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ADSORPTION OF HYDROGEN SULFIDE BY MODIFIED CELLULOSE NANO/MICROCRYSTALS

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ABSTRACT

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Adsorption of hydrogen sulfide using modified cellulose nano/micro crystals

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Hydrogen sulfide is toxic and hazardous pollutant. It has been under great interest for past few years because of all the time tighten environmental regulations and increased interest of mining. Hydrogen sulfide gas originates from mining and wastewater treatment systems have caused death in two cases. It also causes acid rains and corrosion for wastewater pipelines.

The aim of this master thesis was to study if chemically modified cellulose nanocrystals could be used as adsorbents to purify hydrogen sulfide out from water and what are the adsorption capacities of these adsorbents. The effects of pH and backgrounds on adsorption capacities of different adsorbents are tested. In theoretical section hydrogen sulfide, its properties and different purification methods are presented. Also analytical detection methods for hydrogen sulfide are presented. Cellulose nano/microcrystals, properties, application and different modification methods are discussed and finally theory of adsorption and modeling of adsorption is shortly discussed. In experimental section different cellulose nanocrystals based adsorbents are prepared and tested at different hydrogen sulfide concentrations and in different conditions.

Result of experimental section was that the highest adsorption capacity at one component adsorption had wet $\mathrm{MFC/CaCO_3}$. At different pH the adsorption capacities of adsorbents changed quite dramatically. Also change of hydrogen sulfide solution background did have effect on adsorption capacities. Although, when tested adsorbents' adsorption capacities are compared to those find in literatures, it seems that more development of MFC based adsorbents is needed.

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
Teknillinen tiedekunta
Ympäristötekniikan koulutusohjelma

Aki Heinonen

Rikkivedyn erottaminen vedestä modifioidulla nano/mikro selluloosalla

Diplomityö

2012

73 sivua, 10 kuvaa, 9 taulukkoa ja 5 liitettä

Tarkastajat: Professori Mika Sillanpää
Professori Risto Soukka

Hakusanat: Rikkivety, adsorptio, nano/mikro selluloosa, kemiallinen modifiointi, pH

Rikkivety on myrkyllinen ja haitallinen yhdiste. Rikkivety on kiinnostuksen kohteena tiukkenevien ympäristölakien ja lisääntyvän kaivosteollisuuden takia. Kaivosteollisuudesta ja vedenpuhdistusprosessista peräisin olevalle rikkivedylle altistuminen on kahdessa tapauksessa johtanut altistuneiden henkilöiden kuolemaan. Luonnossa rikkivety hapettuu rikkihapoksi, joka aiheuttaa happosateita. Rikkivety on korroosiota aiheuttava aine betoniputkistossa.

Tämän diplomityön tarkoituksena oli tutkia, voidaanko kemiallisesti modifioituja nano/mikro selluloosaa käyttää rikkivedyn erottamiseksi vedestä adsorbenttina, sekä mitkä ovat eri adsorbenttien adsorptiokapasiteetit. Veden pH:n ja suolapitoisuuden muutoksen vaikutuksia adsorbenttien adsorptiokapasiteetteihin tutkittiin. Työn teoriaosassa tutustutaan rikkivedyn ominaisuuksiin sekä muihin tutkittuihin puhdistusmenetelmiin. Lisäksi perehdytään nanoselluloosan valmistukseen, ominaisuuksiin, käyttökohteisiin sekä pinnan kemialliseen modifiointiin. Vesinäytteessä olevan rikkivedyn analyyttisiin määrittämiskeinoihin perehdytään. Lisäksi lyhyesti tutustutaan adsorption teoriaan ja mallintamiseen. Kokeellisessa osassa valmistetaan erilaisia nanoselluloosapohjaisia adsorbentteja ja tutkitaan niiden adsorptiokapasiteettejä sekä eri pH:n ja liuoksen taustan vaikutusta adsorptiokapasiteetteihin.

Kokeellisen osan perusteella paras adsorptiokapasiteetti on kostealla $\mathrm{MFC/CaCO_3}$:llä. pH:n muuttaminen vaikutti adsorbenttien adsorptiokapasiteetteihin melko voimakkaasti. Lisäksi liuoksen taustan muuttamisella on vaikutusta adsorptiokapasiteetteihin, mutta vaikutus ei ollut niin suuri kuin pH:n säädöllä. Kirjallisuudesta löydettyihin adsorbentteihin verrattuna nanoselluloosaan perustuvia adsorbenttejä tulee jatkossa kehittää.

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This Master Thesis is made in Laboratory of Green Chemistry, Mikkeli between April and October of 2012 as part of TEKES-project where the possibility to use of cellulose nano/micro crystals as adsorbent or nanocatalyst were studied. I would like to thank both of my examiners Professor Mika Sillanpää, head of LGC and Professor Risto Soukka for giving me opportunity to study this interesting subject. I would like to thank to both of my instructors Eveliina Repo and Sanna Hokkanen and rests of the researchers from Laboratory of Green Chemistry for advises and help during this process.

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Lots of time it has taken, but like Norwegian ski coach said: “*It is not the hours you put into your works that counts. It’s the work you put into those hours.”*

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Acronyms

AGU	equivalent anydroglucose unit
ARE	average relative error
ASA	alkyenyl succinic anhydride
CNC	cellulose nanocrystal
CNC-CA	cellulose nanocrystal
CNC-HEC	cellulose nanocrystal with epoxy etanol
CNC-HPC	cellulose nanocrystal with epoxy propane
DTA	differential thermal analysis
EABS	sum of absolute errors
EPA	Environmental protection Agency
ERRSQ	sum of the square of the errors
GC	gas chromatography
GC-FPD	gas chromatography with flame photometric detector
GC-PFPD	gas chromatography with pulsed flame photometric detector
HPLC	high performance liquid chromatograph
HPTMAC-CNC	hydroxypropyltrimethyl ammonium chloride cellulose nanocrystals
HYBRID	hybrid error function
IC	ion chromatograph
ICP	inductively coupled plasma
ICP-OES	inductively coupled plasma optical emissions spectrometry
ISE	ion selective electrode

LC50	lethal concentration for 50%
LOD	limit of detection
MCC	microcrystal cellulose
MFC	micro fibrillated cellulose
NACEWA	nano cellulose water
NMR	nuclear magnetic resonance
PAA	poly(acrylic acid)
PS-1	Pseudo-first adsorption model
PS-2	pseudo-second adsorption model
PTFE	Polytetrafluoroethylene
PVOH	poly(vinyl alcohol)
RSC	reduced sulfur compounds
SD	Substitution degree or degree of substitution
SEM	scanning electron microscopy
TEKES	the Finnish Funding Agency for Technology and Innovation
TGA	thermal gravity analysis
TOC	total organic compound
VG-ICP-AES	vapor generator inductively coupled plasma atomic emission spectroscopy
VG-ICP-OES	vapor generation inductively coupled plasma optical emission spectrometry
VG-ICP-QMS	vapor generator coupled inductively coupled plasma quadruple mass spectrometry

WHO	world health organization
VSC	volatile sulfur compounds
WVTR	water vapor transmission rate
XAFS	X-ray adsorption fine structure
XPS	X-ray photoelectron spectroscope
XRD	X-ray powder diffraction
AMP	2-amino-2-methyl-1-propanol
APS	ammonium persulfate
$bmimHSO_4$	1-butyl-3-methylimidazolium hydrogen sulfate ionic liquid
$CaCO_3$	calcium carbonate
$\mathrm{Co(CH_3COO)_2}$	cobalt porphyrin
DIPA	di-isopropanolamine
DMAc	N,N-dimetylhyacetamide
DMSO	dimethyl sulfoxide
EDTA	ethylenediaminetetraacetic acid
EPTMAC	2,3-epoxypropyltrimethyl ammonium chloride
iso-ODSA	iso-octadecenyl
MDEA	N-methyldiethanolamine
N2	N-[3-(trimetloxysily)prolyl]ethylenediamine
N3	N’-(3-trimethoxysilylpropyl) diethylenetriamine
THF	tetrahydrofuran

n-TDSA	n-tetradecenyl succinic anhydride
TEMPO	2,2,6,6-Tetramythylpiperidine-1-oxyl

1 Introduction

Hydrogen sulfide is toxic and hazardous pollutant. It has been under great interest for past few years because of all the time tighten environmental regulations and increased interest of mining. Hydrogen sulfide gas originated from mining process has been a cause of death in mining accident in Talvivaara Finland (Tukes 2012, 10). Also in Japan wastewater treatment plan four workers death was caused by hydrogen sulfide gas, which originated from wastewater (Kage *et al*. 2004, 182). Hydrogen sulfide can corrode to wastewater pipelines (Vollertsen *et al*. 2008, 162). Because of the corrosion the wastewater pipelines needs better pipes and more frequently have to be changed and that costs money. When hydrogen sulfide evaporates it oxidized to sulfuric acid and this causes acid rains

Adsorption has shown a great potential to be very useful method in purification of different water types. Different materials have been used as sorbents. Two different adsorbents have been studied for hydrogen sulfide adsorption in aqueous solutions. Crushed oyster shells have been tested by Asaoka *et al.* (2009, 4127-4132). Alum and ferric water treatment residuals have been tested by Wang & Pei (2012). Also other methods for purifying hydrogen sulfide out of water have been studied.

Cellulose nanocrystals are suggested to be the next big thing in green chemistry. They have been tested and studied to replace crude oil in polymers producing, function as biosensor, do a drug delivery or work as catalyst in variety of reactions. Cellulose nanocrystals can be prepared by two different but quite similar processes and they can be chemically modified by several different ways. (Lam *et al*. 2012, 2-6; Habibi *et al*. 2010, 3483-3485; Man *et al*. 2011, 726-731)

This master thesis is part of larger TEKES-project, called NACEWA, where nano- and micro cellulose based materials for water treatment applications are studied and developed. In this project functionalized nano- and micro cellulose adsorbents and nanocatalysts are studied in the removal of certain contaminants.

1.1 Objectives and contents

The main object of this master thesis was to study if chemically modified cellulose nanocrystals could be used as adsorbents to purify hydrogen sulfide out from water and what are the adsorption capacities of these adsorbents. The effects of different pH and backgrounds on adsorption capacities of different adsorbents are tested. Obtained results are compared to literature.

In theoretical part the properties of hydrogen sulfide and its effects for example on humans and sewer pipelines are examined. To test hydrogen sulfide adsorption the quantity of it has to be measured, so the analytical methods to quantify hydrogen sulfide from water samples are also studied. Cellulose nanocrystals, their different properties, applications and how the surface of CNC could be modified are investigated. Finally, the adsorption theory is also shortly discussed. In experimental section several different chemically modified MFC based adsorbents are prepared and their adsorption capacities determined.

For this master thesis large number of articles concerning hydrogen sulfide detection methods from water samples was read and five analytical methods selected based on their accuracy, reliability and most importantly the possibility to be able to use that method in Laboratory of Green Chemistry in Mikkeli. Awareness of cellulose nanocrystals, its properties and applications are growing fast. During this six months period several articles related to CNCs properties and applications, have been published.

2 Hydrogen sulfide

Hydrogen sulfide H_2S is colorless gas, which can easily be identified from its odor, strong rotten eggs smell. It is reducing agent so it is easily oxidized in suitable conditions. Hydrogen sulfide is corrosive to metals and concrete. When hydrogen sulfide is adsorbed for example on concrete sewer, it is most likely oxidized to elemental sulfur, which is then slowly oxidized to sulfuric acid. (OVA-website; Vollertsen *et al*. 2008, 162) According to EPA (1991, 32) Hydrogen sulfide can cause corrosion rate up to 3.6 mm/year for concrete wastewater pipe. There has been found certain conditions, low H_2S concentration (1.36 mg/L) pH between 3 to 5 and immersion time more than 2 hours, when hydrogen sulfide can cause inhibiting effect for iron corrosion (Ma *et al*. 2000, 1683).

Hydrogen sulfide is a byproduct of many industrial processes. It is formed in the production of cellulose and more precisely sodium cellulose liquor or white liquor containing sodium sulfide and sodium hydroxide. Crude oil refining is another major source of hydrogen sulfide. In refining process sulfur is removed by reducing sulfur compounds to hydrogen sulfide. In wastewater purification system hydrogen sulfide is also produced. When the temperature and pH are suitable organic matter can produce hydrogen sulfide under anaerobic conditions. Sludge containers are the most promising places from wastewater treatment facilities to produce hydrogen sulfide. Viscose fiber production and tannery productions are some sources of this gas. Furthermore, natural gas can contain hydrogen sulfide from concentration level ppm to vol% of total volume. (OVA-website; Reddy *et al*. 2012, 87)

Hydrogen sulfide is toxic to almost all kinds of forms of life (Balasubramanian & Pugalenthi 2000, 4201). Taste threshold of hydrogen sulfide is estimated to be between 0.05 and 0.1 mg/L (WHO 2008, 216). Concentration between 10 to 20 ppm (15-30 $\mathrm{mg/m^3}$) causes irritation for eyes. If the concentration is between 50 to 100 ppm it causes burning pain, blurred vision and tearing of the eyes. Also nose and throat starts to dry and irritate.

When the concentration is between 100 to 150 ppm hydrogen sulfide paralyzes the sense of smell. If the concentration is over 1000 ppm or 1400 mg/m^3 it causes instant loss of consciousness and death because respiration stops. In nature hydrogen sulfide is oxidized to sulfuric acid and it causes acid rains. Hydrogen sulfide is water soluble (4-6 g/L) and it is highly toxic to aquatic organism and its LC50 values for fish are between 0.01- 0.77 mg/L. (OVA-website) For drinking water there are no limits set by WHO, because of occurred concentration levels are much lower than the concentration, which may cause some toxic effect (WHO 2008, 185). Quantity of hydrogen sulfide from different water types has been measured. Table 1 shows the concentration of hydrogen sulfide and sulfide from different countries and water types.

Table 1. Hydrogen sulfide and sulfide concentration on different kind of waters round a world.

Source	**Concentration [mg/L]**	**Forms**	**Reference**
Spring water, Chezh Reb.	0.06-20.2	H_2S	Cmelik *et al*. 2008, 1780
Black Sea	9.5	H_2S	Baykara *et al*. 2007, 1246
Wastewater, Kuwait	7.2-7.8	H_2S	Tomar & Abdullah 1994, 2545
Wastewater, Brazil	5.59	H_2S	Santos *et al*. 2009, 3360
Lake water, Sri Lanka	0.03-0.247	H_2S	Kularatne *et al*. 2003, 906
Spring water, Japan	0.07-2.89	H_2S	Toda *et al*. 2012, 45
Tannery wastewater	250 - 525	sulfide	Wieman *et al*. 1998, 774-780
Anaerobic treated effluent wastewater from paper mill	35-55	sulfide	Dutta *et al*. 2010, 2564
Reclaimed urban wastewater, Tenerife Spain	0.09-1.8	sulfide	Delgado *et al*. 1999, 541

2.1 Water purification methods for hydrogen sulfide

Different water purification methods for hydrogen sulfide have been studied. Oxidation is one of the most studied processes and different chemicals have been used as oxidants. These are for example oxygen, hydrogen peroxide, hypochlorite, chlorine, potassium permanganate, ferrate and iron (hydro)oxides (Poulton *et al*. 2002, 826). Another oxidation method is to add solid oxidant like magnesium peroxide (MgO_2) (Chang *et al*. 2007, 478).

The third oxidation method is catalytical oxidation, where different catalysts are used to upgrade oxidation process. Activated carbon, granular activated carbon, and pyrolysed cobalt(II) mesotetra-4-methoxyphenylporphyrin and carbon supported CoN_4 structure, which is prepared by the heat treatment of $Co(CH_3COO)_2$ and imidazole impregnated carbon black have been studied as catalysts. (Goifman *et al*. 2006, 296)

Biological conversion of hydrogen sulfide to elemental sulfur has been studied by Henshaw & Zhu (2001, 3605-3610) by using fixed-film bioreactor with C. *thiosulfatophilum* bacterial. The average sulfide concentration before the test was 257 mg/L and after test no sulfide was discovered. For electrochemical conversion of sulfide to elemental sulfur electrochemical sulfide oxidation fuel cell was used. In this process two identical rectangular champers were separated by cationic exchange membrane to anode and cathode. The removal percentage of sulfide was between 10 to 80% of original sulfide. 80% removal was achieved at when the fuel cell was operated less than 15 days and after that the removal percentages started to drop until after 90 days the test was finished. (Dutta *et al*. 2008, 4971)

Microfiltration combined by chloride oxidation has been tested and studied by Thompson *et al*. (1995, 287-291). In this method chloride is added to water for oxidation of hydrogen sulfide to elemental sulfur. After oxidation microfiltration of water removes elemental sulfur. Advantages of this system compared to direct air stripping are that combined oxidation with chloride and microfiltration improves disinfection efficiencies, enhances elimination of noxious off-gases, lowers finished water turbidity and lowers the amount of sulfur transferred to distribution network. (Thompson *et al*. 1995, 287)

3 Adsorption

In adsorption process, a component, which can be in liquid or gas phase, accumulates at the common boundary of two phases. The accumulating component is called adsorbate and adsorbing component, which is usually a solid adsorbent. (Repo 2011, 15)

Adsorption can be categorized in two categories. Van der Waals, hydrogen bonding and hydrophobic interaction based physical adsorption, physisorption or covalent bond interaction based chemical adsorption, chemisorption. Physical adsorption is effective at low or close temperatures of critical temperature of an adsorbed substance. Physical adsorption is reversible process, which can happen in mono- or multilayers. Chemical adsorption occurs only as a monolayer and at temperatures above the critical temperature. Physical adsorption causes decrease of free energy and entropy of the adsorption system which means that physical adsorption is exothermic process. (Repo 2011, 15; Dabrowski 2001, 139-140)

Adsorption kinetics or dynamics is term, which is used when time evolution of adsorption process is dealing with time. Adsorption kinetics can be divided in four phases. In the first phase, diffusion of molecules from the bulk phase towards the interface space occurs. In the second phase, solute adsorbate diffuses across the so-called liquid film, which surrounds adsorbents particles. The third phase includes diffusion of solute in the liquid contained in pores of adsorbent particle and along the pore walls. Because of most of the adsorbents have porous structure this can influence on the rate of adsorption (Repo 2011, 34-35). In the fourth phase adsorption and desorption of adsorbate molecules on/from the adsorbent surface take place. (Dabrowinski 2001, 166; Plazinski *et al*. 2009, 2).

3.1 Modeling of adsorption

There are several different adsorption isotherms and all of those describe the amount of component adsorbed on the surface of adsorbent versus the adsorbate amount in fluid phase. Isotherm modeling can be conducted in one- or multi-component systems. Moreover, kinetics of the adsorption can be modeled. (Repo 2011, 19)

In most of the cases, adsorption theory is considered in one-component systems. One-component isotherms are for example Langmuir and Freundlich isotherms and also Sips, Redlich-Peterson, Temkin, Toth and Dubinin-Radushkevich and some other isotherms. All of these isotherms describe adsorption phenomena at different perspective. For example, Langmuir isotherm assumes that surface of accumulation is homogenous when the adsorption energy is stable, adsorption of adsorbent is localized and one adsorption site can bind only one adsorbate. Langmuir isotherm is calculated using equation (1). (Repo 2011, 21-22)

$$Q_e = \frac{Q_m K_L C_e}{(1+K_L C_e)} \tag{1}$$

Where

Q_e is adsorption capacity of adsorbent [mg/g]

Q_m is maximum adsorption capacity of adsorbent [mg/g]

C_e is initial adsorbate concentration [mg/L]

K_L is the affinity constant [L/mg]

Freundlich isotherm is based on the idea that the surface of adsorbent is heterogeneous. It also can be used with multilayer adsorption. Freudlich isotherms are calculated using equation (2). (Repo 2011, 22)

$$Q_e = K_f C_e^{\frac{1}{n_f}} \tag{2}$$

Where

$Q_e$is adsorption capacity of adsorbent [mg/g]

C_e is initial adsorbate concentration [mg/L]

K_f is Freudlich adsorption constant $[(\frac{mg}{g})/(\frac{L}{mg})^{n_f}]$

n_f is Freudlich adsorption constant

The Sips isotherm is combination of previous isotherms and it can be derived by equilibrium or thermodynamic approach. The Sips isotherm is calculated using equation (3). (Repo 2011, 23)

$$Q_e = \frac{Q_m(K_s C_e)^{n_s}}{(1+(K_s C_e)^{n_s})} \tag{3}$$

Where

$Q_e$is adsorption capacity of adsorbent [mg/g]

Q_m is maximum adsorption capacity of adsorbent [mg/g]

C_e is initial adsorbate concentration [mg/L]

K_s is affinity constant [L/mg]

n_s describes surface heterogeneity

In more complicated systems, multi-component isotherms are needed. These isotherms were developed to describe situation where there are more than one adsorbate. Langmuir is most developed isotherm of two component isotherms having three different models. Other models are for example extended Sips, Redlich-Peterson isotherms and extended BiLangmuir model. (Repo 2011, 27)

Furthermore, the kinetics of adsorption is frequently modeled. Kinetic models were developed to understand and predict how different phases of adsorption develop. Pseudo-first (PS-1) and Pseudo-second order (PS-2) models are the most known and most often used adsorption kinetics models. Those are also the simplest models. Both pseudo models are based on the assumption that adsorption kinetics is governed by surface reaction. (Repo 2011, 35)

One important part of adsorption isotherms and modeling is error functions. The error function is used to minimize the difference between experimental data and the theoretical isotherms. Examples of used error functions are: the sum of the square of the errors (ERRSQ), the hybrid error function (HYBRID), the sum of absolute errors (EABS) and the average relative error (ARE) (Repo 2011, 31) For example ERRSQ is calculated using equation (4) (Repo 2011, 31).

$$\sum_{i=1}^{n}(Q_{e,exp} - Q_{e,isoth})_i^2 \tag{4}$$

Where

$Q_{e,exp}$ is experimental adsorption capacity of adsorbent [mg/g]

$Q_{e,isoth}$ is calculated adsorption capacity using isotherm [mg/g]

4 Analytical methods for hydrogen sulfide determination in aqueous matrices

A few potential analytical methods to determine hydrogen sulfide from aqueous sample have been developed. Some of them are old but still useful to determine concentration of H_2S. Some of them will be thoroughly discussed in this chapter. The purpose is to find reliable and sensitive method for hydrogen sulfide measurement from water sample. Reason for the selection of these four detection processes is that inductively coupled plasma ICP, Gas chromatograph (GC) and high performance liquid chromatograph (HPLC) are methods, which were possible to use in Laboratory of Green Chemistry, where the experimental part of this master thesis was conducted.

4.1 Inductively coupled plasma (ICP)

Analysis method with ICP was developed to determine low concentrations of H_2S. VG-ICP-QMS (vapor generator coupled to an inductively coupled plasma quadruple mass spectrometer) was developed and tested for this purpose. Base idea of this analytical method is to separate sulfur from the water form of H_2S by using hydrochloric acid. A specific reaction cell, which uses hydrogen and helium gas, is used. Reason for using reaction cell is that in water matrix there will be some polyatomic isobaric interference because of oxygen. One of the main targets was to study, if reaction cell can prevent those interferences. To compare the results obtained by VG-ICP-QMS potentiometric system was used. (Colon *et al.* 2007, 470)

Results of study are presented in Table 2. Limit of detection (LOD) was also studied for VG-ICP-QMS and it was 2 μg/L. If that is compared to the limit of detection of potentiometric methods 20 μg/L, it can be seen that VG-ICP-QMS is more sensitive than potentiometric methods for low concentration of sulfur. Interference caused by polyatomic isobaric was managed by using vapor generator and reaction cell with hydrogen and helium gas streams. (Colon *et al*. 2007, 473)

Table 2. Results of potentiometric method and VG-ICP-QMS (Colon *et al.* 2007, 473).

	Potentiometric method		VG-ICP-QMS	
Sample concentration [µg/L]	µg/L	standard derivation	µg/L	standard derivation
20	<LOD	-	14.9	0.4
50	46.1	0.8	45.1	0.4
90	88	1	87.6	0.4

The second study was conducted by using vapor generator inductively coupled plasma atomic emission spectroscopy (VG-ICP-AES) to measure low concentrations of H_2S. Two different systems were used for H_2S production. In Figure 1 main differences of two studied technology are described. For setup a (Figure 1a) they used only two channels, one for sample and one for hydrochloric acid. Acid was added to the sample flow via a T-piece placed before the reaction coil. Generation of H_2S was completed by using polytetrafluoroethlylene (PTFE) capillary, which measurements are 1 m x 0.8 mm. To complete the release of H_2S vapor phase, an argon stream was added to reaction coil. In setup b (Figure 1b) gas separator was replaced by conventional liquid sample introduction system. This system consists a pneumatic concentric nebulizer. Nebulizer is coupled to cyclonic spray chamber, which volume is 40 cm^3. Difference of Figure 1a is that they did add gas (Ar), to avoid degradation of nebulization process. To compare results of those two methods potentiometric method was used. (Colon *et al*. 2008, 161)

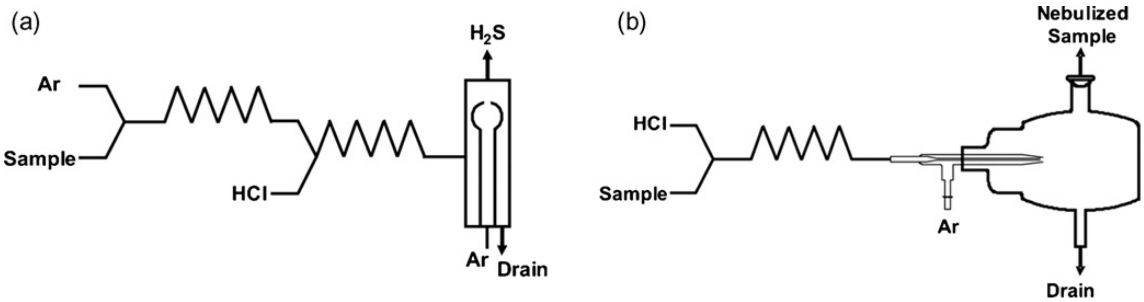


Figure 1. Different sample processing methods for separating hydrogen sulfide for aqueous matrix. (Colon *et al*. 2008, 161)

Sulfide in aqueous solution is very unstable so it must be preserved in a basic solution with a reducing agent. According to Colon *et al*. Environmental protection Agency (EPA) recommends to use SAOB buffer which consist of NaOH, ascorbic acid and ethylenediaminetetraacetic acid (EDTA). Colon *et al*. (2008, 162) also studied how different buffers, NH_3/NH_4^+ with ascorbic acid and SOAB, would work in this solution. Differences of buffers were tested in both setups and varying the gas flow rate and the sample or acid flow rate.

Results of comparison of Figure 1 setups and potentiometric methods are in Table 3. Limits of detection (LOD) for VG-ICP-AES both setups were also measured and calculated to be 5 μg/L compared to potentiometric methods 20 μg/L. As it can be seen in Table 3 setup b values are higher than spiked values. Reason for this is that in setup b, all components of sample reached the plasma. This means that all the sulfur forms contributed to the emission intensity. According to Colon *et al*. real sample must be analyzed twice, because in that case emission intensity greatly increase. When sample is analyzed twice: the sulfur signal can be obtained by replacing HCl with ultrapure water at the reaction coil while the sulfide signal is obtained by subtracting the signal obtained using water from the signal obtained using HCl at the reaction coil. Eight determinations for sulfide concentration in environmental water were also conducted for both methods. Samples' hydrogen sulfide concentrations for one to five were too low for potentiometric methods, but last four were able to be measured by all three methods and there were no significant difference between those results. (Colon *et al*. 2008, 165-166)

Table 3. Result obtained for spiked samples VG-ICP-AES and potentiometric methods (Colon *et al*. 2008, 166)

Spiked sample	Spiked values	VG-ICP-AES (setup a)		VG-ICP-AES (setup b)		Potentiometric methods	
	μg/L	μg/L	standard derivation (n=3)	μg/L	standard derivation (n=3)	μg/L	standard derivation (n=3)
1	24.7	22.4	0.6	28	3	19.1	0.6
2	75.8	75	3	75	4	75	3
3	102.2	101	2	114	5	111	6
4	152	152.3	0.4	158	2	154	1

Third study for vapor generation inductively coupled plasma spectrometric (VG-ICP-OES) techniques for determination of sulfide in water samples was published in 2010 by Cmelik *et al*. (2010, 1777-1781). VG-ICP-OES was used for similar study than previous reference (Colon *et al.* 2007;2008). One of the main tasks for this study was to find out why some chemicals cause interference to other analytical methods: iodometric titration and spectrophotometric determination of sulfide. Studied chemicals were SO_4^{2-}, HCO_3^-, $NO_3^-, NO_2^-, SO_3^{2-}, Fe^{3+}, Fe^{2+}$ and Cu^{2+}. (Cmelik *et al.* 2010, 1777-1781).

Results can be classified in three categories. First are chemicals, which do not interference determination. Sulfate SO_4^{2-} is one of those chemicals. Reason for this is that sulfate does not form volatile species after acidification and in gas/liquid separation it separates in liquid waste. Nitrate (NO_3^-) do not interference determination if the concentration stays below 100 mg/L. The second group includes chemicals, which have negative influence for determination. When the HCO_3^- concentration is higher than 100 μg/L it has negative effect for determination. This could be a problem because HCO_3^- concentration levels higher than 100 μg/L can be found frequently in natural waters. Other problem is dissolved free carbon dioxide because it forms (bi)carbonate with alkaline reagent used for sample preservation. Negative interference is also caused by nitrite at concentration over 1 mg/L. Reason for this is that nitrite has oxidative properties in acidic solution. Sulfide is oxidized by nitrite to elemental sulfur and that causes signal suppression. Sulfide is oxidized by Fe^{3+}, Fe^{2+} and Cu^{2+} so these also cause signal suppression. For Fe concentration over 10 mg/L and in case of Cu^{2+} 0.1 mg/L starts to have effect for determination. (Cmelik *et al*. 2010, 1779-1780)

The third group is chemicals, which have positive interference on determination. Sulfite has positive influence for the determination even from lowest concentration level 0.1 mg/L. Reason for this interference is that sulfite forms volatile compound's, which cannot be distinguished in detector. Hydrogen sulfide and sulfur dioxide cannot be distinguished in detector. (Cmelik *et al*. 2010, 1779)

Cmelik *et al*. (2010, 1779) also compared VG-ICP-OES and iodometric titration for real water samples. Results of that comparison are presented in Table 4. Limit of detection was measured to be 30 μg/L, which is about five times higher than in previous reference (Cmelik *et al*. 2010, 1779; Colon *et al*. 2007, 173; Colon *et al* 2008, 160).

Table 4. Result of the real sample of water with different concentration analyzed by iodometric titration and VG-ICP-OES. (Cmelik *et al.* 2010, 1780)

Sample	Iodometric titration [mg/L]	VG-ICP-OES [mg/L]
A	0.06±0.01	0.06±0.01
B	1.05±0.07	1.14±0.02
C	3.10±0.05	3.18±0.05
D	3.7±0.1	3.5±0.1
E	6.2±0.1	6.2±0.1
F	6.5±0.2	6.4±0.3
G	7.2±0.1	7.26±0.08
H	20.3±0.8	22±2

4.2 Gas chromatography (GC)

Gas chromatography with flame photometric detector (GC-FPD) is useful analytical method to determine concentration levels for hydrogen sulfide (H_2S), methyl mercaptan, dimethyl sulfide and dimethyl disulfide in aqueous matrices. There are few studies where GC has been used to determine hydrogen sulfide form aqueous matrices.

First study was made by Sola *et al*. (1997, 329-335) to quantify volatile sulfur compounds in polluted water. In this study Sola *et al*. used special cryogenic trap-gas chromatographic method with flame photometric detection. Reason for the usage of this technology was according to Sola *et al*. that in the cases where volatile sulfur compounds (VSC) concentrations are high, normal GC-FPD systems cannot make quantitative determination of VSC composition. Description of cryogenic trap GC-FPD is in the reference. In this study line of calibration for different VSCs were determined. For H_2S results were good. Linear regression coefficients were 0.9989; 0.9895 and 0.9920 for concentrations between 0.5-13; 13-110 and 110- 370 ηg/L. (Sola *et al*. 1997, 329-335)

Second study was made by Berube *et al*. in 1999. In this study methods that could solve most of the problems related to direct injection of aqueous sample into a GC-FPD system were tried to find. (Berube *et al*. 1999, 485-489)

One problem is that, when sample is injected to the system, the water can extinguish the detector flame and non-volatile material contained in the aqueous sample coat the GC injection port and column. Solution for this problem is to use either purge and trap techniques or headspace gas sampling for separating volatile compounds from aqueous matrices before analysis. Using purge and trap techniques involves some disadvantages when used for aqueous solution. First disadvantages are price and complex of purge and trap apparatus. The second disadvantage is level of hygiene what is required. Sulfur in gaseous forms adsorb strongly to glass, which may lead to poor recoveries if the glassware is not properly cleaned. The third disadvantage is the times that purge and trap system needs. Hydrogen sulfide is unstable and characteristics of the sample can change during the process. The fourth disadvantage is that it is often difficult to be sure that the entire compounds are purged when the compound has low volatility. This may lead to poor recovery. The fifth problem is the sample volume, which is needed in purges and trap apparatus. 100 mL is a large volume of sample when many samples are withdrawn in laboratory or bench-scale system. Finally, the biggest disadvantage associated with the injection of the head-space gas from a sample vial directly into a GC. Disadvantage is that the relationship between the concentration of volatile sulfur compounds in the head-space and those of the aqueous sample is highly influenced by temperature of the sample. For this reason all the samples must be analyzed in the same temperature. This requires constant temperature monitoring and temperature automatic sampler, which increases the cost of laboratory analysis and makes process more complex. (Berube *et al*. 1999, 485-486)

Direct injection of aqueous sample to gas chromatograph with flame photometric detector was developed to solve previous problems. System measures the concentration of hydrogen sulfide, methyl mercaptan, and dimethyl sulfide and dimethyl disulfide in aqueous matrices. Those matrices can consist of either tap water, distilled water, kraft pulp mill condensates of mixed liquor from MBR. Results of using GC-FPD are presented in Table 5. The accuracy of the concentration measurement of dimethyl sulfide and dimethyl disulfide is satisfactory, but the accuracy of hydrogen sulfide and methyl mercaptan are significantly lower. Reason for the low accuracies is associated for their highly volatile nature. This and effect of sampling error may cause low accuracy. The accuracy can be improved by analyzing multiple samples. (Berube *et al*. 1999, 488-489)

Table 5. Calibration curve result for different reduced sulfur compounds (RSC) (Berube *et al*. 1999, 488).

RSC	Range [mg/L]	Confidence interval for concentration measurement [mg/L]
hydrogen sulfide	0.49-4.87	±0.15-±1.52
methyl mecaptan	0.69-6.88	±0.12-±1.13
dimethyl sulfide	0.33-3.28	±0.02-±0.18
dimethyl disulfide	0.41-4.06	±0.06-±0.59

Various detection limits for gas chromatography with pulsed flame photometric detector (GC-PFPD) has been studied by Catalan *et al*. (2001, 89-98). Task of their study was to find out various detection limits for GC-PFPD. Gas chromatography with flame photometric detector (GC-FPD) analysis has been used to determine hydrogen sulfide concentration in animal tissues (Ubuka *et al*. 2001, 31-37) and biotrickling filter process to determine process success (Zhang *et al*. 2009, 595-601).

4.3 High performance liquid chromatography (HPLC)

High performance liquid chromatography (HPLC) has been used to determine $\mathrm{H_2}S$ from seawater. Base idea was to study oxidation of $\mathrm{H_2}S$ by hydrous Fe(III) oxides in seawater. HPLC was used as analytical method to find out how the oxidation process succeeded. (Yao & Millero. 1996, 4-5) Other HPLC study was made to find out analytical method to determine $\mathrm{H_2S}$ from different kinds of biological matrices. This study was mainly focused on the tissue samples. (Shen *et al*. 2011, 1021-1022)

4.4 Ion selective electrode (ISE)

Ion selective electrode (ISE) has been used to determine sulfur concentration from waste water. Base idea was to compare ISE and iodimetric methods for determination of sulfide in tannery wastewater. First part was to study tannery wastewater samples without any modification. Results of those samples are in Table 6. Table 6 clearly shows that variations of results are huge and modification for ISE must be done, because iodimetric method was found to be accurate for sulfur concentration below 50 ppm. Some modification for ISE was made and reasonable causes for large variation were thought, but not tested in tannery effluent. (Balasubramanian & Pugalenthi. 2000, 4201-4206)

Table 6. Concentration of sulfide in tannery waste water measured by ISE and iodimetry (Balasubramanian & Pugalenthi. 2000, 4202)

Sample	Sulfide concentration (ppm)	
	ISE	Iodimetry
1.Delium liquor	101.5	152
2. Lime liquor	73	64.1
3. Composite liquor	72.5	176.4
4. Chrome liquor	4.31	14.9
5. Aeration tank	0.22	5.7
6. Washing liquor	0.28	72

Ion selective electrode (ISE) can be used for field measurement of free sulfides from seawater sediment (Brown *et al*. 2011, 821–839). It can also be used for on-line monitoring for gas-phase hydrogen sulfide and liquid-phase S^{2-} concentration for bio trickling process (Redondo *et al.* 2008, 789-798).

4.5 Other methods

There are several studies about different analytical methods to determinate hydrogen sulfide from samples. In sediment sample X-ray adsorption fine structure (XAFS) has been used (Asaoka *et al*. 2009; Asaoka *et al*. 2012). Ion chromatograph (IC) has been used to determine H_2S from animal tissues (Ubuka *et al*. 2001). IC has been used to determine sulfide, sulfate, thiosulfate and sulfite concentrations from water sample, which was treated by fuel cell. (Dutta *et al*. 2008).

5 Cellulose nano/microcrystals

Cellulose based biodegradable products have been under great interest for past few years. Cellulose is basic structure off different kind of materials such as cotton and cotton linters pulp, flax, ramie, hemp, palm, sisal, wheat straw, bacterial cellulose, tunicates, sugar beet pulp and bleached softwood and hardwood. The annual production has been estimated to be more than $7{,}5 \times 10^{10}$ tons. (Habibi *et al*. 2010, 3480; 3484) In references CNC have names like cellulose nanocrystal, nanocrystal cellulose, CNX or CNN, in this study cellulose nanocrystals or CNC is used.

Cellulose nano/microcrystals have applications, which are based on highly developed porous structure and large specific surface area (Lam *et al*. 2012, 283-290). The surface of CNC is easy to modify chemically (Habibi *et al*. 2010, 3493). Activated carbon, which probably is the most used adsorbent, has similar feature than CNC (Razvigorova *et al*. 1998, 2135). However, activated carbon is expensive and regeneration of it is difficult and expensive process, because of high energy demand (Sabio *et al*. 2004, 2285-2286). Based on those features modified CNC could be used to replace activated carbon as an adsorbent. At the moment, there is only one reported study where modified micro fibrillated cellulose has been used as adsorbent to remove arsenate from aqueous solution (Islam *et al.* 2011, 755-763).

5.1 Preparation of cellulose nanocrystals

Cellulose nanocrystals can be prepared from pure cellulose by using strong acid hydrolysis with sulfuric or hydrochloric acid, which time, temperature and agitation are controlled (Habibi *et al*. 2010, 3484). For example bleached cellulose is acid hydrolyzed in 65w-% sulfuric acid for 40 min at temperature of 50 °C (Siqueira *et al*. 2009, 426). After acid hydrolysis the resulting suspension is diluted with water and then washed with successive centrifugations. To remove free acid molecules, dialysis against distilled water is then performed. Additional process such as differential centrifugation, filtration or ultracentrifugation can be used to prepare special CNC. Specific hydrolysis and separation methods have been developed for different source of cellulose. For example combination of acid hydrolysis and high-pressure homogenization techniques has been used to prepare CNC from microcrystalline cellulose (MCC). (Habibi *et al*. 2010, 3484; Liu *et al*. 2010, 5685.)

Other method to prepare CNC is to use ionic liquid as catalyst in ionic hydrolysis. Microcrystal cellulose (10% w/w) was mixed with 1-butyl-3-methylimidazolium hydrogen sulfate ionic liquid ($bmimHSO_4$) in hydrolysis process. MCC and $bmimHSO_4$ was treated for 1 h at 70, 80 and 90 °C using stirring speed of 400 rpm. To stop this reaction, 20 mL of deionized cold water was added into the mixture. After this the mixture was sonicated in water bath at room temperature and the suspension was washed with deionized water several times followed by centrifugation at 2000 rpm for 15 min. The supernatant was isolated by centrifugation at 7500 rpm for 30 min. (Man *et al*. 2011, 726-727)

The hydrolysis of MCC by $bmimHSO_4$ ionic liquid and acid hydrolysis is found to be quite similar. Ionic liquid causes hydrolytic segmentation of glycosidic bonds between two anhydroglucose units. This causes rearrangement of the interlinking chain ends. The dissolves of amorphous portion is caused by ionic liquid and result of this is crystalline regions. Combination of ionic liquid treatment and mechanical stirring causes disintegration of the MCC structure into CNC particles. (Man *et al*. 2011, 727)

Result of this ionic liquid treatment is that it could be used to synthesize CNC from MCC. According to Man *et al*. (2011, 730) the crystallinity index increases, basic structure of CNC maintains and the ionic liquid is not consumed during this treatment so it can be regenerated. This CNC and acid hydrolysis prepared CNC have similar features. For example their thermal properties are similar.

5.2 Properties of cellulose nanocrystals

Cellulose nanocrystals geometrical dimensions (length *L* and width *w*) are found to vary widely depending on original source of cellulose and hydrolysis conditions. For example from soft wood prepared CNC is 3-5 nm wide and 100-200 nm long and CNC from tunicate is 10 nm wide and 500-1000 nm long. (Habibi *et al*. 2010, 3485) Different derivate cellulose (MFC, CNC and MCC) geometrical dimensions (length *L*, diameter *d* and aspect of ratio *L/d*) are show in Table 7.

Table 7. Derivate celluloses geometrical dimensions(Abdul Khalil *et al* .2012, 967)

Cellulose structure	diameter [nm]	Length [nm]	Aspect ratio [l/d]
Microcrystal cellulose (MCC)	>1000	>1000	~1
Microfibrillated cellulose (MFC)	10-40	>1000	100-150
Cellulose nanocrystal (CNC)	2-20	100-600	10-100

5.2.1 Thermal properties on cellulose nanocrystals

The difference between CNC's and cellulose's thermal properties is significant. Cellulose has shown typical decomposition with onset temperature just over 300 °C and after that great mass loss leaving only 2.87% from its original weight at 600 °C. CNC decomposition is different. CNC lost 40% of its original weight in temperature between 150- 300 °C and 30% in temperature between 300-600 ℃. At 600 °C 30% of its original weight was still remained. This great difference in thermal behavior between CNC and cellulose may have been caused by the difference between decomposition- gasification processes. Cellulose decomposed at 180 °C by levoglucosan (1,6-anhydro-β-d-glucopyranose) and gasified at 300 ℃. Gradual weight loss of CNC at temperatures between 150-300 °C and the small endotherms between 160-190 °C suggest that the decomposition mechanism is different. It could be a direct solid-to-gas phase transition, which is catalyzed by sulfate groups on the surface of the CNC. (Lu & Hsieh. 2010, 333-334)

Hydrolysis duration has shown some influence on the thermal properties of CNC. According to Kargarzadeh *et al*. (2012, 855-866) the duration of hydrolysis has effect on thermal stability of CNC. CNC was made from kenaf bast fibers by alkaline and bleached treatment and then subsequently hydrolyzed. The hydrolysis time effect on thermal stability was studied and compared to bleached kenaf fibers value. Hydrolysis times were 20, 30, 40, 60, 90 and 120 min. Result of this study was that at 600 °C the residual masses of different CNCs were quite similar, about 30%, except CNC with 120 min hydrolysis time. Its residual mass at 600 °C was 45 %. (Kargarzadeh *et al*. 2012, 855-866)

5.2.2 Cumulative pore volume of cellulose nanocrystal

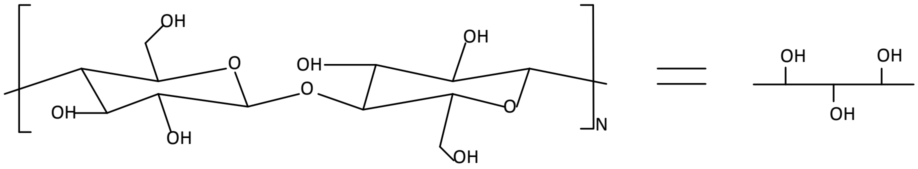
Cellulose and CNC have also great difference in cumulative pore volume. According to Lu & Hsieh (2010, 334) CNCs cumulative pore volume is 0.03396±0.00059 cm^3/g and for cellulose it is 0.00839±0.00026 cm^3/g. Greater pore volume of CNC was increased after loosely packed structure formed huge amount of mesopores among the nanocrystals.

5.2.3 Crystallinity of cellulose nanocrystal

Crystallinity for MCC was found to be between 55-80% (Wei *et al.* 1996). For CNC the crystallinity was found to be around 67% (Liu *et al*. 2010, 5689). Crystallinity of CNC depends of hydrolysis duration. According to Kargarzadeh *et al*. (2012, 855-866) the hydrolysis duration have some effect on the crystallinity of CNC. Hydrolysis time was studied at 20, 30, 40, 60, 90 and 120 min and crystallinities of CNC were 75.1%; 80.0%; 81.8%; 81.6%; 76.9% and 75.3%. Those can be compared to bleached kenaf fibers with crystallinity of 72.8%.

5.3 Chemical modification of cellulose nano crystals

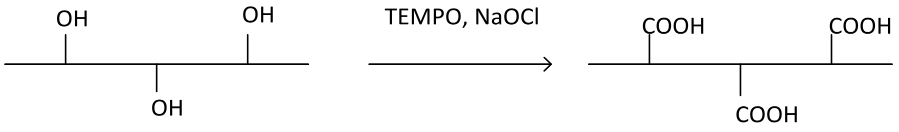
Cellulose nanocrystals can be modified by several different ways for making suitable products for different kinds of purposes. Chemical modification is the way to modify CNC or MFC surface to improve its properties for different kind of purposes. Reactions to accomplish such goal are for example oxidation, acetylation, cationazation, sulfonation, silylation and grafting via acid chloride, acid anhydride or isocyanate. There has also been prepared more homogenous CNC by using ammonium persulfate (APS). Basic idea is to introduce positive or negative electrostatic charges on the surface of the CNC or MFC. Purpose of this is to obtain better dispersion. Other idea to chemically modify the surface is to tune the surface energy characteristics of CNC to enhance its compatibility, especially when hydrophobic matrices in nanocomposites or conjunction with nonpolar matrices were used. Biggest challenge in chemical modification of CNC is not to change the original morphology, avoid any polymorphic conversion and maintain the integrity of the crystal. (Lam *et al*. 2012, 283; Habibi *et al*. 2010, 3486) The reaction equation (5) shows the basic structure of CNC (Lam *et al*. 2012, 284).



(5)

5.3.1 TEMPO oxidation

Objective to oxidize CNC by 2,2,6,6-Tetramythylpiperidine- 1-oxyl (TEMPO) is convert the hydroxylmethyl groups from surface of the cellulose to carboxylic form (Habibi, *et al*. 2010, 3487). Reaction between TEMPO and cellulose surface is shown in equation (6). (Lam *et al*. 2012, 284)

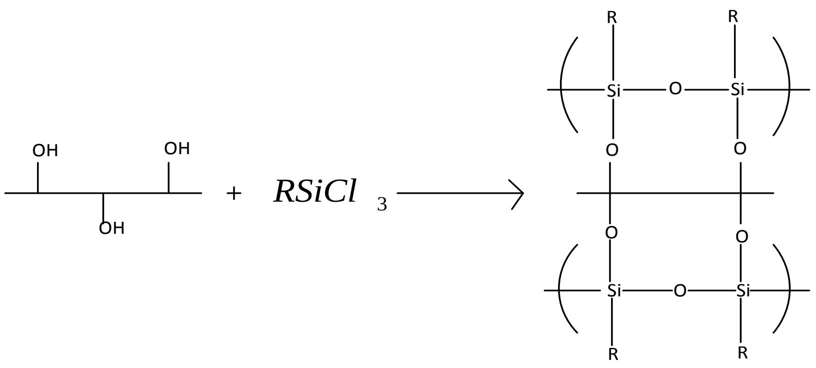


$$-\overset{\text{OH}}{|}-\underset{\text{OH}}{|}-\overset{\text{OH}}{|}- \xrightarrow{\text{TEMPO, NaOCl}} -\overset{\text{COOH}}{|}-\underset{\text{COOH}}{|}-\overset{\text{COOH}}{|}- \qquad (6)$$

When CNC are prepared by sulfuric acid methods, the main disadvantage is that, in that process rather labile sulfate moieties are formed on the surface of CNC. TEMPO - oxidation is promising alternative to convert those hydroxyl ions into carboxyl groups, which are not so labile. (Habibi *et al*. 2006, 680) In TEMPO oxidation process 510 mg or 3.15 mmol of equivalent anydroglucose unit (AGU) of CNC is suspended in 100 mL of distilled water and sonicated. After sonication 14.75 mg of TEMPO with 162 mg of NaBr are added into suspension. Then certain amount of 1.24 M NaOCl is slowly added to cellulose suspension. This amount corresponds to 0.06-0.5 molar ratio of NaOCl/AGU. The suspension is stirred for 30 to 45 min and pH is maintained at 10 by using 0.5 M NaOH. The synthesis is stopped by adding methanol and pH is adjusted to 7 with 0.5 M HCl. The fraction, which is not dissolved in water, is centrifuged and washed with water. Oxidized CNC is then dialyzed with distilled water. (Habibi *et al*, 2006, 680)

5.3.2 Silylation

Silylation is one of the chemical methods to modify CNC surface. In silylation CNCs dissolved in water (0.6% w/v) are exchanged to acetone and dry toluene. After solvent is exchanged the solution is precipitated so that the water content is around 1% v/v. Required amount of chlorosinales is added to solution to neutralize and derivate residual water. The reaction time can be changed up to 16 hours at room temperature with vigorous stirring. To end silylation a mixture of methanol and tetrahydrofuran (THF) 20/80 is added to terminate grafting and dissolve imidazolium chloride. Finally suspension is washed twice by THF to remove all impurities. (Gousse *et al*. 2002, 2646-2647) Reaction equation of silylation process is shown in equation (7). (Lam *et al*. 2012, 284)



(7)

Partial silylation process starts rapidly and after few hours it slows down. After slowing down it reached state where no silylation is found. One problem for silylation is that it is very sensitive to changes in reaction conditions. If the silylation reaction time is too long or the concentration of reagent is too high, then the morphological integrity of CNC is lost. If the morphological integrity of CNC is wanted to keep intact, then the substitution degree of silanization is low. (Gousse *et al*. 2002, 2648-2650) By using limited reaction conditions it is possible to silylate the surface of nano-scale cellulose microfibers without losing the morphological integrity of MCC (Gousse *et al*. 2004, 1573).

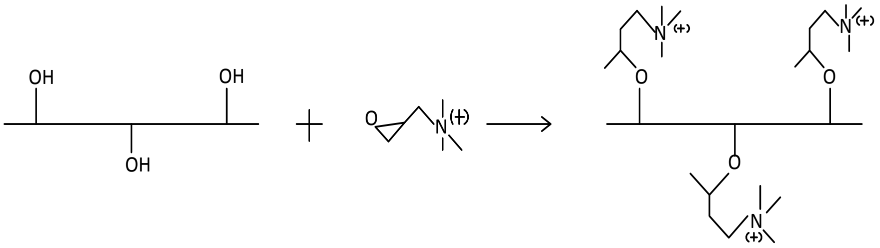
5.3.3 Cationization

CNC surface can be chemically modified by using cationization. Cationization with 2,3-epoxypropyltrimethyl ammonium chloride (EPTMAC) was studied by de la Motte *et al*. (2011, 738-746) Basic procedures of CNC is to use high amount of EPTMAC in alkaline water solution at relatively low temperature and long reaction time. Other method, which was tested for softwood kraft pulp, was relying on low amount of EPTMAX in dry conditions at high temperature and short reaction time.

In cationization process CNC is mixed with sodium hydroxide solution, concentration is 2 M and consistency 5.9%. This mixture is stirred for 30 min at room temperature. After that

EPTMAC, with molar ratio of EPTMAC/AGU= 3, is added and stirred for 5 h at temperature of 65 °C. After stirring the reaction mixture is diluted 5-fold with water and then dialyzed against de-ionized water for 15 days. The reaction suspension of hydroxypropyltrimethyl ammonium chloride cellulose nanocrystals (HPTMAC-CNC), which concentration is 1% (w/w), is sonicated. (de la Motte *et al*. 2011, 739-740)

After previous process the 200 mg HPTMAC-CNC is hydrolyzed by using 3 mL of 72% sulfuric acid. The sample is then subjected to vacuum for 15 min and then heated in water bath at temperature of 30 °C for 1 h. After heating 84 g of distilled water is added and then the sample is autoclaved at temperature of 125 °C for 1 h. Hydrolysate is then filtered, neutralized with barium hydroxide and then filtered again. Result of filtration, filtrate is then concentrated to dryness in reduced pressure. Result of this study was that cationic epoxide EPTMAX can successfully react with CNC and softwood kraft pulp despite the differences in procedures. (de la Motte *et al*. 2011,740-746) Basic cationization reaction equation between of CNC and epoxides is shown in equation (8) (Lam *et al*. 2012, 284).



(8)

5.3.4 Grafting

CNC can be chemically modified by using grafting reactions. In grafting reaction CNC surface is chemically modified by acetylation, hydroxyethylation or hydroxypropylation reaction. Basic grafting reactions with acetylation and hydroxyethylation are described. (Wang *et al*. 2007, 228)

About 10 g of CNC suspension and 40 mL of isopropyl alcohol was added to the 100 mL three-necked flask. After that proper amounts of acetic anhydride and sulfuric acid were added with stirring. The reaction mixture was maintained at 40 °C by using thermostatic water bath for 3 h to make the product. Product was neutralized by washing it and to get sample of CNC-CA. (Wang *et al*. 2007, 228)

To produce CNC-HEC 10 g of CNC suspension, 60 mL of isopropyl alcohol and 1.5 g of NaOH were added into the 100 mL three-necked flask with stirrer and stirred at temperature between 20 to 25 °C for 1h. After stirring the flask was transferred into ice water bath, which temperature was between of 2 to 5 °C where it was allowed to cool for 30 min. After cooling proper amount of epoxy ethane was added into the flask, which still was in the ice water bath for 30 min. Ice water bath was then heated gradually to 50 °C where it was kept for 8 h to obtain the products. To neutralize the sample it was filtered and washed. To produce CNC-HPC sample same process can be used, only epoxy ethane is replaced by epoxy propane. All samples were dried in thermostatic chamber for 48 h and at 80 °C and then cooled down at room temperature in desiccator. (Wang *et al.* 2007, 229)

Properties of these grafting modified CNCs were investigated. Degree of substitution was measured using nuclear magnetic resonance (NMR). In modified CNCs the amount of un-reacted cellulose chains disturbed the results and because of that these modified CNCs should be further treated by dissolving derivatives in organic solvents. CNC-CA was treated by propionylation and CNC-HEC and CNC-HPC was modified by acylation. Substitution degree SD was measured to be respectively 0.081; 0.18 and 0.3 for CNC-CA, CNC-HEC and CNC-HPC. (Wang *et al*. 2007, 229)

Dispersibility of modified and unmodified CNCs was studied. Dried CNC samples were added in proper amount of solvent and then treated with an ultrasonic oscillator for required time. After 2 h of ultrasonic treatment CNC-HEC and CNC-HPC dispersed in de-ionized water and CNC-CA dispersed in weak acetic acid but unmodified CNC was not dispersed in de-ionized water after 4 h treatment. (Wang *et al*. 2007, 230)

Crystallinity was also studied and result of that study was that for unmodified CNC and CNC-CA the crystallinities were 81% and 82% but for CNC-HEC and CNC-HPC 50% and 59%. Thermal properties were also studied by thermogravimetric analyses (TGA). Result of studies was that weight loss of unmodified and modified CNC was quite different. Modified CNC started to lose its weight later, at temperature of 200 °C, than unmodified CNC, which started to lose its weight at 175 °C and the drop was faster than for unmodified CNCs weight loss. Also the compostable weight for modified CNC was little bit less than for unmodified CNC. Particularly CNC-CA weight loss was greater than that of other modified CNCs. At temperature of 600 °C, the remaining weight of CNC-CA was about 18% and other CNCs it varied around 30%. According to Wang *et al*. (2007, 230) reason for the thermal properties variations was that although, unmodified CNC were neutralized by washing, there still seemed to be sulfate groups on its surface and this caused the decomposition at lower temperatures.

5.3.5 Acetylation

In experimental acetylation process 18.5-185 mg of iso-octadecenyl succinic anhydride (iso-ODSA) or 15.5-155 mg of n-tetradecenyl succinic anhydride (*n*-TDSA) was dispersed in 3.6 mL of distilled water and then the solution was put to homogenizer to obtain white emulsion. Solution was then mixed with 1 mL of 1.5% (w/w) cellulose nanocrystals and then stirred for five min. After stirring, the solution was filtrated with 0.45 μm membrane filter by suction. Then quantity of an alkyenyl succinic anhydride (ASA) added was 2 to 20 times molars to the surface hydroxyls of cellulose nanocrystal. The solution was then filtrated and CNCs collected as filter cake. After that CNCs were freeze-dried and then heated to 105 °C for 5 to 240 min. The dry sheet of CNC was dispersed in acetone using sonication and the unreacted alkyenyl succinic anhydride and its hydrolyzed product, ASAcid, removed completely by filtering the acetone dispersion solution several times. After this purified CNCs were collected after filtration to membrane filter. (Yuan *et al*. 2006, 696-697)

The degree of substitution was measured in both acetylated CNC using XPS calibration method. For iso-ODSA acetylation the SD was measured, at 2 h heating time, to be 0.0162 and for *n*-TDSA acetylation SD was measured, at 15 min heating time, to be 0.0176. The morphology was also studied and in both acetylation processes no morphological changes of CNCs were discovered. (Yuan *et al*. 2006, 696-697)

5.3.6 Calcium carbonate

One method to modify CNC or MCC surface is to use calcium carbonate $\mathrm{CaCO_3}$ at the surface of cellulose. This new method has been developed by Jia *et al.* (2012, 179-184). In this hydrothermal synthesis 7.00 g of NaOH and 12.0 g urea are added into 81 mL of distilled water under vigorous stirring. Then 3.24 g of MCC is added into NaOH-urea solution, stirring is kept vigorous. This solution is then cooled at -12 ºC for 12 h.

After cooling 10 mL of cellulose NaOH-urea solution is mixed with 5 mL of $\mathrm{Ca(NO_3)_2 \cdot 4H_2O}$ solution, which concentration is 0.40 mol/L and 5 mL of $\mathrm{Na_2SiO_3 \cdot 9H_20}$ which concentration is 0.40 mol/L under vigorous stirring. The mixture is then transferred into 25 mL Teflon-lined stainless steel autoclave and temperature set for 160 °C and time between 2 to 12 h. (Jia *et al*. 2012, 180)

This cellulose/$CaCO_3$ was characterized with its phase, microstructure and morphologies and different heating times and temperatures were tested. The phase of cellulose/$\mathrm{CaCO_3}$

bionanocomposites was characterized by X-ray powder diffraction (XRD). According to Jia *et al*. (2012, 180-181) when the heating time is long, 12 to 24 h, there is more calcite and when the heating time is short 2 to 6 h, there is more aragonite. Aragonite is metastable phase of $\mathrm{CaCO_3}$ and calcite is thermodynamically stable phase of $\mathrm{CaCO_3}$. Changes of morphology at bionanocomposites by different heating time and temperature were tested by SEM. When the heating temperature was 160 ºC and time varied between 2 to 12 h there was some changes. Within time between 2 to 4 h morphology did not change, but when the heating time was 6 h the aggregation and growth of $\mathrm{CaCO_3}$ was observed. When the time was increased to 12 h, the porous structure of $\mathrm{CaCO_3}$ agglomerates appeared.

Different heating temperatures were tested with 24 h heating time. When the temperature was 120 ºC there were no significant changes of morphology of cellulose/$\mathrm{CaCO_3}$ bionanocomposites. When the temperature was increased to 180 ºC, there were no $\mathrm{CaCO_3}$ congregates found. According to Jia *et al*. (2012, 182) the heating temperature has some effect on morphology of bionanocomposites.

Thermal stability was tested by TGA and DTA at cellulose/$\mathrm{CaCO_3}$ which was prepared at heating temperature of 160 ºC and time 2 h, 12 h and 24 h. 5% weight loss was discovered at temperature between 20 ºC and 150 ºC. At around 250 ºC to 350 ºC the first weight loss was discovered and it was respectively 25% for every heating time. Second weight loss happened at temperature between 350 ºC to 500 ºC and then the weight loss was 20%. Total weight loss was 46.8% for 2 h heating time, 43.4% for 12 h and 47.3% for 24 h heating time. (Jia *et al*. 2012 182-183)

Other method was also tested. Islam *et al*. (2011, 755-763) studied arsenate removal from aqueous solution by cellulose-carbonated hydroapatite nanocomposites. In this method beginning is the same as presented by Jia *et al*. (2012, 180) except the cooling was done at 0 ºC for 12 h. After cooling, 0.110 g of $\mathrm{CaCl_2}$ and 0.094 g $\mathrm{NaH_2PO_4}$ were added into the 5 mL mixture of cellulose-NaOH-urea solution with 40 mL of distilled water under vigorous stirring. This mixture was then heated to 90 ºC for certain time by microwave. After microwave treatment the product was separated from the solution by centrifugation and washed with water and ethanol and then dried at 60 ºC.

5.3.7 Other methods

Cellulose nanocrystals can be used in synthesis of metal oxides. Syntheses of silver (Li *et al.* 2011, 422-429) and titanium oxide (Zhou *et al.* 2007, 5050-5052) have been developed. Titanium chloride and CNC was synthesized to produce $\mathrm{TiO_2}$ nanocubes. In this process distilled water of CNC homogenous dispersion (3w-%) was obtained through ultrasonic treatment. Titanium chloride $TiCl_4$, which titanium concentration was 0.015 mol/L was dropped into provided dispersion in 250 mL rounded bottom flask and then vigorously stirred for 4.5 h at 90 ºC. Above solution was then centrifuged and washed with distilled water three times and then filtered and desiccated in vacuum at 70 ºC. (Zhou *et al.* 2007, 5051)

Cellulose-silver synthesis was prepared by Li *et al.* (2011, 422-429). In this synthesis 3.044 g of LiCl was added into 40 mL of DMAc under vigorous stirring to produce LiCl/DMAc solution. After that 2.848 g of MCC was dissolved directly into aqueous LiCl/DMAc solution under vigorous stirring to produce cellulose solution. This solvent was then heated at 90 ºC for 3 h. After heating 5 mL of cellulose-silver solution was added directly into 30 mL of DMAc and then 3.00 g of ascorbic acid and 0.338 g of $\mathrm{AgNO_3}$ were added into resulting colloidal solution under vigorous stirring. This solution was then heated by microwave at 150 ºC for 40 min. After heating, solution was air cooled to room temperature naturally. The final product was prepared by centrifugation from solution and washing three times with ethanol and then dried at 60 ºC in vacuum.

Both cellulose-metal synthetic products were characterized. Thermal gravity analysis (TGA) was tested in both synthesis. CNC-TiO_2 started to lose its weight first time at temperature below 130 ºC, when it lost 8% of its original weight. According to Zhou *et al*. (2007, 5052) this was caused by water evaporation. Second weight lost happened at temperature between 130 ºC to 330 ºC when it lost approximately 10% of its weight. This was caused by oxidation and carbonization of the three polymers of CNC. Final weight loss happened at temperature between of 330 ºC and 540 ºC when 20% from its original weight was lost caused by combustion of the packed CNC in TiO_2 particles. (Zhou *et al*. 2007, 5052)

Cellulose-silver nanocomposites' thermal behavior was characterized in different ascorbic acid concentrations. Concentrations were 0.352; 1.000; 2.000 and 3.000 g. For all of those the first weight loss was between of 100 ºC and 120 ºC, which was caused by loss of hydrate and coordinated water. Second and bigger weight loss happened at temperature between of 300 ºC to 500 ºC. At low concentrations of ascorbic acid 0.352 g and 1.000 g weight loss was greatest. These two lost 94.5% and 89.2% of original weight when the temperature was reached to 600 ºC. For 2.000 g and 3.000 g total weight losses were smaller. Weight losses for different ascorbic acid concentrations were 42.7% for 2.000 g and 65.3% for 3.000 g. (Li *et al*. 2011, 424-425)

5.4 Applications for cellulose nano/micro crystals

Cellulose nanocrystals have been under great interest in past few years. Different applications have been studied and tested. Because of CNC's large surface area and nonporous structure CNC has been tested as agent for protein or/and enzyme immobilization. Because of CNC biocompatibility, good strength and high water holding capacity the interest of using CNC as antimicrobial and medical applications has grown. Hydrogels derived from CNC can be processed into spheres, tubes or films and CNC can be used to produce carbon based nanotube-cellulose conducting films. After synthesis of silver (Ag) the product can be used to generate an antimicrobial wound dressing material. Because of similar properties of collagen and its low cytotoxic and genetoxic properties, CMC has been used in tissue engineering for 3D model. Also the hydrogels of bacterial cellulose have been used after casting as tubes, which are suitable for artificial blood vessels. CNC from bacteria has been thought as potential source of tissue replacement, by itself or as scaffolds for the replacement material. (Lam *et al*. 2012, 2-4)

CNCs can be used as biosensors and bioimaging. As known, functional groups at the surface of CNC can be modified, but also it can be conjugated with different biological moieties or used as binding site for metallic nanoparticles. Those can be used as biosensors and bio imaging. Another possible application for CNC could be drug delivery. MCC has been used as blender with other pharmaceutical excipients to form drug-loaded tablets. Some derived cellulose such as ethyl cellulose has been used in injectable, oral and topical formulations. (Lam *et al*. 2012, 5)

CNC has been used as reinforcing filler in polymer matrices. CNC morphology is unique, dimensions are nanoscale, it has large surface area, low density, and high mechanical strength and its surface can be easily modified. Because of those features CNC has been incorporated into wide range of different polymer matrices. For example poly(vinyl alcohol), epoxides and polysulfonates. (Habibi *et al*. 2010, 3493) Barrier membrane, which is made from poly(vinyl alcohol) (PVOH) with CNC and crosslinked by poly(acrylic acid) (PAA) the water vapor transmission rate (WVTR) is lower than in pure poly(vinyl alcohol) membrane. When the membrane is prepared at 10% CNC, 10% PAA and 80% PVOH the WVTR is around 10 $\mathrm{g/m^2h}$ and for pure PVOH it is 32 $\mathrm{g/m^2h}$. The carboxylation of CNC surface did not affect the initial result. (Paralikar *et al*. 2008, 254-255)

MFC gel as film or nanocomposite and paper can be combined. To use of combination of MFC and paper could improve the mechanical and barrier properties of paper. This has been tested in food packing industry with good results. For example water vapor transmission rate (WVTR) for 25 μm thick film was $7-8\ \mathrm{g/m^2d}$ which is close to WVTR value 5 $\mathrm{g/m^2d}$, which is value of high moisture barrier material. MFC has been studied for printing applications. When using MFC as coating on paper it might increase the sheet resistance to penetration. It also improves inks density at paper. (Lavoine *et al*. 2012, 758-760)

The use of MCC based nanocomposites for water purification process has been studied by Islam *et al*. (2011, 755-763) Islam *et al*. studied arsenate removal from aqueous solution using MCC-carbonated hydroxyapatite nanacomposites in different conditions. Result was that adsorption maximum was 12.2 mg/g and best conditions were when pH was ranging from 4 to 8. $\mathrm{MFC/TiO_2}$ sol-gel synthesis at mild reaction conditions product have been tested for destroying organic pollutants from water. The $\mathrm{MFC/TiO_2}$ was used as nanocatalyst for catalytic adsorption of methylene blue. According to Virkutyte *et al*. (2012, 292) adsorption capacity of nanocatalyst was 0.13 mg/g, which is better than that of commercial catalyst 0.065 mg/g.

6 Experimental testing for modified micro fibrillated cellulose for water purification process

6.1 Used analytical methods

Chapter 4 presented different kind of analytical methods to determine hydrogen sulfide from water. ICP, GC and HPLC have shown their potential for measuring hydrogen sulfide from water. In this study ICP was used. Reason for this is that Laboratory of Green chemistry has ICP, GC and HPLC and according to chapter 4 it seems that ICP could be more simple and reliable way to measure hydrogen sulfide from aqueous matrix than GC or HPLC. Also the Colon *et a.l* (2008, 160-168) developed methods seems to work with the Asaoka *et al.*(2009) developed hydrogen sulfide adsorption test method.

6.1.1 ICP

In this study ICP was used to measure hydrogen sulfide from water samples with few modifications on Colon *et al*. (2008, 160-168) system in Figure 1b. Operation parameters were kept as close as possible to be same as Colon *et al*. optimized. Operation parameters are in Table 8. ICP was Thermo, Electron Corporations Icap 6000 Series ICP-OES Spectrometer. Auto sampler was Cetac ASX- 260.

For washing the rinse nitric acid is normally used. To determine hydrogen sulfide 5% HCl was used for rinsing. 10 M HCl was used as acid to produce hydrogen ions. When sulfide reacts with hydrogen ion in acidic environment it produces hydrogen sulfide. Other change was in nebulizer. According to Colon *et al.* (2008, 161) no argon was used in nebulizer. In this study argon was used. Colon *et al*. used different inner diameter tubes to have ratio of sample flow rate acid flow rate to optimal balance as 5.3. In this study outside pump was used to manage the same task. Pump was Watson Marlow 120s. As it is in Table 8 sample acid flow rate ratio is the same, but flow rates are smaller than used by Colon *et al* (2008).

Table 8. ICP operation parameters

ICP operation parameters	
RF power	1350 W
Nebulizer gas flow	0.5 mL/min
Auxiliary gas flow	0.2 mL/min
Plasma gas flow	15 L/min
Sample flow rate	3.529 mL/min
Acid flow rate	0.643 mL/min
S wavelength	180.731; 180.034nm

To test this method spiked samples were made. Spiked samples were made by using Colon *et al*. (2008, 160-168) method with some modification. 10 mL of spiked samples, which concentrations were 2.0 and 5.0 mg/L of hydrogen sulfide were prepared as follows. 5 mL of buffer, which was made according to Colon *et al*. (2008, 162), 0.2 mol/L of ascorbic acid and 2.0 mol/L of NaOH were mixed in Millipore water. L-ascorbic acid came from Sigma-Aldrich and it was bioultra pure (≥99.5%). NaOH came from Merck and its purity was 99-100%. Then appropriate amounts of sodium sulfide-y-hydrate was diluted in buffer and filled to mark at 10 mL by Millipore water. Also hydrogen sulfide concentration of 15.0 mg/L was measured, but this was not spiked sample. In the case of 15 mg/L, 3 mL of hydrogen sulfide solution, which concentration was 30 mg/L was diluted with 3 mL of buffer and measured.

6.2 Sample preparation

In chapter 5.3 different kinds of CNC and MFC synthesis were presented. For this study five different syntheses with some modifications were tested. Basic idea of those syntheses was to use chemicals, which have been studied and tested for hydrogen sulfide adsorption and then study and test how it would work with MFC. In some cases no data or articles were found to support synthesis.

6.2.1 Cellulose with amines

Amines have been used for gaseous hydrogen sulfide adsorption by aqueous 2-amino-2-methyl-1-propanol (AMP) and *N*-methyldiethanolamine (MDEA). Also other hindered amines, for example diisopropanolamine (DIPA) have been used as adsorbent in gaseous hydrogen sulfide adsorption. (Mandal *et al*. 2004, 192)

Nanocrystal cellulose was prepared by silanization with modification. In this study N2 (N-[3-(trimetloxysily)prolyl]ethylenediamine) and N3 **(**N'-(3-trimethoxysilylpropyl) diethylenetriamine) were used to silanizate cellulose with simple process. N2 and N3 came from Sigma-Aldrich and purity was ≥ 98% and technical grade.

In process 10 g of MFC, 5 g of N2 or N3, and 100 mL of ethanol/water solution (80/20) was stirred for 2 h by magnetic stirrer. Ethanol was Aa glass and it was delivered by Altio. After stirring, solutions were centrifuged at 4000 rpm for 4 to 5 min and washed with ethanol/water (80/20) solution for several times.

6.2.2 Cellulose with calcium carbonate

Calcium carbonate ($CaCO_3$) has not been directly used as adsorbent for hydrogen sulfide, but according to Asaoka *et al*. (2009, 4129) crushed oyster shell, which was used to adsorb hydrogen sulfide, was consisted primarily of calcium carbonate.

In chapter 5.3.4 basic processes for cellulose/$CaCO_3$ bionanocomposites preparation is described. This process was used without significant modification. Used chemicals sodium hydroxide came from Merck and its assay was 99-100% and urea came from Sigma

Aldrich. Sodium dihydrogen phosphate came from Merck and assay was >99% and calciumchloride-2-hydrate came from Sigma-Aldrich and its assay was >99%.

In typical synthesis 7.00 g of NaOH and 12.0 g urea were added into 81 mL of distilled water under vigorous stirring. Then 3.24 g of MFC was added into NaOH-urea solution and stirring kept vigorous. (Jia et al. 2012, 180) This solution was then cooled at 5 ºC for 12 to 18 h.

After cooling 50 mL of MFC-NaOH-urea solution was mixed with 25 mL of $\mathrm{CaCl_2 \cdot 2H_2O}$ solution, which concentration was 0.402 mol/L and 25 mL of $NaH_2PO_4 \cdot H_2O$, which concentration was 0.802 mol/L under vigorous stirring. The mixture was then transferred into oven where the temperature was set to 160 ºC for 6 h. After heating cellulose/$\mathrm{CaCO_3}$ mixture was centrifuged at 4000 rpm for 5 min. Cellulose/ $\mathrm{CaCO_3}$ mixture was washed by water and ethanol and centrifuged several times and then dried at 60 ºC for 15 min. (Jia et al. 2012,180)

Other synthesis for MFC/ $\mathrm{CaCO_3}$ was also tested. Process was the same as Jia *et al*. (2012, 180) presented except concentrations, volumes and treatment time were changed. In this synthesis after cooling 25 mL of MFC-NaOH-urea solution, 100 ml of $\mathrm{CaCl_2 \cdot 2H_2O}$ solution, which concentration was 0.049 mol/L and 100 ml of $\mathrm{NaH_2PO_4 \cdot H_2O}$ solution, which concentration was 0.039 mol/L were added to mixture, stirred vigorously approximately for 5 min. After stirring, the solution was put to oven for 24 h at temperature of 160 ºC. After heating solution was centrifuged and MFC/$CaCO_3$ was washed with ethanol/water (80/20) solution several times.

After washing there was two different preparation conducted. In the first one $MFC/CaCO_3$ was dried in the oven at 60 ºC for 15-25 min and then crushed. In other method after washing the $MFC/CaCO_3$ bionanocomposite was left wet. The first $cellulose/CaCO_3$ synthetic product was dropped out and adsorption tests made by using the product from the second synthesis.

6.2.3 Titanium oxide nanocubes

Titanium oxide TiO_2nanocubes were synthesized using the method developed by Zhou *et al.* (2007, 5050-5052). Synthesis is described in chapter 5.3.5. In this study 0.7 g of MFC was added to 200 mL of distilled water and then 340 μL of $TiCl_4$ was added and stirred in water bath for 4.5 h at temperature around 55-60 °C. After stirring resulting precipitates were centrifuged at 4 000 rpm for 10 min and washed with water for 3 times. After that sample was filtrated and heated at 70 °C for 5 min. and then transferred in vacuum.

6.2.4 Cellulose membrane paper

Cellulose membrane papers were synthesized by using method of Gou & Ruckenstein (2001, 131-140; 2002, 53-62). Filter paper was used as source of cellulose. Forty filter papers were first mercerized by using 400 ml of 8 M NaOH solution at room temperature for 20 min. Then those papers were washed with millipore water and then immersed in reducing 0.2w-% $NaBH_4$ solution to avoid oxidation. (Guo & Ruckenstein 2001, 132) After mercerization cellulose papers were prepared by crosslinking the filter papers at mixture which composed 40 mL of 6.25 M NaOH, 100 mL of epichlorohydrin and 150 mL of DMSO (dimethyl sulfoxide). Filter papers were immersed sequentially into mixture and then allowed to react with all 40 sheets with 2 h at 50 °C with shaking the mixture to keep concentration uniform. After reaction the filter papers were washed with millipore water until neutral conditions were achieved. (Gou & Ruckenstein 2002, 55)

6.2.5 MFC cationization via epoxides

MFC was epoxied by using method of Gou & Ruckenstein (2001, 131-140; 2002, 53-62). Exception was that in this process cellulose membrane filter papers were replaced by MFC. In this process 5.07 g of MFC was first mercerized using 200 mL of 8 M NaOH solution at room temperature for 20 min. Then the solution was centrifuged and washed with ultra-pure water for several times. After mercerization MFC was prepared by crosslinking in mixture which composed 20 mL of 6.25 M NaOH, 50 mL of epichlorohydrin and 75 mL DMSO. MFC-NaOH-epichlorohydrin-DMSO solution was stirred for 2 h at 50 °C. Then the solution was centrifuged and washed with ultra-pure water until neutral conditions were achieved.

Activation of MFC by epoxy reagent was carried out by using Gou & Ruckenstein’s (2001, 131-140; 2002, 53-62) method with some modifications. According to Cou & Ruckenstein cellulose membranes were packed into cartridges, which through solutions were pumped. In this case cartridge could not be used, because MFC was used. MFC was added into reacting solution containing 32.5 mL of DMSO, 17.5 mL of 1,4-butanediol diglycidyl ether and 17.5 mL of 1 M NaOH. This was stirred for 2 h at room temperature. After reaction MFC/epoxide was centrifuged, washed until neutral conditions were achieved and filtered. After process weight of MFC/epoxide was measured and it was 0.109 g.

6.3 Adsorption tests for hydrogen sulfide

6.3.1 Adsorption tests for one component adsorption

Series of samples were made in ultra-pure water in sodium sulfide-y- hydride $\mathrm{Na_2S \cdot 3H_2O}$ at the concentration of 116.25 mg/L. This corresponds the 30 mg/L of hydrogen sulfide. Sodium sulfide-y-hydride came from VWR and its purity was more than 60 %. Sample was put into TOC bottles with magnetic stirring rod. Figure 2 shows the basic system of adsorption test. Stirring velocity was kept quite low to avoid evaporation of sulfide. Nitrogen gas was used to inhibit the evaporation of sulfide from the solution.

After 10 min of stirring, 3 mL of sample was injected to test tube containing 3 mL of buffer. When the sample was injected from the adsorption test, access of modified MFC into the sample was tried to avoid. In every series of different hydrogen sulfide concentration, reference sample was made without modified MFC. That was made to see how much sulfide was evaporated at 10 min treatment time.

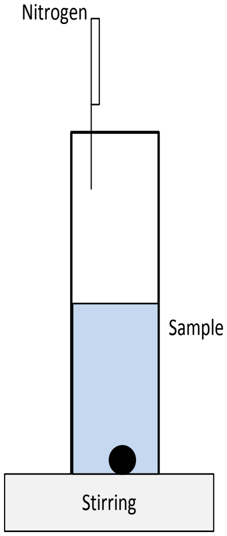


Figure 2. Adsorption test system

Tested modified MFCs were N2 and N3 silanized MFC, both dry and wet $\mathrm{MFC/CaCO_3}$ cellulose membrane with crosslinking and MFC without any modification. In this study, in standard adsorption test 10 mL of sodium sulfide-y-hydride solution and respectively 100 mg of modified/unmodified MFC was stirred in TOC bottle for 10 min. Sometimes 50 mg of dry/crushed $MFC/CaCO_3$ was used with 10 mL of sodium sulfide-y-hydride solution. Tested hydrogen sulfide concentrations were 20, 30, 50, 70, 80 and 100 mg/L for MFC/N2 and MFC/N3. In case of dry $\mathrm{MFC/CaCO_3}$ 100 mg/L adsorption test was not measured. For modified membrane filter hydrogen sulfide concentrations 80 and 100 mg/L were not measured. In case of unmodified MFC and wet $MFC/CaCO_3$ only concentrations of 20, 30 and 50 mg/L were tested. Some adsorption tests were also made for MFC/TiO_2 nanocubes and for MFC/epoxide. Tested method is similar which Asaoka *et al*. (2009, 4128) used at their adsorption test for hydrogen sulfide.

6.3.2 Adsorption test in different pH

Changes in solutions pH can cause difference in adsorption capacity. According to Rahman *et al*. (2009, 277) pH affects the surface charge of adsorbent and ionization degree and speciation of adsorbate during adsorption. When the hydrogen sulfide concentration was 30 mg/L the pH was 10.8. Effect of different pH was tested by using dry $MFC/CaCO_3$, modified membrane filter, MFC/N2 and MFC/N3. pH of samples solutions was adjusted using 0.1 M HCl (Asaoka *et al*. 2009, 4128). Tested pHs were 9, 8, 7 and 6. The adsorption tests were carried out by same procedure as in one component adsorption test.

6.3.3 Effects of different matrix

Two previous adsorption experiments were tested in ultra-pure water. In this test 1w-% sodium chloride solution was used to find out how other chemicals affect hydrogen sulfide adsorption. Tested modified MFCs were dry $MFC/CaCO_3$, MFC/N2 and MFC/N3. Also modified membrane filter was tested. The adsorption tests were carried out using the same procedure as in one component adsorption test.

7 Result of experimental testing

7.1 Result of ICP testing

Results of ICP testing are in Table 9. Calibration of ICP was made in range of 0.5 to 20 mg/L and correlations of calibration curve for wavelength of 180.731 nm was 0.99918 and for 180.034 nm 0.99938. As discussed in chapter 6.1.1 the Ref I was measured from reference samples. As it presented at Table 9 for all tested concentration levels the results are close to spiked or reference concentration. In Tables 4 and 9 measured hydrogen sulfide concentration are in same concentration level and in both cases ICPs results are close to initial hydrogen sulfide concentrations.

Table 9. Results of ICP testing

Sample	Initial concentration [mg/L]	Measured concentration [mg/L]	Stddev
Test I	2.00	1.928	0.052
Test II	5.00	5.503	0.139
Ref I	15.00	14.5252	

7.2 Adsorption capacities of different MFC or membrane filter based adsorbents

Adsorption capacity describes the amount of adsorbate that can be adsorbed on the surface of adsorbent. To calculate adsorption capacity the initial concentration of adsorbate and its concentration after adsorption process have to be known. Also solution’s volume and weight of adsorbent needed. Adsorption capacities of different MFCs based adsorbents were calculated using equation (9).

$$Q_e = \frac{(C_0 - C_h - C_a)V}{W} \quad (9)$$

Where

Q_e is adsorbents average adsorption capacity of hydrogen sulfide [mg/g]

C_0 is initial concentration of hydrogen sulfide [mg/L]

C_h is average concentration which evaporate during the treatment time [mg/L]

C_a is average concentration which is measured at the sample after adsorption test [mg/L]

V is sample volume [L]

W is average mass of adsorbent [g]

C_h Was calculated for reference samples, which were obtained without any modified/unmodified MFC or membrane filter. During 10 min adsorption time evaporating concentration of hydrogen sulfide is calculated by using equation (10).

$$C_h = C_o - C_{ref} \quad (10)$$

Where

C_0 is initial concentration of hydrogen sulfide [mg/L]

C_{ref} is measured average hydrogen sulfide concentration at reference sample [mg/L]

Adsorption capacities of different adsorbent were calculated using equation (9) and (10). Results of ICP-OES measurements for pure water hydrogen sulfide adsorption test, which were calculated to obtain right concentrations, are found in appendices I. Also in appendices I the average weights of adsorbents are presented. Figure 3 shows all the adsorption capacities as a function of hydrogen sulfide concentration. For the MFC, MFC/N2, MFC/N3 and wet MFC/$CaCO_3$ the average weights were measured for moist mass. MFC, MFC/N2 and MFC/N3 were all quite heterogeneous adsorbents, which may have affected the results.

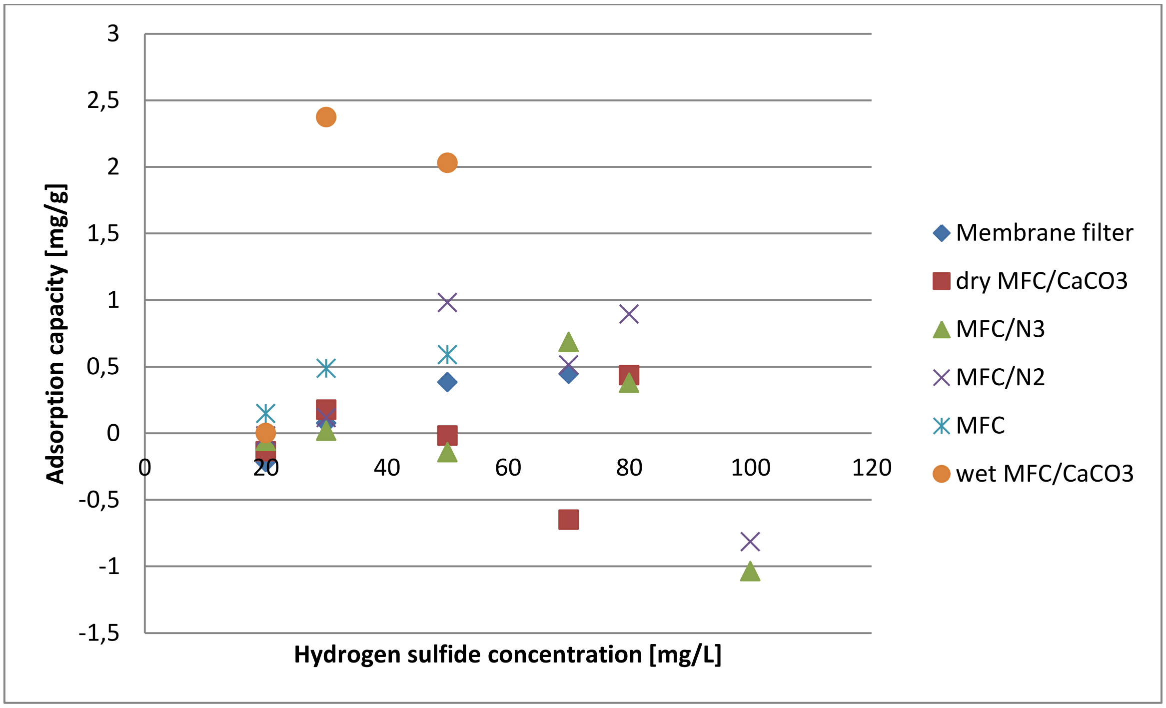


Figure 3. Adsorption capacities for modified/unmodified MFC and modified membrane filter

For demonstration, adsorption capacity of modified membrane for hydrogen sulfide concentration of 70 mg/L is calculated. In reference samples average concentration was 71.16 mg/L which is also initial concentration of hydrogen sulfide. Because of that there was no evaporation so C_h is 0 mg/L and according to Appendices I the measured hydrogen sulfide concentration is 66.78 mg/L and average weight of sample 0.0983g. Volume of solution was always 10 mL.

$$Q_e = \frac{\left(\frac{71.16mg}{L} - \frac{66.78mg}{L}\right) x0.01L}{0.0983g} = 0.445mg/g$$

Adsorption capacities of dry MFC/$CaCO_3$, MFC/N3 and MFC/N2 for low hydrogen sulfide concentration were close to zero, even unmodified MFC's adsorption capacity was higher. There are also some results that do not fit. For example adsorption capacity of dry MFC/$CaCO_3$ crashed at hydrogen sulfide concentration of 70 mg/L to -0.64 mg/g and then at hydrogen sulfide concentrations of 80 mg/L to 0.434 mg/g. Figure 3 shows that the best adsorption capacity of hydrogen sulfide was obtained for wet MFC/$CaCO_3$ bionanocomposites.

7.3 pH effects on adsorption capacity

Effect of different pH was tested using modified membrane filter, MFC/N2, MFC/N3 and dry MFC/$CaCO_3$. Figure 4 shows adsorption capacities of different adsorbents. All the measurements were done at hydrogen sulfide concentration of 30 mg/L. When hydrogen sulfide concentration was 30 mg/L, the solution pH was 10.8. The average adsorption capacities are calculated using equation (9). The ICP-OES measurement, average weight of adsorbent and calculations are shown in Appendices II.

The effect of different pH seems to be quite similar for all the adsorbents. For pH levels 6 and 9 the adsorption capacities are higher than for pH 7 and 8. The difference in adsorption capacities for different pH levels seems to be quite big for MFC/N3 and dry MFC/$CaCO_3$. For dry MFC/$CaCO_3$ at pH 6 the adsorption capacity is almost double what the adsorption capacity is at pH 7. For the MFC/N2 at pH 8 tests did not work so the real adsorption capacity might be higher than what the Figure 4 shows.

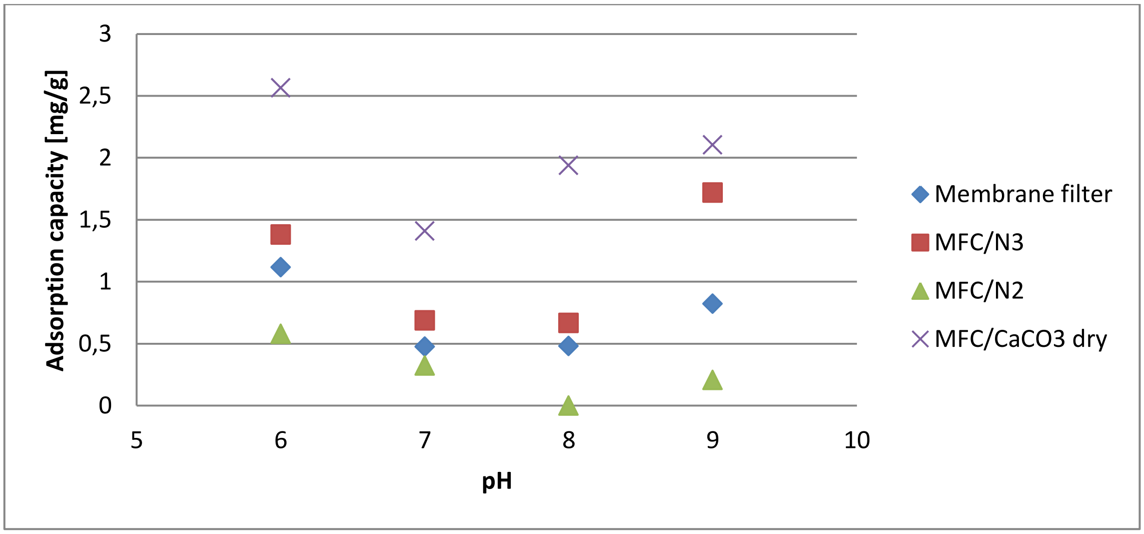


Figure 4. Effect of different pH for adsorption capacities of different pH.

7.4 Salinity and its effect on adsorption capacity

An effect of salinity was tested by using 1w-% NaCl solution as background. Figure 5 shows adsorption capacities of tested adsorbents. If these results are compared to result in Figure 3 it is found that MFC/N2 has lost more than half of its capacity when the hydrogen sulfide concentration is 50 mg/L. In pure water test it was 0.989 mg/g and now it is 0.41 mg/g, although its adsorption capacity has grown at lower concentration of hydrogen sulfide. MFC/N3 seems to work better with sodium chloride solution. During this 10 min adsorption time adsorbent dry $MFC/CaCO_3$ became brown. In one component adsorption test and at different pH it stayed white as it was before the tests. The hydrogen sulfide concentrations after adsorption process, average weight of adsorbent and adsorption capacities are presented in Appendices III

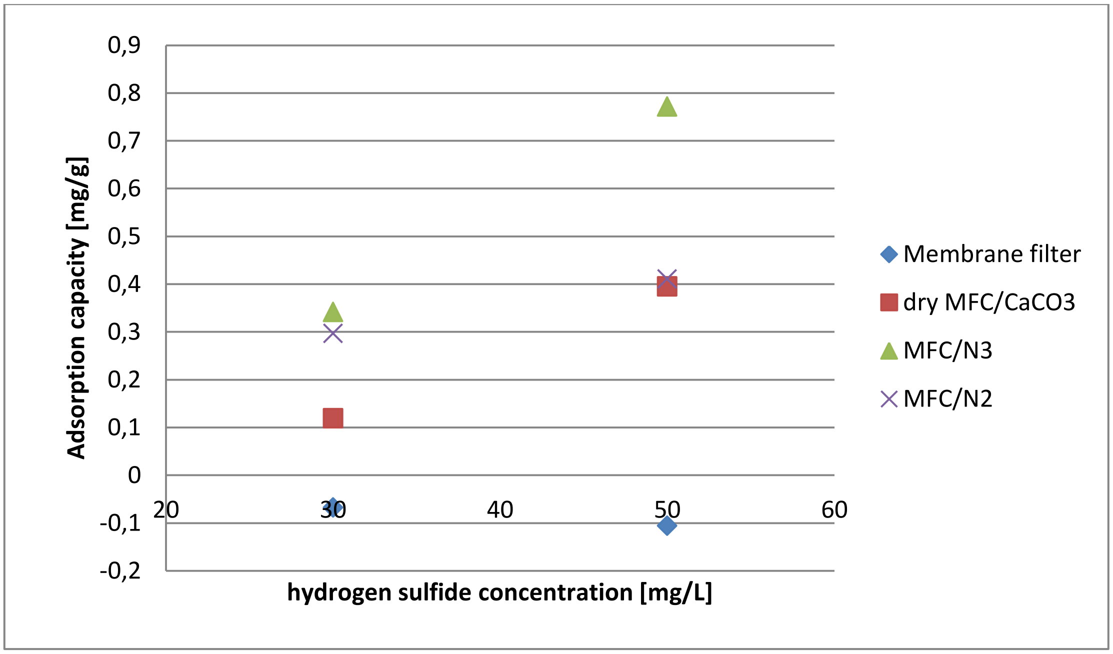


Figure 5. Adsorption capacities of membrane filter, $MFC/CaCO_3$dry, MFC/N2 and MFC/N3 in 1w-% sodium chloride solution.

7.5 Adsorption isotherms

Adsorption isotherms were presented shortly in chapter 3.1. Some of those were tested for different modified/unmodified MFC and membrane filter. Tested isotherms were Langmuir, Freudlich and Sips isotherms and error function used was ERRSQ. The fitting and calculations were conducted using Microsoft Excel-program Solver. The initial calculations for different adsorbents are in Appendices IV. In Figure 6 to 9 the adsorption capacities and previously mentioned isotherms are depicted. For membrane filter the best fitting is obtained using the Sips isotherm. The ERRSQ value was also the smallest 0.0475 compared to Langmuir 0.156 and Freudlich 0.273. Reason for pretty good fit of Sips isotherm, according to Repo (2011, 23.) could be that it takes into account the heterogeneity of adsorbents surface.

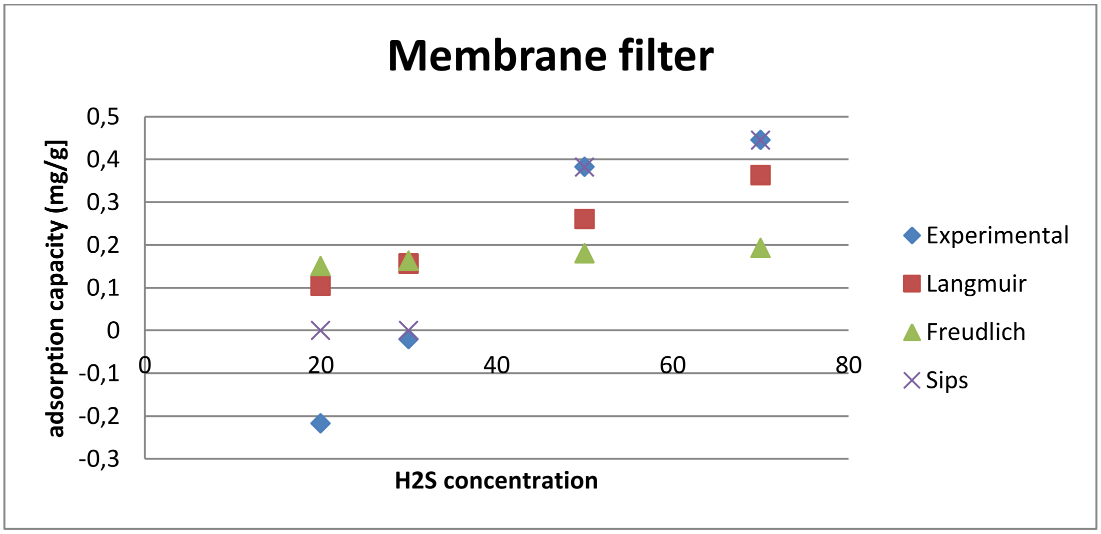


Figure 6. Adsorption capacity and different isotherms of membrane filter

Figure 7 shows MFC/N3 adsorption capacities and adsorption isotherms, which do not fit at all to experimental data. Reason for poor fit could be result of adsorption capacities at experimental measurement for concentrations 50 mg/L, 70 mg/L and 100 mg/L. The ERRSQ values are for Langmuir 0.437, Freudlich 0.439 and Sips 0.259.

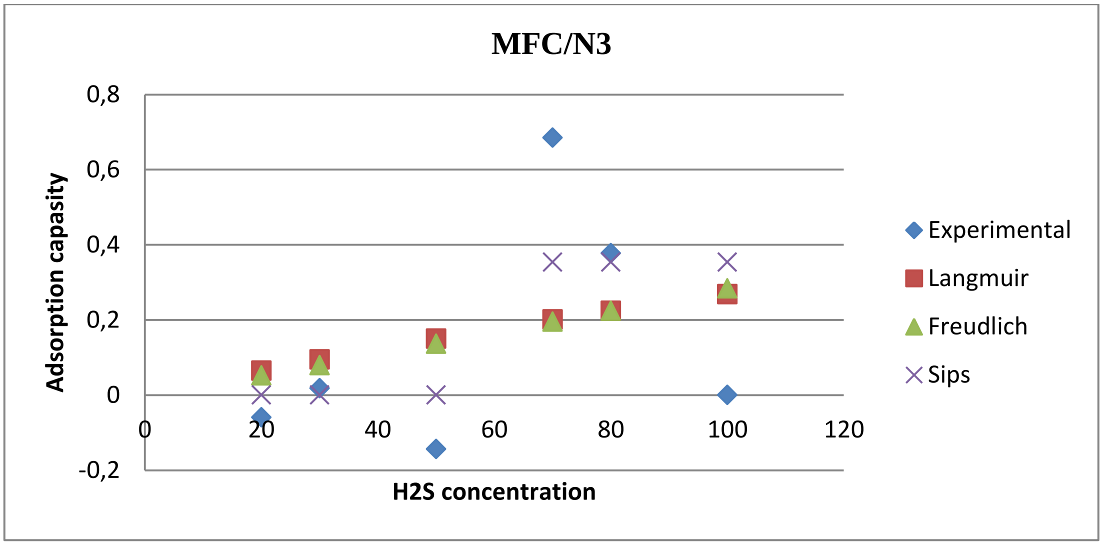


Figure 7. Adsorption capacity and different isotherms for MFC/N3

In Figure 8 adsorption curve for MFC/N2 is shaped like S-isotherm, where the adsorption capacity rises slowly in low concentrations, but in inflection point grows faster. (Repo 2011, 27). Although the adsorption capacity value at hydrogen sulfide concentration of 100 mg/L does not support this. Best fit was given by Sips isotherm. The ERRSQ values for Sips is 0.600, Langmuir 0.877 and for Freudlich 0.943.

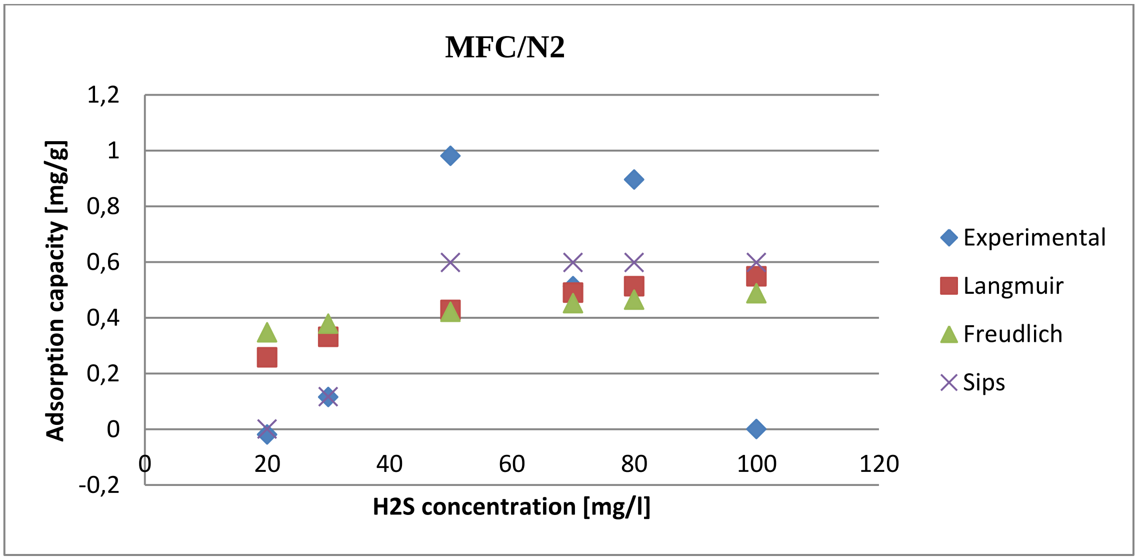


Figure 8. Adsorption capacity and different isotherms for MFC/N2

Figure 9 shows adsorption capacity and adsorption isotherms for dry MFC/$CaCO_3$. The isotherm curves are shape of L-isotherm, where the adsorption capacity raises fast at low adsorbate concentration, reaches its maximum level and stays there, but the experimental data do not support that. (Repo 2011, 27) The best fit is given by Sips isotherm. This can be due to the heterogeneity of adsorbents surface. The ERRSQ value for Sips is 0.0319, Langmuir 0.1197 and Freudlich 0.142.

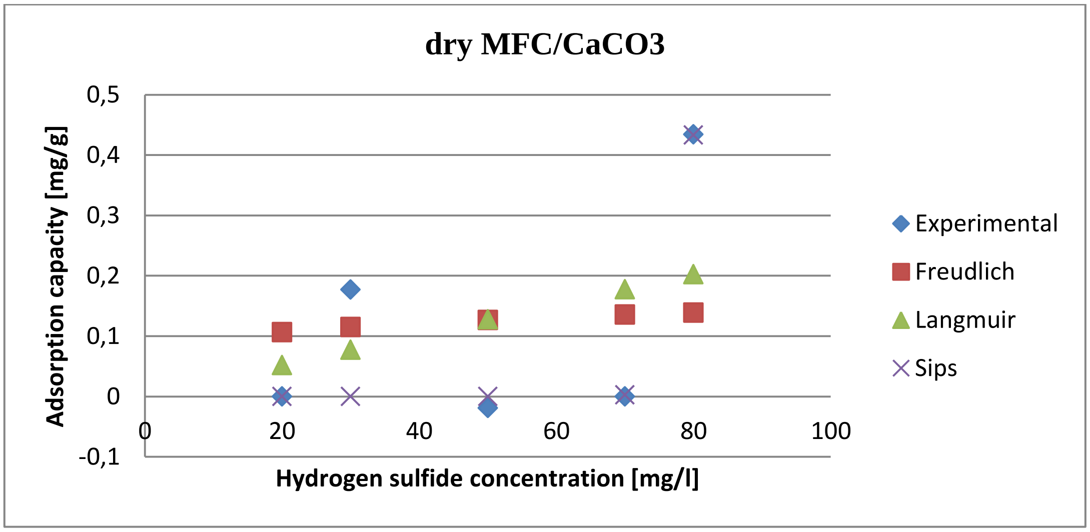


Figure 9. Adsorption capacity and different isotherms for dry MFC/$CaCO_3$

In Figure 10 an unmodified MFC adsorption capacity and adsorption isotherms are shown. The adsorption curve recalls L-isotherm, but it is hard to discover, because of only three concentrations were measured. The Sips isotherm seem to fit the best and this is also confirmed by ERRSQ value, which are for Sips 4.22×10^{-11}, Langmuir 0.0238 and Freudlich 0.0615. The reason could be that the Sips isotherm takes into account adsorbents surface heterogeneity. In the case of unmodified MFC not only the surface but the adsorbent is heterogenic. The MFC consist mainly of water.

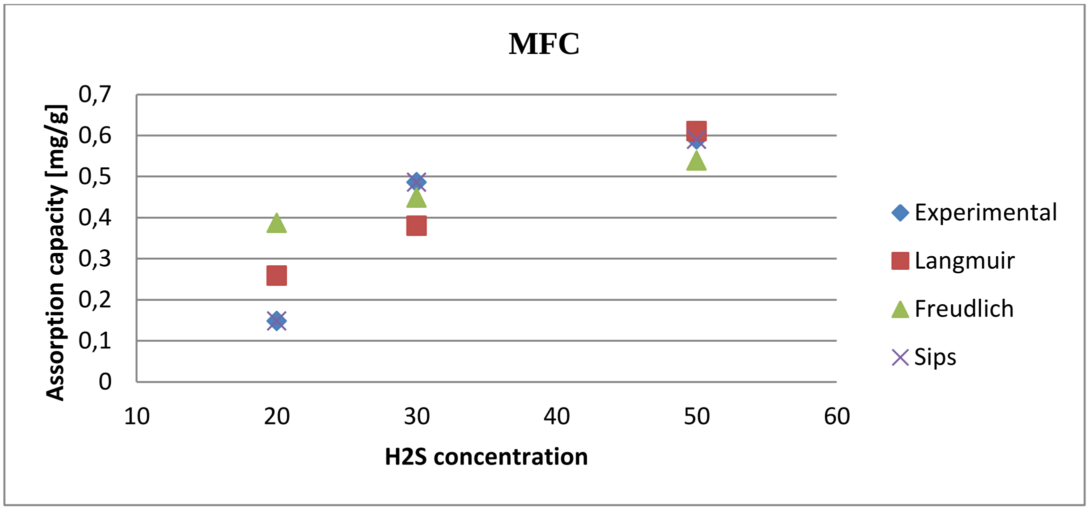


Figure 10. Unmodified MFC and adsorption isotherms.

8 Conclusion for experimental study and development proposal

Hydrogen sulfide adsorption by modified/unmodified MFC and membrane filter was tested. Pure water adsorption tests show that there are great differences in adsorption capacities between different adsorbents. Pure water or one component adsorption, which does not contain other adsorbate or other reagents, is ideal situation, which is highly unlikely to ever occur, but it may give some direction for which adsorbent is most promising. Titanium oxide nanocubes were prepared and some test made, but results of those tests are not reported, because lack of result and in the process MFC was used as basis, which the titanium oxide nanocudes were built. In other syntheses the morphology of MFC was tried to keep intact. Also the MFC/epoxy synthesis was conducted, but because of lack of the results it was not published.

In literature it was discovered that there was only one adsorption study reported where hydrogen sulfide was only target component. (Wang & Pei 2012, 1178-1183) This adsorption study was conducted using ferric and alum water treatment residual. Result from that study cannot be compared directly to results of present study, because of much higher hydrogen sulfide concentration. Also the pH of one component adsorption test was different and if Figures 3 and 4 are compared it can be seen that pH does have effect on adsorption capacity. Unfortunately the best adsorbent at pure water adsorption test wet $\mathrm{MFC/CaCO_3}$ was discovered at the end of the experimental studies and therefore, its adsorption capability was not tested in different pH and salinity conditions.

As discovered pH does have effect on adsorption process. For every adsorbent studied lower pH increased the adsorption capacity. For example for dry $\mathrm{MFC/CaCO_3}$ at pH 6 adsorption capacity at hydrogen sulfide concentration of 30 mg/L was more than ten times higher than that at pH 10.8. The results of Wang & Pei (2012, 1182) have similar features. When the pH was 10.2 the adsorption maximum at hydrogen sulfide concentration of 400 mg/L was 14.74 mg/g and at pH 7.2 for same concentration 40.12 mg/g. To a certain point lower pH gives better adsorption capacities. Difference between the study of Wang & Pei and this study is that in this study pH was measured at the solution without adsorbent. Reason for better adsorption maximum at lower pH could be according to Woodward & Curran (2006, 312) that most adsorbents have weak negative surface charge at lower pH values caused by hydrogen ions. If the dissolved or suspended adsorbate has negative surface charge in lower pH levels the adsorption will increase (Woodvard & Curran 2006, 312). Other possible reason for better adsorption at low pH could be that in low pH up to 6 $\mathrm{H_2}S$ is dominant and when pH increases to 7 to 9 bisulfide $\mathrm{HS^-}$ percentage increases. After pH 9 the sulfide is dominant sulfur species. (Thompson *et al.*1995, 288) This may affect the surface charge of hydrogen sulfide and increase the adsorption at low pH.

The effects on other chemicals were tested using 1w-% sodium chloride solution as background for adsorption experiments for membrane filter, MFC/N2, MFC/N3 and dry $\mathrm{MFC/CaCO_3}$. The results are shown in Figure 5. If these results are compared to pure water adsorption tests it can be seen that change of background has improved the MFC/N2 and MFC/N3 adsorption capacities. It has not affected on the dry $\mathrm{MFC/CaCO_3}$ adsorption capacity at hydrogen sulfide concentration of 30 mg/L. The dry $\mathrm{MFC/CaCO_3}$ and MFC/N3 results at hydrogen sulfide concentration of 50 mg/L at pure water test are so inconsistent that no real conclusion can be made. Dry $\mathrm{MFC/CaCO_3}$ became brown during this adsorption test. This possible contamination may have effected on its adsorption capacity. Asaoka *et al.* (2009, 4127-4132) studied removal of hydrogen sulfide using crushed oyster shell as adsorbent from pore water. The salinity was measured to be respectively 2.85-3.13% and the pH 8.0-8.4. The adsorption maximum was calculated to be 12 mg/g. 3w-% Sodium chloride solutions was tested as background, but no useful data was collected because of problems with ICP.

To find out adsorption maximum at salinity test of MFC/N2, MFC/N3 and dry $\mathrm{MFC/CaCO_3}$ the adsorption isotherms were calculated. Results of the calculations are in Appendices V. The best fit for MFC/N2 was Langmuir isotherm and MFC/N3 and dry $\mathrm{MFC/CaCO_3}$ using the Sips isotherm. The adsorption maximum was 1.13 mg/g for MFC/N3, 0.97 mg/g for MFC/N2 and 0.51 mg/g for dry $\mathrm{MFC/CaCO_3}$. The pH of the solution was measured to be approximately 10. The difference of crushed oyster shells, which mainly are calcium carbonate and dry $\mathrm{MFC/CaCO_3}$ is big. The reason for this difference can be that in this study the adsorption maximum was calculated using quite close concentrations and Asaoka *et al*. (2009, 4130) used larger concentration window from 20 mg/L to 800 mg/L. Also the pH was different.

To compare effects of change in pH and background of sample the difference of adsorption capacities is significant. As it has come to knowledge that difference on the pH seems to have greater effect on adsorption capacity than solutions background. Both of those have positive effect for adsorption capacities of some adsorbents.

There were lots of inconsistencies in the results, which may arise from mistakes in sample preparation or other parts of test protocol. Other source might be ICP-OES. There were times that results were not what they should have been. Possible problem for ICP-OES might have arisen from the used buffer, which was strongly alkaline and contained lots of sodium, which could cause problem at measurement process. Of course in laboratory everything can happen, but no outside reason was discovered and all the tests were done minimum twice to make sure that results were consist and statistically correct.

To develop MFC based adsorbents further the first thing is to conduct more tests with MFC/epoxy adsorbent, despite the lack of results in this master thesis. The synthesis should be also improved, because of pore yield of 5.0 g of MFC was measured at start and 0.109 g MFC/epoxy was measured at the end. Better yield should be reached without big changes in synthesis. Now centrifugation and washing was used between different synthesis steps for neutralization. Filtration could be used to neutralize MFC between different phases of synthesis. Also the wet $\mathrm{MFC/CaCO_3}$ adsorbent should be under interest, not only because of its adsorption capacity at low hydrogen sulfide concentrations, but also its better yield of synthesis when compared to dry $\mathrm{MFC/CaCO_3}$. According to Table 1 the measured hydrogen sulfide concentrations are quite low and because of that it is important that adsorbent works also in low hydrogen sulfide concentrations. Also different adsorption times should be used. Asaoka *et al.* (2009, 4128) used adsorption time up to 24 h. Adsorption times more than 1 h would describe better the dynamics of adsorption, which was not studied in this master thesis.

9 Summary

In this master thesis main object was to study, if functionalized nano- and microcellulose could be used as adsorbent for hydrogen sulfide and what would be the adsorption capacities of those adsorbents.

Hydrogen sulfide is toxic and hazardous pollutant. It causes problems in wastewater treatment systems and pipelines. It is toxic for fish and in nature it most likely will oxidize to sulfuric acid causing acid rains. Because hydrogen sulfide is unstable it is likely to be evaporated and that can cause problems for mining and wastewater treatment sites, if the safety of the workers is not been taken care of. Hydrogen sulfide can be purified from water using different purification methods. Oxidation has been used in most references and also in real purification systems. Also other methods have been studied. Adsorption of hydrogen sulfide has been studied recently and the results are quite good.

In adsorption adsorbate, which can be in liquid or -gas phase, accumulates at the common boundary of two phases. Adsorbent, which is usually solid just like cellulose nanocrystal, adsorbs the adsorbate. The adsorption process can be divided in four phases and adsorption can be categorized in two categories. Those categories are based on the difference on bonds between adsorbent and adsorbate. There are several different adsorption isotherms and all of those describe the amount of components adsorbed on the surface of adsorbent versus the adsorbate amount in fluid phase.

Many methods to quantify hydrogen sulfide in aqueous samples are presented in literature. Some of those, ion chromatography (IC), high performance liquid chromatography (HPLC) and gas chromatography with flame photometric detector (GC-FPD), are used for tissue samples. HPLC was also used when hydrogen sulfide concentrations were measured from seawater. Ion selective electrode (ISE) was tested for tannery waste water. Iodimetric and potentiometric titration have been used as reference methods to test other analytical methods for hydrogen sulfide measurement. Vapor generator coupled to inductively coupled plasma (VG-ICP) has been studied for low hydrogen sulfide concentration and it has shown its potential for measurement of hydrogen sulfide from aqueous samples. ICP was selected as analytical method to measure hydrogen sulfide concentration in this master thesis. ICP was experienced by both spiked samples and reference samples. Results prove that selected analytical method works.

Cellulose nanocrystals (CNC) and micro fibrillated cellulose (MFC) have been under great interest for past few years. CNCs properties are: large surface area, nonporous structure, biocompatibility, good strength and high water holding capacity up to 7-8 $\mathrm{g/m^2d}$. CNC can be prepared by two different methods. Another and more used methods is acid hydrolysis of microcrystal cellulose with strong sulfuric or hypochlorite acid. Another method is synthesis by ionic liquid. Cumulative pore volume of CNC is higher than that of cellulose. CNC’s heat stability is better than celluloses. CNC crystallinity and heat stability depends on acid hydrolysis conditions. CNC/MFC surface can be chemically modified to adjust the CNC for certain purpose. Modification methods are TEMPO-oxidation, acetylation, cationization, sulfonation, silylation and grafting via acid chloride, acid anhydride or isocyanate. Also carboxylation and different metals can be synthesized on the surface of CNC and MFC. CNC can be used for agent for protein or/and enzyme immobilization, as antimicrobial and medical applications, carbon based nanotube-cellulose conducting films, antimicrobial wound dressing material, and in tissue engineering for 3D model. Other applications could be in food packing or printing applications.

MFC based adsorbents were prepared from MFC via different synthesis. These adsorbents were tested in pure water test, in which only reagent was sodium sulfide-y-hydrate. The effects of pH changes and change of solutions background was tested with different MFC and membrane filter based adsorbents. At adsorption test 50 or 100 mg of adsorbent and 10 mL of hydrogen sulfide solution were stirred for 10 min. For pure water adsorption test, adsorption capacity of wet $\mathrm{MFC/CaCO_3}$ was the highest. The changes of pH did have effect on adsorption capacities and results have similar directions than in literature. Lower pH gave better adsorption capacity. The change of background solution for 1 w-% sodium hydroxide did have effect on adsorption capacities of used adsorbents. The increasing effect on adsorption capacities, caused by change of background, was smaller than effect for pH variations. More development for the MFC based adsorbents needs to be conducted.

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APPENDICES

Appendices I One component adsorption test

ICP-OES measurement for different hydrogen sulfide concentration in adsorbents and reference sample

Original concentration [mg/L]	10 min stirred reference [mg/L]	Membrane filter [mg/L]	CaCO3 dry [mg/L]	N3 [mg/L]	N2 [mg/L]	MFC [mg/l]	CaCO3 wet [mg/l]
20	19.799	22.084	21.16	20.4377	20.0077	18.144	
30	29.0504	29.256	27.28	28.86	27.7	24	3.594
50	51.4760295	47.8409568	51.6677	53.0844	41.3397	44.97923	31.3673
70	71.1623325	66.782125	77.78222	63.8509	66.0332		
80	72.71202		68.294187	68.5431	62.863		
100	85.951404			111.1	109.067		

Average weight of different adsorbent for one component adsorption test

Concentration [mg/l]	Membrane filter [g]	CaCO3 dry [g]	N3 [g]	N2 [g]	MFC [g]	CaCO3 wet [g]
20	0.105	0.1	0.1083333	0.10667	0.11207	
30	0.1	0.099875	0.104015	0.11667	0.10393	0.10728
50	0.095	0.100005	0.1122068	0.10333	0.11005	0.09909
70	0.098333333	0.10187	0.1067602	0.1	0.10703	0.098327
80		0.101675	0.1104983	0.11		
100			0.107	0.11117		

Average adsorption capacities of different adsorbent

Average adsorption capacity Qe [mg/g]

Concentration [mg/l]	Membrane filter	CaCO3 dry	N3	N2	MFC	CaCO3 wet
20	-0.217619048	-0.1361	-0.058954	-0.0195	0.14768	
30	0.0744	0.177261577	0.0183051	0.11575	0.48594	2.372893
50	0.382639232	-0.01916609	-0.143339	0.98093	0.59036	2.029341
70	0.445444831	-0.6498368	0.6848486	0.51291		
80		0.434505336	0.3772854	0.89536		
100			-1.037383	-0.8156		

Appendices II pH effect on adsorption capacity

ICP-OES measurement for different hydrogen sulfide concentration in adsorbents and reference sample

Measurment result [mg/L]					
pH	Reference	Membrane filter	N3	N2	CaCO3 dry
9	27.16	21.556	10.7485	24.96	19.827
8	24.13	24.875	23.14		18.233
7	21.13	23.155	23.163	26.6066667	17.445
6	6.948	15.0265	11.7435	18.5213332	16.986

Average weight of different adsorbent

average weight of sample [g]				
pH	Membrane filter	N3	N2	CaCO3 dry
9	0.1049725	0.103968333	0.10615	0.0496325
8	0.102655833	0.10277	0.09806667	0.049635
7	0.107190833	0.101025	0.1016	0.0498175
6	0.102558333	0.107108333	0.10483333	0.05199

Average adsorption capacity of different adsorbent

pH	Membrane filter	N3	N2	CaCO3 dry
9	0.82200097	1.716992171	0.20725389	2.10424099
8	0.480813499	0.667509974	0	1.93770297
7	0.474456107	0.687954935	0.32245803	1.40885432
6	1.116281966	1.378913451	0.57837367	2.56336577

Appendices III Effect of 1 w-% sodium chloride solution

ICP-OES measurement

Original concentration [mg/L]	10 min stirred reference [mg/L]	Membrane filter [mg/L]	CaCO3 [mg/L]	N3 [mg/L]	N2 [mg/L]
30	21.94	30.73333333	21.249	26.48	26.6866667
50	43.16666667	51.04444444	46.083333	42.466667	45.5833333

Adsorbent average weight

Concentration [mg/l]	Membrane [g]	CaCO3 dry [g]	N3 [g]	N2 [g]
15	0.104856667	0.099875	0.1069667	0.1117667
30	0.108456667	0.057885	0.1030333	0.1117
50	0.098786667	0.09909	0.0976333	0.1075933

Adsorption capacities [mg/g] of different adsorbent

concetration [mg/l]	Membrane filter	CaCO3 dry	N3	N2
15				
30	-0.06761533	0.119374622	0.341637	0.2966279
50	-0.105727269	0.395263565	0.7715944	0.4104963

Appendices IV Adsorption isotherm for pure water test

Isotherms for membrane filter

				qm	35.11375
Langmuir	membrane filter			Kl	0.000149
	experimental	Model			
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	-0.217	0.104557	0.103399		
30	-0.02056	0.156603	0.031387		
50	0.3826	0.260231	0.014974		
70	0.4454	0.363246	0.006749		
sum			0.156509		

Freudlich	Membrane filter			n	5.0052
	experimental	model		K	0.0825
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	-0.217	0.150153	0.134801		
30	-0.02056	0.162823	0.033629		
50	0.3826	0.180318	0.040918		
70	0.4454	0.192856	0.063778		
sum			0.273127		

				qm	0.44513
Sips	Membrane filter			K	0.021874
	experimental	model		n	19.98744
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	-0.217	2.9656E-08	0.047089		
30	-0.02056	9.8091E-05	0.000427		
50	0.3826	0.3814492	1.32E-06		
70	0.4454	0.44504067	1.29E-07		
sum			0.047517		

N3 isotherms

langmuir	N3			Qm	1.269985
	experimental	Model		Kl	0.002684
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	-0.05898	0.064694	0.015295		
30	0.018305052	0.09463	0.005826		
50	-0.143339354	0.150253	0.086197		
70	0.684848627	0.200849	0.234255		
80	0.377285419	0.224471	0.023352		
100	0	0.268714	0.072207		
sum			0.437132		

Freundlich	N3			n	0.9467
		Model		K	0.0022
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	-0.05898	0.051918	0.012298		
30	0.018305052	0.079675	0.003766		
50	-0.143339354	0.136667	0.078403		
70	0.684848627	0.194993	0.239959		
80	0.377285419	0.224531	0.023334		
100	0	0.284212	0.080776		
sum			0.438537		

				qm	0.353792
Sips	N3			K	0.01697
	experimental	Model		n	87.04382
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	-0.05895	5.0247E-42	0.003476		
30	0.018305	1.0685E-26	0.000335		
50	-0.14334	2.1844E-07	0.020546		
70	0.684849	0.35379157	0.109599		
80	0.377285	0.35379168	0.000552		
100	0	0.35379168	0.125169		
			0.259676		

N2 Isotherms

			qm	0.764784
langmuir	N2		Kl	0.025439
Ce [mg/l]	experimental qe [mg/g]	Model qe [mg/g]	ERRSQ	
20	-0.0195625	0.257896	0.076983	
30	0.115748571	0.33103	0.046346	
50	0.980933597	0.428165	0.305553	
70	0.51291005	0.489755	0.000536	
80	0.895364727	0.512807	0.146351	
100	0	0.548982	0.301381	
sum			0.87715	

Freundlich	N2			n	4.7411
	experimental	Model		K	0.1844
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	-0.0195625	0.346863	0.134267		
30	0.115748571	0.377832	0.068688		
50	0.980933597	0.420815	0.313733		
70	0.51291005	0.451765	0.003739		
80	0.895364727	0.464669	0.185499		
100	0	0.487062	0.237229		
sum			0.943155		

				qm	0.597318
Sips	N2			K	0.03148
	experimental	Model		n	24.76433
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	-0.01956	6.31E-06	0.000383		
30	0.115749	0.11655702	6.54E-07		
50	0.980934	0.59730995	0.147167		
70	0.51291	0.59731785	0.007125		
80	0.895365	0.59731785	0.088832		
100	0	0.59731785	0.356789		
sum			0.600296		

Dry MFC/$CaCO_3$ isothems

Langmuir			qm	6.744616
			KL	0.000387
Ce [mg/l]	experimental qe [mg/g]	Model qe [mg/g]	ERRSQ	
20	0	0.05175	0.002678	
30	0.177261577	0.077328	0.009987	
50	-0.019166092	0.127902	0.021629	
70	0	0.177715	0.031582	
80	0.434505336	0.202341	0.0539	
sum			0.119777	

Freundlich				n	5.1654
	experimental	model		K	0.0595
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	0	0.106351	0.011311		
30	0.177261577	0.115036	0.003872		
50	-0.019166092	0.126994	0.021363		
70	0	0.135542	0.018372		
80	0.434505336	0.139091	0.08727		
sum			0.142186		

				qm	2.118649
Sips				K	0.012079
	experimental	Model		n	39.70461
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	0	6.781E-25	4.6E-49		
30	0.177262	6.6516E-18	0.031422		
50	-0.01917	4.279E-09	0.000367		
70	0	0.00270862	7.34E-06		
80	0.434505	0.43305614	2.1E-06		
sum			0.031798		

MFC isotherms

Langmuir	MFC			qm	6.660673
	experimental	Model		Kl	0.002017
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	0.147678854	0.258245	0.012225		
30	0.485942461	0.380001	0.011224		
50	0.590362943	0.610129	0.000391		
sum			0.023839		

Freundlich	MFC			n	2.7722
	experimental	model		k	0.1315
Ce [mg/l]	qe [mg/g]	qe [mg/g]	ERRSQ		
20	0.147678854	0.38735	0.057442		
30	0.485942461	0.448357	0.001413		
50	0.590362943	0.539076	0.00263		
sum			0.061485		

				qm	0.595396
sips	MFC			K	0.042058
	experimental	Model		n	6.411767
Ce [mg/l]	qe (exp) [mg/g]	qe [mg/g]	ERRSQ		
20	0.147679	0.14767725	2.5785E-12		
30	0.485942	0.48594441	3.80706E-12		
50	0.590363	0.59036893	3.57928E-11		
sum			4.21783E-11		

Appendices V Best adsorption isotherms for MFC/N2, MFC/N3 and MFC/$CaCO_3$ after salinity test

MFC/N2 langmuir adsorption isotherm calculation

Langmuir Ce [mg/l]	MFC+N2 expermimental qe [mg/g]	Model qe [mg/g]	ERRSQ	qm K	0.969576 0.014685
30	0.296627872	0.2965209	1.14E-08		
50	0.410496313	0.4105061	9.54E-11		
sum			1.15E-08		

MFC/N3 Sips adsorption isotherm calculation

Sips Ce [mg/l]	MFC+N3 experimental qe [mg/g]	Model qe [mg/g]	ERRSQ	qm K n	1.129826 0.025538 3.138605
30	0.341637011	0.341626	1.32E-10		
50	0.771594401	0.771585	8.08E-11		
sum			2.13E-10		

Dry MFC/$CaCO_3$ Sips adsorption isotherm calculation

Sips Ce [mg/l]	CaCO3 dry Experimental qe [mg/g]	Model qe [mg/g]	ERRSQ	qm K n	0.51407 0.025837 4.694295
30	0.119374622	0.119366	6.783E-11		
50	0.395263565	0.395261	6.444E-12		
sum			7.427E-11		