high surface areas and porosity but also on its chemical properties from which hydrophobic properties play a key role. (Mars & Reinoso, 2006)

2.1 Structure

Activated carbon has a microcrystalline structure which is close to the basic structure of graphite, however, activated carbon has some differences in the structure. It has smaller interlayer distances inside of molecule structure and less organized crystalline structure than graphite. The disorganized structure of activated carbons can be referred to as non-graphitizable structure whereas graphite's structure is known to be graphitizable. A graphical design of activated carbon and graphite structures are represented in Figure 1 and scanning electron microscope (SEM) images in Figure 2. (Mars & Reinoso, 2006) The disorganized crystalline structure is the reason for internal holes, known as pores, in activated carbon. The porous structure defines the adsorption capacity of activated carbon. (Bansal & Goyal, 2005) The term adsorption capacity refers to the maximum amount of material that an adsorbent can adsorb per its own volume or mass. (Mokhatab et al., 2019)

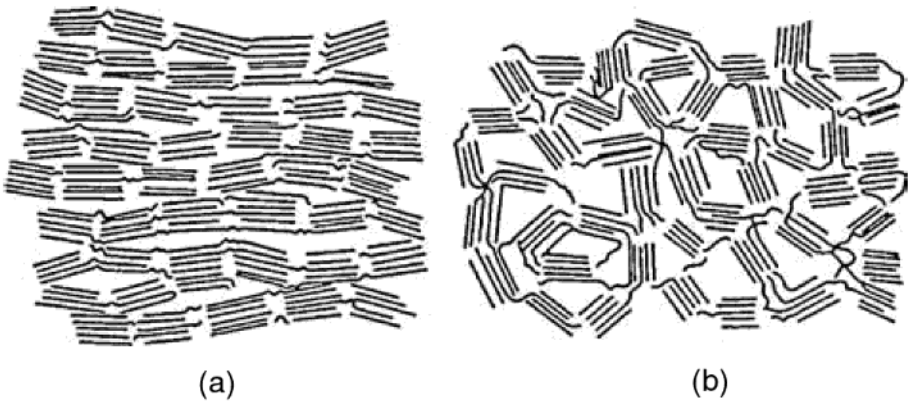

Figure 1 Designs for a) graphitizable structure of graphite and b) non-graphitizable structure of activated carbons. (Mars & Reinoso, 2006)

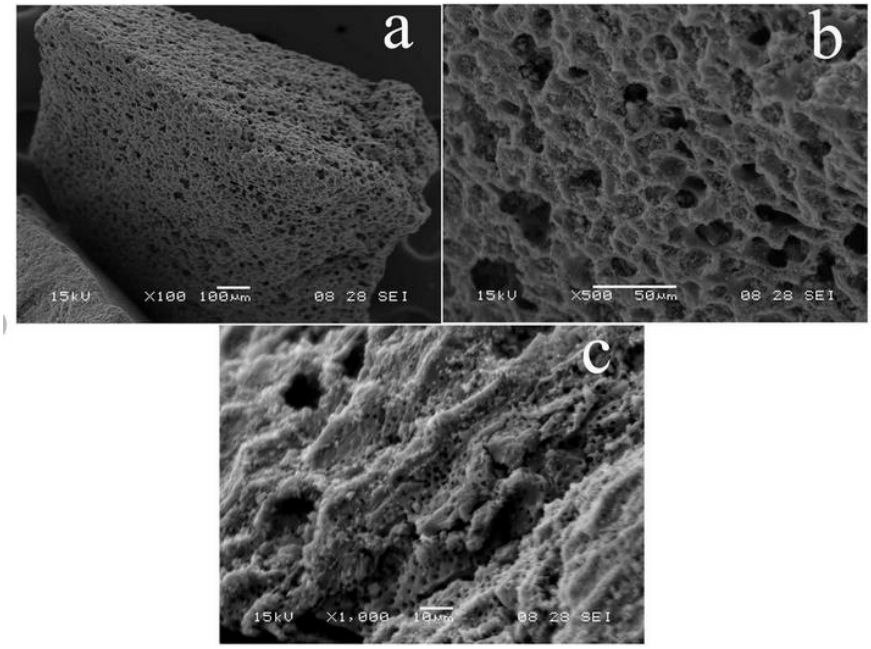

Figure 2 Illustration of activated carbon structure taken by scanning electroscope microscope (SEM) with three different scale bars: a) 100 µm, b) 500 µm and c) 1000 µm. (Yao et al., 2019)

The pores in activated carbons are divided into three categories, namely as micropores, mesopores and macropores based on their radius sizes. Porous structure includes all 3 pore categories together. (Inamuddin et al., 2021) The radius of micropores is under 2 nm, mesopores 2-50 nm and macropores 50-200 nm. Micropores have pore volume of 0.15-0.7 cm^3/g and they cover typically 95% of the surface area of activated carbons. Micropores have the most effective adsorption efficiency of the three pore types due to their high surface area share and superior adsorption forces. The pore volumes of mesopores are from 0.1 to 0.2 cm^3/g and have a share of under 5% of activated carbon's surface area. Macropores have pore volume of 0.5 cm^3/g and their share of the surface area is less than the share of mesopores. Porous structure of carbon particle surfaces created by micro, meso and macropores is represented in Figure 3. (Bansal & Goyal, 2005)

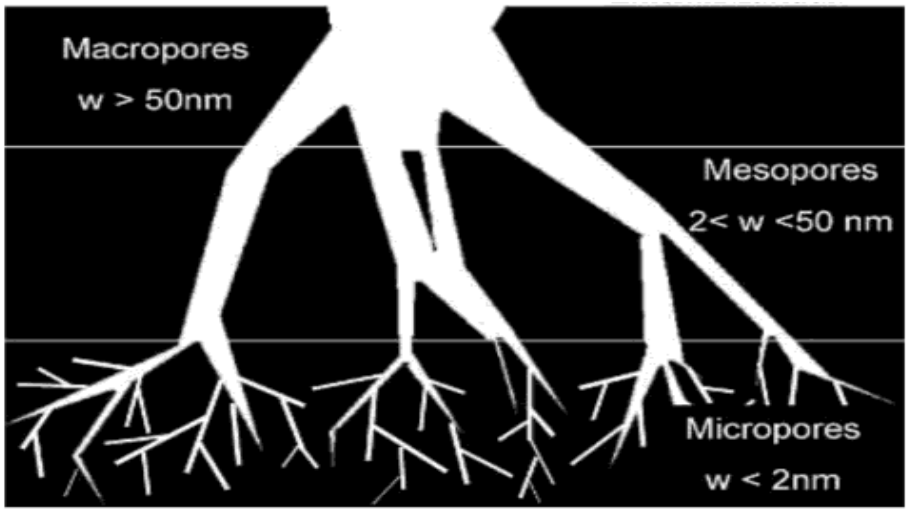

Figure 3 Illustration of micro, meso and macropores on activated carbon surfaces. (Bandosz, 2006)

Chemical properties of activated carbons include elemental surface groups. The most significant surface group on the activated carbon surface is carbon-oxygen (C-O). (Yang et al., 2019) Groups are divided into acidic, basic and neutral surface groups. Surface groups can modify the characteristics and properties of activated carbon. Carbon-oxygen surface groups affect polarity, acidity and wettability of surface features. Chemical and physical

properties such as chemical, electrical and catalytical reactivities are also affected by carbon-oxygen surface groups. Acidic surface groups such as phenolic, lactone and carboxylic groups create polarity and hydrophobicity into the surface of carbon. Typical functional surface groups formed by carbon-oxygens are represented in Figure 4. (Bansal & Goyal, 2005)

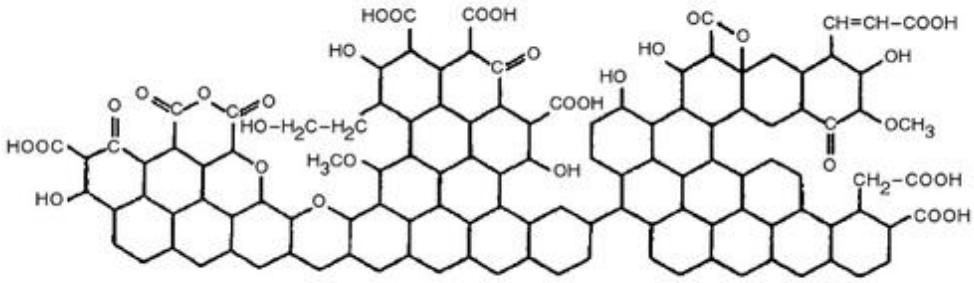

Figure 4 Typical structural formula of oxygen groups on activated carbon. (Bansal & Goyal, 2005)

2.2 Carbon raw materials

Activated carbon raw materials are usually carbon-based and non-graphitic solid materials. Used raw material sources comprise of wood-based lignocellulosic materials, coal, lignite and peat. Raw material coals can be bituminous or sub-bituminous coals. (Bandosz, 2006) The most common raw materials are coal, wood and coconut shells (Inamuddin et al., 2021)

Important properties of raw materials include high carbon contents, high volatile solid, low inorganic content and low ash content. (Inamuddin et al., 2021) Final properties of activated carbon depend on a combination of 2 factors: raw material source and the characteristics of activation process. In addition, factors such as density and hardness and are important in selection of raw material. Inorganic material content is desired to be low in the purpose of ensuring an effective adsorption capacity. This is because inorganic compounds do not possess porous structures, consequently they reduce adsorption capacity. High density and hardness of the raw material are usually important properties for adsorbent operability and performance. (Bandosz, 2006)

Cost of raw materials and activation process are also important. If the activation process and the raw material are expensive, activated carbon might not be economical in comparison to other commercial adsorbents. (Mars & Reinoso, 2006) Currently activated carbon production has started to utilize more agricultural residues and other biowastes as raw materials. Benefits of biowastes are their low cost and more eco-friendly source. (Inamuddin et al., 2021)

3 Activation process of carbon

Activation of activated carbon is a method that modifies the structure and the chemical compound content of carbon raw materials. Activation is also known as a structure transformation of materials. Activation process can be performed to almost all organic materials, however, only some materials can be made into effective adsorbents. (Mars & Reinoso, 2006) Activation process of carbon consists of two main methods: chemical and physical activation. Physical activation method requires a carbonization procedure for organic materials before the activation phase. The carbonization phase modifies organic materials into a carbonized form. Chemical activation method performs activation and carbonization at the same time. The goal of both activation methods is to enhance porosity, surface areas and adsorption capacities. (Hayashi et al., 2000) A block diagram of a typical activation process is represented Figure 5.

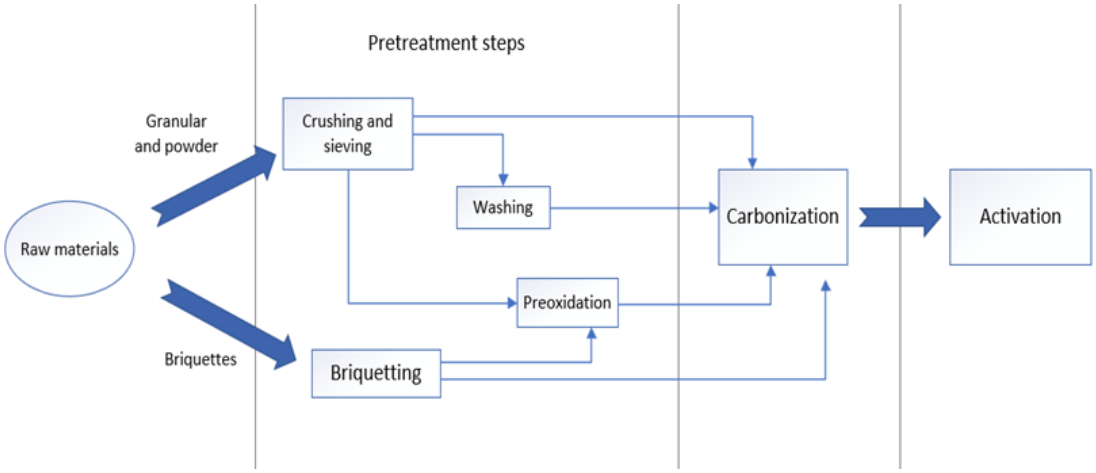

Figure 5 Production block diagram for activated carbon. (Bandosz, 2006)

In some situations, pre-treatment steps are required before the activation processes. Pre-treatment steps include crushing, sieving, washing, pulverizing, briquetting and peroxidation of raw materials which are presented in Figure 5. Purpose of crushing and sieving is to achieve desired particle sizes for raw materials. Washing is executed to those raw materials that contain prominent amounts of dirt. Pre-oxidation is performed when stabilization of raw material structure is needed as, for example, coking coal requires stabilization. Pulverizing and briquetting are executed to those raw materials that generate pores insufficiently in the activation process. (Bandosz, 2006)

3.1 Physical activation

Physical activation process consists of carbonization and activation phases. Carbonization phase practically means a thermal degradation of a carbonaceous raw material. (Mars & Reinoso, 2006) In the carbonization phase there occurs a devolatilization where volatile components are separated in a form of a gaseous mixture from solid raw materials. These separated gaseous mixtures consist of hydrogen and light hydrocarbons. In the carbonization process microporous structure begins to develop into the solid raw materials. (Bandosz, 2006) Carbonization temperature usually varies between 450 and 850 °C (Ioannidou & Zabaniotou, 2007). An important factor in carbonization process is the heating rate where high heating rates have been found to produce more meso and macropore development in the carbon structure than lower heating rates. Micropore development is not dependent on the heating rate. Low heating rates produce structures with higher density and hardness in comparison to higher heating rates. (Bandosz, 2006)

Carbon's porous structure is still too weak after the carbonization phase to be an effective adsorbent and therefore activation phase is always required. Physical activation phase is basically a thermal activation process. Activation phase improves the porous structures of solid carbons after the carbonization and makes them effective adsorbents. Activation of carbons is a gasification process where carbon is oxidized. Gasification is done with carbon dioxide gas ($CO_{2(g)}$), air or steam from which steam activation process is the most popular activation method used in industries due to its superior controllability at high temperatures. These gases are also known as activating agents. (Mars & Reinoso, 2006) Temperatures used in the gasification are generally around 600-900 °C (Ioannidou & Zabaniotou, 2007). Carbon

atoms are removed from carbon material during gasification, when activating agents react with solid carbon material. Removal of carbon atoms from raw materials internal structures enhances micropore development in carbons. In activation phase the microporous structures are fully developed. (Bandosz, 2006)

When carbon dioxide is used as an activation agent, it reacts with carbon and forms carbon monoxide. Carbon dioxide gasification reaction is represented in equation (1) (Mars & Reinoso, 2006):

$$CO_2 + C \longrightarrow 2CO \quad \Delta H = 159\ \mathrm{kJ/mol} \qquad (1)$$

When steam is an activation agent, it forms hydrogen and carbon monoxide as seen in equation (2) (Bandosz, 2006):

$$C + H_2O \longrightarrow H_2 + CO \quad \Delta H = 132\ \mathrm{kJ/mol} \qquad (2)$$

When activation is performed with air, oxygen reacts with carbon and forms carbon dioxide and carbon monoxide. Unlike in carbon dioxide and steam activation reactions, air activation reactions are exothermic. Reaction equation with air as an activation agent are represented by equations (3) and (4) (Bandosz, 2006):

$$C + O \longrightarrow CO_2 \quad \Delta H = -387\ \mathrm{kJ/mol} \qquad (3)$$

$$2C + O_2 \longrightarrow 2CO \quad \Delta H = -226\ \mathrm{kJ/mol} \qquad (4)$$

3.2 Chemical Activation

Chemical activation is an activation method where the activation is done with a chemical reagent. The most popular chemical reagents in industries are zinc-chloride, phosphoric acid

or potassium hydroxide. (Mars & Reinoso, 2006) Chemical activation performs carbonization and activation steps at same time. Used reagents react with carbon atoms and generate porous structures into carbon, while thermal degradation simultaneously modifies the overall structure of the raw material structure. (Molina-Sabio & Rodríguez-Reinoso, 2004) Porous structures vary significantly between final carbon products based on which reagent is used. Simultaneous activation and carbonization phases are usually performed at temperatures 350-500 °C (Wong et al., 2018). Washing of activated products after chemical activation is always required (Yahya et al., 2015)

Zinc chloride activation is often used with lignocellulosic raw materials like wood-based materials. (Yahya et al., 2015) Use of zinc chloride as a reagent produces open microporous structures that are effective adsorbents for liquids. (Malik et al., 2006) Phosphoric acid activation is also targeted for lignocellulosic raw materials and materials with volatile components. (Yahya et al., 2015) Like zinc chloride activation, it also produces open microporous structures which are effective adsorbents for liquids. (Molina-Sabio,& Rodríguez-Reinoso, 2004)

Potassium hydroxide activation is able to create superior porous structures with surface areas as large as 3000 m^2/g (Maciá-Agulló et al., 2004). Raw materials used in this method have a high carbon content and don't have highly volatile composition. Popularly used raw materials in potassium hydroxide activation are coals, chars and petroleum cokes. Unlike in phosphoric acid and zinc chloride activation, potassium hydroxide generates narrow microporous structures with excellent adsorption capacity. There are almost no mesopores in the final structure of adsorbents made by potassium hydroxide. Adsorbents produced by potassium hydroxide method are suitable for instance gas adsorption. (Molina-Sabio & Rodríguez-Reinoso, 2004)

4 Activated carbon adsorption

Adsorption on activated carbon can be performed in liquid and gas phases which differ considerably from each other. Gas phase adsorption generally focuses on one adsorbate. (Radovic et al., 2004) Adsorption in solution is based on two forces: attraction between adsorbent and adsorbate and rejection between adsorbent and water. Activated carbon

adsorbents used in liquid solutions are usually hydrophobic and therefore they reject water molecules. Liquid phase adsorptions from solutions are usually non-ideal. Gas phase adsorption behaves more commonly like multilayer adsorption than liquid phase adsorption. (Moreno-Castilla, 2004) It is relevant to recognize in activated carbon adsorption that adsorption capacity and adsorption efficiency are different concepts and are affected by different factors. Adsorption efficiency describes how effectively adsorbent can adsorb different compounds (Bansal & Goyal, 2005), while adsorption capacity refers to the maximum amount that activated carbon can adsorb (Mokhatab et al., 2019).

4.1 Adsorption in liquid solutions

Activated carbon adsorption in solutions is a spontaneous phenomenon which consists of two categories of interactions: electrostatic and non-electrostatic. Electrostatic interactions occur when there are electric charges on adsorbent's surface or in aqueous solutions like ionized electrolyte solutions. (Yang et al., 2019) Ionic strength of aqueous solutions and surface charge densities of adsorbent and adsorbate determine the characteristics of electrostatic interactions in adsorption process. Non-electrostatic interactions are based on hydrophobicity, van der Waals forces and hydrogen bonds between adsorbent and adsorbate. (Moreno-Castilla, 2004) Overall, adsorption process of activated carbon is affected by properties of adsorbent and adsorbate, solution chemistry and temperature of the adsorption. (Hadi et al., 2015)

4.1.1 Effects of activated carbon properties in adsorption

The properties of activated carbons that effect adsorption process are surface chemistry and textural composition. Surface chemistry of activated carbons refers to surface charge and functional groups. Textural properties consist of pore size, surface area, pore size distribution. Pore size distribution refer to the proportion of micropores, mesopores and macropores in the activated carbon. (Hadi et al., 2015) Porosity is considered one of the most important factors to adsorption capacity, however, it does not determine the adsorption capacity. Molecular sizes of adsorbates are an important factor that affects adsorption capacity since adsorbates with molecules larger than some pores are not able to access inner

surface of adsorbent. Here comes the importance of pore sizes between micro, meso and macropores. Micropores allow only molecules with small sizes in, where meso/macropores allow larger molecules in them. Meso/macropore can also create diffusion resistances for adsorbates, which affect adsorption rate. (Moreno-Castilla, 2004) Another point of view is that pore sizes can be used to block adsorption of unwanted molecules. This is called closed porosity where certain pores holes are too small for certain molecules with larger size than the pore holes, thus these pores resist the access of the larger molecules. (Mileeva et al., 2012)

Chemical properties of activated carbon determine the surface chemistry in adsorption process. As said in the Chapter 2 the most important surface groups of activated carbons are carbon-oxygen complexes. (Yang et al., 2019) The surface groups affect the surface charge, hydrophobicity and electronic densities of activated carbon. Surface charges are created when surface groups of activated carbon dissociate in liquid solutions. Ions in liquid solutions can also create surface charges into activated carbon. Influencing factors for whether the surface charge is negative or positive are caused by surface groups of the adsorbent or pH of the liquid solution. Positive charge can be a result of various factors like basic properties of surface groups or basic behaviors of graphene layers of carbon structure. (Moreno-Castilla, 2004) The main cause for negative surface charges is dissociations of acidic carbon-oxygen surface groups like phenol and carboxyl. Figure 6 illustrates different surface groups of activated carbon and their results on acidity and surface charges. (Radovic et al., 2004)

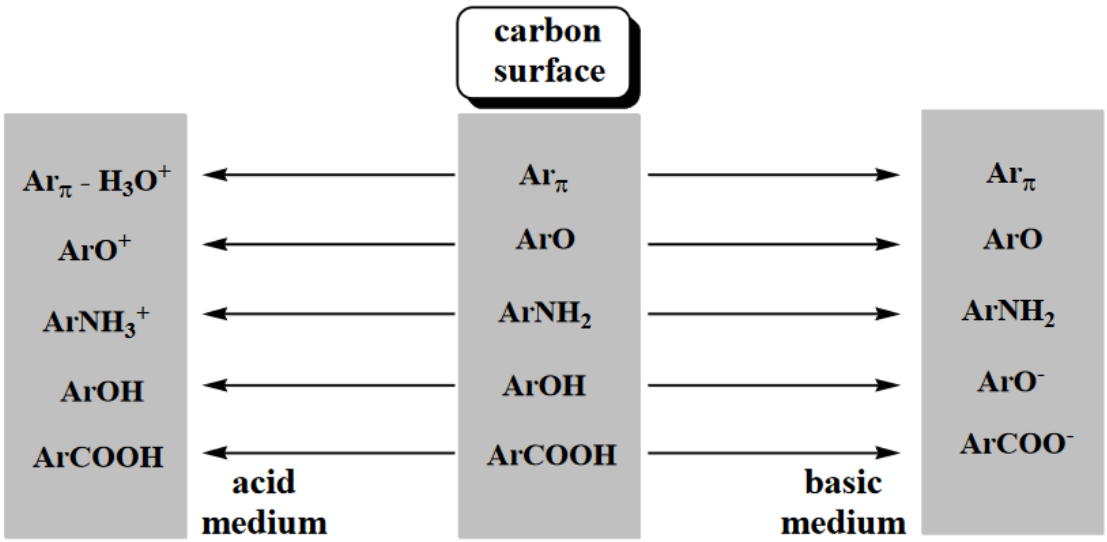

Figure 6 Illustration of surface groups effects on surface charge of activated carbon. (Kwiatkowski, 2012)

As stated before, hydrophobicity is influenced by oxygen compounds. Hydrophobicity decreases when oxygen compound quantity increases on the activated carbon surfaces. Consequently, if oxygen compound quantity decreases the hydrophobicity increases. The reason for this behavior is that oxygen groups make hydrogen binds with water molecules in liquid solutions thus blocking access for hydrophobic adsorbates into carbon pores. (Derylo-Marczewska, & Swiatkowski, 2011)

4.1.2 Effects of adsorbate properties in adsorption

Properties of adsorbate have a major role in adsorption process. They are also an important factor in characteristics selection for adsorbent material. (Radovic et al., 2004) Affecting properties in adsorbate for adsorption process are molecular size, acid dissociation constant (pK_a), solubility and aromaticity characteristics. (Derylo-Marczewska et al., 2018) The molecular size of adsorbate restricts diffusion on pores therefore it can be used as a condition for adsorbent porosity selection. The acid dissociation constant (pK_a) is a key influencing factor for solution pH due to a fact that it determines the dissociation of the adsorbate. (Moreno-Castilla, 2004) The solubility of adsorbate affects the hydrophobic forces between it and the adsorbent (Derylo-Marczewska et al., 2018). Solubility can be also expressed in

terms of molecular weight. The higher the molecular weight is the less soluble in water it is, thus molecules with higher molecular weight are easier to adsorb than molecules with lighter molecular weight. The aromaticity of adsorbate influences interactions between adsorbate and adsorbent because aromatic substituents can make hydrogen bonds and dispersion interactions with surface oxygen groups on the activated carbon surface. (Moreno-Castilla, 2004)

4.1.3 Effects of solution chemistry in adsorption

Liquid solution properties enable solution chemistry and affect the adsorption process. Solution pH, ionic strength, temperature, and adsorbate concentration affect the adsorption. (Moreno-Castilla, 2004) Solution pH affects the electrostatic interactions, surface charges of activated carbon and dissociations which have a major role in adsorption. (Hadi et al., 2015) Acidic dissociation constant of the adsorbate and the solution pH are connected to each other in case of acidic electrolytes. In the acidic electrolyte solutions adsorbates dissociate if the value of pH is larger than the value of pK_a. For example, in organic compound adsorptions, lower pH is beneficial for adsorption process and higher pH unfavorable. High pH values can be determined values over 7 and low pH values under 7. In adsorption process high pH values tend to cause negative surface charges and low pH values positive charges. Value of pH affect also adsorbent bed dimensions in adsorption columns. Acidic solutions require smaller adsorbent beds than basic solutions. (Moreno-Castilla, 2004) The ionic strength of solution also affects the attractive and repulsive electrostatic interactions and thus the adsorption efficiency. (Al-Degs et al., 2008) In the case of attractive forces between adsorbent and adsorbate, increase of ionic strength reduces adsorption efficiency. And when there are repulsive forces between adsorbent and adsorbate, increase of ionic strength will enhance the adsorption. (Moreno-Castilla, 2004)

Effect of temperature on adsorption process is a controversial subject on the basis that adsorption itself is a spontaneous phenomenon. It is an exothermic process and thus increase in temperature should weaken adsorption. (Hadi et al., 2015) It is known that increasing temperature effects the solubility of the dissolved compounds in solutions by enhancing their solubility. Increased solubility of adsorbates in aqueous solutions reduces the adsorption efficiency of activated carbons. Solubility of adsorbates is connected to the hydrophobicity

of the adsorbates. Hydrophobicity of adsorbates decreases when their solubility increases and therefore adsorption becomes more difficult. Generally increased temperatures in influent solution are considered to reduce adsorption efficiency of activated carbon adsorbents. (Marczewski et al., 2016) Effect of adsorbate concentration in solution is straightforward, increase of adsorbate concentration increases the adsorption efficiency. (Ju et al., 2008)

4.2 Activated carbon coalescing

Activated carbon is capable for performing coalescing phenomenon in addition to adsorption. (Sole, 2007) Coalescing is commonly used in separation and filtration processes where oily organic compounds are removed from water or from aqueous electrolyte solutions. (Li & Gu, 2005) Filter materials that have coalescing abilities also have hydrophobic and oleophilic properties. (Sole, 2007) Coalescing process of oily organics is enhanced by hydrophobic surfaces in filter material. Affecting properties in the coalescing phenomenon are solution's density, viscosity and interfacial tension, but also properties of filter material such as pore size, permeability and wettability. (Almeida et al., 2019)

Gathering organic compounds on the filter surface and unification of organic droplets into each other on hydrophobic filter surfaces are the basic working principles of coalescence filters. When enough droplets are joined together and formed large droplets, the large droplets can diverge from filter material and float upwards in aqueous solutions. (Almeida et al., 2019) Since activated carbons have hydrophobic surfaces, they are able to perform coalescing, however, activated carbon primary function is adsorption. Gathering of oily organic compounds onto activated carbon surface occurs by adsorption. Coalescing can occur only after activated carbon's adsorption capacity is full or when adsorbent bed is fully exhausted in fixed bed columns. (Sole, 2007) Adsorption followed by coalescence is referred as wetting adsorption coalescence in the removal of oily organics. This includes removal mechanisms such as adsorption, coalescence and floatation. (Li et al., 2008)

5 Activated carbon adsorbents

Activated carbon manufacturing is a large industry and it produces approximately 1962000 tons/year in 2018 with a market value of USD 4,72 billion (Grand View Research, 2019). There are several different kind of activated carbon adsorbents, that vary with particle sizes and structure forms. Adsorbents can be split into two major categories based on their particle sizes: granular activated carbons (GAC) and powdered activated carbons (PAC). (Mars & Reinoso, 2006) Common commercial activated carbon adsorbents are represented in Figure 7.

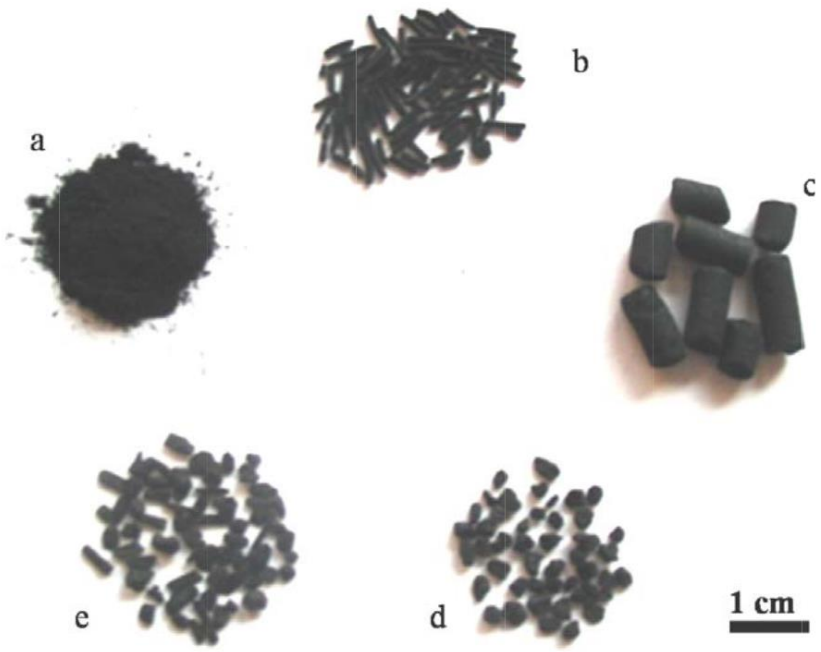

Figure 7 Common commercial activated carbon adsorbents. A) Powered activated carbon, B) and C) Pelletized and extruded carbons, D) and E) Granular activated carbons. (Kwiatkowski, 2012)

5.1 Granular activated carbon (GAC)

Granular activated carbons mean particle size is averagely 1-5mm (Inamuddin et al., 2021), whereas particle sizes range can vary between 0.2-5mm (Çeçen & Aktas, 2011). GACs can be split to two subgroups called shaped GACs and broken GACs. Shaped GACs are the most used activated carbon in industries and the typical choice for water filtration. GACs are

suitable for continuous adsorption processes with liquid or gas. (Bandosz, 2006) They have wide range of adsorption applications like solvent recovery, air filtering, purification of gas and gas separation. (Dwivedi et al., 2008) Its liquid adsorption abilities are notable, and it can be effectively applied to wastewater treatment, drinking water purification and metal extraction from liquids. (Çeçen & Aktas, 2011). Toxic metal adsorption is one the most popular water environmental purification applications of GACs. (Inamuddin et al., 2021)

The most important benefit of GACs is that they can be regenerated. GAC operability in fixed bed adsorption columns allows low pressure drops. (Inamuddin et al., 2021) GACs produced with steam activation process obtain well-developed internal porosities and have some of the highest densities and hardness's among commercial activated carbons. (Bandosz, 2006)

5.2 Powdered activated carbon (PAC)

Powdered activated carbon particle sizes are usually in a range of 15-25 um. (Inamuddin et al., 2021) PACs have large portion of total activated carbon products, but their role is weakening due to increasing popularity of GACs. PACs have weaker density, hardness and abrasion resistance than GACs, therefore they are not able to tolerate as much pressure as GACs. Main weakness of PACs is that they can't be regenerated. (Bandosz, 2006) They can't be used have in fixed beds due to their higher pressure drops. (Kwiatkowski, 2012). They are also capable to do faster adsorptions in some adsorption processes where GACs require too much time (Tancredi et al., 2004) Notable is that they are cheaper to produce than granular activated carbons (Saputra et al., 2013) PAC are used often as part of a combination with another adsorbent material. PAC applications include l wastewater treatment. purification of discharge gases, toxic metal removal. Mercury removal from gases is one of the most effective applications of PACs. (Inamuddin et al., 2021)

5.3 Other activated carbon adsorbents

Other activated carbon adsorbents include carbon fibres, pellets, and carbon nanotubes. (Kwiatkowski, 2012) Activated carbons fibres (AFC) are carbon-based fibres. They are produced with physical or chemical activation. (Lee et al., 2014) They have larger adsorption

capacity than basic GACs. This is due to the AFC structure, which has a microporous structure on the outer surfaces. This provides better access for materials to adsorb than in GACs where components adsorb into mesopores and then into micropores. AFCs have only minor proportion of mesopores in its pore size distribution and there are no macropores in the structure. AFC structure have minor diffusion resistances in comparison to GACs. AC-fibers provide straight access for adsorbates due to the micropores. A significant disadvantage of AFCs is their high cost. (Hassan et al., 2020)

Pelletized and extruded activated carbons are cylinder-shaped combinations of PACs and coal-based materials, such as anthracite. Their typical particle size is 0.8-130mm. Carbon films are carbon are membranes. They are popular in gas purification applications. (Inamuddin et al., 2021) Activated carbon nanotubes are adsorbents that have graphitic shells in their structure. Diameters of nanotubes is typically around 1nm.Their applications include sensors and detector technology and electrochemical separation processes (Kwiatkowski, 2012)

5.4 Commercial activated carbon suppliers

World’s largest granular activated carbon supplier is Calgon Carbon Corporation which has business and production in North America, Europe and Asia (Research and Markets, 2016). Chemviron is Carbon Calgon’s operational branch which is responsible of business and manufacture in Europe (Carbon Calgon, 2020). Other Major suppliers are Carbon Activated Corporation (USA), Cabot Carbon Corporation (USA), Osaka gas Chemical Corporation (JPN), Fujian Yuanli Active Carbon (CHN), Datong Coal Mining Jinding Activated Carbon (CHN) and Shanxi Xinhua Chemical (CHN). (Research and Markets, 2016)

In Finland the major activated carbon suppliers are Haarla Oy, Polynova Oy, Brenntag Nordic, Akva Filter Oy. From which Haarla represents Chemviron products, Polynova Oy Jacobi Carbons’ products, Brenntag Nordic Carbon Activated’s products and Akva filters Silcarbon’s products. In 2020 Vapo Oy launched Finland’s first activated carbon factory in Ilomantsi, making it the first activated carbon manufacture in Finland.

6 Regeneration of activated carbons

Regeneration of activated carbon refers to a desorption process where carbon's adsorption capacity is restored by removing or destroying adsorbed material from activated carbon. (Bandosz, 2006) Generally, only granular activated carbons are regenerated (Inamuddin et al., 2021). Industry usage of carbon adsorbents takes usually place in packed columns where activated carbon performs adsorption. Activated carbon's adsorption efficiency decreases over time in a continuous adsorption process due to its limited adsorption capacity; consequently, a change or reactivation of GAC material is required at regular intervals. (Kwiatkowski, 2012)

Replacement of activated carbon in adsorption columns can be done in two ways. The first method is to replace used carbon adsorbent with an entirely new set of unused activated carbon. The second method is regeneration of used activated carbon which can be done inside of column or off-site. Both methods have their own benefits and weaknesses. (Bandosz, 2006) On-site regeneration is considered to be profitable only if consumption of carbon is higher than 900 kg/day (Hendricks, 2006). Regeneration enables savings in raw material consumption and costs but has its downsides in usability. (Bandosz, 2006) Regenerated activated carbon's adsorption capacity decreases during regeneration times. There is also a limit for regeneration times in activated carbon usage. Eventually activated carbon loses its regeneration ability. (Srivastava et al., 2021) Regeneration is also important, since fully exhausted activated carbons that have adsorbed toxic adsorbates, are harmful to environment. (Bhagawan et al., 2015)

Replacement of activated carbon uses more adsorbent material the regeneration option but may offer more profitable option. This is due to high costs of typical regeneration processes that can exceed the costs of new carbon materials. Selection between these methods is case related. Some adsorption processes require more expensive adsorbents and some less expensive. (Zanella et al., 2014) Powdered activated carbons are relatively inexpensive adsorbents which are not worth of regeneration due to their poor regeneration ability (Saputra et al., 2013). Selection criterions are thereby done based on what adsorbent material is used and regeneration costs in comparison to corresponding new activated carbon. (Zanella et al., 2014)

There are various types of regeneration methods for activated carbons. The most common ones are thermal regeneration, steam regeneration, chemical regeneration. Other regeneration methods are biological, electrochemical, super critical fluid regeneration and microwave regenerations. (El Gamal et al., 2018)

6.1 Thermal regeneration

Thermal regeneration of activated carbon is the ruling method for exhausted adsorbents regeneration and solvent recovery. It heats exhausted activated carbons until adsorbates from carbon pores are desorbed or destroyed. Some adsorbates are removed by thermal decomposition if desorption is ineffective. (Salvador et al., 2015) Heating is done at generally temperatures 800-1000 $^{\circ}$C (Yuen & Hameed, 2009). Heating is performed in furnaces outside of adsorption columns or in some cases inside of columns. Used furnaces for heating include rotary kilns, multiple-heart furnaces and fluidized beds. (El Gamal et al., 2018) On-site regeneration can be done in fluidized beds or fixed beds with integrated heating systems. Thermal regeneration weaknesses are high energy consumptions, long process time and a material loss of heated material. (Zanella et al., 2014) Microwave furnaces are an alternative option for thermal furnaces (Liu & Han, 2007).

6.2 Steam regeneration

Steam regeneration is widely used on-site industrial regeneration method. Steam can be also replaced with other gases like nitrogen and air (Ramalingam et al., 2012). Steam activation is considered a low cos method (Srivastava et al., 2021). Regeneration with steam consists of three steps: desorption, drying and cooling. Desorption is performed with hot steam which flows through adsorbent bed. The drying step removes moister from adsorbent with hot inert gas and the cooling step returns adsorbent bed into operating temperature. Major benefit of steam regeneration is that steam is generally available in many industries. Steam is also relatively easy to produce with boilers. Recovery of adsorbates is possible after desorption if adsorbates are separated from steam. Desorption with steam provides an effective removal of organic hydrophobic adsorbates from activated carbon. Desorption of hydrophilic adsorbates is less profitable for steam regeneration since their removal requires more energy.

Steam regeneration generally prefers desorption of adsorbates with a low boiling point. It is performed at lower temperatures than thermal regeneration. When adsorbates have relatively high boiling points, then thermal regeneration is generally more profitable. Adsorbates that are immiscible with water and have low boiling points are generally less expensive to regenerate with steam than thermally. (Irfan et al., 2013) Used temperatures in steam regeneration vary between 100-850 °C based on adsorbate boiling point and activated carbon's heat capacity. Volatile compounds can be desorbed at temperatures as 100-260 °C, non-volatile compounds in 200-650 °C and some adsorbates with very high boiling points require steam temperature as high as 650-850 °C (Shah et al., 2013). Column operation pressures can reach as low values as 0.7 bar in superheated steam method (Tggelbeck & Goyak, 1991). Figure 8 shows illustration of on-site steam regeneration in wastewater treatment. (Mishra et al., 2021)

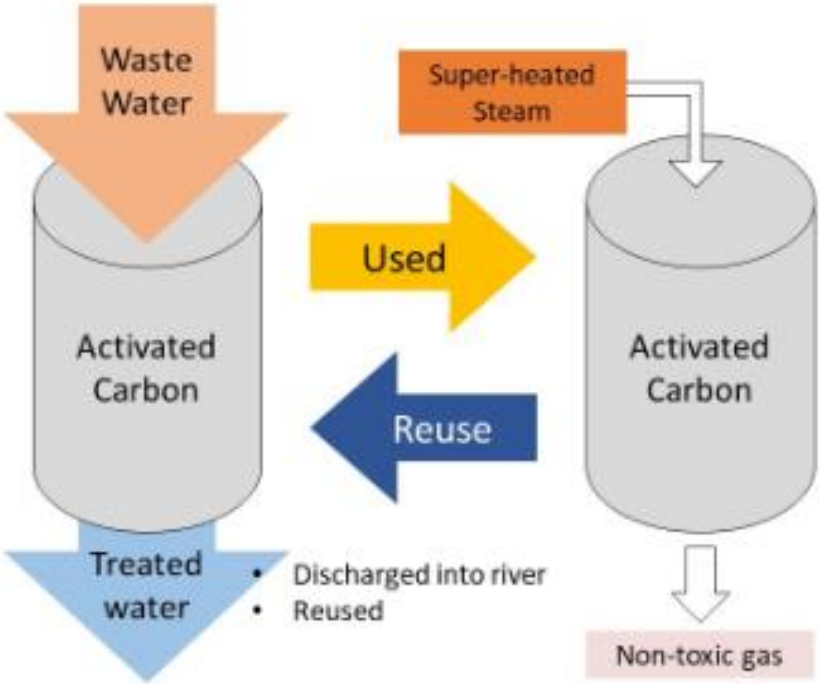

Figure 8 Illustration of on-site steam regeneration process. (Mishra et al., 2021)

6.3 Chemical regeneration

Chemical regeneration can be performed inside adsorption columns where chemicals react with adsorbent and adsorbates. Chemical reactions either desorbs adsorbates or destroy them. (El Gamal et al., 2018) Used chemicals in this method include acids, sodium hydroxide and sodium bicarbonates (Lu et al., 2011). Benefits for chemical regeneration are minimum attrition for activated carbon and therefore almost no mass loss during regeneration. Affecting factors for chemical regeneration are solubility and reactivity of activated carbon and properties of adsorbate. (El Gamal et al., 2018) Weaknesses of this method is that some chemical can forge carbon structures. (Lu et al., 2011)

6.4 Other regeneration methods

Biological regeneration is done with microbial colonies. It is suitable in situations where adsorbates are easy desorb from adsorbent. Regeneration with microbial colonies has two phases: desorption and biological removal. Affecting factors for biological regeneration are adsorbate biodegradability, interactions between adsorbent and adsorbate and activated carbon properties. This method is not widely used in industries. (El Gamal et al., 2018)

Super critical regeneration is based on fluids in critical conditions. This method generally has lower energy consumption and adsorbent material loss than thermal regeneration. (Madras et al., 1993) The most used supercritical fluids are carbon dioxide and water. (Bandosz, 2006) SFC is effective in hydrometallurgy applications where metals are removed and recovered from activated carbon adsorbents. (Sunarso & Ismadji, 2009) Typical pressure and temperature for carbon dioxide fluid in processes are 7.28 MPa and 31 $^{\circ}$C (Díaz-Reinoso et al., 2006).

7 Activated carbon applications

Activated carbon is used in a broad scale of applications. The main application fields include environmental treatment, wastewater treatment, healthcare sector, gas purification, food industry and hydrometallurgy. (Kwiatkowski, 2012) Applications include both liquid and

gas phase where liquid phase covers approximately 80% of total applications. Activated carbon adsorbents are also used in many other industrial filtrations process. It is estimated that activated carbon has over one thousand different applications. (Dias et al., 2007)

7.1 Water treatment

The main water treatment applications for activated carbon are wastewater, drinking water and industrial process waters. In drinking water treatment activated carbon filtration is used mainly for purification of surface and ground waters of organic compounds and toxic metals. Toxic heavy metal that can be removed with activated carbon include lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr) and arsenic (As) (González-García, 2018). Wastewaters from industries that end up in surface and ground waters contaminate the waters; therefore, there is general demand for activated carbon in wastewater and drinking water filtration. (Çeçen & Aktas, 2011)

Activated carbon is used for removal of organic compounds, odours, pharmaceutical residue, chlorides, dyes, toxic metals and other harmful compounds from wastewaters (González-García, 2018). Organic compounds such as aromatic compounds, phenols, aliphatic acids, esters, amines and alcohols can be removed in activated carbon wastewater filtration. Wastewater treatment can be divided into industrial and municipal. In municipal treatment activated carbon is used generally as a tertiary filtration unit for removal of organic compounds and dissolved material. (Çeçen & Aktas, 2011)

In industrial wastewater treatment activated carbon is used for purification of waters that are released into nature but also for purification of receiving waters. The goal of filtration is to reach necessary environmental restrictions for pollutant content in the wastewaters or to achieve specific degree of purity for receiving waters. (Çeçen & Aktas, 2011) Common industries for activated carbon wastewater filtrations include textile, food, pharmaceutical, chemical, petroleum refineries, mining and mineral processing where wasters are discharged. Other major fields are pesticide, ammunition, explosive, dye and detergent manufacture. (Kwiatkowski, 2012)

Activated carbon industrial wastewater filtration is generally set as a final purification step to clean wastewaters from remaining pollutants. It is also used as a primary filtration unit in

cases where pollutant contents are relatively low. The most common application is a tertiary filtration column in the wastewater treatment set-up where activated carbon is used remove remaining organic and inorganic compounds. Preceding treatment units before carbon filtration include coagulation, flotation and a primary filtration unit. (Çeçen & Aktas, 2011)

A major application for activated carbon filtration is industrial process waters that are used in boilers, heat exchangers and cooling towers. (Çeçen & Aktas, 2011) Activated carbon is currently used widely in boiler water feed filtration where petroleum refinery industry is the most common. Condensate waters used in boilers to produce steam may contain hydrocarbons derived from other instruments that can cause coking in the boilers which is harmful for boiler efficiency. Jacobi carbon has even developed a specific GAC product for boiler feed water filtration called PetroSorb HS-D. (Jacobi Group, 2020)

7.2 Applications in hydrometallurgy

Activated carbon is known to be effective adsorbents in industrial hydrometallurgy processes as filtration media for purification and metal recovery. Important metal recovery applications are gold and silver recovery from cyanide solutions. (Yalcin & Arol, 2002) It is also used recovery of uranium, copper, nickel and zinc (Carbon Calgon, 2020).

7.2.1 Gold recovery

Activated carbon is widely/globally used in industrial gold extraction from cyanide leaching. Gold recovery is effective since activated carbon has a strong adsorption efficiency for gold. The most popular gold recovery processes are Carbon-in-Pulp (CIP), Carbon-in-Leach (CIL), and Carbon-in-Column (CIC). The CIP process focus on adsorption of gold from aurocyanide solutions. (Soleimani & Kaghazchi, 2008.) The first industrial carbon-in-pulp plants is recorded from 1949 and 1951 (Marsden & House, 2006). Gold is removed from activated carbon by either elution or stripping process. Recovery of cold after elution is commonly performed with electrowinning. There are two prime industrial elution methods using activated carbon for gold extraction: the Anglo-American Research Laboratory (AARL) process the Zadra process. (Oladele et al., 2015) Both processes methods use chemical regeneration with sodium cyanide solution in the elution of gold from activated

carbon adsorbent. Gold is desorbed from adsorbent in the form of aurocyanide ion $[Au(CN)_2]^-$. The Zandra process is a older method and it requires more time than AARL. The AARL is more used elution method due to its shorter process time and preferable gold recovery ability. Difference between these two elution methods is that the ARRL uses also hot water flow to in desorption. (Soleimani & Kaghazchi, 2008.)

7.2.2 Purification of metal electrolyte solutions

Activated carbon filtration is used widely on metal-finishing applications where electroplating is used to make solid metals from metal electrolyte solutions (Sole et., 2007) (Sole et al., 2005), (Bello et al.,2019), (Neira et al., 1992), (Raghavan et al., 1999), (Feather et al., 1999), (Jansen, 2012).The most common electroplating processes, where activated carbon is used for purification of organic impurities from metal electrolyte solutions, are nickel, zinc, copper and cobalt electroplates. In nickel-electrolyte solution purification activated carbon filtration is stated to be the most used technique (Jansen, 2012). The reason for using activated carbon is that organic compounds can harm electrolysis and precipitation of metal ions in electrolytic cells. Demands for purification efficiency can be as high as 2 ppm limit of organic impurities in electrolyte solution. (Sole et., 2007)

7.3 Other applications

In healthcare and pharmaceutics activated carbon applications include poison treatment, anti-flatulents, cholestasis, wound care, haemodialysis and catalysts for pharmaceutical products. (Jansen, 2012) Protective filtration for human health is one of activated carbon application which includes protective cloths, respirators and decontamination wipes. These application use activated carbon fibres as filter medias. (Hassan et al., 2020) In food industry activated carbon is used in forms of filtration membranes. Filtration targets comprise of removal of acids, steroids, oils sugars, vitamins and caffeine. Colour and odour removal from wines, juices and beer is also one of the important food industry usages. (Jansen, 2012) Caffeine removal from coffee (Castillo et al., 2020) and tea (Vuong & Roach, 2014) is occasionally executed with activated carbons.

In gas phase separation applications activated carbon is used in air purification, carbon dioxide separation from flue gases, solvent recovery, sulphur removal from exhaust gases gas storages and methane-carbon dioxide separation from biogases and landfills (Sircar et al., 1996), (Sun et al., 2011). Activated carbon fibres are usen successfully in gas storage applications (Hassan et al., 2020). The most major gas phase application is adsorption of volatile organic compounds from industrial emissions (Jansen, 2012). A notable application for gas filtration is also mercury adsorption from gases, especially from coal-fired plants where activated carbon filtration is used to restrain mercury emissions. (Sjostrom et al., 2010)

8 Biochar

Biochar is carbonized material which derived from carbon-based biomass. (Mohan et al., 2014) Materials obtained from living matter are referred to as biomass. Biochar consists mainly of carbon (C) but also hydrogen (H) and oxygen(O). Typical biochar raw materials derived from biomass are lignocellulosic matters like wood, bagasse and corn straw. In Finland the most used raw materials for biochars are birch and spruce (Siipola et al., 2018). They are considered as low-prized materials with an environmentally friendly reputation. Biochar is used commonly as adsorbents, fuel and in soil remediation. Typical biochar products are shown in Figure 9. (Cha et al., 2016) Biochar has many structural similarities in comparison to activated carbon. They have porous structures with high surface areas, aromatic features and rich mineral contents. They have surface groups with functional features which are important factors of biochar adsorption mechanism. Biochar is considered a strong adsorbent and is expected to be used in various adsorption applications in the future. (Mohan et al., 2014) Illustrations of biochar surfaces are shown in Figure 10.

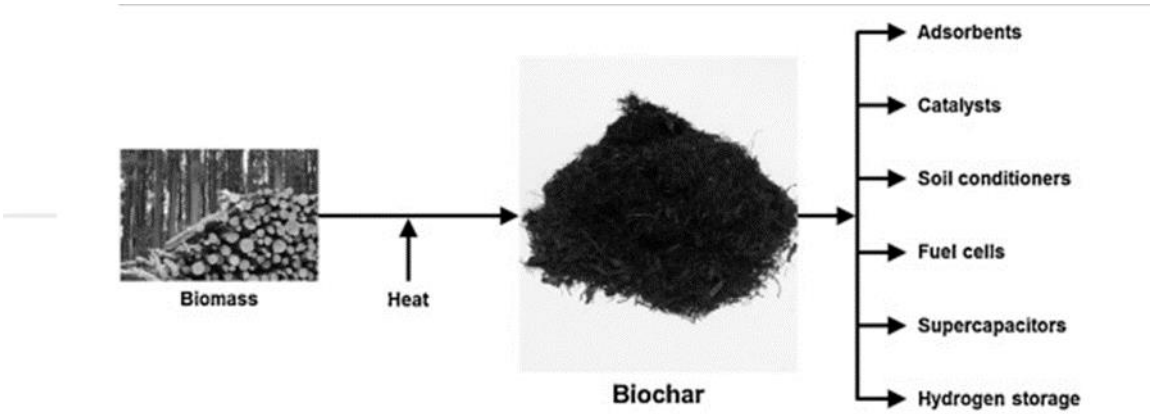

Figure 9 Biochar products. (Cha et al., 2016)

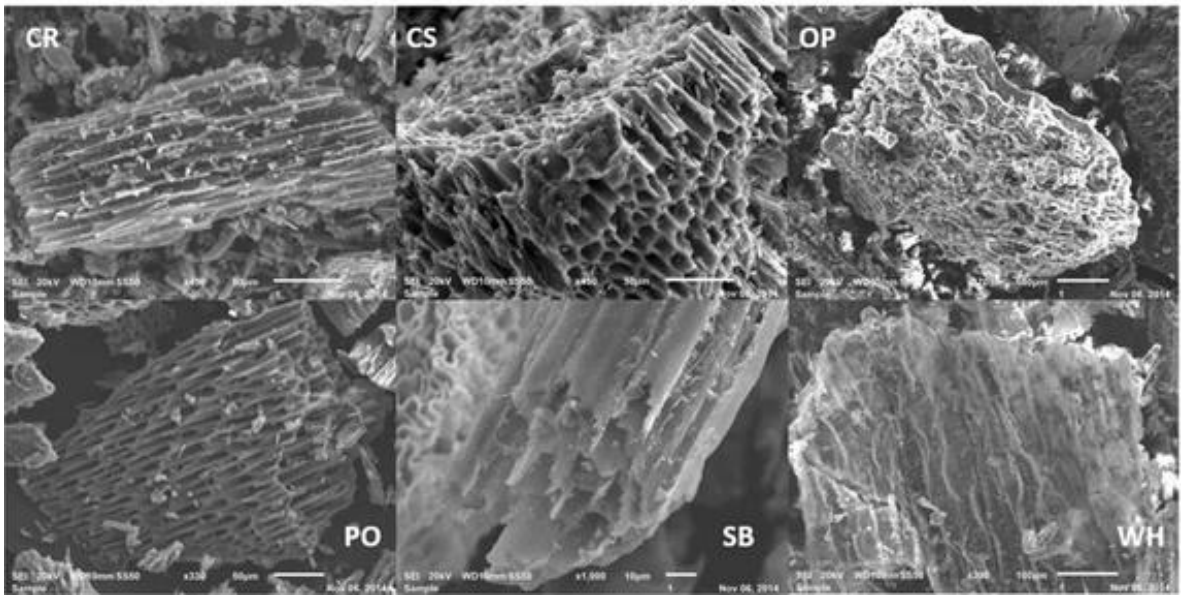

Figure 10 Surface structure of biochar. (Batista et al., 2018)

8.1 Biochar production and activation

Production of biochar is a well-known procedure, and its benefits are simplicity and operability. Global production of biochar is a growing industry with a production quantity of 85,000 tonnes in 2015. (IrBEA, 2018) Like in activated carbon production, carbonization is performed to biochar raw materials. Carbonization of biomass into biochar is performed with thermal degradation including pyrolysis and gasification. Gasification is partial

combustion method which is aiming in making gaseous fuel products. (Mohan et al., 2014) Biochar regeneration follows same theory as regeneration of activated carbon, where biochar is regenerated either by desorption of adsorbate or by destroying the adsorbate. Biochar regeneration is not yet a common procedure in industrial usage. (Dai et al., 2018)

Pyrolysis is the most used biochar production method. It is performed at temperatures 300-900 ℃ depending on what pyrolysis technique is used. Basic principle is the same as in activated carbon carbonization phase, it removes hydrocarbons from the structure to transform raw material into a porous form. There are two kind of pyrolysis methods: fast and slow. Slow pyrolysis is the original method, and it is used to produce mostly biochar in the form of a solid material. (Wang et al., 2020) Its product yield is generally 35% solid biochar and 30% bio-oil. It produces more aromatic properties into biochar products in comparison gasification or fast pyrolysis. (Mohan et al., 2014) Heating rates are slow in slow pyrolysis and top temperatures are around 400-500 ℃ and heating residence time is between 5 and 60min (Sekar et al., 2021). Fast pyrolysis operates with fast heating rates at temperatures 400-500 ℃ and has a residence time of 1-5s (Lima et al., 2020). Product of fast pyrolysis is mostly in a fluid form. Its production ratio is generally 75% bio-oil and only 12% biochar. (Mohan et al., 2014)

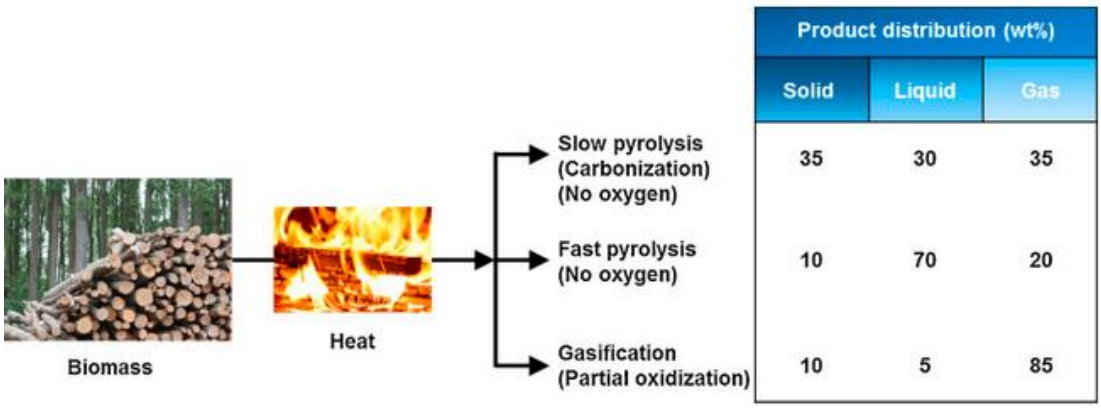

Figure 11 Typical production methods of biochar. (Mohan et al., 2014)

Reaction temperature, heating rate and residence time affect the biochar structure results during the pyrolysis, but the initial raw biomass properties also affect the outcome (Zhao et al., 2018). Especially mineral content of biomass will affect biochar characteristics. Biochar

products favour slow heating rates with long residence times. Higher pyrolysis temperatures are found to produce more rich carbon contents, larger surface areas and more porous structures than lower temperatures, while lower pyrolysis temperatures tend to produce more oxygen surface groups. (Cha et al., 2016)

Biochar properties such as porosity, specific surface area and functional group content can be enhanced with an activation process after pyrolysis. Typical specific surface area values for biochars made by pyrolysis are 10-100 m^2/g whereas biochars modified with activation have areas around 400-500 m^2/g (Siipola et al., 2018). There are two main activation methods for biochar: physical and chemical activation (Cha et al., 2016). In physical activation biochar is typically treated with carbon dioxide or steam in temperatures over 700 C. Physical activation can be executed during pyrolysis or after pyrolysis. (Siipola et al., 2018) Chemical activation of biochar is similar to chemical activation of activated carbon. It uses basic and acid chemicals like kalium hydroxide (KOH), sodium hydroxide (NaOH), phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) to enhance porosity. Chemical activation is more expensive than physical and therefore it is used more rarely. (Cha et al., 2016) The difference between activated carbon and activated biochar are minor but generally activation of biochar is less expensive than activation of activated carbon. (Wang et al., 2020)

8.2 Biochar adsorption and potential applications

Biochar is relatively close to activated carbon with their adsorbent properties. Oxygen surface groups, aromaticity, porosity, carbon content and surface area play an important role in biochar adsorption. (Zhang et al., 2019) There is not granular biochars developed into industrial applications. Biochar adsorbents with rich oxygen surface group content are found be effective in adsorption of polar compounds because oxygen surface groups can make hydrogen bonds with polar compounds. Non-polar compounds adsorb more effectively into biochar adsorbents with rich carbon content because of hydrophobic attraction forces between biochar and the non-polar compounds. (Cha et al., 2016)

Current commercial biochar filtration systems focus on stormwater treatment, where underground container filters are used to treat the stormwaters. Stormwaters include rain and meltwaters that are accrued on buildings and residential areas. (Siipola et al., 2018) Underground biochar filtration prevents stormwater pollutants from ending up in lakes and

rivers. In agriculture and garden care biochar is used in soil improvement where biochar prevents flushing of nutrients from soil by adsorbing the nutrients. (Cha et al., 2016)

Biochar potential adsorption applications can be divided into organic compounds removal from water, toxic metal removal from water, inorganic anion removal from water and air purification. (Mohan et al., 2014) Biochar industrial applications are in few. Industrial wastewater application for biochar do not yet exist, however, there is several studies done on the subject. During recent years there have been a strong desire to develop biochars to filter media for wastewater filtration. Biochar adsorbents are planned to be replacement products for activated carbon in wastewater filtration (Wang et al., 2020), (Siipola et al., 2018). One of important potential environmental application of biochar is reducing GHG emissions, where its mission is to be gas storage for gases such as CO_2, CH_4 and N_2O (Paustian et al., 2016), (Zhang et al., 2019), (Dong et al., 2013).

8.2.1 Organic compound adsorption with biochar

Organic compound adsorption possibilities include removal of dyes, phenols, herbicides, pesticides solvents, antibiotics (Zhang et al., 2019). Affecting properties for adsorption of organics are surface area, porosity, aromaticity and oxygen-surface group content of biochar. Larger surface areas are observed to adsorb more organic than biochar with smaller surface areas. (Cha et al., 2016) Polar surfaces in terms of oxygen-groups have also a major role since they enable formation of hydrogen bonds and other electrostatic interactions between char and organic compounds (Zhang et al., 2019). Higher pyrolysis temperatures tend to produce biochar adsorbents more suitable for organic compound adsorption. (Mohan et al., 2014)

Dyes in wastewaters are from textile industry and they consist of toxic compounds, acids, and basses (Dai et al., 2018). Biochar adsorbents produced with slow pyrolysis are able to adsorb these compounds from wastewater. Phenolic compounds are also one biochar's possible applications. Phenols are usually leaked from plastics and drugs. Pesticides and polyaromatic hydrocarbons (PAHs) from agriculture waste can also be removed from wastewaters with biochar. (Mohan et al., 2014) Biochars made from almond shell in slow pyrolysis have been observed to achieve 100% efficiency in removal of soil fumigants such as dibromochloropropane (DBCP). Activated carbon is the current industrial application in

DBCP removal, but biochar offers a cheaper option in adsorbent material selection. (Klasson et al., 2013)

8.2.2 Toxic metal adsorption with biochar

Biochar adsorbents provide a rival to activated carbon in toxic metal removal from wastewaters and other solutions. Heavy metals such as Fe, Hg, Cr, Cu, Cd, As, Pb, Cd and Zn ions are possible adsorb with biochar. (Mohan et al., 2014) Based on former studies its adsorption efficiency can equal or even surpass activated carbon's adsorption efficiency in metal adsorption (Zhang et al., 2019), (Inyang et al., 2016), (Komkiene & Baltrenaite, 2016) (Tan, 2016), (Xu et al., 2016), (Tong et al., 2011).

Biochar has set of functional surface groups, such as aliphatic, that commercial activated carbon lacks in. These functional groups enable more ion exchange capacity for biochar which enhances cation adsorption. (Gray et al., 2014). Activated carbons can have some aliphatic groups on its surface but their quantity is decreased in the activation step. Certain highly processed activated carbons can have rich aliphatic group content, but these kinds of activated carbons are expensive to produce. (Mohan et al, 2014)

Biochar adsorbents generally have less surface area than commercial activated carbons but some them have more oxygen-surface groups that attract metal cations. Biochar adsorbents with richer oxygen-surface group content are found to be more effective in metal adsorption than those with low oxygen-surface group content. (Mohan et al., 2014) Based on former studies (Kim et al., 2016) and (Samsuri et al., 2014) oxygen-surface group content is more important than biochar surface areas in the metal ion adsorption. Also increased carbon/oxygen ratio (O/C) and polarity index [(O + N)/C] are observed to enhance metal adsorption.

Certain biochars have also functional groups like carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) which enable precipitation of metals on the biochar surface. In copper remediation ion-exchange biochar surface and metal cations is more effective metal collector than the adsorption process in biochar pores (Cho et al., 2013). Biochar's chemical characteristics can be stated have more major role in metal adsorption than its surface area and porosity. Producing high porosity adsorbents with very high surface areas such as activated carbon is

much more expensive than production of biochar. This makes biochar an excellent alternative to activated carbon. (Cha et al., 2016)

8.3 Biochar versus Activated carbon

Activated carbon and biochar have several similarities in their structure and adsorption abilities. Both adsorbents have carbonized structure, high porosity, functional surface groups and high surface area. While activated carbon surpasses biochar in micro porosity and surface area, biochar has other effective adsorption properties. Adsorption efficiency of biochar is based on its surface groups. (Mohan et al, 2014)

In terms of packed column adsorbent operability, biochar loses to activated carbon. Biochar adsorption requires more time than activated carbons, thus filtrations with biochar requires slower linear flowrate or larger adsorbent dosage. (Alhashimi & Aktas, 2017) Biochar structures have weaker bulk densities and mechanical hardness than activated carbon, thus making it adsorption capacity weaker in columns. Biochar material can also break in columns due to their low hardness and density. Adsorption applications where packed columns are not required its low density can provide benefits to adsorption. (IrBEA, 2018) A comparison of biochar and typical GACs is represented in the Table I.

Table I Typical physical properties for biochar and granular activated carbon.

Property	GAC	Source	Biochar	Source
Surface area, [m^2/g]	800-1500	(Bansal & Goyal, 2005)	10-500	(Siipola et al., 2018)
Bulk Density, [kg/m^3]	440-520	(Moosa et al., 2016)	90-500	(Lehmann & Joseph, 2015)
Particle density, [g/cm^3]	0.92-15	(Çeçen & Aktas, 2011)	1.0-1.5	(Lehmann & Joseph, 2015)
Pore volume, [cm^3/g]	0.2-0.6	(Bansal & Goyal, 2005)	0.05-0.21	(Chatterjee et al., 2020)
Mean particle size, [mm]	1-5	(Bansal & Goyal, 2005)	5-50	(Tisserant & Cherubini, 2019)

Biochar's major benefit is its low material cost in comparison to activated carbon. Biochar production usually occurs at smaller temperatures than production of activated carbons, and biochar production lacks the activation step. Production of biochar is significantly less energy consuming than activated carbon production. (Mohan et al., 2014) Energy consumption biochar production is estimated to be averagely 6,1 MJ/kg, while activated carbon production is averagely 97 MJ/kg (Alhashimi & Aktas, 2017). Raw material sources are wilder for activated carbon since biochar is produced from biomass while activated carbon is produced from organic and non-organic raw materials. The global cost for biochar is 1,750 € /tonne while it is 2,000-2,500 € /tonne for granular activated carbon and 2,500-3,500 € /tonne for powdered activated carbon. Some highly processed and modified activated carbons can cost up to 25 000 € /tonne. (IrBEA, 2018) In addition to energy consumption, biochar production is considered to have less GHG emissions than production of activated carbon. Biochar production can reach zero emissions, while activated carbon production is estimated to averagely emit 6,6 kg CO_2/kg. (Alhashimi & Aktas, 2017)

9 Activated carbon filtration

Activated carbon filtration is one of the most common applications of activated carbon. Commercial carbon filtration reactors generally use granular activated carbon. (Kwiatkowski, 2012) Filtration is generally performed in adsorption column reactors. Used columns include fixed beds, fluidized beds and expanded beds, from which fixed beds are the most used option. Fixed bed adsorber is the most used option in process wastewater treatment. There are also filtration systems for short time use such as carbon canister which can be rechargeable or disposable. (Çeçen & Aktas, 2011)

9.1 Fixed bed filters

Fixed bed filter columns are the most common adsorption vessels for both liquid phase and gas phase applications. Working principle of fixed beds is a simple filtration process where influent flow is fed through a packed bed inside of the column. The feed of the filter column can either be downflow or counter-flow where downflow is more common. Mass-transfer

between adsorbent media and the flow occurs when feed passes through the column. Adsorbent media beds must be exchanged at regular intervals into new ones since activated carbon adsorbents have a limited adsorption capacity. The exchange of adsorbent material is done when adsorbent is fully saturated or when target values of treated effluent are surpassed. The new set of adsorbent media can be derived either by regenerating used adsorbent or by acquiring a new unused adsorbent. The regeneration can be done by both onsite and offsite, however, offsite regeneration with thermal regeneration is the most used method. (Çeçen & Aktas, 2011)

Fixed bed filtration systems often include a parallel process set-up where two or more filtration columns are placed in parallel. This enables a continuous filtration process while the regeneration or the exchange of filter media can be executed in one column. In this situation column set up is design to handle operation flow rates while one column is not in commission. Filtration columns can be also set in series. (Hendricks, 2006)

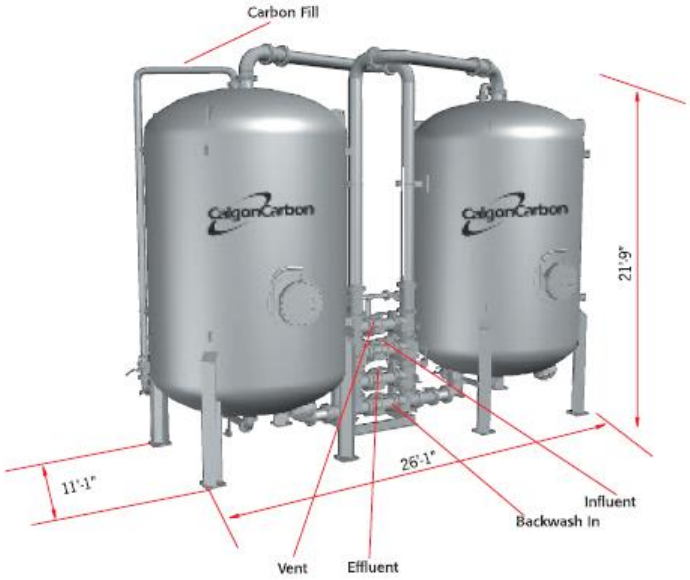

Figure 12 Illustration of fixed-bed GAC filters in series (Calgon Carbon, 2020)

9.1.1 GAC filter column dimensions and operational factors

Filter column sizes and operational parameters vary widely between activated carbon fixed bed filters depending on the application and the scale of treated process stream. There is no specific dimensions or operational guidelines for industrial wastewater or municipal GAC filters, however, there are some similarities. The operational parameters include empty bed contact time (*EBCT*), linear flow rate, packed bed depth (L_b) / bed volume (V_B). The most important parameters for column sizing are bed depth (L_b) of the adsorbent in the column and linear flow rate (v_L). (Hendricks, 2006) An illustration of fixed-bed filter for granular activated carbon is represented in Figure 13.

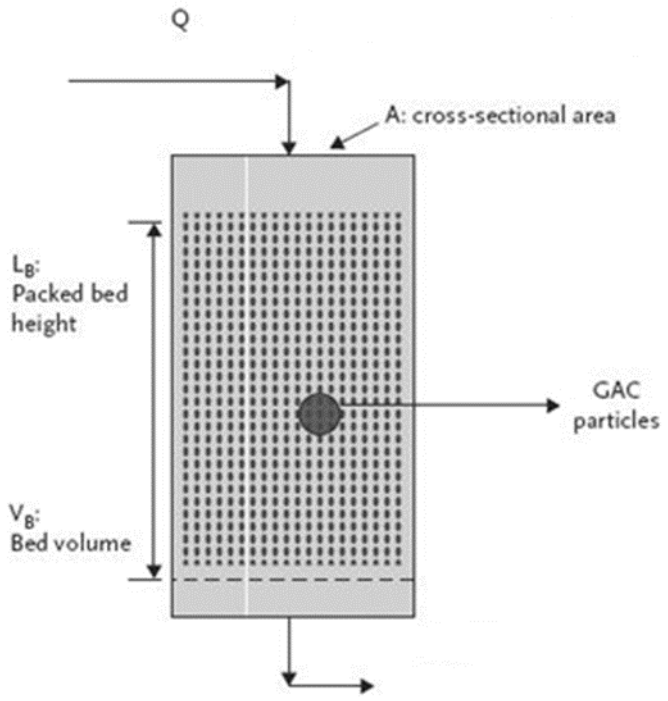

Figure 13 Illustration on a typical fixed-bed filtration column for activated carbon where L_B is bed height, V_B is bed volume, A is cross-sectional surface area and Q is total flow rate. (Çeçen & Aktas, 2011)

The depth of packed carbon bed in filter columns is a key parameter. In addition to column size designing, it can be used in estimating filter efficiency. Volume of the packed bed is dependent on column diameter from which cross-sectional area is derived. Linear flow rate represents the flow velocity inside of filter columns with a specific cross-sectional area. It can be calculated by dividing total volume flow with cross-sectional area shown in Equation (7). (Hendricks, 2006)

$$V_f = \frac{Q}{A} \qquad (7)$$

where

Q total volume flow rate, [m^3/h]

A cross sectional area of packed bed, [m^2]

v_f linear flow rate, [m^3/h/m^2] [m/h]

Residence time of the fixed bed columns is illustrated with the term EBCT, in other words, it represents the time for flow to go through packed bed in the filter column. The EBCT is a useful parameter in comparison of filter column performances. It can be evaluated from bed depth and linear flow rate in Equation (8) or by dividing bed volume with total volume flow rate in Equation (9). (Hendricks, 2006)

$$EBCT = \frac{L_B}{Q/A} \qquad (8)$$

$$EBCT = \frac{V_B}{Q} \qquad (9)$$

where

EBCT Empty bed contact time, [min]

L_b packed bed depth, [m]

A cross sectional area of packed bed, [m^2]

Q/A linear flow rate, [$m^3/h/m^2$]

V_B packed bed volume, [m^3]

Consumption of activated carbon in the fixed bed filters is generally represented with the term carbon usage rate (CUR). It tells how much activated carbon mass per treated volume of water flow is needed until carbon bed is fully exhausted. It can be calculated from Equation (10). (Hendricks, 2006)

$$CUR = \frac{M_c}{V_t} \qquad (10)$$

Where

CUR carbon usage rate, [kg/m^3]

M_c activated carbon mass, [kg]

V_t treated volume of water flow, [m^3]

9.1.2 Backwash in GAC filters

Backwash is a counterflow washing procedure for filter columns. The general purpose of backwash in GAC filters is to prevent stratification of solid particles in the GAC bed and to maintain a stable filtration efficiency. (Çeçen & Aktas, 2011) In biological GAC filtration backwash is used to prevent growth of unwanted micro-organisms on to GAC surfaces (Kim et al., 2014). Accumulation of particles in GAC bed leads stratification, head loss and clogging in the filters, which are disadvantageous for filtration efficiency. These phenomena can be avoided by backwashing the GAC beds at regular intervals. Intervals of backwashing depends on the filtration application. In general, applications with more solid particles in water are more prone to clogging than application with less solid particles in the water and therefore require more frequent backwash. (Çeçen & Aktas, 2011) In electrolyte filtration applications GAC filters are also backwashed (Sole, 2007).

9.1.3 Typical operational parameters for GAC wastewater filters

Fixed-bed columns are stated to be the most used filters for granular activated carbon in water and wastewater treatment. Wastewater treatment can be divided into municipal and industrial applications. Operational parameters and column dimensions differ between these industrial and municipal. In municipal wastewater treatment treated volume flows and filter column dimensions are generally larger than in industrial applications. The wastewater GAC filters in industrial applications have also a wide variance in column dimensions and operation parameters. Used particle sizes for GACs are between mesh 12/40 (1.7-0.425) and mesh 6/12 (3.35-1.7mm). In table II there is represented typical and general values for GAC filters in wastewater treatment, which includes industrial, municipal and overall values for wastewater filters. (Çeçen & Aktas, 2011).

Table II Typical and general operation and design parameters for water and industrial wastewater activated carbon filter columns. (Çeçen & Aktas, 2011)

Operation parameter	Range
Flow rate (Q), [m^3/h]	
Water treatment	50-400
Industrial wastewater treatment	0.8-670
Municipal wastewater treatment	90-1600
Embty-Bed Contact Time (EBCT), [min]	
General	10-50
Typical	30
Water treatment	5-30
Industrial wastewater treatment	30-540
Municipal wastewater treatment	17-66
Linear Flow, [m/h]	
General	5-25
Typical	12
Water treatment	5-15
Industrial wastewater treatment	7-16
Municipal wastewater treatment	6-15
Bed volume (V_b), [m^3]	
Typical	10-50
Bed height, [m]	
Typical	1.8-9
Bulk filter density, [kg solid /m^3 bed]	
Typical	430-480
GAC particle density, [g/cm^3]	
Typical	0.92-15

9.1.4 Commercial wastewater fixed bed filters

Commercial fixed-bed GAC filters have similarities between them. In table III there are gathered operational parameters and column dimensions of commercial GAC filters from different manufacturers. Filter diameters, maximum volume flows and carbon media mass capacities are given by manufactures in their product datasheets. Packed bed volumes and carbon bed heights are estimated based on apparent densities and weights of used GACs inside the columns, as given by the manufacturers. Linear flow rates were calculated with equation (7). As an exception, General Carbon corp. informs typical operational linear flow rates of its columns. EBCT values are calculated with equation (8) using estimated bed volumes and maximum volume flows. The GAC filter manufacturers only inform the maximum volume flows that their filters can perform, therefore the EBCT values may be shorter than real operational values and linear flow rate values larger. Backwash flowrates are on only given by Calgon Carbon and Jacobi Services, where the backwash values are approximately 1.4-2.4 times larger than given maximum volume flows.

Announced applications for Table III filters include industrial wastewaters, receiving process water streams, chemical spill purifications. General removal targets are organic compounds. Filters are informed to able used in parallel or series, however Dual Module and Model 6-14 from Carbon Calgon are 2 columns systems with are operated in series. Regeneration of GAC beds in these commercial filters is stated to be performed outside of filter columns. Most of the manufacturers inform that customers can send used activated carbon back for regeneration.

Table III Operational parameters for commercial wastewater GAC filters.

Manufacturer, model	Diameter [mm]	Flow max [m³/h]	Bed volume [m³]	Bed height [mm]	Linear flow [m/h]	EBCT [min]	Resource
Galgon Carbon							
CYCLESORB-HP	1524	14	1,7	922	7	7,4	(Galgon Carbon, 2020)
Dual Module	3050	68	16,8	2301	9	14,8	(Galgon Carbon, 2020)
Model 6	1830	45	5,0	1901	17	6,6	(Galgon Carbon, 2020)
Model 8	2440	80	8,4	1796	17	6,3	(Galgon Carbon, 2020)
Model 10	3050	159	16,8	2301	22	6,3	(Galgon Carbon, 2020)
Model 12	3660	159	16,8	1598	15	6,3	(Galgon Carbon, 2020)
Model 14	4267	234	50,4	3528	16	12,9	(Galgon Carbon, 2020)
Chemiviron							
CYCLESORB HP2	1500	14	2,0	1132	8	8,6	(Chemiviron, 2020)
General Carbon corp.							
HP-48	1220	14	1,8	1728	12	8,5	(General Carbon corp, 2020)
HP-72	1830	32	4,5	1911	12	9,4	(General Carbon corp, 2020)
HP-96	2440	57	9,1	2176	12	10,7	(General Carbon corp, 2020)
HP-120	3050	91	18,1	2530	12	13,4	(General Carbon corp, 2020)
TL-MP	1220	14	0,9	864	12	3,8	(General Carbon corp, 2020)
J-24	610	3	0,4	1239	12	6,6	(General Carbon corp, 2020)
J-30	762	5	0,6	1311	12	6,8	(General Carbon corp, 2020)
EVOQUA							
HP2000SS	1370	23	1,9	1301	15	5,1	(Evoqua, 2020)
AQUA-SCRUB	559	2	0,2	827	9	5,4	(Evoqua, 2020)
AQUA-SCRUB	1220	11	1,0	821	10	5,1	(Evoqua, 2020)
AQUA-SCRUB	1220	23	1,9	1640	19	5,1	(Evoqua, 2020)
Carptrol corp							
L-4	1220	11	0,9	777	10	4,8	(Carbtrol corp., 2020)
L-5	1520	11	1,6	899	6	8,6	(Carbtrol corp., 2020)
HP-600	762	8	0,5	1193	18	4,1	(Carbtrol corp., 2020)
HP-1100	1070	17	1	1112	19	3,5	(Carbtrol corp., 2020)
HP-1900	1397	28	1,7	1125	18	3,7	(Carbtrol corp., 2020)
HP-9300	3000	136	18,6	2631	19	8,2	(Carbtrol corp., 2020)
Jacobi Services							
Aquaflow P250	700	3	0,4	859	6	8,0	(Jacobi Services, 2020)
Aquaflow 2000	1550	20	2,0	1060	11	6,0	(Jacobi Services, 2020)
Aquaflow V2	1400	20	2,0	1299	13	6,0	(Jacobi Services, 2020)
Aquaflow V20 H	2550	80	24	4699	16	18,0	(Jacobi Services, 2020)

9.2 Fluidized bed filtration reactors

Fluidized-bed adsorption columns are commonly for large scale treatment processes where large amounts of wastewaters or emission gases are treated continuously. A typical fluidized bed system is represented in Figure 14. Working principle of fluidized beds is based on a counter-flow system instead of a downflow. Influent comes into bottom of the column and effluent comes out from the top of the column. (Johnson & Massey, 1979) The main

difference in comparison to fixed bed columns is that fluidized beds have an adsorbent mass recycle system which enables a continues fresh activated carbon adsorbent inflow into the

column and simultaneous outflow of saturated adsorbent (Hendricks, 2006). Adsorbent recycle flow can be a counter-flow or a downflow. There is generally a regeneration unit connected to fluidized beds that regenerates the saturated adsorbent and thereby produces the fresh adsorbent. The most common regeneration units in fluidized bed systems are thermal regeneration furnaces. Benefit of fluidized beds is that their adsorption performance stays a constant since the adsorbent bed is never fully saturated. Downsides include expensive operating costs due to the regeneration units. (Johnson & Massey, 1979)

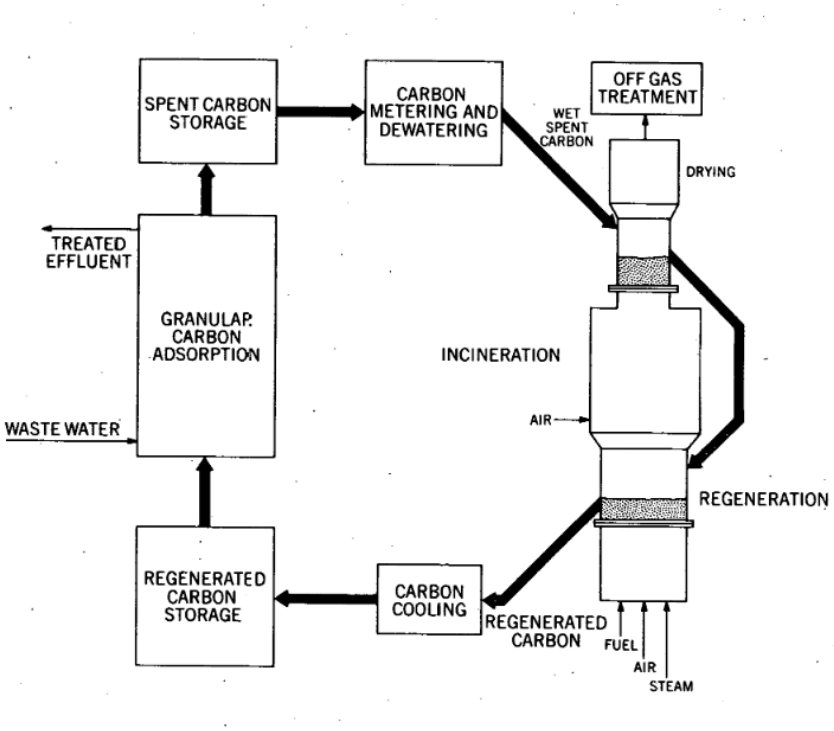

Figure 14 Fluidized bed adsorber system. (Johnson & Massey, 1979)

9.3 Moving-bed filtration reactors

Moving bed filters have counter-flow system. Their columns resemble fixed bed columns, however, inside they have two rotational cylinders packed with adsorbent material. The purpose of these cylinders is to allow continuous regeneration of the adsorbent while process stream is being filtered in the other cylinder. Regeneration is commonly performed with integrated steam regeneration. (Çeçen & Aktas, 2011)

9.4 Activated carbon canisters

Activated carbon canisters commonly small-scale filtration unit for both liquid phase and gas phase applications where average size is 200-300 liters. Carbon canister can be either rechargeable or disposable. The rechargeable unit are commonly regenerated off-site. The working principle is close to fixed bed filters since uniform flow is fed through adsorbent media inside of the canister units. Common set up for water purification applications is 2 or more in series. (Carbtrol Corporation, 2018)

Figure 15 A typical carbon canister set up for liquid phase purification. (Carbtrol Corporation, 2018)

9.5 Activated carbon adsorption theory in fixed bed columns

Activated carbon filtration fundamental theory is easy to explain with adsorption in fixed bed columns. Adsorption columns have adsorbent beds inside of them which can be refer to as stationary phase or solid phase. Solution inflow into the column is referred as influent and solution and the column outflow is referred to as effluent. (Al-Degs et al., 2009) The adsorption process inside of columns is basically a mass transfer between mobile phase and solid phase, where adsorbent represents the solid phase and solution refers to the mobile phase. Behavior of adsorption process in fixed bed columns can be studied with

breakthrough curves, mass transfer zone adsorption isotherms and adsorption models. Examination of adsorption process is commonly done by studying effluent concentrations, equilibrium state of adsorption and saturation of activated carbon bed. (Hamdaoui & Naffrechoux, 2007)

9.5.1 Adsorption isotherms of activated carbon

The adsorption isotherms describe the behavior of adsorption process and can be used in estimating adsorption capacity of adsorbents and in scaling of filtration process dimensions. (El Qada et al., 2006) Adsorption isotherms illustrate the relationship between adsorbate concentration in solution and absorbate concentration in solid at equilibrium. Adsorption equilibrium describes the phase of adsorption process where amount of adsorbate is a constant value in solution and in the adsorbent or in other words a phase where adsorption capacity of adsorbent is full. Adsorption isotherms are an efficient method to estimate adsorption capacity of activated carbon beds and optimal bed heights for adsorbents. (Hamdaoui & Naffrechoux, 2007)

The most common adsorption isotherms for activated carbons are Langmuir and Freundlich. Langmuir model equation is represented in equation (11) and Freundlich in (12). (Hamdaoui & Naffrechoux, 2007)

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (11)$$

where

q_e equilibrium concentration of adsorbent, [mg/g]

q_m maximum adsorption capacity, [mg/g]

b Langmuir free energy constant, [dm^3/g]

C_e equilibrium concentration for liquid, [mg/dm^3]

$$q_e = K_F C_e^{1/n} \quad (12)$$

where

K_F Freundlich constant for adsorption capacity, [(mg/g)/(dm^3/mg)^n]

n adsorption intensity constant

Langmuir isotherm is the simplest version for adsorption equilibrium. Its default is that adsorption process is homogeneous on adsorbent surfaces and that adsorbate compounds do not interact with each other in the solution or during the adsorption. (El Qada et al., 2006) Freundlich isotherms is a step more complicated than Langmuir. Its default is that adsorption process takes place on heterogeneous adsorbent surfaces. It enables non-ideal adsorption modelling where adsorption is not identical with every adsorbent site. (Hamdaoui & Naffrechoux, 2007)

Langmuir and Freundlich are typically represented in linearized forms where Langmuir have five forms and Freundlich only one. Linear forms of adsorption isotherms are used in finding out of parameters that can be used in the modeling of isotherms. The linear forms for the isotherms are represented in Table IV. (Hamdaoui & Naffrechoux, 2007)

Table IV Linear forms and plots for Langmuir and Freundlich isotherm models. (Hamdaoui & Neffrechoux, 2007)

Isotherm	Linear form	Plot
Langmuir-1	$\frac{1}{q_e} = \frac{1}{bq_m}\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}\ vs.\frac{1}{C_e}$
Langmuir-2	$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{bq_m}$	$\frac{C_e}{q_e}\ vs.\ C_e$
Langmuir-3	$q_e = -\frac{1}{b}\frac{q_e}{C_e} + q_m$	$q_e\ vs.\frac{q_e}{C_e}$
Langmuir-4	$\frac{q_e}{C_e} = -bq_e + bq_m$	$\frac{q_e}{C_e}\ vs.\ q_e$
Langmuir -5	$\frac{1}{C_e} = bq_m\frac{1}{q_e} - b$	$\frac{1}{C_e}\ vs.\frac{1}{q_e}$
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	$\ln q_e\ vs.\ln C_e$

9.5.2 Breakthrough curve and mass transfer zone

Breakthrough curves are used to describe adsorption process in filtration columns by examining effluent concentration during adsorption. There are also used in defining of column parameters such as residence times, flow rates and column dimensions. (Al-Degs et al., 2009), (Qian et al., 2019) Mass transfer zones and breakthrough curves can be also used as a tool when studying effects of adsorption process parameters, such as flow rate, adsorbent bed height, column diameter, solution pH, solution temperature, initial adsorbate concentration, adsorbent particle size and the properties of activated carbon adsorbent and adsorbate. (Taty-costodes et al., 2005)

A common plot for breakthrough curve is adsorbate concentration in effluent divided by concentration in influent ($C_{effluent}$ / $C_{influent}$) as a function of past time (t) or throughput volume (V) during adsorption. A typical breakthrough curve is represented in Figure 16. According to Figure 16 there are 3 concentration points that determine the nature of breakthrough curve. Adsorbate concentration in influent is C_0 when it comes to the adsorption column. At the start of the adsorption, adsorbate concentration in effluent is zero since the flow has not reached the bottom of column. The breakthrough point is at C_b which illustrates the desired

value of adsorbate concentration in effluent. At end of the curve, effluent concentration is same as the influent concentration C_0 since the adsorption capacity of the adsorbent is limited. Adsorbent is expected to be fully exhausted at C_x when effluent concentration is approximately 90-95% of influent concentration. The zone between C_b and C_x in breakthrough curve represents the mass transfer zone (MTZ) of adsorbent bed in column which is considered as a meter for adsorption efficiency in the column. The length of MTZ zone illustrates the rate of adsorption. MTZ starts to develop in the top of the column at the beginning of adsorption when fluid enters adsorbent bed and then advances till the end of the column. The breakthrough point in MTZ equals the phase in column where maximum permitted concentration comes out within effluent. (Al-Degs et al., 2009)

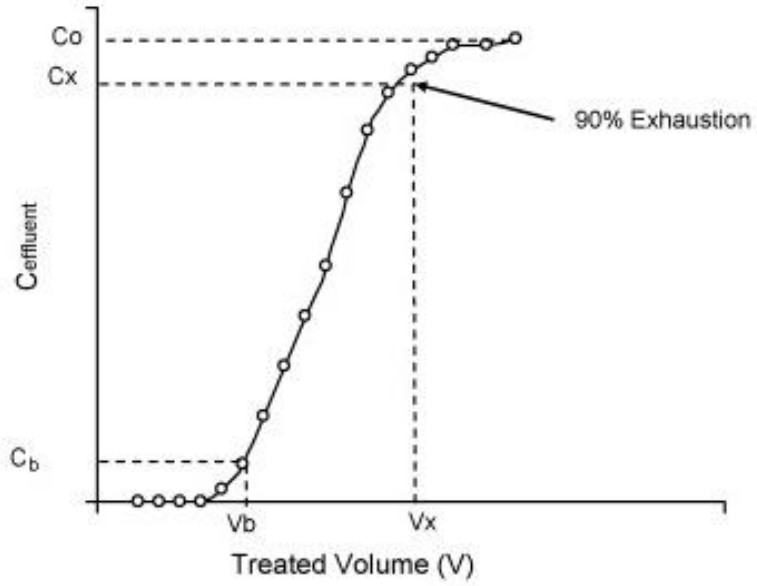

Figure 16 Illustration of an ideal breakthrough curve for activated carbon. (Al-Degs et al., 2009)

9.5.3 Effects of operational parameters in fixed bed filtration

Affecting operational parameters in fixed bed filtration include feed concentration, linear flow rate, carbon bed height and the diameter and particle size of the activated carbon. The initial concentration of influent affects adsorption process by influencing saturation rate of adsorbent and breakthrough time of the filtration. Concentration of adsorbate affects the concentration gradient of solutions. Larger concentration gradients enhance the adsorption

of the adsorbate, thus increased initial concentration increases saturation rate and decreases the breakthrough time of the fixed bed. (Ahmad & Hameed, 2010)

Generally smaller flow rates increase the adsorption efficiency of the fixed bed columns. Increasing flow rate reduces adsorption residence time. Shorter residence times equal less contact with the adsorbent, and thus less adsorbate is adsorbed into adsorbent. Due to shorter contact times the adsorption capacity decreases when flow rate increases in the column. (Ahmad & Hameed, 2010)

Larger height of adsorbent beds equal more adsorbent mass if the column diameter is held as a constant. Increased column bed heights also equal more residence time due to the increased mass transfer zone. Adsorption capacity increases when the adsorbent bed height is increased due to increased residence time and mass transfer zone. (Ahmad & Hameed, 2010) Larger column diameters may cause channelling fixed bed columns and too small diameters radial dispersion. It stated that reasonably thin diameters favour adsorption process efficiency. Ratio of column diameter and activated carbon particle diameter is also an important factor. (Augier et al., 2008)

Activated carbon materials with smaller particle sizes have generally more faster adsorption rates and more accessible micropores than larger carbon particles. This is because smaller particle sizes have lower diffusion resistance in the adsorption than larger ones. Adsorption equilibrium is reached faster with larger particle sizes than with smaller particle sizes and therefore the adsorption capacity fills up faster with larger particles. Downside for small particles is that they can cause channelling in filter media bed. (Roostaei & Tezel, 2004)

Experimental Part

The experimental part is divided into two parts: wastewater filtration and electrolyte solution filtration. The main focus of the experimental part was the filtration of the electrolyte solution with activated carbon. The wastewater part was an additional filtration application.

10 Wastewater filtration

In the wastewater part, a typical wastewater solution from mining industry was chosen for the filtration. The goal was to test if activated carbons are suitable for mining water filtration. The filtration target was to separate anions and toxic metals from the mining waters. The composition of the mining water solution was obtained from a mining water treatment study (Mamelkina et al., 2019). The anions to be separated were nitrate, sulfate, and chloride, while the metals to be separated were copper, zinc, and nickel. Aside from the filtration, it was also intended to examine how effectively the activated carbons and biochar products can adsorb anions and toxic metals from the mining water solution over a 24- hour period.

10.1 Materials

Materials used in making of the synthetic mining wastewater included $CuSO_4 \cdot 5H_2O$ (99%) by SIGMA-ALDRICH, $NiSO_4 \cdot 6H_2O$ (99%) by ACROS Chemicals, $ZnSO_4 \cdot 7H_2O$ (>99,5%) by MERCK, Na_2SO_4, $NaNO_3$ (>99,5%) by Riedel-de Haën, NH_4Cl (>99%) by VWR Chemicals and NaCl (99,4%) by TABLETEKI SOLNE. The composition of the solutions is presented in Table V, where there are three different levels for the metal and anion concentrations. The medium level was chosen for the filtration and adsorption tests.

Table V Mining water composition. (Mamelkina et al., 2019)

Ions	Concentration, [mg/l]		
	Low	**Medium**	**High**
Sulphate (SO_4)	1000	2000	3000
Nitrate (NO_3)	20	40	60
Chloride (Cl)	100	200	300
Copper (Cu)	2	5	8
Nickel (Ni)	2	5	8
Zinc (Zn)	5	10	15
Ammonium (NH_4)	10	20	30

There were nine different filter medias in the wastewater experiments shown in Table VI. In the wastewater filtration test only activated carbon Norit GAC 1240W was used. In the adsorption all 9 materials were used. All the filter medias listed in Table VI were also used in the electrolyte filtration part.

Criteria for the activated carbon selection was to get commercial granular activated carbons for the filtration tests. The chosen commercial activated carbons are widely used in various water filtration processes. The activation method of the activated carbon was not a selection criterion. However, all the selected activated carbons were produced by steam activation. The biochars were also chosen from commercial products. The applications of the used biochar materials include gardening and runoff water filtration. All three biochars were manufactured with slow pyrolysis. Carbofex Oy's spruce-based biochar is manufactured at pyrolysis 600 ℃ pyrolysis with a residence time of 10 were used. Carbons Finland Oy's birch-based biochar is produced at 450-550 ℃ with a residence time of 90 min and spruce-based biochar at 600 ℃ with 30 min residence time.

Table VI Properties of used activated carbons and biochars.

Filter media	Supplier	Material	Particle size range	Surface area	Bulk density
			[mm]	[m^2/g]	[kg/m^3]
Filtrasorb 300	Chemviron Carbon	Activated carbon	0,6-2,36	950	560
Filtrasorb 400	Chemviron Carbon	Activated carbon	0,425-1,7	1050	540
AquaSorb H150	Jacobi Carbon	Activated carbon	0,425-1,7	1010	520
LGCO 100	Sorbotech	Activated carbon	0,6-2,36	1000	550
K835	Silcarbon	Activated carbon	0,5 - 2,5	1100	500
Norit GAC 1240 W	Brenntag-nordic	Activated carbon	0,425-1,7	1100	470
Birch	Carbons Finland	Biochar	0-2,0	225	330
Spruce (1)	Carbons Finland	Biochar	0-2,0	280	
Spruce (2)	Carbofex	Biochar	0-2,0	550	200

10.2 Analysis methods

The anion concentrations of the mining water were analyzed in LUT by IC (Ion Chromatography) analysis and the toxic metal concentrations by ICP (Inductively Coupled Plasma) analysis.

10.3 Filtration equipment

In figure 17 there is shown a flowsheet of the equipment used in the wastewater filtration. There are three columns in the filtration equipment, shown in Figure 18. The heights of the columns are 70 cm and the diameters 22 mm. Flowrates in the filtration columns were adjusted with flowmeters. The used flow meters were rotameters from which two were ABB's A6146C061INAOAAS models and one was Kytölä's LH-5BA-HV model. The pumps of the filtration equipment were Flowjet Nemp 25/5 models. The pressure difference meters were Müller MDHS-200-00282 models. Each column had also a temperature meter and a pressure meter. The mining water was contained in a 1000 dm^3 feed tank.

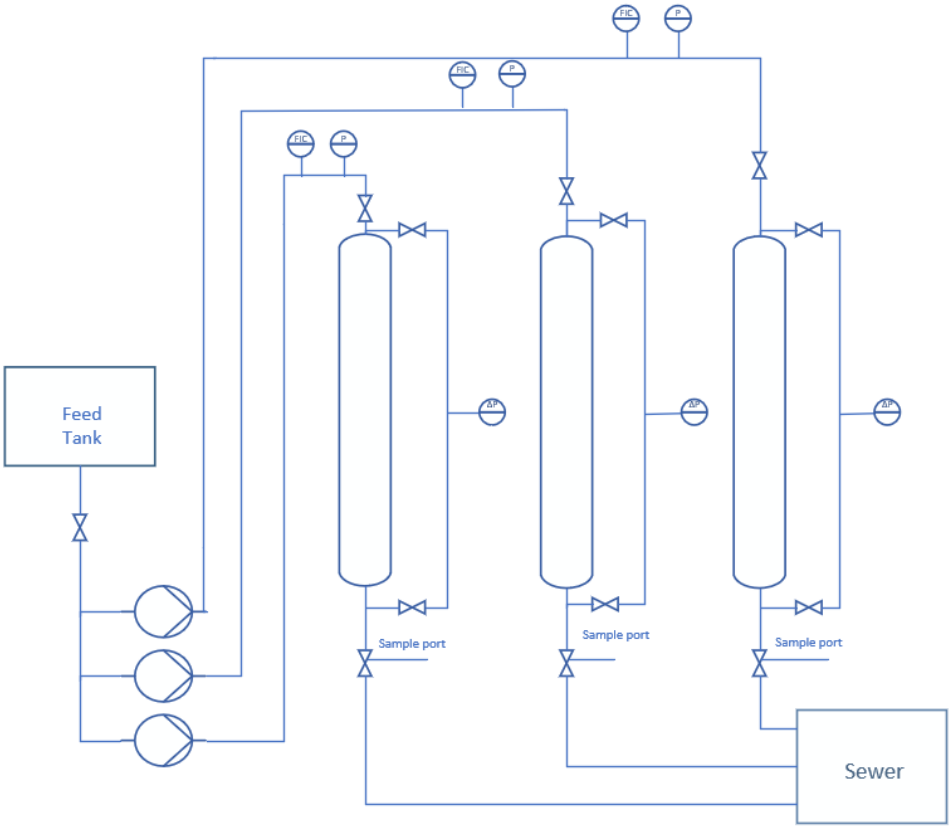

Figure 17 Wastewater equipment flowsheet

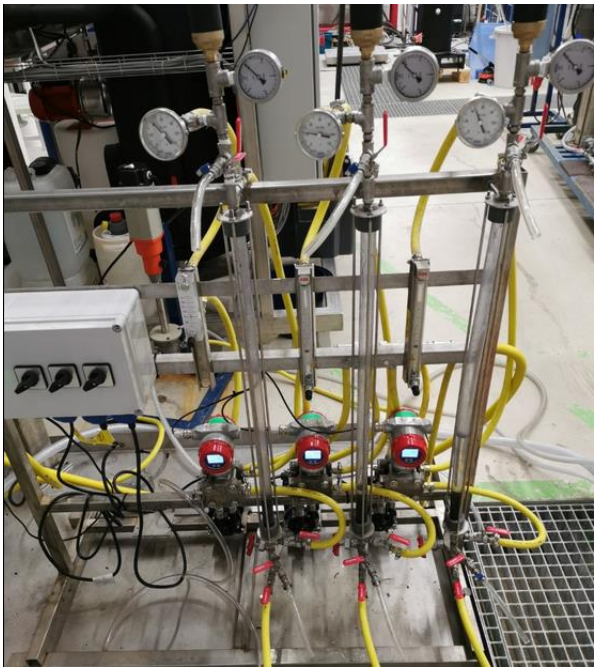

Figure 18 Filtration columns.

10.4 Wastewater experiment procedures

Wastewater filtration tests were performed with two filtration columns. Norit 1240 W activated carbon was used as a filter media in both columns. The duration of the filtration was six hours. Temperature of the wastewater feed solution was 22 ℃ which remained constant during the filtration. Used bed heights in the columns were 11.4 cm in the Column 1 and 5.5 cm in the Column 2. Chosen linear velocity (m/h) for the filtration test runs was 12 m/h which is a typical rate in commercial GAC filters (Çeçen & Aktas, 2011). The flow meters were set at 4.56 l/h which corresponds to the target value for linear flow. It was noticed during the test run that the flow meters had problems in maintaining a steady flow rates and therefore the linear flow value varied between 10-12 m/h during the test runs.

Filtrate samples were gathered from the column outlets and feed samples from the column inlets. Sampling interval was once every 15 minutes during the first hour of test run and once every 30 min thereafter. Only anion concentrations were measured from the effluent samples.

A long duration adsorption test was decided to be performed for the mining wastewater to see if activated carbons or biochars can adsorb toxic metals or anions from the wastewater. The used adsorption time in the test was 24 hours. The used wastewater solution was the same as in the filtration test. Temperature for wastewater solution was 22 ℃. All the activated carbons and the biochar products in Table VI were used as adsorbents in the test. The used dosages were 20 grams of the activated carbons and the biochar products. Each adsorbent was placed to 500ml Erlenmeyer flasks with 300ml wastewater in them. Magnetic stirrers were used in the flasks to make a mixing effect on the wastewater solution. A stirring speed of 900-1100 rpm was used during the adsorption test.

10.5 Wastewater results

The anion and toxic metal concentrations of the prepared wastewater feed solution are shown in Table VII. In the filtration test only anion concentrations were measured due to difficulties in analysing the samples. In the 24-hour adsorption test both toxic metal and anion concentrations were measured.

Table VII Concentrations (mg/l) of nitrate, chloride, sulphate and metals in wastewater feed solution.

Concentration, [mg/l]	**Nitrate**	**Chloride**	**Sulphate**	**Nickel**	**Copper**	**Zinc**
	39	182	2013	5,0	6,5	10,2

10.5.1 Wastewater filtration results

Filtration results are presented in Table VIII that shows the anion concentration of the effluent samples. The lowest measured anion concentrations of the effluent samples were 30.2 mg/l for nitrate, 171 mg/l for chloride and 1982 mg/l for sulphate, while the average effluent concentrations were 36 mg/l for nitrate, 182 mg/l for chloride and 2060 mg/l for sulphate. The results indicate that the used activated carbon failed to separate chloride, nitrate and sulphate properly from the wastewater, since effluent concentrations are only slightly different from feed concentrations.

It can also be seen in table VIII that many of the measured values of sulphate concentrations were higher than their concentrations in the feed solution, likely due to measurement errors in the analysis of the samples. The measured effluent concentration values for nitrate and chloride were more accurate than for sulphate, although they also had a few outliers in the measurements. The measurement errors of sulphate values were probably caused by the high concentration and the dilution of the samples.

Table VIII Effluent concentrations (%) of nitrate, chloride and sulphate anions after activated carbon filtration. The bed height was 11.4 cm in Column 2 and 5.5 cm in Column 2. The linear flow was 12 m/h. Used feed solution contained 39 g/l of nickel, 182 mg/l of chloride and 2013 mg/l of sulphate.

	Nitrate, [mg/l]		**Chloride, [mg/l]**		**Sulphate, [mg/l]**	
Time, [min]	**Column 1**	**Column 2**	**Column 1**	**Column 2**	**Column 1**	**Column 2**
0	30,2	36,9	189	181	2152	2000
15	32,6	36,8	194	179	2003	2006
30	33,4	33,9	188	174	2081	1989
45	NA	35,2	NA	175	NA	2079
80	35,3	37,9	207	187	1993	2112
105	NA	NA	NA	NA	2144	2037
140	31,6	36,7	171	182	NA	2226
170	35,9	39,3	178	179	2034	2103
200	33,8	39,2	171	182	2063	2087
230	38,2	38,9	186	180	2140	2023
260	36,9	35,5	184	180	2022	1982
290	39,8	39,5	183	181	2170	1988
320	39,1	35,5	184	178	NA	2036
360	37,7	36,3	184	176	NA	2000

The term removal efficiency (%) was used to describe how much the filter media adsorbs the adsorbates from the influent concentrations. The calculated removal efficiencies are shown in Table IX. The filtration efficiency was averagely 4.3 % for nitrate, 1.8% for chloride and 0.4% for sulphate. Due to the inaccuracy of the sulphate values, it can be assumed that sulphate removal efficiency was zero. Based on the effluent concentrations in Tables VIII and IX, it can be said that the nitrate was separated most effectively from the feed solution even though the filtration efficiency for nitrate was also very poor. The sulphate separation was so minor that it can be assumed that it was not removed from the solution during the filtration.

Table IX Removal efficiencies (%) of nitrate, chloride and sulphate anions after activated carbon filtration. The bed height was 11.4 cm in Column 2 and 5.5 cm in Column 2. The linear flow was 12 m/h. Used feed solution contained 39 g/l of nickel, 182 mg/l of chloride and 2013 mg/l of sulphate.

	Nitrate, [%]		**Chloride, [%]**		**Sulphate, [%]**	
Time, [min]	**Column 1**	**Column 2**	**Column 1**	**Column 2**	**Column 1**	**Column 2**
0	21,7	4,2	0,0	0,7	0,0	0,7
15	15,4	4,3	0,0	1,9	0,5	0,3
30	13,2	12,0	0,0	4,7	0,0	1,2
45	Na	8,5	NA	3,9	NA	0,0
80	8,4	1,6	0,0	0,0	1,0	0,0
105	NA	NA	NA	NA	0,0	0,0
140	17,9	4,6	6,3	0,1	NA	0,0
170	6,7	0,0	2,2	1,8	0,0	0,0
200	12,2	0,0	6,5	0,3	0,0	0,0
230	0,8	0,0	0,0	1,3	0,0	0,0
260	4,2	7,8	0,0	1,2	0,0	1,5
290	0,0	0,0	0,0	0,9	0,0	1,3
320	0,0	7,8	0,0	2,7	NA	0,0
360	2,1	5,6	0,0	3,7	NA	0,7

Filtration figures for nitrate, chloride and sulphate are shown in Figures (19), (20) and (21). Based on these filtration figures, the used activated carbon did not get saturated during the filtration since the effluent concentrations of the anions remained approximately constant. The figures also demonstrate that bed heights did not significantly affect the filtration efficiency since only minor differences can be seen in the effluent concentrations between the column 1 and the column 2. In the nitrate filtration there is a bit more difference between the effluent concentrations of the columns than in chloride and sulphate filtrations. A noteworthy observation in the nitrate filtration is that the filtration in the column 1, where bed height was 11.4 cm, achieved slightly lower effluent concentrations than the column 2, where bed height was 5.4cm. Therefore, it can be stated that the larger bed height had a positive effect on the nitrate filtration. This is a logical result since a raise in bed height

increases the residence time and mass transfer zone of the adsorption (Ahmad & Hameed, 2010) (Al-Degs et al., 2009) (Augier et al., 2008).

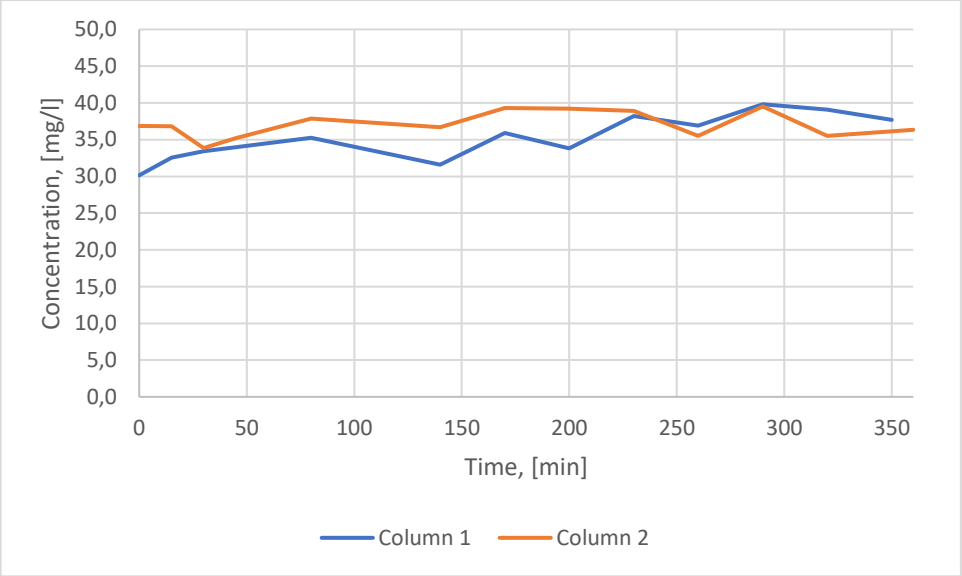

Figure 19 Nitrate concentrations (mg/l) in the wastewater filtration effluents. The bed height was 11.4 cm in Column 2 and 5.5 cm in Column 2. The linear flow was 12 m/h. Used feed solution contained 39 g/l of nickel.

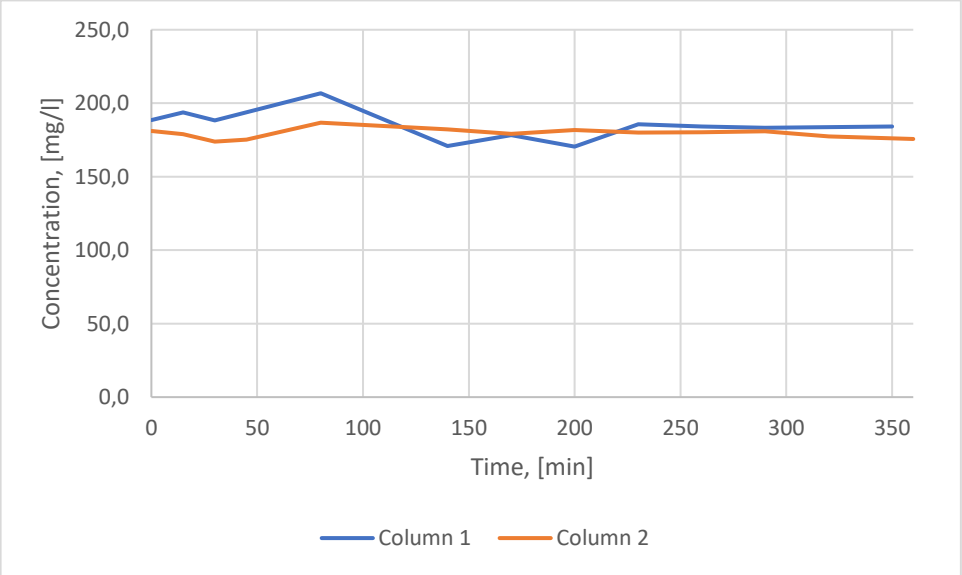

Figure 20 Chloride concentrations (mg/l) in the wastewater filtration effluents. The bed height was 11.4 cm in Column 2 and 5.5 cm in Column 2. The linear flow was 12 m/h. Used feed solution contained 182 mg/l of chloride.

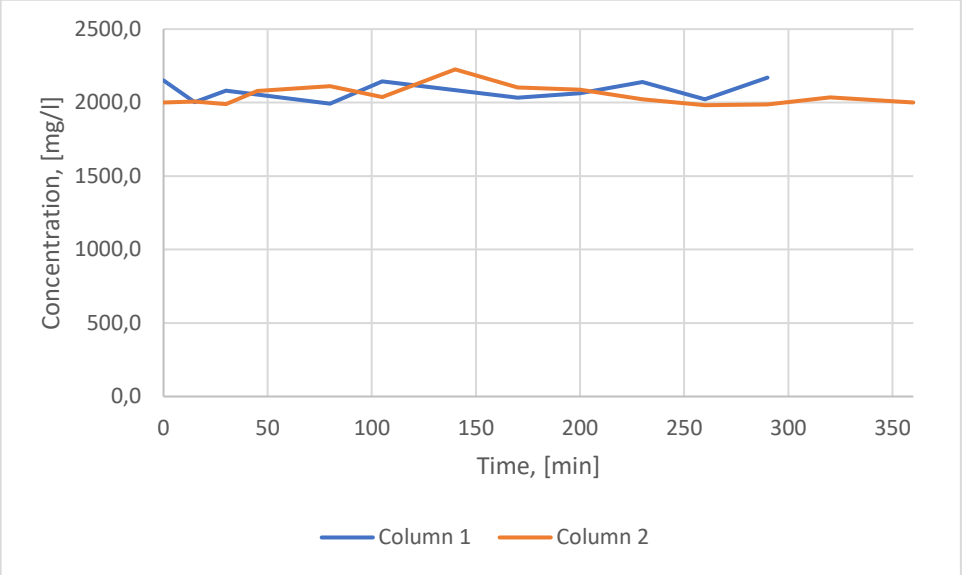

Figure 21 Sulphate concentrations (mg/l) in the wastewater filtration effluents. The bed height was 11.4 cm in Column 2 and 5.5 cm in Column 2. The linear flow was 12 m/h. Used feed solution contained 2013 mg/l of sulphate.

10.5.2 Wastewater adsorption test results

The results of the 24-hour adsorption test are presented in Table X, where there is shown the anion concentrations and removal efficiencies. Based on removal efficiencies, the used activated carbons adsorbed nitrate more effectively than chloride or sulphate. The activated carbons adsorbed averagely 76% of nitrate, 13% of chloride and 19% of sulphate. However, it is notable that the initial concentrations of chloride and sulphate were significantly higher than the initial concentration nitrate. Based on the adsorbed masses, sulphate was adsorbed the most. The used biochar products adsorbed averagely lower amounts of chloride and sulphate than the activated carbons. The adsorption of nitrate was significantly less effective with biochars since they adsorbed less than 17% of the nitrate. It can be stated that activated carbons adsorbed anions more efficiently than the biochar products. Notable, is that biochars adsorbed averagely more efficiently sulphate than nitrate and chloride.

Table X Concentrations (mg/l) and removal efficiencies (%) of nitrate, chloride and sulphate anions after 24-hour adsorption. Used feed solution contained 39 g/l of nickel, 182 mg/l of chloride and 2013 mg/l of sulphate.

Adsorbent	Nitrate		Chloride		Sulphate	
	Concentration, [mg/l]	Removal efficiency, [%]	Concentration, [mg/l]	Removal efficiency, [%]	Concentration, [mg/l]	Removal efficiency, [%]
Filtrasorb 400	5,7	85,1	137,4	24,5	1555	22,7
Filtrasorb 300	5,7	85,1	130,6	28,3	1561	22,4
Aquasorb H150	5,7	85,2	NA	NA	1600	20,5
LGCO 100	13,9	63,8	183,2	0,0	1715	14,8
K835	12,9	66,5	157,5	13,5	1648	18,1
Nordic GAC 1240W	11,5	70,2	156,4	14,0	1681	16,5
Birch	35,0	9,2	177,2	2,6	1715	14,8
Spruce (1)	32,0	16,8	169,0	7,2	1703	15,4
Spruce (2)	34,9	9,3	173,3	4,8	1706	15,2

The differences in the anion adsorption between the adsorbents are shown in Figure 22. The most effective activated carbons in the nitrate adsorption were Filtrasorb 400, Filtrasorb 300 and Aquasorb H150 with a removal efficiency of 85%. Filtrasorb 300 and Filtrasorb 400 also adsorbed chloride and sulphate more than other activated carbons. From the biochar products Spruce (1) was the most effective adsorbent in the nitrate removal. In chloride and sulphate removal, there were no significant differences among the biochars.

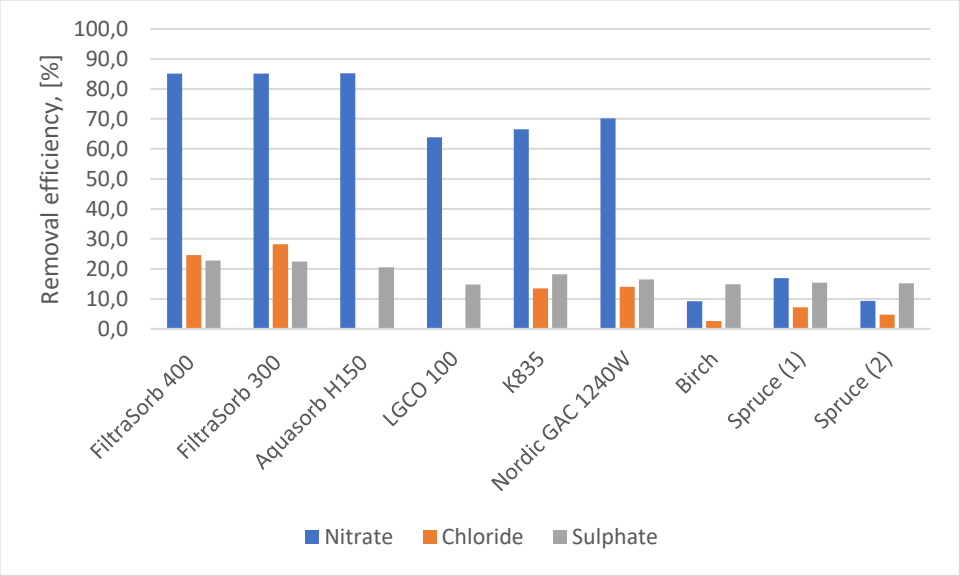

Figure 22 Removal efficiencies (%) of nitrate, chloride and sulphate after 24-hour wastewater adsorption test.

The results of the metal adsorption are presented in Table XI that shows the concentrations and removal efficiencies of nickel, copper and zinc. Based on the results, the activated carbons adsorbed at least 99.9% of the copper (II) ions, 99.5% of the zinc (II) ions and 97.3% of the nickel (II) ions. The used activated carbons adsorbed copper (II) ions slightly more effectively than nickel (II) and zinc (II) ions, though the differences between metal adsorptions were minor. The biochar products were not as effective in the nickel and zinc adsorptions as the activated carbon since they adsorbed only 40-62% of the nickel (II) ions and 50-81% of the zinc (II) ions. However, in the copper (II) adsorption they achieved almost equally effective adsorption, adsorbing over 99% of the copper (II) ions. The adsorption results also indicate that both activated carbons and biochar products adsorbed the metals in order: copper (II)>zinc (II)>nickel (II).

Table XI Concentrations (mg/l) and removal efficiencies (%) of nickel (II), copper (II) and zinc (II) ions after 24-hour adsorption. Used feed solution contained 5.0 mg/l of nickel, 6.5 mg/l of copper and 10.2 mg/l of zinc.

Adsorbent	Nickel		Copper		Zinc	
	Concentration [mg/]	Removal effiency, [%]	Concentration [mg/]	Removal effiency, [%]	Concentration [mg/]	Removal effiency, [%]
Filtrasorb 400	0,00	100,0	0,00	100,0	0,00	100,0
Filtrasorb 300	0,00	100,0	0,00	100,0	0,00	100,0
Aquasorb H150	0,06	98,8	0,01	99,9	0,04	99,6
Sorbotech LGCO	0,13	97,3	0,00	100,0	0,05	99,5
K835	0,01	99,8	0,00	100,0	0,02	99,8
Norit GAC 1240W	0,00	100,0	0,00	100,0	0,00	100,0
Birch	1,91	61,5	0,00	99,9	1,99	80,5
Spruce (1)	2,94	40,6	0,04	99,4	4,00	60,6
Spruce (2)	2,98	39,8	0,06	99,0	5,01	50,8

The differences in the metal adsorption between the adsorbents are shown in Figure 23. Based on the results, the copper (II) ions were adsorbed equally effectively among the activated carbons. In the nickel and zinc adsorption Filtrasorb 300, Filtrasorb 400 and Norit GAC 1240W were the most effective adsorbents, although LGCO 100, K835 and Aquasorb H150 adsorbed only 0,2-3% less. The biochar products were almost equally effective in the copper (II) ion adsorption, since differences among the were less than 1%. However, in nickel and zinc adsorption the birch-based biochar was the most effective adsorbent. The

birch-based biochar adsorbed 20% more nickel and 20-30 % more zinc than the spruce-based biochars. Spruce (2) was approximately as effective as Spruce (1) in the nickel and copper adsorption, while in the zinc adsorption it removed 10% less.

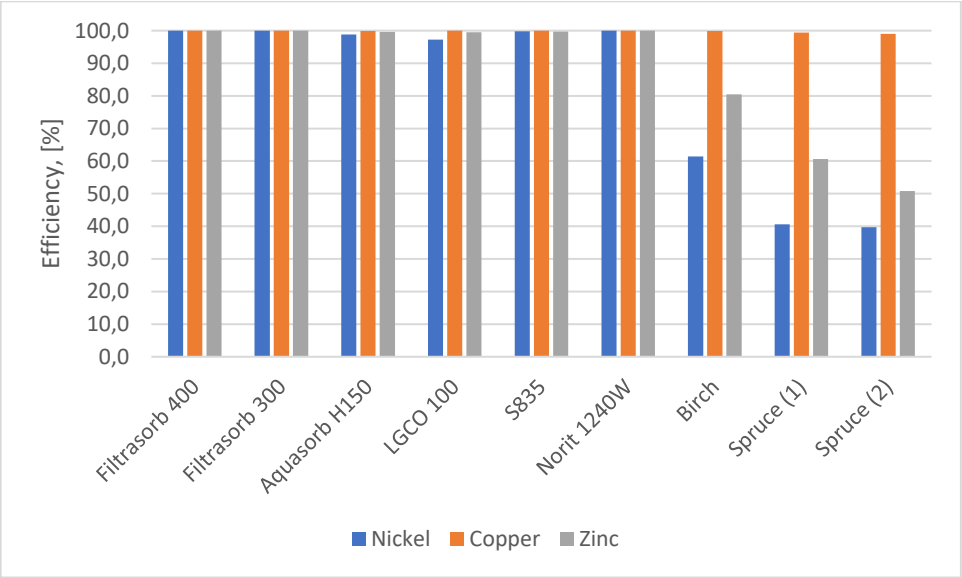

Figure 23 Removal efficiencies for nickel, copper and zinc in the 24 hours wastewater adsorption test.

10.6 Conclusions of wastewater experiments

The purpose of the wastewater filtration test and the adsorption test was to determine if commercial activated carbons can separate anions and toxic metals from a mining water solution. Biochar products were also tested in the adsorption test. Due to analysis problems, only anions were measured in the filtration test. The target anions were nitrate, chloride and sulphate, while the target metal ions were nickel, copper and zinc. The filtration test was performed at a linear flow of 12 m/h and the adsorption test was a 24-hour laboratory test with magnetic rod stirring.

The wastewater filtration test indicated that the used commercial activated carbon was almost incapable of separating anions from the mining water solution at 12 m/h. Since there were limited number of filtrations and only one commercial activated carbon was used in the filtration, many reliable conclusions cannot be drawn from the filtration test. Based on

the filtration results, the commercial activated carbon was not suitable for anion filtration from the mining water.

The adsorption test showed that anions adsorbed significantly more effectively with 24-hour contact time than in the filtration. The commercial activated carbons adsorbed 63-85% of the nitrate, 0-28% of the chloride and 14-23% of the sulphate during the test. The nitrate adsorption was the most effective among the activated carbons based on removal efficiencies. It is still notable that in 24 hours the activated carbons failed to adsorb all the nitrate from the mining water solution where the initial concentration of nitrate was 39 mg/l. A noteworthy fact was also that the activated carbon adsorbed sulphate more in masses than chloride or nitrate. The adsorption test indicated that the commercial activated carbons are not suitable for the removal of nitrate, chloride or sulphate from mining waters.

The results of the adsorption test demonstrated that the commercial activated carbons adsorb more effectively toxic metal ions than anions. Copper (II), nickel (II) and Zn (II) metal ions were removed almost entirely from the wastewater solution by the activated carbons during the 24-hour adsorption test. The commercial activated carbons adsorbed at least 99.9% of the copper, 99.5% of the zinc and 97.3% of nickel. The removal order of the metal ions for the activated carbons was: Cu (II)>Zn (II)>Ni (II). Although the activated carbons were more effective in the metal ion adsorption than in the anion adsorption, it is notable that the initial concentrations of the metals were significantly lower than with the anions. The removal of the toxic metal ions should be examined in a mining water filtration test to if the activated carbons can remove effectively metal ions at 12 m/h. Based on the adsorption test results, the activated carbons have potential to succeed in removing metal ions in the filtration.

The used biochar materials were discovered to be even less effective in the anion adsorption than the activated carbons. They adsorbed less than 17% of all the anions during the 24 hours. The biochar products were more successful in the metal adsorption than in the anion adsorption. Like the activated carbons the biochar products removed more than 99% of copper from the wastewater. However, in the removal of nickel and zinc, they adsorbed only 39-62% of the nickel and 50-80% of the zinc. It can be stated that the biochar products were almost as effective in the copper removal than the activated carbon but significantly less effective in the nickel and zinc removals. The adsorption test indicated that biochar raw material affected the metal adsorption, since the birch-based biochar adsorbed more nickel

and zinc than the spruce-based biochars. However, in the anion adsorption birch-based biochar was not more effective than the spruce-based biochars.

11 Electrolyte filtration

The electrolyte filtration test runs aimed to remove organic phase from electrolyte solutions. In addition to activated carbons, biochar products and alternative filter media were tested in the electrolyte filtration tests. The main objective was to determine how effectively commercial activated carbons can remove organics. Biochar was examined as a possible substitute filter media for the activated carbon. Filtration with the alternative filter medias focused on the effect of linear flow rate in the organic removal. There were two different electrolyte solutions in the filtration tests: impurity raffinate and cobalt raffinate. The Impurity raffinate is an electrolyte stream derived from the extraction of metal impurities such as iron and aluminum, whereas the cobalt raffinate is derived from cobalt extraction. Both raffinates have a similar organic phase composed of a kerosene-based extraction solvent and of a phosphoric or phosphinic acid-based extraction reagent. The target limit of the organic phase in the electrolyte filtration effluents was 2-5 mg/l.

11.1 Materials

Preparation of electrolyte solutions required $NiSO_4 \cdot 6H_2O$ (>98%) by VWR Chemicals, $CoSO_4 \cdot 7H_2O$ (>99%) by ACROS Organics and H_2SO_4 (93%) by MERCK. Both raffinates were prepared in tap water. The target metal contents were 17 g/l nickel and 3 g/l cobalt in the impurity raffinate and 17 g/l nickel in the cobalt raffinate. To achieve the target metal concentrations, the impurity raffinates was prepared using $NiSO_4 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ while the cobalt raffinate was prepared using $NiSO_4 \cdot 6H_2O$ only. Sulphuric acid content was 0.45 mass-% in the impurity raffinate 0.092 mass-% in cobalt raffinate. Acidity targets at pH numbers were 2.7 for impurity raffinate and 5.5 for cobalt raffinate.

The organic phase was added to the filtration feed stream with a syringe pump. In the cobalt raffinate solution the organic phase consisted of oil-based solvent Shellsol D70 by Kremer Pigmente and extraction reagent bis 2, 4, 4-trimethylpenthyl phosphinic acid Cyanex 272 (85%) by American Cyamid Co. In the impurity raffinate the added organic phase consisted

of NESSOL D100 by Neste Oyj and di-(2-ethylhexy) phosphoric acid called D2EHPA (93%) by Albright & Wilson Americas Inc. The organic phase in impurity raffinate was made from 80 vol.% of Nessol D100 and 20 vol.% of D2EHPA, while the organic phase in cobalt raffinate was made from 87 vol.% of Shellsol D70 and 13 vol.% of Cyanex 272. The solvent and reagent combinations were mixed with a magnetic stirrer before adding them to a syringe. The organic target in the feed was 50 mg/l with both raffinate solutions.

In addition to the commercial activated carbons and biochar products listed in Table VI, alternative filter materials were tested in the electrolyte filtrations tests. Table XII shows the physical properties of the alternative filter medias.

Table XII Physical properties of alternative filter medias.

Filter media	Particle size range	Bulk density
	[mm]	[kg/m^3]
Media (1)	0,4 - 0,6	1470
Media (2)	0,75 - 1,0	1500
Media (3)	0,4 - 0,6	2390

11.2 Analysis methods

The concentration of the organic phase in the column effluents was analyzed in LUT by TOC (Total Organic Carbon) analysis, which analyses total carbon content (mg/l) of the samples. Electrolyte solution pH values were measured with a Mettler Toledo pH meter. LUT's ICP was used in analyzing of nickel and cobalt concentrations in the 24-hour electrolyte adsorption test. Total carbon concentrations were converted to organic phase concentrations. The conversion was done using data from the manufacturers about the molecular masses and carbon numbers of the extraction solvents and reagents listed in table XIII. Equation (13) shows the conversion calculation:

$$C_{op} = x\frac{M_s}{M_{Cs}}C_{tc} + y\frac{M_r}{M_{Cr}}C_{tc} \qquad (13)$$

where

C_{op} organic phase concentration, [mg/l]

C_{tc} total carbon concentration, [mg/l]

M_s molar mass of extraction solvent, [g/mol]

M_r molar mass of extraction reagent, [g/mol]

M_{Cs} molar mass of carbons in extraction solvent, [g/mol]

M_{Cr} molar mass of carbons in extraction reagent, [g/mol]

x portion of extraction solvent in organic phase

y portion of extraction reagent in organic phase

Table XIII Molar masses (g/mol) and carbon numbers of extraction solvents and reagents.

	Molar mass, [g/mol]	Carbon number	Reference
Nessol D100	208	13-18	(Neste, 2021)
Shellsol D70	178	11-14	(Kremer Pigmente, 2021)
D2EHPA	322	16	(Lanxess, 2021
Cyanex 272	290	16	(Solvay, 2021)

11.3 Equipment

Figure 25 shows the flowsheet of the equipment used in the electrolyte filtration tests. The filtration columns were the same as in the wastewater filtration tests. The electrolyte feed solution was kept in a 200-liter reactor with a thermal jacket. Used reactor is shown in Figure 24. The temperature in the reactor was maintained constant with a Lauda RP 855 heat exchanger. The organic phase was fed into feed stream with an Aladdin AL-1000 syringe pump. An organic mixing tank with a stirrer was used to break the size of the organic phase droplets, and to mix the organic phase with the electrolyte feed solution. The used stirrer Ystral D-7801 has a mixing efficiency of 50 Hz (300 RPM). A 1000 dm^3 container was used as a waste tank for electrolyte effluents.

Figure 24 Electrolyte filtration equipment.

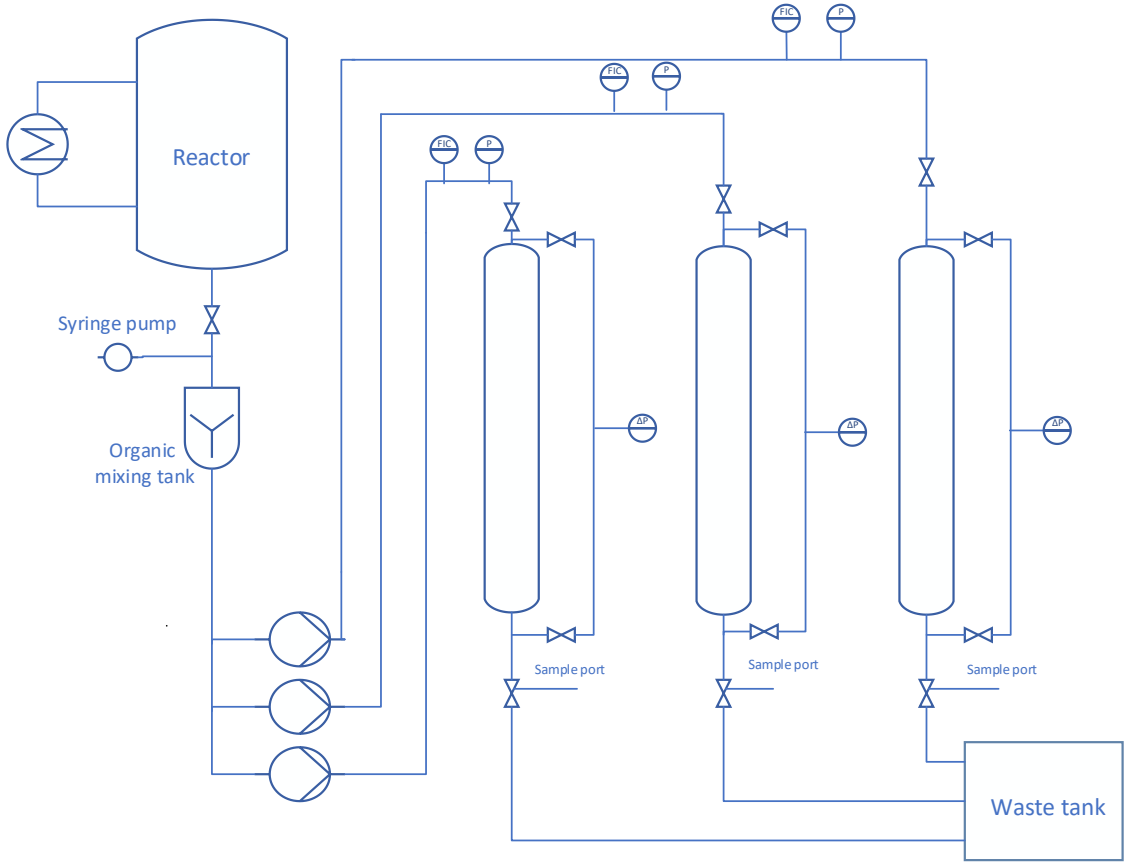

Figure 25 Flowsheet of the electrolyte filtration equipment.

Figure 26 Aladdin AL-1000 syringe pump used for pumping the organic phase.

Figure 27 Organic mixing tank and stirrer (Ystral D-7801) used in electrolyte filtration.

11.3.1 Biochar particle sieving

The biochar products were sieved with a Retsch sieve shaker for the electrolyte filtration test runs. The sieving duration was 4 hours for each biochar media. The biochar particle size range was 0-2.0mm in the impurity raffinate filtration and 0.425-2.0mm in the cobalt raffinate filtration.

11.4 Filtration procedure

The electrolyte filtration runs were performed with all three columns of the filtration equipment working simultaneously. The used filter media in the electrolyte filtrations are listed in Tables VI and XII where there are 6 activated carbons, 3 biochar products and 3 alternative media products. Each media was tested in both electrolyte solutions. Altogether 8 filtration tests were executed, 4 with impurity raffinate solution and 4 with cobalt raffinate. The filtration samples were taken from the column effluents.

The heights of filter media beds in the columns were 7 cm in all the test runs and bed volumes 26.6 cm^3. The duration of the filtration was 6 hours for the activated carbon and biochar test runs. The linear flow rate of the activated carbon and the biochar filtrations was 12 m/h which corresponds to a volumetric flow rate of 4.56 l/h. In the filtration with the alternative medias the duration was 215 min. The first 90 minutes of the filtrations with the alternative medias were performed with a linear flow of 16 m/h and the rest 125 min with 24 m/h. The flow rates were not very accurate during the electrolyte filtrations since the rotameters were unable to maintain a steady flow rate. An estimated variation for the linear flow was ±2 m/h.

The sampling frequency was once every 15 minutes during the first hour and once every half hour after the first hour. In addition to effluent samples, also four feed samples were taken from each test run and pH value was measured from them. The target temperature was 40 °C in the impurity raffinate and 50 °C in the cobalt raffinate. During the first test, it was noticed that the stirrer in the organic mixing tank caused a rise in the solution temperature. A running water flow from tap water was connected into the jacket of the organic mixing tank to prevent the excessive warming. The temperatures varied from 35 °C to 42 °C in the impurity raffinate filtrations and from 45 °C to 52 °C in the cobalt raffinate filtrations.

In addition to the filtration test, a 24-hour adsorption test with activated carbons was performed for the impurity raffinate solution to determine if the activated carbons can remove nickel or cobalt from the electrolyte solution. The metal concentrations of the electrolyte solution were 3 g/l cobalt and 30 g/l nickel. The test was performed with similar methods as the wastewater adsorption test. A dosage of 30 grams was taken from each activated carbon medias and placed into 500 ml Erlenmeyer flasks with 300 ml of electrolyte solution in them. Magnetic stirrers were used in the flasks to make a mixing effect on the solutions. A stirring speed of 900-1100 rpm was used during the test.

12 Electrolyte filtration results

The electrolyte filtration results are presented as organic concentrations in the filtration effluents. The effects of the physical properties of the filter media on the filtration was examined using the average organic effluent concentrations of the filtration test runs. Filtration efficiencies were not calculated since there is no precise profile available for the organic concentrations of the electrolyte feeds. The organic droplet formation in the syringe pump feed was cyclical, leading to large variations in the organic concentrations of the feed samples. Since only 4 feed samples were taken from each test run, the information about the filtration feed profiles was limited. In the interpreting of the results, the organic content of the feed was considered as the target value of 50 mg/l. The assumption of the target value was based on the calibration of the syringe pump and the measurement of the syringe volume after each test.

12.1 Preliminary test results

The results of the 24-hour electrolyte adsorption test are presented in Table XIV that shows cobalt and nickel concentrations and removal efficiencies. The removal efficiencies are also shown in Figure 28. The activated carbons adsorbed only small percentages of the cobalt and nickel amounts, since they averagely removed less than 10% of the initial amounts. An exception was made by Silcarbon K835 adsorbed 56,1% and Norit GAC 1240W 22,1% of the initial cobalt content. It was decided that cobalt and nickel adsorptions from the electrolyte solution were low enough for the activated the filtration. Since the contact time in the filtration is significantly shorter than in the adsorption test, the metal ion removal was assumed to be close to zero during the filtration. Metal ion adsorption from electrolyte solution was also not considered as a competitive factor for the organic phase adsorption.

Table XIV Concentrations (mg/l) and removal efficiencies (%) of cobalt and nickel after 24-hour adsorption. Used feed solution contained 3 g/l cobalt, 30 g/l nickel and 1 % H_2SO_4.

Adsorbent	Cobalt		Nickel	
	[g/l]	Removal efficiency, [%]	[g/l]	Removal efficiency, [%]
Filtrasorb 400	3,1	0,0	30,5	0,0
Filtrasorb 300	2,7	9,5	27,1	9,6
Aquasorb H150	2,8	7,7	27,8	7,5
LGCO 100	2,9	5,0	28,4	5,5
S835	1,3	56,1	27,6	8,2
Norit 1240W	2,3	22,1	27,8	7,5

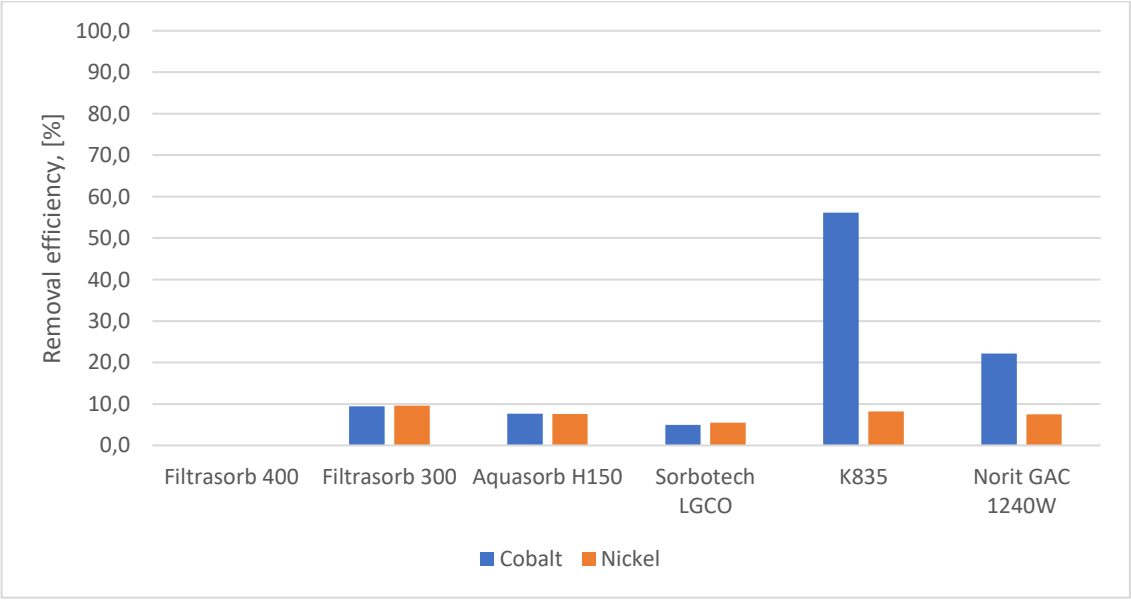

Figure 28 Removal efficiencies (%) of cobalt and nickel after 24-hour adsorption. Used feed solution contained 3 g/l of cobalt, 30 g/l nickel and 1 % of H_2SO_4. Adsorbent dosages were 30 g for each activated carbon.

12.2 Activated carbon filtration results

The cobalt raffinate filtration results of the commercial activated carbons are represented in Table XV that shows the organic phase concentrations of the filtration samples. The table XV shows that the organic phase concentrations of the impurity raffinate effluents vary between 2.5-8.0 mg/l. The average organic phase concentration by activated carbon filtration was 4.8 mg/l in the impurity raffinate effluents. The lower concentrations of 2.5-3.6 mg/l achieved with medias Filtrasorb 300, Filtrasorb 400 and Aquasorb H150 during the first 45 min were caused by a linear flow of 8-10 m/h. The lower flow rate provided more contact time for the organic removal than the target flow rate of 12 m/h, thus the filtration was more effective.

As shown in Figures 29 and 30, the organic concentration values follow a steady line with all the activated carbons and there are no significant deviations among the values. It can be also seen, that the are no significant differences in the filtration among the activated carbon medias. The average organic concentration in the effluents per filter media was 4,0 mg/l with Fitrasorb 300, 3.8 mg/l with Filtrasorb 400, 4.4 mg/l with Aquasorb H150 5.7 mg/l with K835, 5.9 mg/l with LGCO 100 and 5.2 mg/l with Norit GAC 1240W.

Table XV Organic phase concentrations (mg/l) of impurity raffinate effluents after activated carbon filtration. The linear flow was 12 m/h, the bed height of activated carbons was 7 cm, the temperature target was 40 °C, the targeted organic feed was 50 mg/l and the pH was 2.2-2.6.

Organic phase concentrations (mg/l) in filtration effluents							
Time, [min]	AquaSorb H150	Filtrasorb 300	Filtrasorb 400	Time, [min]	K835	LGCO 100	Norit GAC 1240W
	[mg/l]	[mg/l]	[mg/l]		[mg/l]	[mg/l]	[mg/l]
0	2,8	2,9	2,8	0	6,6	7,4	5,0
15	2,5	2,9	2,5	15	4,6	5,4	3,7
30	3,1	4,2	3,1	30	4,9	5,8	5,3
45	3,6	3,0	3,6	45	4,9	4,9	5,8
75	4,0	3,9	4,0	75	5,2	5,3	5,0
115	4,2	3,8	4,2	105	4,9	5,8	5,1
150	4,4	3,5	4,4	135	5,7	6,2	6,3
180	4,3	3,8	4,3	165	5,5	6,1	4,5
205	4,5	4,3	4,5	195	5,0	5,7	6,4
235	4,1	4,2	4,1	225	5,6	5,8	5,4
265	6,0	5,2	6,0	255	5,3	6,2	4,6
295	4,3	3,9	4,3	285	6,0	5,8	5,3
325	3,8	4,2	3,8	320	8,0	6,4	5,0
360	4,4	3,7	4,4	360	7,3	5,4	6,0

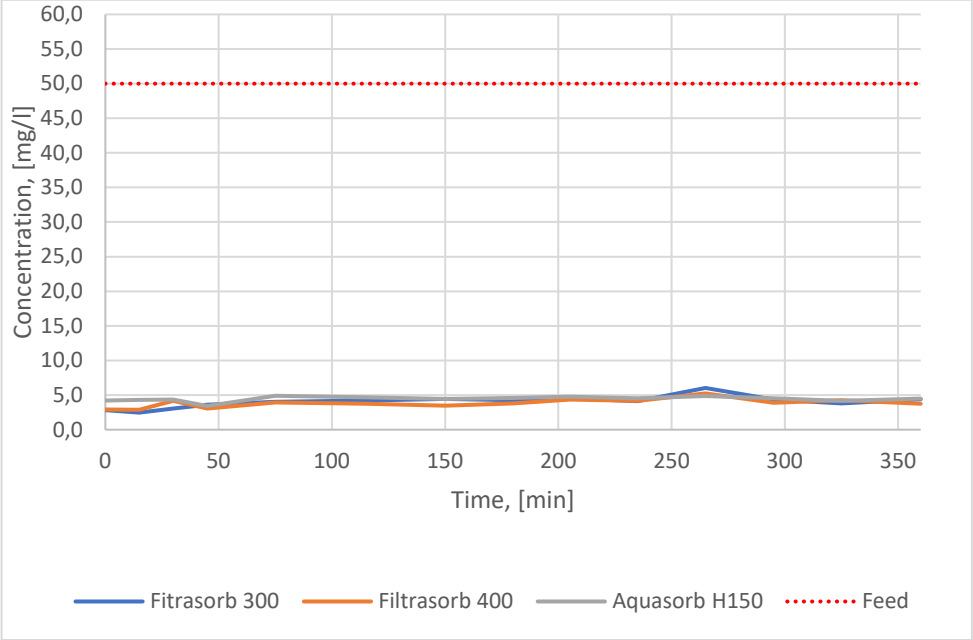

Figure 29 Organic phase concentrations (mg/l) of impurity raffinate filtration effluents with Filtrasorb 300, Filtrasorb 400 and Aquasorb H150. The duration was 6 hours, the linear flow was 12 m/h, the bed height was 7 cm, the temperature was 37-39 °C, the targeted organic feed was 40 mg/l and the pH was 2.2-2.5.

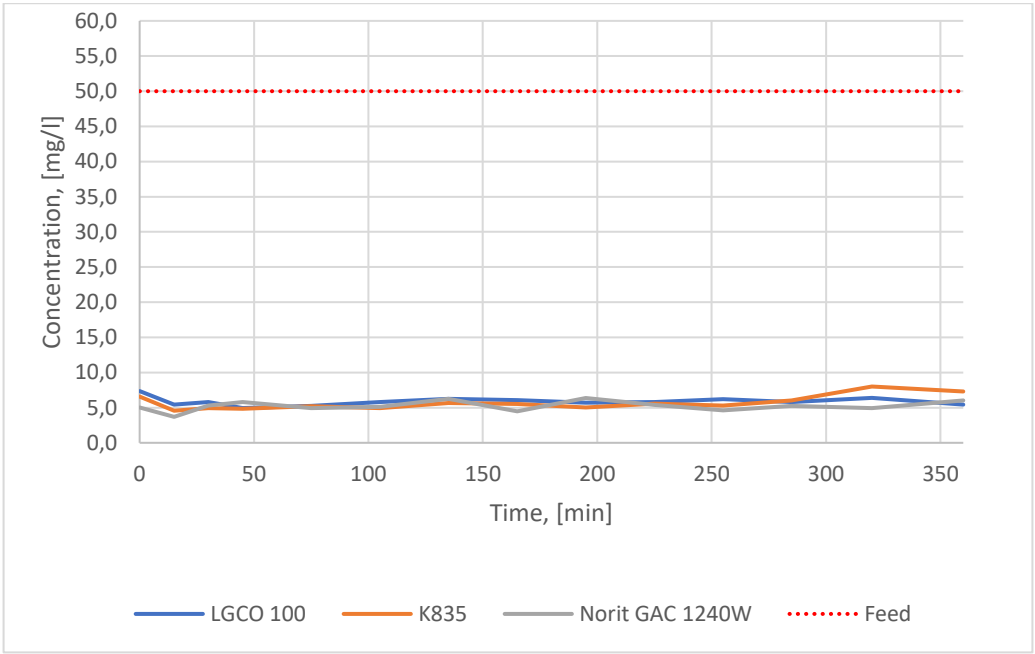

Figure 30 Organic phase concentrations (mg/l) of impurity raffinate filtration effluents with LGCO 100, K835 and Norit GAC 1240W. The duration was 6 hours, the linear flow was 12 m/h, the bed height was 7 cm, the temperature was 38-42 °C, the targeted organic feed was 50 mg/l and the pH was 2.4-2.6.

The Table XVI shows that the organic phase concentrations of the cobalt raffinate effluents fall between values 2.9-12.3mg/l. The average organic concentration in the cobalt raffinate effluents was 5.0 mg/l. It can be seen in Figures 31 and 32, that the organic concentrations of cobalt raffinate effluents follow the same behavior as the organic concentrations in the impurity raffinate. Filtration with AquaSorb H150 and Filtrasorb 300 had a few larger values in the organic phase concentrations. However, the deviations were under 15mg/l and the rest of the organic concentrations follow line between values 4-7 mg/l. The deviations of 8-12.3mg/l were likely due to a cluster of organic droplets in the feed since majority of the organic concentration was close to 5 mg/l. The average organic concentration in the effluents per filter media was 6.0 mg/l with Fitrasorb 300, 4.8 mg/l with Filtrasorb 400, 5.8 mg/l with Aquasorb H150, 4.4 mg/l with K835, 4.9 mg/l with LGCO 100 and 3.7 with Norit GAC 1240W. Norit GAC 1240W achieved the lowest organic concentrations in the cobalt raffinate filtration and was only activated carbon to reach 2.9 mg/l at 12 m/h.

Table XVI Organic phase concentrations (mg/l) of cobalt raffinate effluents after activated carbon filtration. The linear flow was 12 m/h, the bed height of activated carbons was 7 cm, the temperature target was 50 °C, the targeted organic feed was 50 mg/l and the pH was 3.2-3.7.

Organic phase concentrations (mg/l) in filtration effluents							
Time, [min]	AquaSorb H150 [mg/l]	Filtrasorb 300 [mg/l]	Filtrasorb 400 [mg/l]	Time, [min]	K835 [mg/l]	LGCO 100 [mg/l]	Norit GAC 1240W [mg/l]
0	8,0	6,4	4,8	0	9,0	7,3	7,4
15	5,4	5,2	4,8	15	3,6	4,5	3,8
30	4,8	4,7	6,0	30	3,5	4,4	3,8
45	6,4	12,3	6,2	45	3,8	4,3	3,3
80	4,9	4,8	5,2	80	3,6	4,2	2,9
105	4,8	4,7	6,1	105	4,1	5,3	3,4
135	4,6	4,7	4,4	135	3,7	5,1	3,0
165	6,6	4,9	4,4	165	3,7	5,1	3,2
195	5,7	5,4	4,3	195	4,0	5,6	3,1
225	8,7	5,9	3,8	225	4,3	4,8	3,5
255	5,2	6,1	4,0	285	4,3	3,6	4,6
285	4,5	9,6	4,5	305	4,8	4,8	3,2
315	5,5	5,2	4,6	335	4,8	5,2	3,4
360	5,9	4,6	4,3	360	4,7	5,1	3,9

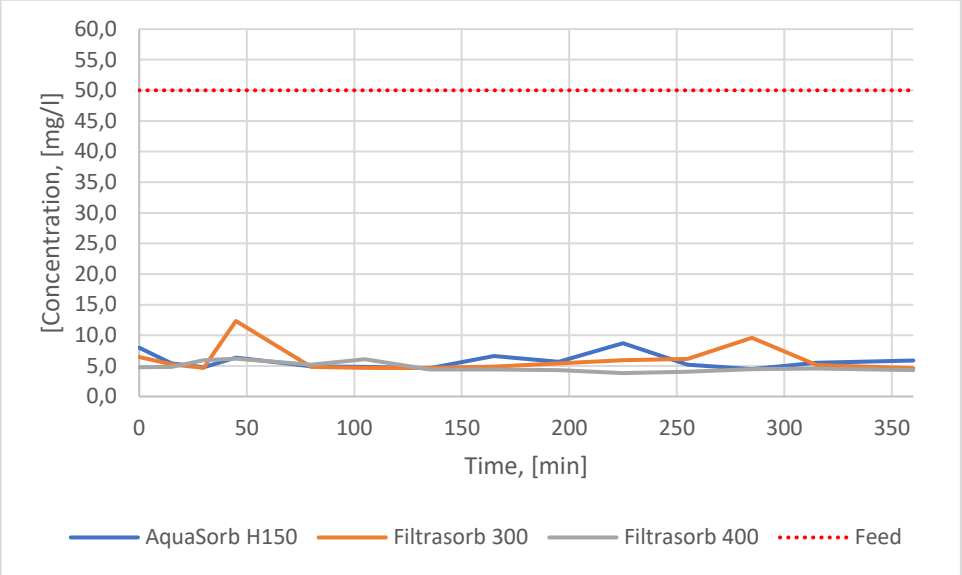

Figure 31 Organic phase concentrations (mg/l) of cobalt raffinate filtration effluents with Filtrasorb 300, Filtrasorb 400 and Aquasorb H150. The duration was 6 hours, the linear flow was 12 m/h, the bed height was 7 cm, the temperature was 45-50 °C, the targeted organic feed was 50 mg/l and the pH was 3.2-3.3.

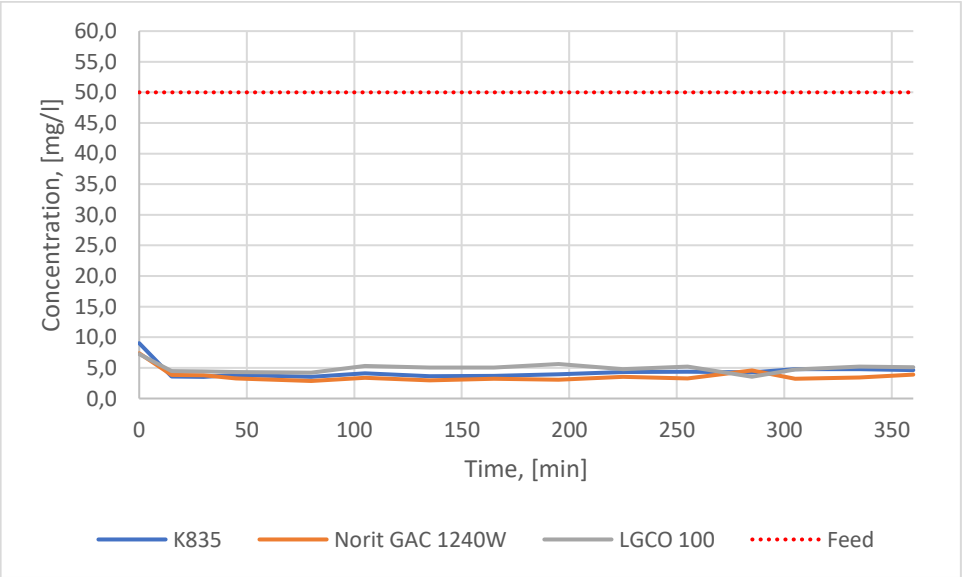

Figure 32 Organic phase concentrations (mg/l) of cobalt raffinate filtration effluents with LGCO 100, K835 and Norit GAC 1240W.The duration was 6 hours, the linear flow was 12 m/h, the bed height was 7 cm, the temperature was 45-48 °C, the targeted organic feed was 50 mg/l and the pH was 3.5-3.7.

There were no large differences in filtration results between the raffinate solutions. Medias Filtrasorb 300, Filtrasorb 400 and Aquasorb H150 performed more effectively with impurity

raffinate than with cobalt raffinate, while medias LGCO 100, K835 and Norit GAC 1240W achieved more effective filtration with the cobalt raffinate. The activated carbons proved to be able reach the organic phase limit of 5 mg/l with both raffinate effluents but not the limit of 2 mg/l. At best, the activated carbons achieved an organic phase concentration of 2.9 mg/l with the target flow rate. It noteworthy that the activated carbons also let organic concentrations above 5 mg/l pass through.

Coalescing phenomenon was not observed during the filtration since no organic droplets were seen on the liquid surfaces in the filtration columns. There is no saturation of the activated carbons to be detected in figures 29, 30, 31 or 32 since the organic concentrations stay around the same values during the filtration runs. Thus, the adsorption capacity of the activated carbons was not filled during 6-hour filtration at a bed height of 7 cm and duration. A full saturation of the activated carbons would require taller bed height, higher organic feed concentration or longer the filtration duration. Adsorption isotherms were not formed for the executed filtrations since the activated carbon beds did not get saturated, and since there are no precise data on the organic phase concentration in the feed solution.

The effect of solution temperature on the filtration can't be determined since half of the activated carbons performed filtration more effectively at 40 °C impurity raffinate and the other half at 50 °C with cobalt raffinate. Based on adsorption kinetics the lower temperature should have been more favorable for the filtration (Marczewski et al., 2016), which applied to filtrations with Filtrasorb 300, Filtrasorb 400 and Aquasorb H150. The target pH of 5.5 for the cobalt raffinate solution was not achieved in the activated carbon filtrations. The effects of pH on the filtration can't be determined either due to low pH differences between the raffinate solutions.

12.2.1 Effects of the physical properties of activated carbon on filtration

The manufactures of the used activated carbons have reported bulk densities, surface areas and particle sizes of their products, listed in Table V. In the comparison of the physical properties, there was used the averages of the organic concentrations of the filtration effluents. Effect of particle size on electrolyte filtration is shown in Figure 33, where there are three different particle sizes for the activated carbons. No significant effect of the particle size of the activated carbon on the filtration was observed, as the average organic effluent

concentrations differ only by 2 mg/l at most from each other. It is noticeable that activated carbons with particle size range of 0.425-1.7 mm (Mesh 12x40) achieved averagely lower organic concentrations in the effluents than activated carbons with particle size 0.6-2.36 (Mesh 6x30) in both raffinate solutions. This indicates that smaller particle size of the activated carbons has a positive effect on the electrolyte filtrations process. The activated carbons with a particle size range of 0.5-2.5 performed the most effectively with the cobalt raffinate and the least effectively with the impurity raffinate. This supports the positive effect of smaller particle sizes on the removal of organic material in the impurity raffinate filtration but negates its effect in the cobalt raffinate filtration.

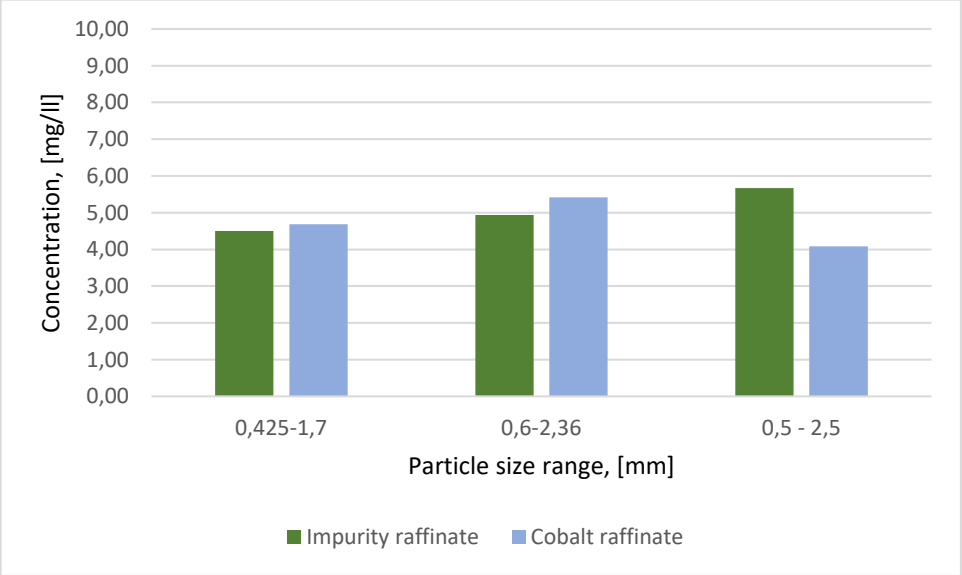

Figure 33 Effect of activated carbon particle size range [mm] on the organic concentrations [mg/l] of the filtration effluents. The average organic concentrations of the filtration effluents were used in the comparison.

The surface areas of the used activated carbons vary only in the range of 950-1100 m^2/g. The effects of the surface areas of the activated carbons are shown in Figure 34. The lowest average organic concentration of the cobalt raffinate filtration was reached with a surface area of 1100 m^2/g by Norit GAC 1240W and in impurity raffinate with 1050 m^2/g by Filtrasorb 400. In cobalt raffinate filtration there is a dim trend to be observed where activated carbons with larger surface areas have lower organic concentration in the effluents, whereas in the impurity raffinate filtration there is no clear indications that larger surface

areas would increase organic removal. Generally, the larger surface areas provide more contact area for compounds to adsorb. It is notable that surface chemistry of activated carbon surfaces also affects the adsorption and if the surface chemistry is not favorable for the adsorption process, the surface area of pores can't be exploited. (Radovic et al., 2000) (Bansal & Goyal, 2005) Pore size distribution of the activated carbon plays also a role in the adsorption, since if the pore radius is too small for the adsorbate to access, the inner surface areas can't be exploited either. (Moreno-Castilla, 2004)

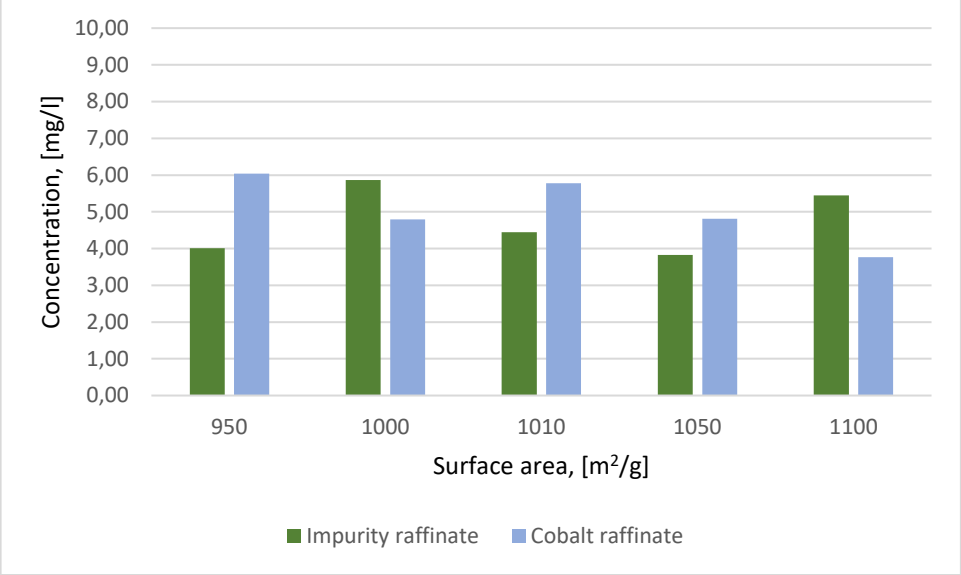

Figure 34 Effect of activated carbon surface areas [m^2/g] on the organic concentrations [mg/l] of the filtration effluents. The average organic concentrations of the filtration effluents were used in the comparison.

The effect of activated carbon bulk density is presented in Figure 35. The bulk densities of the used activated carbons vary between 470-560 kg/m^3. There is no trend to be seen, that bulk density would affect organic removal since the average organic concentrations vary back and forth in the bulk density range. In general, there is little information about the effects of activated carbon bulk densities on adsorption processes. Activated carbon manufactures provide the bulk density value since it is a useful tool for dimensioning activated carbons filters.

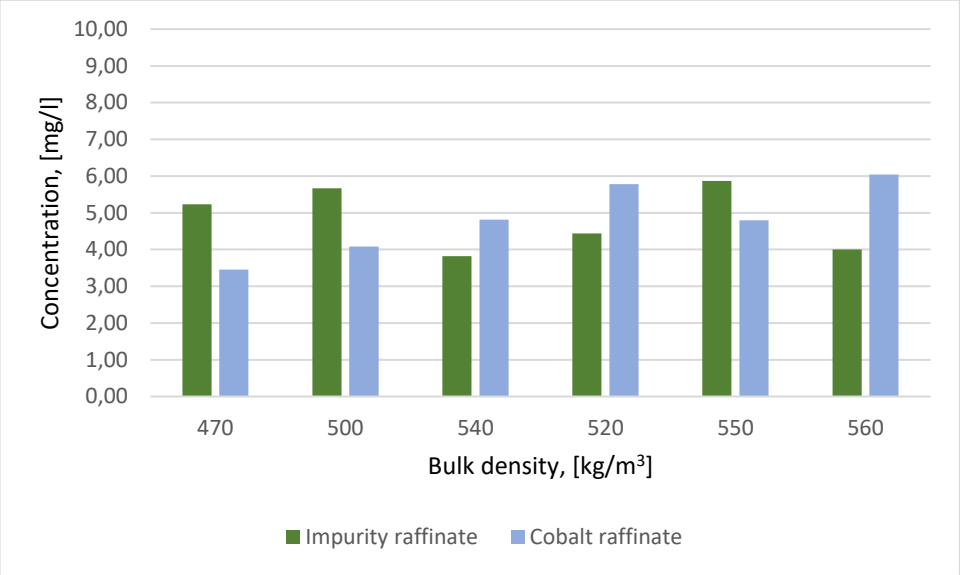

Figure 35 Effect of activated carbon bulk densities [kg/m^3] on the organic concentrations [mg/l] of the filtration effluents. The average organic concentrations of the filtration effluents were used in the comparison.

12.3 Electrolyte filtration with biochar

The electrolyte filtration results of the biochar products are presented in the Table XVII where there is shown the organic phase concentrations of the filtration samples. Table XVII shows that of the organic concentrations of the impurity raffinate effluents vary between 3.8-6.2 mg/l, whereas the organic concentrations of the cobalt raffinate effluents vary between 7.7-27.5 mg/l. The average organic concentration was 4.7 mg/l in the impurity raffinate effluents and 13.2 mg/l in the cobalt raffinate effluents. Particle size difference of biochar is affected greatly on the organic phase removal since the biochar particle range 0-2mm removed significantly more effectively organic phase from the impurity raffinate than the biochar particles with size range of 0.425-2mm from the cobalt raffinate.

Table XVII Organic phase concentrations (mg/l) of impurity and cobalt raffinate effluents after biochar filtration. The linear flow was 12 m/h, the bed height of biochars was 7 cm, the targeted organic feed was 50 mg/l.

Organic phase concentrations (mg/l) in filtration effluents							
Impurity raffinate				Cobalt raffinate			
Time, [min]	Birch	Spruce (1)	Spruce (2)	Time, [min]	Birch	Spruce (1)	Spruce (2)
	[mg/l]	[mg/l]	[mg/l]		[mg/l]	[mg/l]	[mg/l]
0	4,9	5,6	6,2	0	22,6	22,7	16,0
15	5,0	4,9	5,2	15	27,5	20,0	22,0
30	3,9	4,5	4,8	30	20,8	13,9	16,4
45	4,4	4,8	5,2	45	16,4	13,6	15,1
75	4,4	4,2	5,1	75	16,4	11,8	14,3
110	3,8	4,6	4,8	115	14,9	10,2	12,8
140	4,4	4,7	4,5	150	14,2	9,2	11,8
170	4,8	4,7	4,7	180	10,1	8,3	10,2
200	4,8	4,8	4,5	205	10,4	10,2	10,2
230	5,0	4,5	4,6	235	10,4	9,1	10,7
260	4,4	4,7	4,1	265	10,7	8,3	10,2
290	4,6	4,8	4,6	295	11,1	9,7	11,1
320	4,7	5,1	4,7	325	11,0	10,3	11,3
360	4,5	4,8	4,6	360	10,3	7,7	9,5

It can be seen in Figure 36 that the organic concentrations of cobalt raffinate effluents follow the same behavior as with the activated carbon filtration, since the concentrations follow approximately a steady line at 5 mg/l. It is notable that in impurity raffinate filtration the columns got clogged several times during filtration runs due to the small particle sizes of the biochars. The clogging of the columns caused increases in column pressures and decreases in flow rates. Linear flow rate varied approximately between 6-12 m/h during filtration run. It can be assumed that lower organic effluent concentrations in cobalt raffinate filtration are due to the clogging since it provided a longer contact time for the filtration.

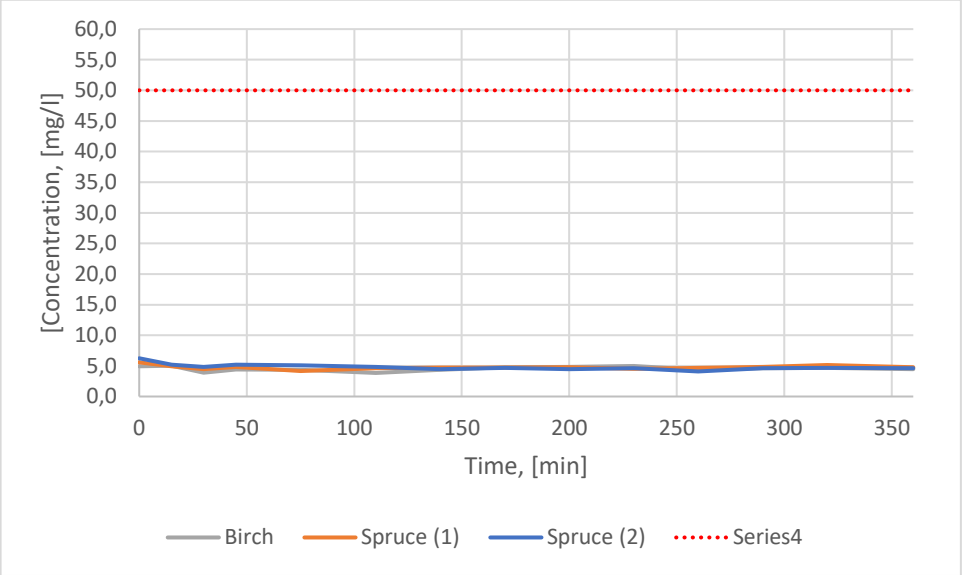

Figure 36 Organic phase concentrations (mg/l) of impurity raffinate filtration effluents with spruce (1), spruce (2) and birch. The duration was 6 hours, the linear flow was 12 m/h, the bed height was 7 cm, the temperature was 38-40 °C, the targeted organic feed was 50 mg/l and the pH was 2.2-2.3.

In figure 37 there can be seen large differences in the organic concentrations of the impurity raffinate effluents. A stabilization in the values can be observed only after 180 min. The large organic effluent concentration of 14-28 mg/l during the first 180 min of the cobalt raffinate filtration were likely due to a wetting of the biochar particles. At beginning of the filtration, the influent probably passed through particles without a proper contact, and during the filtration, the biochar particles were more tightly packed into the column due to the wetting of the particles. The wetting of the particles and the tighter packing of the biochar bed explain the decreasing and the stabilization of the organic phase concentrations.

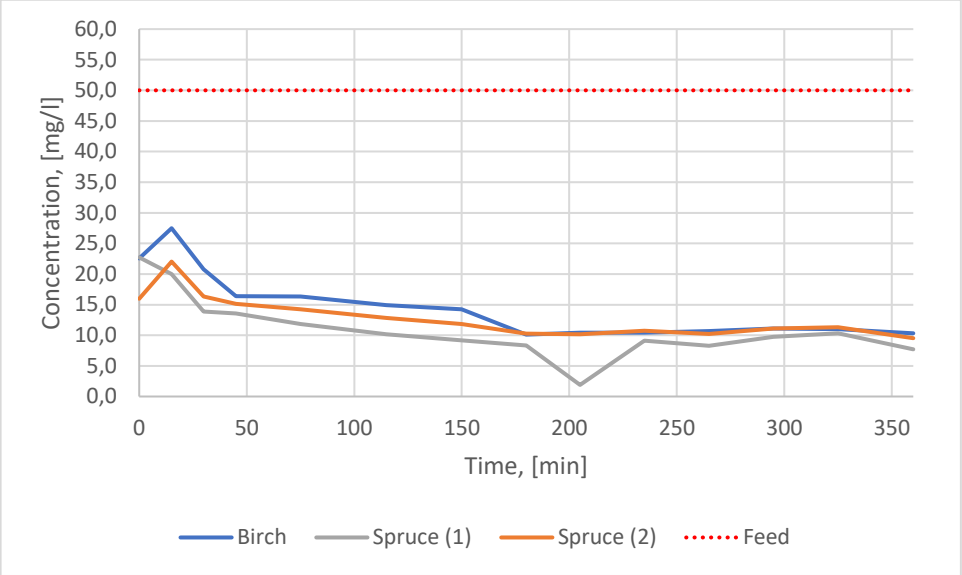

Figure 37 Organic phase concentrations (mg/l) of cobalt raffinate filtration effluents with spruce (1), spruce (2) and birch. The duration was 6 hours, the linear flow was 12 m/h, the bed height was 7 cm, the temperature was 45-52 °C, the targeted organic feed was 50 mg/l and the pH was 5.3-5.5.

In Figure 38 there is shown the average organic concentrations of the biochar filtration effluents. There were no significant filtration differences between biochar materials in the impurity filtration. In the cobalt raffinate test spruce (1) removed averagely more organic matter than spruce (2) or birch. Notable is that spruce (2) with surface area of 550 m^2/g did not remove organic matter more than spruce (1) with 280 m^2/g or birch with 280 m^2/g. This indicates that the surface chemistry of the biochars affects the filtration more than the surface areas.

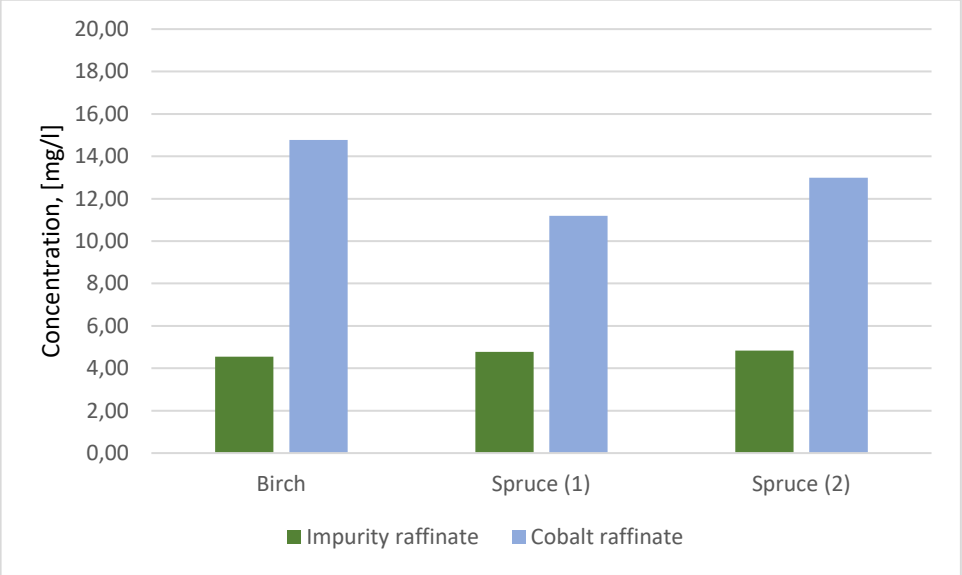

Figure 38 The average organic concentrations [mg/l] of the filtration effluents with biochar materials.

12.4 Electrolyte filtration with alternative medias

The electrolyte filtration results of the alternative medias are presented in the Table XVIII where there is shown the organic phase concentrations of the filtration samples. The organic concentrations of the electrolyte effluents were between 4.4- 10.9 mg/l in the impurity raffinate and 4.2-20.4 mg/l in the cobalt raffinate. Averagely the medias performed more effectively with impurity raffinate solution than cobalt raffinate since the average organic concentration was 5.8 mg/l in the impurity raffinate effluents and 6.8 mg/l in the cobalt raffinate effluents.

The alternative medias performed steady filtrations with both raffinate solutions shown in Figures 39 and 40. There were a few organic bursts in the cobalt raffinate effluents which can be seen in Figure 8. The rest of the organic phase concentrations followed a steady trend in both raffinate filtrations. Figures 7 and 8 also show that increasing the linear flow rate from 16 m/h to 24 m/h did not affect the filtration, since the organic concentrations remain at the same value range after the change. It is noteworthy that the medias achieved equally low organic concentration at flow rates of 16 m/h and 24 m/h. In general, filter medias perform less effectively with higher flow rates since the contact time of the filtration is shorter.

Table XVIII Organic phase concentrations (mg/l) of impurity and cobalt raffinate effluents after filtration with alternative medias. The linear flow was 16-24 m/h, the bed height was 7 cm, the targeted organic feed was 50 mg/l.

Organic phase concentrations (mg/l) in filtration effluents								
Linear flow, [m/h]	Impurity raffinate				Cobalt raffinate			
	Time, [min]	Media (1) [mg/l]	Media (2) [mg/l]	Media (3) [mg/l]	Time, [min]	Media (1) [mg/l]	Media (2) [mg/l]	Media (3) [mg/l]
16	0	9,8	10,9	5,8	0	7,4	11,2	6,3
16	15	5,7	6,5	4,7	15	14,1	20,4	12,3
16	30	5,7	6,6	4,6	30	6,7	6,0	6,8
16	45	5,9	6,3	5,0	45	5,3	5,5	5,0
16	60	5,4	6,2	4,4	60	4,9	4,6	4,5
16	90	5,4	6,4	4,8	90	5,4	6,7	6,7
24	95	5,0	5,7	5,0	95	7,6	10,4	7,3
24	110	6,2	6,1	5,3	110	7,9	8,9	7,1
24	120	5,7	5,6	5,0	125	5,3	4,6	5,0
24	135	5,2	4,6	4,9	140	4,7	5,0	4,7
24	150	6,0	4,9	4,7	155	4,8	4,2	5,9
24	180	5,5	5,9	4,7	185	4,8	5,1	5,1
24	215	7,5	6,0	5,3	215	4,8	5,8	5,3

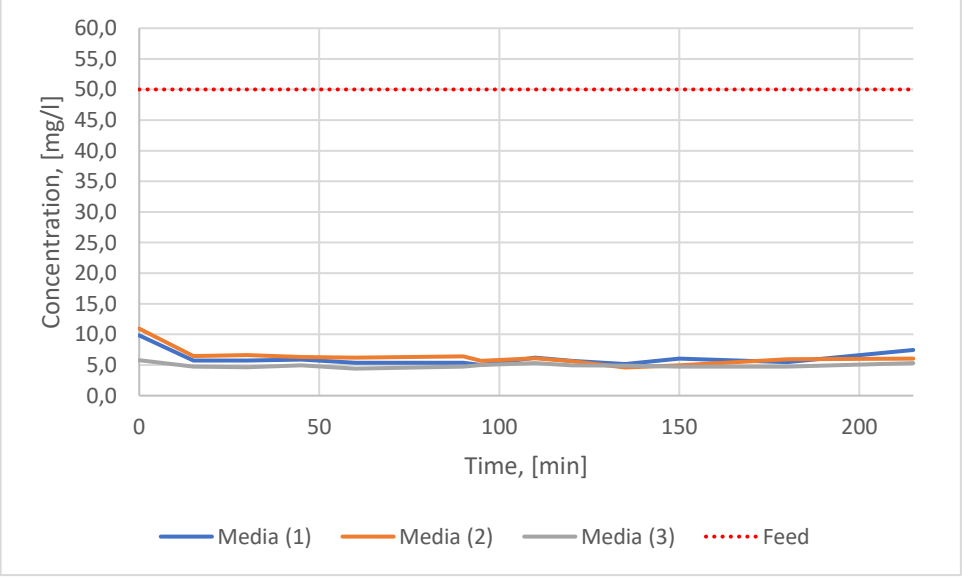

Figure 39 Organic phase concentrations (mg/l) of impurity raffinate filtration effluents with alternative filter medias. The duration was 215 min, the linear flow was 16 m/h at 0-90 min and 24 m/h at 90-215 min, the bed height was 7 cm, the temperature was 39-42 °C, the targeted organic feed was 50 mg/l and the pH was 2.2-2.5.

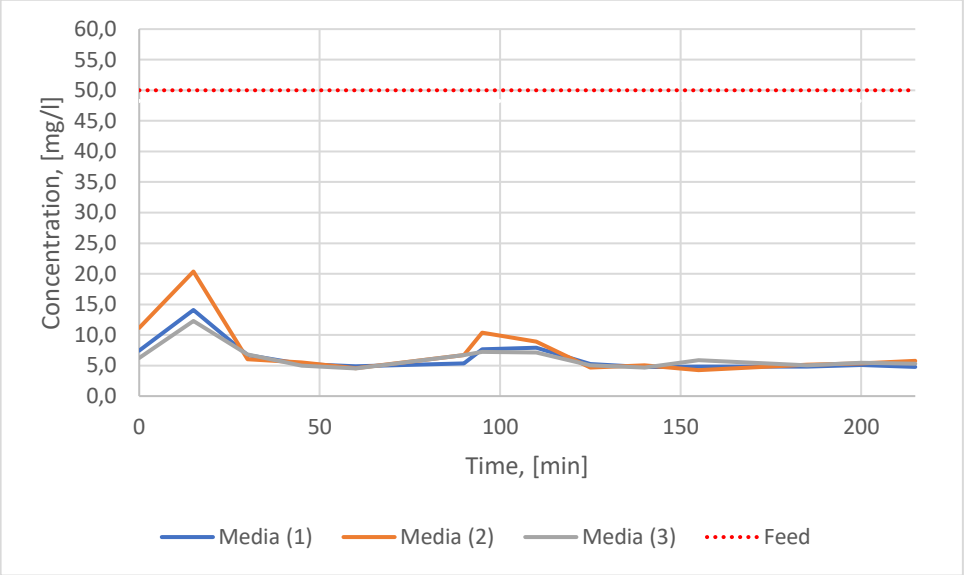

Figure 40 Organic phase concentrations (mg/l) of cobalt raffinate filtration effluents with alternative filter medias. The duration was 215min, the linear flow was 16 m/h at 0-90 min and 24 m/h at 90-215 min, the bed height was 7 cm, the temperature was 45-52 °C, the targeted organic feed was 50 mg/l and the pH was 3.6-3.7.

Filtrations between the alternative medias are compared in Figure 41 where there is shown average concentrations of organic phase in filtration effluents. It can be seen in Figure 12 that media (1) and media (3) with particle size range of 0.4-0.6 mm removed slightly more effectively organic matter from both raffinate solutions than media (2) with particle size of 0.75-1 mm. Media (3) with bulk density of 2390 kg/m^3 achieved lower organic concentrations in both raffinate effluents than media (1) and media (2) with densities of 1470-1500 kg/m^3.

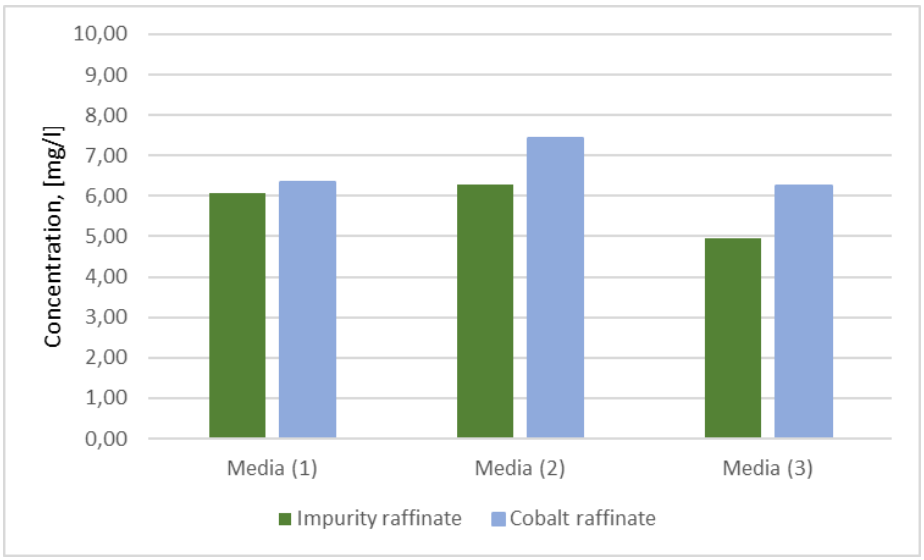

Figure 41 The average organic concentrations [mg/l] of the filtration effluents with alternative filter medias.

13 Conclusions

The purpose of the electrolyte filtration tests was to determine if commercial activated carbons are suitable filter media for organic phase removal from electrolyte solutions. Linear flow rate of 12 m/h was used in the filtrations. Target organic feed concentration was 50 mg/l. In addition to activated carbon filtration, also biochar products and the alternative filter media were used in the electrolyte filtrations tests. The target limit of the organic concentrations in filtration effluents was 2-5 mg/l. An additional purpose was to determine experimentally an optimal bed height for activated carbon filtration but since the used activated carbons did not get saturated during the filtration tests, it was not possible to model adsorption isotherms for the activated carbon filtrations or to determine the optimal bed heights.

Based on the filtration test runs, the commercial activated carbons were able to reach the upper organic phase limit of 5 mg/l in the electrolyte effluents but not lower limit of 2 mg/l. At best the activated carbons achieved 3-4 mg/l organic concentrations at the flow rate of 12 m/h. There were no large differences in the organic effluent concentration between the electrolyte raffinate solutions. Averagely the organic phase concentrations were 5 mg/l in the impurity raffinate and cobalt raffinate effluents. When the linear flow rate was under 12 m/h, the activated carbon reached 2,5-3 mg/l organic concentrations. This indicates that the commercial activated carbons could be capable of reaching the lower organic limit of 2 mg/l with lower flow rates.

The effects of the physical properties of the activated carbons on filtration were also examined. It was observed from the effects of the physical properties that activated carbons with particle size of 0.425-1.7 mm removed slightly more effectively organic phase than activated carbons with larger particle size. Surface areas or bulk densities of the activated carbons did not affect significantly on the filtration. However, activated carbons with larger surface of 1050 m^2 or higher achieved slightly lower organic phase concentrations in the cobalt raffinate effluents than activated carbons with smaller surface areas.

Unexpectedly the biochar products achieved equally effective filtration results with the impurity raffinate solution than the activated carbons. However, in the cobalt raffinate filtration the organic effluent concentrations were averagely more than two times larger with the biochar products than with the activated carbons. Organic concentrations after the

biochar filtration were averagely 5 mg/l in the impurity raffinate effluents and 13 mg/l in cobalt raffinate effluents. It is notable that the low organic concentrations in the impurity raffinate filtration were due to small biochar particles which caused clogging in the filter columns. Biochar products are not yet suitable filtration materials since they can fall apart during the filtration or cause clogging if the particle size is too small.

Linear flow rates of 16 m/h and 24 m/h were tested in filtration with the alternative filter materials. A notable observation from the test results was that filtration at a higher flow rate of 24 m/h removed organic phase as effectively as at the lower flow rate of 16 m/h. The filter medias achieved averagely 6 mg/l organic concentrations in the filtration effluents at both flow rates. A recommendation for further filtration studies with the alternative filter media is to test even higher flow rates than 24 m/h and to determine at what flow rate the organic effluent concentrations start to rise.

Further studies are recommended for activated carbon filtration since accurate profiles of organic feed concentrations or organic removal efficiencies could not be determined. It is recommendable to test the limits of activated carbon filtration in organic removal at higher concentrations of organic feed, such as 100-200 mg/l, to see how the organic feed concentrations affect the filtration. Determining the optimal height of the activated carbon bed for filtration at 12 m/h requires additional tests since the saturation point of activated carbons was not reached in the filtrations. To reach the saturation point of the activated carbons, the filtration requires a longer filtration duration, a shorter activated carbon bed height or a higher organic feed concentration. A coalescing phenomenon was not detected with the activated carbons during the filtration. If the activated carbons perform coalescing after saturation, it would be important to compare removal efficiencies between adsorption and coalescing.

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