UNIVERSITY
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SECONDARY MATERIALS IN WATER TREATMENT

Taru Välikangas

ENVIRONMENTAL ENGINEERING
Master's Thesis
January 2017

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Supervisors: Lic.Sc.(Tech.) Kaisu Ainassaari, D.Sc.(Tech.) Minna Pirilä,
D.Sc.(Tech.) Satu Ojala and Prof. Riitta Keiski

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ABSTRACT FOR THESIS

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Abstract

In the World the availability of the clean drinking water is a serious problem. The appearance of this problem is different in developed and developing countries. Even though water treatment technologies are widely studied and improved, the developing countries do not have the same economic capacities to utilize the sufficient treatment methods. This thesis concentrates on the utilization of secondary materials in water treatment as adsorbents. These materials are potential for the low-cost treatment of water.

For the testing of the secondary materials, two pollutants were chosen as model compounds: organic pharmaceutical diclofenac and inorganic arsenic As(V), since they have been recognized to be problematic in water treatment. Two industrial by-products were chosen as secondary materials to be tested as adsorbents. Sachtofer is a by-product from titanium dioxide TiO_2 production and Red mud is a waste material originating from aluminium oxide Al_2O_3 production. Third material tested was sand from Brazil obtained via cooperation with the Federal Institute of Goias in Goiania, Brazil. In this thesis a commercial adsorbent CFH-12 (Kemira) was chosen as a reference material.

The literature part of the thesis contains theoretical considerations on the utilization of adsorption in water treatment. In addition the effect of organic and inorganic impurities in water bodies are discussed in a general level.

The experimental part of the thesis presents first the characterization results of the secondary materials. The specific surface areas (BET) were measured for all the secondary materials. The surface structures were studied with scanning electron microscopy (SEM). For some of the adsorbents, the pH of the point of zero charge was determined as well as the elemental composition with XRF. One part of this thesis concentrated on studying the effect of pre-treatment on the adsorption efficiency of the materials. In this case, the adsorption materials were washed with distilled water and treated with hydrochloric acid. The adsorption experiments were carried out as batch experiments.

Diclofenac concentration during the experiments was analyzed with spectrophotometry and HPLC. The best removal, i.e. 16% of diclofenac was achieved with HCl-activated Brazilian sand. With Red mud the HCl-activated sample was the most effective with 8% removal. The HCl-activated Sachtofer removed only 4% of diclofenac. The change in the arsenic concentration during the experiments was analyzed by ICP-MS. With Sachtofer, all three pre-treated samples removed 100% of arsenic. All Red mud and Brazilian sand samples were able to remove arsenic in significant amount. Though, after HCl-activation, the removal of arsenic was higher giving 98% for Red mud and 100% for the Brazilian sand.

The diclofenac removal was assumed to be difficult and the 16% removal was a quite good result. The problem seems to be too high pH. By adjusting pH to a lower level, the higher removal efficiency might be achievable. All arsenic removal results were promising, and with all the material samples the removal was higher than 90%. These results confirm that the secondary materials are potential adsorbents for in water treatment. With certain adsorbents, the removal was high even without any pre-treatment. This is economically interesting possibility that should be studied more, especially due to the possibility of improving the water treatment in developing countries.

Additional Information

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Tiivistelmä

Puhtaan juomaveden puute on todellinen ongelma maailmassa. Se on ongelma jossa erityisesi kehittyvät ja kehittyneet maat ovat eriarvoisessa asemassa. Vaikka vedenpuhdistusprosesseja tutkitaan paljon ja ne ovat pitkälle kehittyneitä, ei kehittyvillä mailla ole välttämättä taloudellisia resursseja hyödyntää riittävää vedenpohditus tekniikkaa. Tässä työssä on tutkittu kierrätysmateriaalien hyötykäyttöä adsorbentteinä vedenpuhdistuksessa.

Puhdistettaviksi malliaineeksi valitiin orgaaninen lääkeaine diklofenakki sekä epäorgaaninen arseeni As(V), koska niiden on havaittu aiheuttavan ongelmia nykyisissä vedenpuhdistusprosesseissa. Adsorptiomateriaaleina tässä työssä käytettiin teollisuuden sivutuotteina syntyneitä Sachtoferia joka on titaanidioksidin valmistuksen sivutuote, sekä punaliejua, joka alumiinioksidin valmistuksessa syntynyttä jätemateriaalia. Kolmantena materiaalina testattiin Brasilialaista -hiekkaa, jota saatiin tutkimustarkoituksiin yhteistyön kautta, Federal Institute of Goias, Goiania, Brasilia toimittamana. Työhön haluttiin valita myös yksi kaupallinen adsorptiomateriaali joka toimisi referenssimateriaalina, ja tämän vuoksi valitsimme adsorptiomateriaaliksi Kemiran CFH-12 -tuotteen.

Työn kirjallisuus osiossa selvitetään adsorption teoriaa sekä sen hyödyntämistä vesienpuhdistuksessa. Myös orgaanisen ja epäorgaanisten haitta-aineiden vaikutuksia veden laatuun tarkastellaan yleisellä tasolla.

Kokeellisen osan alussa työssä käytettyjen adsorbenttien ominaisuuksia tutkittiin erilaisilla menetelmillä, joilla arvioitiin materiaalien kykyä adsorboida malliaineita. Materiaaleille määritettiin mm. pH jossa materiaalin pintavaraus on nolla (point of zero charge). Lisäksi materiaaleille tehtiin BET-analyysi ominaispinta-alan selvittämiseksi ja niiden pintaa ja rakennetta tutkittiin elektronimikroskoopilla. Osalle aineista tehtiin myös alkuaineanalyysi. Työssä haluttiin myös tutkia vaikuttaisiko materiaalien esikäsittely adsorptiotehokkuuteen. Tämän vuoksi adsorptiomateriaaleja pestiin tislatulla vedellä sekä käsiteltiin suolahapolla. Adsorptiokokeet toteutettiin laboratoriomittakaavassa panoskokeina.

Diklofenakin pitoisuutta seurattiin kokeen aikana spektrofotometrillä sekä HPLC analyysi menetelmällä. Paras tulos diklofenakin poistossa saatiin HCl -aktivoidulla Brasilialaisella hiekalla, jolloin poistuma oli 16 %. Punaliejulla käsitellyistä näytteistä paras poistuma, 8 %, saatiin myös HCl -aktivoidulla näytteellä. HCl -aktivoidulla Sachtoferilla poistuma oli vain 4 %. Arseenin pitoisuuden muutosta kokeen aikana analysoitiin ICP-MS menetelmällä. Kaikkilla kolmella Sachtofer -näytteellä arseenin poistuma oli 100 %. Kaikki punaliejú ja Brasilialainen hiekka näytteet adsorboivat arseenia merkittävästi. Kuitenkin HCl -käsitellyillä näytteillä poistuma oli paras, punaliejulle 98 % ja Brasilialaiselle hiekalle 100 %.

Diklofenakin poistamisen vedestä oletettiin olevan haastavaa, ja saavutettu 16 % poistuma oli hyvä tulos. Ongelmana diklofenakin poistossa oli todennäköisesti liian korkea pH ja mikäli pH:ta onnistutaan säätämään enemmän happamaksi, poistuma voisi olla korkeampi. Arseenin adsorptio kokeiden tulokset olivat todella lupaavia, ja kaikilla materiaaleilla poistuma oli vähintään 90 %. Näiden tulosten perusteella voidaan todeta että kierrätysmateriaalit ovat hyvin potentiaalinen vaihtoehto vedenkäsittelyadsorbenteiksi. Osa materiaaleista toimi arseenin poistossa tehokkaasti myös ilman esikäsittelyä. Tämä on taloudelliselta kannalta mielenkiintoinen tulos, jota tulisi tutkia lisää, erityisesti kehittyvien maiden vedenpuhdistuksen tehokkuuden parantamiseksi.

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Taru Välikangas, Oulu, January 2017

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LIST OF SYMBOLS AND ABBREVIATIONS

A	Absorbance
b	Langmuir adsorption coefficient
c_e	Equilibrium concentration
c_f	Concentration of model compound at certain time of experiment
c_i	Concentration of model compound at the beginning of experiment
K	Henry’s law adsorption equilibrium constant
k	Freundlich constant for adsorption strength
n	Freundlich exponent, related to the energy of the surface of the adsorbent
p	Sorbate partial pressure
p_s	Saturated vapor pressure of the saturated liquid
q	Sorbate concentration
q_e	Adsorbate loading or density at equilibrium
q_{max}	The maximum adsorbent loading or density

BET	Brunauer-Emmett-Teller, a multilayer adsorption isotherm model
EQS	Environmental Quality Standards
FIWA	Finnish Water Utilities Association
HPLC	High-Performance Liquid Chromatography
ICP-MS	Inductively coupled plasma-mass spectrometry
$\mathrm{pH}_{\mathrm{Final}}$	Final pH after determination of the point of the zero charge
$\mathrm{pH}_{\mathrm{Initial}}$	pH in the beginning of the determination of the point of the zero charge
$\mathrm{pH}_{\mathrm{PZC}}$	pH of the point of the zero charge
PCD	Pulsed corona discharge method
PZC	Point of the zero charge
SEM	Scanning electron microscopy
XRF	X-Ray fluorescence analysis

1 INTRODUCTION

The water contamination is a major problem in the World, since about 768 billion people are not able to have access to clean drinking water (Unicef 2016). Industrial growth, increasing pollution and waste production have created a growing problem to handle the emissions. The low-cost solutions to handle emissions and waste have become more and more interesting during the recent years. (Worch 2012 p. 18) In developing countries and in rural areas low-cost water treatment methods are needed to ensure the safe drinking water (Chowdhury et al. 2016).

In the Baltic Sea, the recent concern is the contamination due to pharmaceutical substances. Most of the pharmaceuticals are originated from households but the removal efficiency of these substances in sewage treatment is only minor. Therefore, pharmaceutical compounds end up in the Baltic Sea from the sewage effluents. The amount of pharmaceutical compounds in sewage has been the interest of certain recent studies. (Haapkylä 2015)

Pharmaceuticals are hazardous to the environment and all the consequences are not clear. In the Baltic Sea, the amount of pharmaceuticals is between 0.01–37 ng/dm^3 but it is enough to cause negative effects on animals and the environment. Pharmaceutical compounds are poorly decomposable and they will accumulate in nature. Carbamazepine for example can cause the deformation of organs in animals that live in the water environment. The elimination of this compound in a wastewater treatment plant is only minor and large amounts of carbamazepine end up in the Baltic Sea. (Haapkylä 2015)

Heavy metal exposures to humans via drinking water have become a problem especially in developing countries since they do not have economic capacity for the proper handling of wastewaters. This leads to situation were heavy metal concentrations in drinking water are alarmingly high in those countries. The heavy metal component can be harmful to humans when the concentration is high. Heavy metals are released in the drinking water by natural processes or they come from anthropogenic action. (Chowdhury et al. 2016)

Arsenic, for example, is carcinogenic and toxic heavy metal. Arsenic is present in its organic and inorganic forms in the environment. (ASROCKS-hanke 2014) 26 million people in the World are estimated to be exposed to arsenic containing waters. Exposures appear typically by drinking arsenic poisoned water, or eating food that has been grown or prepared with contaminated water. Some people are also exposed by inhalation or dermal contact, but these exposure paths are minor. The responses for exposure to arsenic are individual and depend on the method and time of exposure. (Murcott 2012)

In nature arsenic is released from bedrock by weathering or it is dissolved in water. Arsenic is also released by human activities. Aggregates produced from crushed bedrock are used in road and infrastructure production. This aggregate production is increasing arsenic emissions when bedrock material is crushed into smaller particles. Mining exposes bedrock also to oxygen and rain water. When sulphide minerals containing arsenic are oxidized, the solubility of arsenic is increased. (ASROCKS 2014)

In this research, the main purpose is to study the use of secondary materials in water treatment. The model compounds used in this study are organic pharmaceutical diclofenac and inorganic heavy metal arsenic. Diclofenac was chosen as a model compound because of the recent interest on the pharmaceuticals in water bodies. Diclofenac seems also more difficult to be removed than some of the other pharmaceuticals. Carbamazepine was also considered as the pharmaceutical model compound, because it is difficult to be treated in wastewater treatment plants as well. However, it appeared that carbamazepine is difficult to dissolve in water and it was decided that the studies will concentrate on diclofenac removal.

In this thesis four different materials were tested as adsorption materials. The first adsorbent material was Sachtofer PR, which is a by-product from the TiO_2 production. The second material was Red mud that is a waste material from aluminium oxide Al_2O_3 production. This adsorbent was pre-treated by M.Sc(Eng.) Sanna Antikainen who treated four different sorts of Red muds. The third adsorbent is a Brazilian sand. It was obtained from partners in the Federal Institute of Goias, Goiania, and it is presumed that it might work as an adsorbent, even though it was never tested before. The fourth adsorbent used in this thesis was Kemira’s commercial adsorbent CFH-12, which was chosen as a reference material.

In the theory part, the absorption phenomena itself is studied as a pollutant removal method in water treatment. Appearance of pharmaceutical compounds and heavy metals in water basins and difficulty of their removal is also considered. In the chapter on Material and methods, all adsorbent materials are presented in detail. Also, the theories related to the used characterization methods are shown. All the adsorbents were characterized with the scanning electron microscopy (SEM), with the Brunauer-Emmett-Teller (BET) analysis and with an elemental analysis with the X-Ray fluorescence (XRF) analysis. The pH of the point of the zero charge (PZC) was also determined for adsorbent materials to be able to adjust the pH of the adsorption experiments at the right level.

In the Experimental part of the thesis, the removal of model compounds were tested in batch adsorption experiments. Sachtofer, Brazilian sand and Kemira’s reference adsorbent were first tested without any pre-treatment. Secondly, the adsorbents were washed with distilled water presumably to achieve higher removal efficiency. Thirdly, activation of adsorbents was done with acid to improve the adsorption efficiency further. Red mud was pre-treated with four different methods earlier containing different acid and washing treatments. The change of diclofenac concentration during the experiments was followed by spectrophotometry and High-Performance Liquid Chromatography HPLC. Arsenic samples were analyzed with inductively coupled plasma-mass spectrometry ICP-MS.

The general aim of the thesis was to create new information on the utilization of secondary materials in the treatment of wastewater, and thus, to decrease the costs of the treatment, as well. Secondary materials can be more environmentally friendly and utilizing the waste stream from industry decreases also the need for industrial production of commercial adsorbents.

2 ADSORPTION

2.1 Adsorption theory

Adsorption is a separation process used to remove pollutants and other impurities from waste streams. In the adsorption process molecules or atoms that are called as the adsorptive are accumulating on the surface of an adsorbent when bind molecules or atoms are called as the adsorbates. Structure of the adsorbent's surface is typically porous and the binding is typically understood as reversible. Desorption is the reverse process for adsorption. During that process, an adsorbate in the condensed phase passes from the adsorbent's surface back to the solution. (Bart and von Gemmingen 2015)

Forces between an adsorbate and an adsorbent can be physical or chemical. In physical adsorption (physisorption) forces are relatively weak mainly van der Waals forces. In chemical adsorption (chemisorption) between an adsorbate and a surface of adsorbents chemical bonds are formed. (Ruthven 1984 p.29-30) Adsorbate molecules can stay in the form of as molecules on the adsorbent surface or they can be decomposed to smaller atoms. The amount of bond adsorbates versus free sites on adsorbents surfaces is called as the coverage. (Manninen and Nieminen 1988 p. 116, 125)

Surface chemistry is one of the most important features to observe when the adsorbent efficiency is studied. In this work pH in the point of the zero charge (PZC) was determined. At this pH, the net charge for the adsorbent is zero. When the pH is lower than pH_{PZC}, the net surface of adsorbent is positively charged and when it is higher the surface is negatively charged. (Worch 2012 p. 34)

For adsorption at low concentrations, the equilibrium relationship between the fluid phase and the adsorbed phase is linear and can be expressed according to the Henry's law (Eq. 1) (Ruthven 1984 p. 43).

$$q_e = Kc_e \tag{1}$$

where q_e is the adsorbate loading or density [µg adsorbate/mg adsorbent]. K is the temperature dependent adsorption equilibrium constant for the component [dm^3/g] and c_e is the equilibrium concentration [$\mu g/dm^3$] (Worch 2012).

The Langmuir model 1918 (Eq. 2) is the simplest theoretical model for monolayer adsorption. This model is based on four assumptions, which are as follows. An adsorbent can have a fixed number of sites where adsorption can be take place. Each of these sites can only adsorb one molecule at a time. All sites still have the same energy to attract molecules. Molecules that have been adsorbed in different sites do not have any interaction. (Ruthven 1984 p. 49)

$$q_e = \frac{q_{max} b c_e}{1 + b c_e} \tag{2}$$

where q_e is the adsorption density [µg/mg], q_{max} is the maximum adsorbent loading [µg/mg], b is the Langmuir adsorption coefficient and c_e is the concentration in liquid phase equilibrium [mg/dm^3].

The Freundlich isotherm 1906 (Eq. 3) is a good model to present the medium concentration range. For very low or high concentration the Freundlich isotherm cannot describe the linear range of the concentration. (Worch 2012 p. 50)

$$q_e = k {c_e}^n \tag{3}$$

where q_e is the adsorption density [µg/mg], k is the constant for the strength of adsorption, c_e is the concentration in liquid phase equilibrium [mg/dm^3] and n determines the curvature of the isotherm and is related to the energy of the surface of the adsorbent.

2.2 General adsorption materials

Adsorbent materials for water treatment can be industrially made or originate from natural sources such as clay, minerals, zeolites, oxides or biopolymers. Typically commercial adsorbents from industry are classified as carbonaceous adsorbents, polymeric adsorbents, oxidic adsorbents, zeolites or molecular sieves. Also using wastes and by-products as adsorbents has been of recent interest in the production of low-cost adsorbents. (Worch 2012 p. 11)

The important quality element to measure is the internal surface area of the adsorbent. Internal surface area is inversely proportional to the mean pore diameter. In adsorbent selection, the size of the adsorptive is determining the minimum size of the pore diameter. The standard method for determining the internal surface area is the BET method.

(Bart and Von Gemmingen 2015 p. 563) Typically, the internal area is larger than the external surface. Industrial adsorbents typically have large internal surface areas. Usually, the large internal surface contains a large range of different sizes and shapes of pores. Pores can be divided into three different categories based on the size of the pores: macropores, mesopores and micropores. Macropores and mesopores are important when considering the mass transfer into the adsorbent. Micropores will determine the internal surface area, and the larger micropore volume will indicate that the adsorbent can adsorb larger amounts of chemical species. (Worch 2012 p. 28)

The internal surface area is an important feature because the adsorption process is more efficient when there is a larger surface for adsorption reaction to take place. Good adsorbents have a large internal surface and high porosity. The commercial adsorbents have high adsorption capacities because they are industrial products and produced under specific conditions. The production of commercial adsorbents that have the required features are typically very expensive. Natural adsorbents on the other hand are cheap but they might not have so high adsorption capacities. (Worch 2012 p. 11-12)

In this work one adsorbent material is a soil from Brazil. Generally speaking, using soil as an adsorbent material would be very cost effective and it would be environmentally friendly when there is no need to use industrial chemicals. However, some soil material could require some treatment like activation with acid to work as adsorbents. There are some investigations which show that at least soil containing clay have potential to remove copper (II) (Saha et al. 2010). Clay minerals have become more interesting for adsorbent materials. Clay minerals have the net structure that is negatively charged. This feature allows the adsorption of positively charged species such as heavy metal cations Cu^{2+}, Zn^{2+} or Cd^{2+}. (Worch 2012 p. 18) Soil material from the earth of Nigeria has also been tested to remove dye chemicals and it has been reported to be an efficient adsorption material. (Dawodu et al. 2016).

Density is used to measure the porosity of solid adsorbents. Density can be determined as a material, particle or bulk density. Material density is measuring the true density of the solid adsorption material. It is defined as the mass of adsorbent divided by the volume of the solid adsorbent without volumes of pores. Particle density is defined in the same way as the material density, but the volume is included in the pore volume. Bulk density is measured by the mass of material divided by the total volume of the reactor. From density, the particle and bulk porosity can be defined. Porosity is defined as the void space in the total volume of material. Particle porosity can also refer to the internal porosity and the external porosity refers to bulk porosity. (Worch 2012 p. 22)

The adsorbents that are utilized in water treatment for drinking water, have to pass strict quality standards, and the adsorption capacity is usually very high. Adsorbents used in drinking water treatment, are usually commercial activated carbons and oxidic adsorbents. Commercial and engineered adsorbents have typically constant properties for efficient adsorption and that is why they are typically more expensive. This will increase the interest of low-cost adsorbents that are produced from wastes and by-products. (Worch 2012 p. 11)

Activated carbon filters are commonly used to remove organic compounds and other impurities from drinking water. Activated carbon is a material that has a positive charge to attract impurities and high surface area to have a large contact area. Half a kilogram of activated carbon can have half square kilometers surface area. Typically in industry there are three materials to produce activated carbon for drinking water filtration: bituminous, wood and coconut shell. The company named Filter Water for example produces commercial activated carbons from a coconut shell. (FilterWater 2016) Water softening is not possible with activated carbon filters. It is not either a proper method to remove sodium, microbes, fluoride and nitrates. Some heavy metals like lead can also require some specific properties of activated carbons. (Water professionals 2016)

A company named Water professionals provides commercial activated carbons of two kinds. With steam activation, the carbon gets the structure of a fine pore. The porous structure is a good feature for liquid and vapor phase adsorption. In steam activation, the water-gas reaction will occur when the temperature of steam is in the range of 800 ºC – 1000 ºC and the carbonized material is gasified. Adding air is then used to burn gases. With chemical activation, the carbon will get more open pore structure, which is good in adsorbing large molecules. In chemical activation a dehydrating agent like phosphoric acid and zinc chloride is added and the temperature is then increased to the level of 500 ºC – 800 ºC to activate the carbon. (Water professionals 2016)

For arsenic removal commercially available synthetic zeolites are noticed to be very useful as adsorbent materials (Shevade and Ford 2004). Zeolites are three-dimensional materials that have micropores and a crystalline solid structure. They are natural minerals, but now there are also synthetically produced zeolites. They contain silicon and aluminum atoms that are placed tetrahedrally with each other in shared oxygen atoms. Zeolites can be used to adsorb a variety of materials and they can be used in drying, purification and separation applications. Zeolyst International is one company that is producing commercial zeolites. They produce zeolites in a powder form, which are re-useable. Regeneration of zeolites is possible and adsorbed materials can be removed with heating, cations can be removed with ion exchange and adsorbed gases can be removed with pressure swing. (Zeolyst International 2016)

When one compares synthetic zeolites to natural zeolites synthetic zeolites have more controlled physico-chemical properties. Arsenic can be adsorbed onto a zeolite via a ligand exchange. It has been investigated that synthetic zeolites can adsorb arsenic in 15 minutes from a contaminated solution. In general, zeolites have been found to be promising materials for water treatment because they promote the cation exchange capacity, anion sorption and acid hydrolysis of organic pollutants. (Shevade and Ford 2004)

2.3 Adsorption technologies

Both gas and liquid adsorption processes, require adsorption and desorption steps. In the adsorption in a liquid phase, the mixture of a solute and a process fluid has higher mass than in a mixture in a gas phase. In a gas phase the temperature effect is more noticeable, because the heat capacity is weak and during condensation heat is released. This will create nonisothermal operation conditions and some safety problems. In the adsorption in a liquid phase the heat capacity is high and the operation conditions are isothermal. (Bart et al. 2012)

The fixed-bed adsorption unit is typically used in gas phase adsorption. In some rare cases moving and fluidized-bed can also be used. In fixed-bed apparatus there is typically two units. One unit is for the purification of adsorptive from mixture to the adsorbent, while the other unit is used for regeneration. (Bart et al. 2012) The particle size of an adsorbent is typically between 0.05−1.2 cm. When the particle size is larger, the pressure drop is smaller but the smaller particle size is better for the more efficient transport of the mixture. (Seader et al. 2011 p. 609) The mixture for purification is entering to a certain layer in the fixed-bed adsorption unit. In this mass-transfer zone, the adsorptive will transfer to the solid phase in pores of the adsorbent. The mixture is moving downstream in a unit and after one layer is loaded, the mass-transfer zone will enter to the next layer until it has passed the whole fixed-bed with in a certain time. The saturated adsorbent in gas-phase adsorption can be regenerated by temperature or pressure swing, displacement or extraction. (Bart et al. 2012)

Both moving- and fluidized-bed operation units can be operated continuously. These require a smaller amount of adsorbent than the fixed-bed unit, because the stationary mass-transfer zone will correspond to a sufficient bed height. In a fluidized-bed unit the mixture with adsorptive is added from the bottom of the unit. When the mixture is heated up, the hot gas will rise to an upper part of the unit. The adsorbent will move countercurrently to the gas mixture over individual trays. In each tray the fluidized bed forms a mass-transfer zone. (Bart et al. 2012) At the bottom of a unit, there is a desorption zone for regeneration. Regenerated solid adsorbents are then transferred back to the top of the adsorption units to repeat the adsorption operation. (Seader et al. 2011 p. 610)

For liquid-phase adsorption, beds of all kinds can be used. In addition the suspension mixers are sometimes used to make sure that adsorbents are finely dispersed. In a mixer the adsorptive in the liquid phase is transferred to the suspended adsorbent. The suspension is then lead through the filter that separates the purified liquid and the loaded adsorbent. Adsorbents in liquid-phase adsorption can in some cases be reusable by washing the adsorbent with water or regenerating with acid. (Bart et al. 2012)

CalgonCarbon is one company that produces liquid and gas phase adsorption units. Most of their applications are using the activated carbon as an adsorbent. The VENTSORB unit is the apparatus for control of vented emissions in industrial plants. It contains approximately 80 kg of activated carbon. This unit is proper for the low air-flow and can handle the organic contaminants and odor emissions. The maximum flow in this unit is 2.83 m^3/min. The FLOWSORB unit is for liquid phase adsorption. It is the best for small water stream purifications. It contains approximately 80 kg of activated carbon granules. The flow rate is 37.8 dm^3/min and the contact time for a mixture and adsorbent is 4.5 minutes. (CalgonCarbon 2015)

3 PHARMACEUTICALS AS IMPURITIES

3.1 Pharmaceuticals in environment

In Finland the presence of pharmaceuticals and their metabolites has been studied in the bile of wild fish that were catched from a lake where sewage effluent is discharged. In nature the typical concentration of pharmaceutical can be between ng/dm^3 and µg/dm^3. Mainly phase II glucuronide conjugates and their phase I metabolites of the pharmaceuticals are found in fish bile. One major pharmaceutical that was found was antiepileptic drug carbamazepine. The anti-inflammatory drug diclofenac was found in all but one bream and one roach sample. (Brozinski et al. 2015)

In this study it was found that in biles of bream and roach the mean concentration of naproxen and ibuprofen was found to be 2–3 times smaller than the concentration of diclofenac. Sewage effluent is discharged into the lake all the year around and pharmaceuticals are accumulating in fish bile. This has led to a situation where the concentration of anti-inflammatory drugs was found to be 1000 times higher in fish bile than in the water of the lake. (Brozinski et al. 2015) It is studied that in hypoxia conditions diclofenac can disturb enzyme activity and circadian rhythm. Diclofenac's long term impacts on nature would also need more investigation. (Kanerva et al. 2014) Even when the acute toxic effects are probably so harmful the chronic effects can be hazardous and cause some serious troubles (Zhang et al. 2008).

Diclofenac has been reported to be the reason in India that has caused vulture population decline. Vultures are exposed to diclofenac when they use carcass of domestic animals as food. If the animals have got resent veterinary dose of diclofenac the vulture will get the contamination. During the investigation in 2000 - 2003 the decline was 22–50% for the oriental white-backed vulture, long-billed vulture and slender-billed vulture. (Green et al. 2004) In the year 2007 the decline was about 99% compared to the situation in 1990, when the decline was first time noticed. In 2006 the Drug Controller General on India has banned the diclofenac formulation that was a veterinary drug. In the year 2015 in India the Union Ministry of Health and Family Welfare banned the formulation that is meant for human use. The drug is still available in 3 cm^3 vials, but these smaller vials will hopefully not be used as drug for cattle when the dose for large animals would be 10–15 cm^3. (The times on India city 2015)

In Pakistan the veterinary diclofenac has been reported to cause decline of vultures. The residues of the anti-inflammatory drug was a cause for the renal failure and visceral gout for vultures. From kidneys of vultures approximately 0.051–0.643 µg/g of diclofenac residues were found. (Oaks et al. 2004) All three vulture species are classified critically endangered in the IUCN's Red list. (IUCN 2016)

The EU directive on Environmental Quality Standards (2008/105/EC) that is amending with the directive (2013/39/EU), contains a list of the priority substances that can have acute and chronic effects on ecotoxicology and also threat for human health. This directive also sets Environmental Quality Standards (EQS) for all these substances. In this directive, a target to create a Watch List of substances, which could cause risk for aquatic environment, is also mentioned. Substances in the Watch List do not have EQS, but they should be still monitored Union-wide. The substances will be monitored only for the maximum of four years and at least 12 months. In the Directive already three compounds were mentioned to be included in the first Watch List, and diclofenac is one of them. (European Union 2013)

Substances that were selected to the Watch List are reported in European Commission's Joint Research Centre Science and Policy Report "Analytical methods for possible WFD 1st watch list substances" (Loos 2015). More information about the selection of compounds, can be found in European Commission's Joint Research Centre Technical Report "Development of the first Watch List under the Environmental Quality Standards directive" (Carvalho et al. 2015).

The purpose of the watch list is to list substances that may cause threat to aquatic environment and via that also to human health. With the list, hazardous substances get attention, and it also produces information concerning the substances. In addition, there is no previous information concerning the exposure of the substances in nature. The list can contain only 10 substances. Purpose of the Watch List is to produce information about the substances of concern. Because of these rules, the substances are monitored only for the necessary time. Substances in the Watch List should also have a known method for analysis and they cannot be prohibited substances in EU. Carbamazepine was proposed to the List, but it was removed together with 15 other substances because there was already sufficient monitoring data available. Diclofenac is on the Watch list. (Carvalho et al. 2015)

In Finland during the years 2013 - 2014 Finnish Water Utilities Association (FIWA) range a project where hazardous substances in wastewater treatment plants were investigated. In this project 42 substances were measured from 64 wastewater treatment plants. All selected substances are either classified for hazardous or recommended to be classified. The Ministry of the Environment has set the regulation Ymra 15/2012, which lists substances that were supposed to be monitored in this project. Also other substances that are listed in Directive 2013/39/EU and in Watch List or are recommended to be in the Watch List were monitored in this project from influent and effluent of wastewater treatment plant. Diclofenac and carbamazepine are also included in the list of 42 substances. EQS values will tell the threshold level for hazardous substances in water basins. It has to be noticed that this value is set for surface water. Diclofenac and carbamazepine do not have EQS values because they are not yet listed as priority substances. (Vieno 2014)

There is no EQS value for diclofenac, but during the revise process of the directive 2013/39/EU, EQS values for diclofenac were presented 0.01 µg/ dm^3 for inland and coastal waters. Target limits of determination for both substances diclofenac and carbamazepine were 0.01–0.05 µg/ dm^3. The mean concentration of diclofenac in sewage influent was 1.02 µg/dm^3 and in effluent 0.90 µg/dm^3, respectively. The observed diclofenac concentration was 92% over the target limit of determination for influent and 100% for effluent, respectively. For carbamazepine the average load was estimated to be 56 kg in one year. In sewage influent the mean value of carbamazepine was 0.65 µg/dm3 and in effluent 0.60 µg/dm^3, respectively. It was 92% over the target limit of determination for influent and 93% for effluent, respectively. For carbamazepine there is no EQS value in legislation. (Vieno 2014)

In Vieno’s report (2007), the concentration of diclofenac and carbamazepine was measured from sewage influent and effluent in the years 2004 - 2006. For diclofenac the mean concentration in influent and effluent was 0.45 µg/dm^3 and 0.35 µg/dm^3, respectively. For carbamazepine mean concentration in influent was 0.35 µg/dm^3 and in effluent 0.72 µg/dm^3, respectively. (Vieno 2007) For both substances, the concentration was lower in Vieno’s report 2007 than in FIWA’s investigation of hazardous substances in wastewater treatment plants (Vieno 2014).

In the FIWA's project, pharmaceutical substances were measured only from larger plants, when the population equivalent value is more than 100 000. The population equivalent value for treatment plant in Finland is average daily load from week when the sewage influent is the biggest in certain treatment plants. There were 11 larger plants in the project and they were located mostly in Southern, Western and Central Finland and also South-West Finland. Only one sample was taken from a plant were the population equivalent value is 50 000 – 99 999 and also one sample from plant were the population equivalent value is less than 10 000. It was noticed that the removal of diclofenac was quite similar in all treatment plants, but the removal of carbamazepine was higher in Southern Finland in 5 treatment plants and in one plant in Eastern Finland. Deposit of carbamazepine was the highest in a treatment plant that does not receive industrial sewage and the smallest in a plant were industrial sewage was 25%. This trend was not seen with diclofenac, but it was noticed that if there was a pharmaceutical industry sewer basin the deposit of diclofenac was 20% more than the mean value. Other industries did not have a significant effect on the results. (Vieno 2014)

The municipal wastewater treatment plants do not have the capacity to eliminate some organic pharmaceutical active compounds. These contaminants can reduce the quality of water basins and cause pharmaceuticals to end up even in drinking water. (Heberer 2002) Not only the organic pharmaceuticals are the problem in wastewater treatment plants, but in households many of the used personal care products, detergents and disinfectants are organic substances and hard to remove. (Joss et al. 2006)

Jukka Mehtonen is telling in Haapkylä´s article (2015) that the group of pharmaceutical compounds can be very heterogeneous and the degradation in wastewater treatment plant can vary a lot. When some pharmaceuticals are hard to remove from water stream, there are some pharmaceuticals which elimination in water treatment plants is very efficient. For example ibuprofen is widely used in Finland, consumption of it is 113 ton per one year. However, it is not causing a huge problem because in a wastewater treatment plant the reduction of ibuprofen is usually around 90%. (Haapkylä 2015)

In the report of FIWA most of the studied wastewater treatment plants used activated sludge as the biological treatment. This process demands oxygen and is called nitrification. When there is oxygen available, ammonium nitrogen is oxidized to nitrate and nitrite. The removal of nitrogen in anitrification process is approximately 30%. In a denitrification process nitrate is reduced to nitrogen gas. This is a method that can remove 60–90% of nitrogen. If there is a need for more efficient nitrogen removal, the treatment plant can use both nitrification and denitrification processes. It has been found that the concentration of chemical compounds might be lower in plants where the removal of nitrogen is high. (Vieno 2014) The biological treatment for degradation of organic pharmaceutical has limited capacity to reduce the whole load of pharmaceuticals. Dilution of the influent for example by rain water can reduce the degradation of organic contaminants. (Joss et al. 2006)

In all wastewater treatment plants in the FIWA's project when most of the wastewater treatment plants used activated sludge as the biological treatment, there were also treatment plants that used denitrification as the biological treatment process. With diclofenac, when the plant uses biological denitrification, the average removal was higher than with activated sludge. With carbamazepine the trend was the opposite, in plant where they used biological denitrification the average deposit was smaller than in plants that used activated sludge. The highest concentration for diclofenac was observed after biological after-filtration and sand filtration. For carbamazepine without after treatment the concentration was higher than in the situation where after treatment was used in wastewater treatment plant. (Vieno 2014)

In the project of FIWA the average load of diclofenac was estimated to be 308 kg in one year, from oral dose the load was 97 kg and from topical gel 211 kg. In this project measured values for load of pharmaceutical components to wastewater treatment plant were higher than estimated values. For diclofenac the load to plants was 895 kg per year. The average reduction was 5% so the load of diclofenac to environment in Finland was 845 kg per year. For carbamazepine the load to plants was 165 kg per year. The average reduction was 5%, so the load of carbamazepine to environment in Finland was 190 kg per year. It was noticed that concentration of carbamazepine was not as stable as diclofenac was. This is probably because carbamazepine can only be bought with prescription so there is only certain amount of people who use it. Diclofenac in the other hand is patent medicine, so there might be larger group using it. Reduction for the carbamazepine was negative, which means that concentration in effluent was then bigger than concentration in influent. This was explained by degradation of glucuronic conjugates during the water purification, which will release pharmacological conjugates to water. (Vieno 2014)

3.2 Removal of pharmaceuticals

Most of the wastewater treatment plants are using the activated sludge for the removal of pharmaceuticals from sewage. In this process, microorganisms are mineralizing pollutants to less harmful form or to water and carbon dioxide. The activated sludge process will require four different mechanisms, biotransformation, air stripping, sorption and phototransformation. (Zhang et al. 2008)

To transfer the pharmaceutical from water solution onto the surface of an adsorbent is studied to be the limiting step in pharmaceutical adsorption. Because diclofenac is an acidic pharmaceutical, it is neutral in acidic conditions and that is why it is more soluble in acidic conditions. In neutral operation conditions, diclofenac is negatively charged. (Urase et al. 2005b) Urase et al. also found out that in the membrane separation bioreactor in the pH area of 6.8−7.6 removal of diclofenac was only about 10%. When the pH was decreased to 4.3−5.0 the removal was increased to around 80%. (Urase et al. 2005a)

In pharmaceuticals removal from water solutions by adsorption, the right ionic properties are necessary between the adsorbent and the pharmaceutical. In interactive adsorption the electrostatic force is a relevant parameter to be measured when the adsorption efficiency is estimated. The non-ionic adsorbents would adsorb the neutral pharmaceuticals efficiently. In these cases the specific surface area and pore size measurement would play a larger role estimating the adsorption efficiency. Pharmaceuticals have a low solubility in water when they are protonated and thus they will be easily remove from the solution onto the adsorbent. It is assumed that this protonation interaction would have major effect on the adsorption efficiency of pharmaceuticals. (Akhtar et al. 2016)

In the study carried out at Lappeenranta University of Technology, 95% removal of pharmaceuticals was achieved. In that research, the water was first led to a membrane bioreactor where biological purification and dialysis was used to remove contaminants from wastewater. After that, the water was led to the reverse osmosis treatment, where the water is pressed through the semipermeable membrane. The second option, was to lead the water to the oxidation process after the bioreactor. The hydroxyl radicals, ozone and other oxidizing components are formed with a pulsed corona discharge (PCD) method in this oxidizing process. Henry Hatakka from the Wapulec company that is producing PCD method devices assumed that the method is more efficient than ozonazation, but consumes 3−6 times less energy. (Hämäläinen 2016)

In the wastewater treatment plant acidic pharmaceutical compounds can be removed more efficiently when using advanced oxidation processes. This would also increase the costs, and that is why there is a market for more economical solutions for the removal. Nowadays in Finland the water supply for both waste and drinking water costs approximately 4–6 €/m^3. Professor Mika Mänttäri from Lappeenranta University of Technology is supposing that utilization of membrane filtration and the PCD-method would increase the supply costs some tens of cents. (Hämäläinen 2016)

A Swedish company named Pharem Biotech has developed enzymes that are attached to filters and transform the harmful and toxic compounds for example diclofenac to less harmful form. This system consist of modules that are placed in the last stage of water purification in a wastewater treatment plant and can filtrate water 15 000 m^3 per day. One module is 3 m^3 large. This method is energy independent and the enzymes are economical to be produced. The exact price for this method is still not clear, but the price could be evaluated to be 2−5 cents/m^3. The idea for these enzymes came from bacteria that are resistant to antibiotics and producing enzymes that can break down the medicine. This method has been tested only in a pilot scale. (Karlsson-Ottosson 2015)

4 HEAVY METALS AS IMPURITIES

4.1 Heavy metals in environment

Heavy metal contamination is caused by natural sources but also anthropogenic activities. The heavy metal containing wastewaters from industries, end up in nature mostly in developing countries. There is quite much knowledge and research done in the field of heavy metal removal, but the bad economic situation in developing countries is the reason not to handle wastes properly. The leaching of metals from a water distribution system, plumbing pipes and hot water tanks are also increasing the heavy metal concentration in water basins. In the coastal areas the intrusion of seawater to groundwater can also increase the heavy metal concentrations (Chowdhury et al. 2016)

The heavy metal contamination is a serious risk for human health. In Table 1 the WHO guidelines to some heavy metals are presented. Exposure of heavy metals can cause differential symptoms depending on concentration and how long the exposures has been. Also the symptoms are different depending if the exposure is dermal, inhaled or via drinking water. (Murcott 2012) Heavy metals like arsenic (As), cadmium (Cd), lead (Pb) and chromium (Cr) are carcinogenic for human. Neurological symptoms are caused by As, Cd, Pb, and mercury (Hg). Previous compounds with addition of copper (Cu) are also causing gastrointestinal problems. Nickel (Ni) and As are known to cause dermal skin problems. For children in growing phase Cd, Pb and Hg can be disturbing. Cd and Pb can also weaken the change to get pregnant. Among these symptoms heavy metals can cause many other health impacts. (ATSDR 2016)

Table 1. WHO guidelines for heavy metals. (WHO 2011)

Heavy metal concentration [µg/dm^3]							
As	Cd	Pb	Cr	Cu	Hg	Ni	Se
10	3	10	50	2000	6	70	40

Co-exposure of multiple heavy metals can increase or decrease the level of toxicity. When the drinking water consists of heavy metals at low concentrations, the toxic effect on human can be observed. The cumulative effect of several heavy metals, even with low concentrations, can cause serious health risks. (Chowdhury et al. 2016) However, other substances together with heavy metals can increase the toxicity. Humic acid for example in water basins can make bonds with inorganic arsenic, and in a gastrointestinal tract the arsenic is released and adsorbed. (Tseng 2005) On the other hand, arsenic and selenium interaction in tissue, can lower the toxicity of both components (Biswas et al. 1999).

As mentioned earlier, heavy metals in drinking water is mainly a problem in developing countries, when they do not have enough resources to use advanced water treatment methods to remove heavy metal contaminations. (Chowdhury et al. 2016) Based on one research in Bangladesh there could be 6.8 million people exposed to the arsenic level above 300 $\mu g/dm^3$ (Chakraborti et al. 2010). In Iran in Kurdistan providence As, Cd and Se concentrations were found to be over the WHO guideline limits (Alasvand et al. 2012). In Latin America it was studied that there could be over 4 million people exposed to As by drinking water where the concentration is over 50 $\mu g/dm^3$ (Bundschuh et al. 2006).

In 70 countries, toxic level of natural origin arsenic has been found, and it could affect over 140 million people. Most of the countries where arsenic contamination can be found are located in Asia. When arsenic exposure to human via food is high, it can lead to arsenicosis that cannot be handled with medical help. Only way to threat arsenicosis is to prevent arsenic contamination. Different act that can be done in countries that have higher concentration of arsenic contamination: monitor arsenic levels, found the wells that have higher level of arsenic, make plans for safe water supplies and distribute knowledge of hazardous heavy metals. (Unicef 2013)

4.2 Removal of heavy metals

Several different applications can be used for heavy metal removal. Adsorption is one common way of removal. The low-costs adsorbents and chemical precipitation are the most economical solutions for removal. Precipitation is a removal method that is only suitable for a large scale and plants where the concentrations of heavy metals are high. Using only one low-cost method for heavy metal removal the guideline values (WHO 2011) may not be reached. The most efficient way is to use different removal methods in conjunction with each other’s. The ion exchange or membrane filtration can also be possible for the removal of heavy metals, but they are more expensive methods. (Chowdhury et al. 2016)

The conventional method for the removal of arsenic is first oxidizing soluble As(III) to less soluble form As(V). Chlorine, potassium permanganate or some other chemicals are typically used as oxidizing chemicals. Adding these chemicals will increase the costs of arsenic removal. Separation of As(V) from water can be done after oxidation by using conventional methods as coagulation-precipitation, adsorption, ion exchange, reverse osmosis or electro dialysis. (Mondal 2006)

In coagulation-precipitation dissolved arsenic is transformed to insoluble solid. Coagulation and flocculation can be then used for separating suspended and colloidal arsenic. Chemicals typically used in this method are ferric salts, aluminum, manganese sulphate, ammonium sulphate, copper sulphate or some other chemicals. Lime can also be used for precipitation removal. The adsorption method for the removal of arsenic is using physical and chemical forces to attach arsenic on the surface of the adsorbent. The efficiency of all these methods is dependent on the pH of the solution. (Mondal 2006)

In ion exchange method arsenic ions are combined to the resin that is a strong base anion and for exchange in the solution similar charge is releasing from the resin. The method of membrane filtration pressure difference is to drive the solution through a permeable membrane that separates the arsenic from water. The disadvantage of this method is that small pores of this membrane are easily blocked by fouling, especially when Fe and Mn are present in water. This will increase the costs of this method. In the method of electrodialysis, an electric field across a semi permeable membrane is creating the driving force for the separation. (Mondal 2006)

5 MATERIALS AND METHODS

5.1 Adsorption materials

Kemira CFH-12 (FeOOH) is used in this work as a commercial reference material. It is a ferric hydroxide in a form of brown or reddish granules. It can be used in water and wastewater treatment to remove water soluble metals and for phosphorus removal. It is not corrosive and it is placed on the top of the support layer in filters. The support layer can be sand or gravel for example. The typical main components are Iron (Fe^{+3}) 44%, water soluble content 4.5% and moisture 16%. (Kemira 2013) The elemental analysis is not done for this adsorbent because it is a commercial product and it was not modified in the experiments. From product datasheet that Kemira company has delivered, the typical impurities that might be present are shown in Table 2.

Table 2. Impurities in CFH-12. (Kemira 2013)

	concentration in try basis (mg/kg)
	CFH-12
As	<1.0
Cd	<1.0
Pb	3
Cu	5
Cr	10
Ni	140
Mn	1000
Zn	300

Sachtofer PR is a product from Huntsman (former Sachtleben) to be used in wastewater treatment. This granular material is a mixture of iron(III)sulfate $Fe_2(SO_4)_3$, calcium oxide CaO and water. It is a by-product from TiO_2 pigment production. The granule size of Sachtofer PR is approximately 2−5 mm. It is an environmentally friendly solution to remove phosphate from wastewater stream. It has been studied as filter material for phosphorous retention. (Klimeski et al. 2014) In Kokemäki there was a project where different methods were used for P retention. Sachtofer was used as a filter that was placed between the ditch and the field to prohibit the overland runoff. Sachtofer was reported to be the most practical solution. (Heino 2015)

Red mud is a solid waste material from aluminium production. Primarily from Bayer process with alumina extraction from bauxite ore utilizing a caustic soda. (Liu et al. 2014) When alumina is produced 1 ton, 1–1.5 tons of red mud waste will generated (Kumar et al. 2006). Also 1 ton of alumina requires about 1.9–3.6 ton of bauxite ore. The average particle size of red mud is <10 µm and the specific surface area (BET) is 10–25 m^2/g. It has to be noticed that red mud contains particles that have large variety of different sizes and shapes, also a porous surface and crystals can be found. (Wang et al. 2008) Finnish Government regulation of waste 19.4.2012/179 is classifying the Red mud as a hazardous waste.

Red mud has also been investigated to be used as adsorbent in gas cleaning, wastewater treatment and as catalysts for waste gas and water treatment. There are environmental and economic benefits in utilization of red mud. It has been investigated that the red mud contains the following minerals that are residuals from bauxite hematite (Fe_2O_3), goethite (α-FeOOH), boehmite (γ-AlOOH), titania (TiO_2), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$) or, cancrinite-type sodium aluminum silicate (CAN), and gypsum ($CaSO_4 \cdot 2H_2O$) those are creating leaching risk in certain conditions. (Wang et al. 2008)

Alumina is mostly used in aluminium production. Aluminium has a wide range of applications to be use in, because it has light weight, low melting point, and good corrosion resistance as well as good thermal and electrical conductivity. For example airplane and maritime industries utilize aluminium. Even though alumina is mainly used in aluminium production, it has other uses for example in catalysis, when producing materials that can resist high temperature. (Hind et al. 1999)

The Brazilian sand is the soil from Amazon area. The specific origin of sand is unknown and the sand has been obtained through the cooperation with the Federal Institute of Goias. The color of the sand is reddish brown and it is known to contain at least iron. The sand could be so called Terra preta soil, but it cannot be sure. Terra preta de indio is highly fertile soils in Central Amazonia. It is also named Dark earth that is anthropogenic origin. Compared terra preta to natural soil terra preta contains more nutrients. (Araujo et al. 2015)

5.2 Material characterization

5.2.1 Surface area and pore size distribution

The BET specific surface area, pore sizes and volume of the pores of adsorbent materials were analyzed with Micromeritics ASAP 2020 analyzer. 100 mg - 1 g of sample was weighted to a sample tube. The sample was first pre-treated, where all moisture and atmospheric vapor is removed. For all samples the heating pressure in pre-treatment was 100 mmHg and the temperature was 300 ºC, but for Kemira's CFH-12 the temperature was 160 ºC. The temperature of the sample was then decreased to the temperature of liquid nitrogen. Nitrogen gas is then adsorbed onto a sample. An adsorption isotherm is then drawn based on compering data from the adsorbed gas quantity to the samples and gas pressure data at one temperature. (Webb and Orr 1997 p. 5-6)

Specific surface area was then determined by treating data with the adsorption theories. One classical adsorption theory assumes that when gas molecules are added to clean, cold surface they form first layer on a deep surface and after that second layer. The data treatment technique takes the quantity of gas that forms the first layer and the surface area is determined from the amount of molecules of the gas and dimensions of the gas molecules. The unit of specific surface area is square meters per gram. (Webb et al. 1997 p. 6)

The classical adsorption theory also assumes that when gas is added to a clean and cold surface the layer on a deep surface is also getting thicker. In the point where the saturation vapor pressure is reached and the bulk liquid condensation begins. Based on this assumption, first technique to determine pore volume information with Mircometrics apparatus is the assessment of the volume of the gas that is required to admitting into samples and condensed in the pores. In the second method, the information of pore size is achieved by forcing liquid mercury into pores and track the quantity that is penetrated. (Webb et al. 1997 p. 8-9)

A simple isotherm model (Eq. 4) developed by Brunauer-Emmett-Teller (BET) is widely used method to characterize the specific surface area of the particle (Ruthven 1984 p. 52). Thought, the available surface area for adsorption, may differ from specific surface area. The BET method is measuring the specific surface area by adsorbing gaseous nitrogen. (Seader et al. 2011 p. 572-573) Model will define multilayer adsorption and Brunauer-

Emmett-Teller used this model to extract the monolayer capacity and specific surface area.

$$\frac{q}{q_{max}} = \frac{b(p/p_s)}{(1-p/p_s)(1-p/p_s+bp/p_s)} \tag{4}$$

where q is the sorbate concentration, p is the sorbate partial pressure and p_s is the saturated vapor pressure of the saturated liquid sorbate at relevant temperature. (Ruthven 1984 p. 53)

5.2.2 Scanning electron microscopy

Scanning Electron Microscopy was used to discover surfaces of the adsorbents. Materials were analyzed with Carl Zeiss EVO50 XVP Scanning electron microscope (SEM) available inGrant4Com company. With this equipment high resolution imaging and elemental composition analysis can be done. All samples can be analyzed with 100 nm resolvability, but for some samples even 10 nm resolvability is possible. The maximum size of sample is 30 mm thick and 75 mm width.

In SEM there is the electron gun that is producing electrons. In the sample chamber electrons are interacting on the surface of sample approximately a depth of 1µm and it will create signals. Electron detectors gather signals those are scatters from surface of sample. Electron beams are penetrated on different range of depth and based on that generate several kinds of signals. Some samples may not have any metallic region on surface and then samples can be coated with gold or copper film so the surface would be metallic. (Khursheed 2011 p. 2, 60) Our samples were coated with gold.

5.2.3 Elemental analysis

The elemental analysis was done with X-Ray fluorescence analysis (XRF), which is a well-established analysis technique. The method is based on the X-rays or gamma rays that will excite the analyzed material. Different elements have the unique set of atomic energy levels and each element will emit exclusive set of X-rays. Based on the emitted X-rays the element can be characterized. Chemicals that are present in analyzed material are identified based on the number of corresponding atoms those define the intensity of X-ray lines. (Poles et al. 2016)

Elemental analysis for material samples in this thesis have been done with forming fused bead with PanAnalytical machine of Eagon2. The fused bead contained 0.5 g of sample material and 8.0 g of Litiumtetraborate:Litiummetaborate 66:34 mixture. The fused beads are analyzed with standarles method of Omnia. Carbon and Sulphur are determined with LECO CS-230 from 0.1 g of sample, 0.8 g iron chip and 1.2 g lecocell. Carbon has been calculated as carbondioxide and it is feed to Omnia analysis and the total composition of element was determined.

5.2.4 Determination of the pH of the zero point charge

The drift method was used to analyze the pH of the point of zero charge (pH_{PZC}). 0.01 M potassium nitrate KNO_3 was prepared and it was bubbled with nitrogen until the pH was stable. For most cases two times with 10 minutes was enough. The bubbling was done to avoid the CO_2 effect. The solution was divided in the 250 cm^3 flasks, one flask containing 50 cm^3 of solution.

The level of pH to reach values between 3 and 10 was adjusted with 0.1 M NaOH and 0.1 M H_2SO_4. For Sachtofer 0.5 M NaOH was used for pH to reach values between 6 and 13. 0.1 g of adsorbent material was added to each flask. They were shaken for 48 hours to reach the equilibrium. After two days adsorbents were filtered and the final pH was measured. The curves $pH_{Initial}$ vs pH_{Finals} and $pH_{Initial}$ vs $pH_{Initial}$ were drawn and from the interception the pH_{PZC} was calculated.

5.3 Model compounds

5.3.1 Diclofenac

Diclofenac is a non-steroidal anti-inflammatory drug (NSAID) that can be used as an oral dosage or dermal applications, eye dropping or injection (Carmen et al. 2008). When the diclofenac dosage is oral, the elimination time is two hours. From oral dosage 65% is excreted in urine and following metabolites are identified: 4’-hydroxydiclofenac, diclofenac acyl glucuronide, 3’-hydroxydiclofenac, 5-hydroxydiclofenac, 4’,5-dihydroxydiclofenac and 4’,5-dihydroxydiclofenac. (DrugBank 2016)

The molecular formula of diclofenac sodium salt used in this thesis is $C_{14}H_{10}Cl_2NNaO_2$ and the molar mass is 318.13 g/mol. Acid dissociation constant pKa for diclofenac is 4.15.

(DrugBank 2016) The diclofenac is acidic pharmaceutical in neutral pH conditions where it will be in ionized form. When the pH conditions are acidic diclofenac's hydrophobicity will increase, because it is not an ion anymore. (Urase et al. 2005b) Van der Waals forces between diclofenac and adsorbent increase when pH decreases and with physical adsorption process diclofenac will adsorb onto adsorbent (Shehdeh 2016). The chemical formula of diclofenac is presented in Figure 1.

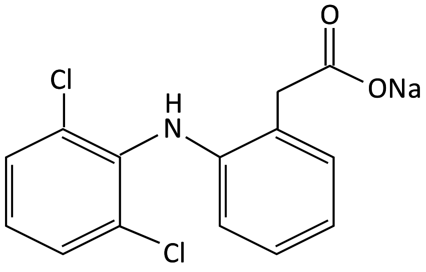

Figure 1. Chemical formula of Diclofenac sodium salt.

In the report of Hazardous substances at wastewater treatment project, diclofenac load for wastewater treatment plants is estimated to be 895 kg/year. (Vieno 2014) Zhang et al. 2008 estimated that in the year 2007 in 76 countries 877 tons of diclofenac was sold. This would present 96% of total pharmaceutical markets in the world. There are different kind of applications for diclofenac. The dermal application is the most popular application in developed countries. Though in worldwide, oral applications are more popular. (Zhang et al. 2008) A popular product in Finland that contains diclofenac is Voltaren, which is a dermal gel application.

5.3.2 Arsenic

Arsenic used in these experiments was arsenite As(V), which commercial name is sodium arsenate dibasic heptahydrate $HAsNa_2O_4 \cdot 7H_2O$. It is a strongly toxic and carcinogenic compound for humans and environment. It includes components that are stable and accumulate in the nature. Molecular weight is 312.01 g/mol and it is a white crystalline component. (Sigma-aldrich 2016a) The WHO guideline value for arsenic is 0.01 mg/dm^3 (WHO 2011). In Figure 2 the chemical formula of sodium arsenate dibasic heptahydrate is presented.

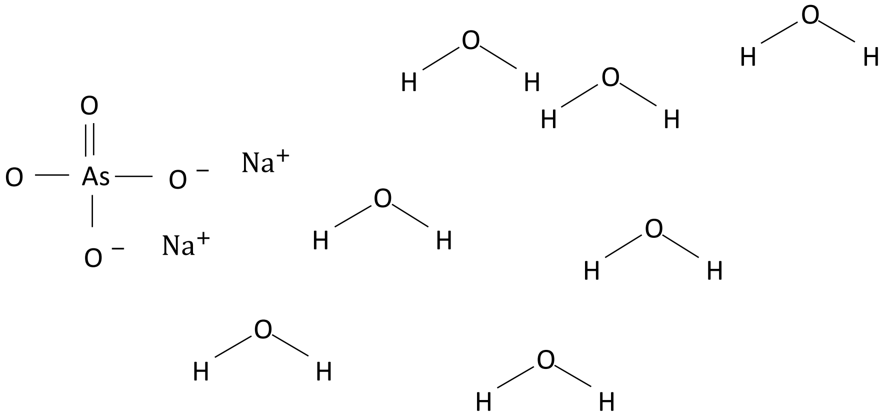

Figure 2. Chemical formula of Sodium arsenate dibasic heptahydrate.

Arsenic is usually found in nature as inorganic form (Smedley and Kinniburgh 2002). The arsenic contamination in water bodies is either from natural sources or anthropogenic sources (Mondal et al. 2006). Arsenic in organic form can be found in surface water, produced by biological activity. Also industrial pollution may cause the appearance of organic arsenic. This organic form is still rarely significant. (Smedley and Kinniburgh 2002) The mobility of arsenic in subsurface can be caused by chemical, physical or microbial forces (McArthur et al. 2001).

In ground, arsenic can be found in oxidation states of -3, 0, +3 and +5 (Smedley and Kinniburgh 2002). In aqueous and aerobic environments the dominant form of arsenic is arsenate $As(V)$. It has limited mobility in solution by its property to adsorb on the surface of common minerals as ferrihydrite and alumina. (Oremland et al. 2003) In aerobic conditions pH less than 6.9 the dominant form of arsenate is $H_2AsO_4^-$, when the pH is higher than 6.9 the dominant form is $HAsO_4^{2-}$. When the conditions are very acidic or alkaline the dominant forms are $AsO_4^0 \; and \; AsO_4^-$. (Smedley and Kinniburgh 2002) In anaerobic environments the dominant form of arsenic is arsenite As(III) and it is not adsorbed so strongly in common minerals so it is more mobile component (Oremland et al. 2003). In the reducing environment predominate form of arsenite is $H_3AsO_3^0$ (Smedley and Kinniburgh 2002).

Into the atmosphere arsenic enters from wind erosion, volcanic emissions, low-temperature volatilization from soils, marine aerosols and pollution. Back to earth arsenic comes through wet and dry deposition. The anthropogenic sources for arsenic pollution are smelter operations and fossil-fuels. These arsenic air pollution emissions are typically handled properly in industrialized countries with air-pollution control. Arsenic concentration in rainfall and snow is higher in areas were natural or anthropogenic sources are located. (Smedley and Kinniburgh 2002)

Arsenic can be converted to another form, but it cannot be destroyed (Mondal et al. 2006). For arsenic decontamination all living organisms have a system to remove it. Metabolism of arsenic is following three steps. First, phosphate transporters and aquaglyceroporins are used to uptake arsenate As(V) and arsenite As(III). Secondly, use arsenate reductases to reduction of As(V) to As(III), and thirdly removal or extrusion of As(III). Phosphate transporters that take up arsenate and arsenite are different for human and prokaryotes. (Barry 2002)

The typical concentration of arsenic in natural waters is less than 1−2 $\mu g/dm^3$. However, in groundwater the concentration can be significantly increased in the worst case of a scenario to 12 mg/dm^3 if the earth contains sulfide mineral deposits that are volcano rocks derivate. Only 25% of arsenic found in food, seems to be in toxic inorganic form and the rest are less harmful organic form. The amount of arsenic, depend on the type of food, but the highest amount can be found in fish and shellfish. Arsenic exposure can be occupational, but in the large scale the highest exposure is through food and drinking water. (WHO 2011 p. 315)

5.4 Experimental procedure

5.4.1 Experimental procedure of adsorption

The adsorption experiment was done with four adsorbent materials. The Kemira's commercial adsorbent CFH-12 was used without any pre-treatment. The Sachtofer and Brazilian sand were tested first without any pre-treatment, then with washed adsorbents and the HCl-activated adsorbents. Red mud was pre-treated earlier with four different methods, washed, calcined, HCl-activated and H_3PO_4-acid activated. All four adsorbent samples were tested.

The amount of adsorbent used in the experiments was 1 g/dm^3 and it was mixed with 200 cm^3 diclofenac or arsenic solution in 250 cm^3 Erlenmeyer flasks that were placed in a shaker that was shacked 280 rpm. All samples were taken according to the timetable 0 min, 5 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, 90 min, 120 min, 180 min, 240 min, 300 min, 360 min and 23 h. From all solutions pH was measured before adding adsorption material, 15 minutes after adding adsorption material in solution and at every hour. The samples were filtered through a 0.45 µm syringe filter.

The diclofenac concentration used in all the tests was 15 mg/dm^3. The pH adjustment was done for diclofenac solution with HCl and H_2SO_4 for untreated Sachtofer and the HCl-activated samples. These acids were decided to be used based on earlier published results (Bahdra et al. 2016) (Shehdeh et al. 2016). For arsenic removal a 100 mg/dm^3 As(V) stock solution was prepared. In the experiments, the stock solution was diluted to the arsenic concentration of 100 µg/dm^3. The stock solution was preserved with (65%) nitric acid (HNO_3) so the final acid concentration was 0.2% in the solution. In arsenic samples nitric acid was added to ensure the preservability of the samples.

The diclofenac samples were analyzed with spectrophotometry and with HPLC. The main analyzing method was spectrophotometry. With some samples there were problems with analyzing samples with spectrophotometry. The results showed that the diclofenac concentration would increase over the starting level. To make it sure, some samples were decided to be analyzed also with HPLC in the laboratory of the Faculty of Medicine. The arsenic samples were analyzed with ICP-MS in the Laboratory of Ahma insinööri Oy in Oulu.

5.4.2 Treatments for adsorption materials

Sachtofer, Brazilian sand and adsorbent from Kemira were first tested for diclofenac without any pre-treatment and pH adjusting. In the first tests, the pH of solution for Brazilian sand was around 6–7 and for Sachtofer it was 8–12. Because of the high pH, Brazilian sand and Sachtofer were washed with distilled water and dried. Both adsorbents were measured around 50 cm^3 and mixed with approximately 500 cm^3 of water. After about 40 minutes the water was changed and for Brazilian sand pH was measured to be 6.95 and for Sachtofer 7.77. After second water change the pH for Sachtofer was 11.06 and for Brazilian sand 6.90. Because washing did not have any effect on Brazilian sand washing was continued only for Sachtofer. Water was changed still two times, but the pH remained both times quite the same 10.71 and 10.31. After washing, both adsorbents were filtered and dried in heat cabinet at 100 ºC for about 3 hours. When the heat cabinet was turned off the adsorbents were left in the cabinet overnight.

Red mud samples were pre-treated by M.Sc.(Eng.) Sanna Antikainen. Red mud adsorbents were divided into four group based on the pre-treatment method. Red mud was first filtered and washed with distilled water and after that dried at 110 ºC overnight. Red mud was then divided into four fractions. The first fraction was washed red mud. The second fraction was calcined red mud and it was calcined in the muffle furnace at 500 ºC for 2 hours. The third fraction was activated red mud. This activation method was introduced by Pratt & Christoverson 1982 and the same method was used for Brazilian sand. Red mud was mixed and stirred with distilled water to reach a 5 wt-% red mud solution. After that hydrocholoric acid was added to reach 8 wt-%. The solution was stirred and boiled for 20 minutes and diluted then with distilled water so that the total volume would reach 1.3 dm^3. With ammonium hydroxide pH of the solution was adjusted at ~8. After pH adjusting the suspension was heated to approximately 50 ºC in 10 minutes and filtered and washed with 50 cm^3 distilled water (40 ºC) three times. At last the activated red mud was dried at 110 ºC overnight and then calcined in muffle the furnace at 500 ºC for two hours. The fourth fraction was activated with mixture of hydrochloric acid HCl and orthoposporic acid H_3PO_4 with the ration aiming for 4 wt-% of phosphorus in calcined material.

The Brazilian sand was treated in the same way as M.Sc.(Eng.) Sanna Antikainen treated the activated Red mud in her work. For this treatment 37.1744 g sand was taken. It was mixed with 700 cm^3 distilled water to reach a 5 wt-% sand solution. Amount of 170 cm^3 hydrochloric acid was then added to reach 8 wt-%. After this solution was stirred and boiled approximately 20 minutes. After that, boiling water was added 2.25 dm^3 and the solution was filtered. Brazilian sand was then washed about with 115 cm^3 of 40 ºC water for three times. After this the adsorbent was filtered and dried at 110 ºC overnight. Then the sand was crushed and calcined in the muffle furnace at 500 ºC for two hours.

Sachtofer was also washed with hydrochloric acid. The adsorbent was washed with 10 cm^3 0.15 M HCl for every gram of Sachtofer. For this treatment Sachtofer was taken 37.048 g and approximately 370 cm^3 of 0.15 M HCl was needed. The adsorbent was in solution for 10 minutes. After that it was filtered and washed with distilled water so the pH reached 6–7. In this test washing and pH measurement was done five times giving as results 1.98, 4.85, 5.06, 5.42 and 8.74. After this the adsorbent was filtered and dried at 110 ºC overnight. Then the adsorbent was calcined in muffle furnace at 500 ºC for two hours.

5.4.3 Analysis method

Spectrophotometry was used to analyze the amount of diclofenac from the samples. Spectrophotometry is a method that measures absorbance, i.e. how much light the sample solution is absorbing and transmission, i.e. how much light is passing through. Depending on the structure of the molecule it can selectively absorb light with certain wavelengths. For following the diclofenac the wavelength was 275 nm. The Beer-Lambert law is explaining that the absorbance is proportional to the concentration. Lambert's law state that the transparent solution is absorbing light equally in entire solution. The Beer's law state that the amount of absorbent light is proportional to concentration in the solution. (Poole and Kalnenieks 2000 p. 2-3)

Spectrophotometry is reporting the amount of absorbance, the concentration can be calculated from the calibration curve. Diclofenac solutions with concentrations 2.5 mg/dm^3, 5 mg/dm^3, 10 mg/dm^3, 12.5 mg/dm^3, 15 mg/dm^3 and 20 mg/dm^3 were prepared and the absorbances were measured with spectrophotometry. The measured values are presented in the Table 3.

Table 3. Light absorbance for certain diclofenac concentrations.

Diclofenac concentration (mg/dm^3)	20	15	12.5	10	5	2.5
Absorbance	0.6251	0.4737	0.3983	0.3159	0.1584	0.0813

From these values the calibration curve is presented in formula (Eq. 5).

$$c_f = 32{,}032A - 0{,}1253 \tag{5}$$

where c_f is the concentration of model compound [mg/dm^3] at certain time of experiment and A is the absorbance.

The second formula (Eq. 6) was used to determine the removal [%] of model compound from the solution.

$$Removal = \frac{c_i - c_f}{c_i} \times 100\% \tag{6}$$

where c_i is the concentration of model compound [mg/dm^3] in the beginning of the experiment.

High-Performance Liquid Chromatography HPLC was used to analyze diclofenac from the solution. Liquid chromatography is one technique of chromatography. This analytical technique is separating a mixture into different components. The separation technique is based on two different phases. The other phase is stationary and the other phase is moving over it. In liquid chromatography the mobile phase is liquid. Components in a mixture are interacting differently in two phases and that is how components are separated. In HPLC the mobile liquid phase is mechanically pumped through the column that contains the stationary phase. (Brown and Weston 1997 p. 1)

There are two different methods to classify the liquid chromatography. The first one is based on separation principle, but it is not the popular way and can be found in literature from 1990 and before. The other way is based on the mechanism of retention where the separation technique can be divided into five different methods: adsorption, partition, size exclusion, affinity and ion exchange. (Brown and Weston 1997 p. 2)

The arsenic analysis was done with inductively coupled plasma-mass spectrometry ICP-MS. In this analysis method the sample is usually in aqueous solutions. The nebulization process used to convert aqueous solution to an aerosol that is then transported to the plasma by an argon gas stream. The formed aerosols are atomized in plasma by ionization. Ions are extracted from plasma and they are measured with a quadrupole mass spectrometer. (Taylor 2001 p. 3)

6 RESULTS AND DISCUSSION

6.1 Material characterization

Adsorbents were analyzed with N_2 adsorption analysis to determine the specific surface areas (BET). Scanning electron microscopy (SEM) analysis was done to get more visual view on the surface structure. To determine the right pH for adsorption tests the values for pH_{PZC} were determined.

Diclofenac and arsenic adsorption tests were performed first for Kemira’s adsorbent. Sachtofer and the Brazilian sand with adsorbents that were pre-treated in this work. For pre-treatment first they were washed with distilled water and second they were activated with HCl to see if the pre-treatment would have an effect on the adsorption efficiency. HCl was chosen for activation, because it was the most efficient method in the pre-treatment of Red mud according to the investigation done by M.Sc.(Eng.) Sanna Antikainen.

6.1.1 Surface area and pore size distribution

Table 4 shows results of BET- analysis. In the table the specific surface area denotes as S_{BET} [$m^2 g^{-1}$]. For ferrous reference materials, the surface area was the largest. In the case of Red mud, it can be seen, that the surface area of the material is increasing when the material is treated with the acid. The HCl-activated Red mud has the highest specific surface area. For Sachtofer the surface area is the smallest. For Sachtofer and the Brazilian sand the surface area are decreased for the samples treated with HCl. This is unexpected, because the surface area was assumed to grow like in the case of Red mud. For the Brazilian sand the surface area was surprisingly high for untreated sample.

Table 4 is also presenting the pore volume V [$mm^3 g^{-1}$] and pore size S [nm] distribution for the CFH-12, Brazilian sand and Sachtofer samples. It should be noticed that for CFH-12 the pore volume is the highest, but the pore size is smaller than pore sizes for the Brazilian sand and Sachtofer samples. The pore volume is smaller for the Sachtofer samples than for the Brazilian sand samples, but the pore size is larger for Sachtofer samples than for the Brazilian samples. For the HCl-activated samples the pore size seems to be larger than for the untreated samples.

Table 4. N_2 adsorption results.

Sample	S_{BET} ($m^2\,g^{-1}$)	V ($mm^3\,g^{-1}$)	S (nm)
CFH-12	187	116	4.2
Washed Red mud	41		
Calcined Red mud	59		
HCl-activated Red mud	144		
H2SO4-activated Red mud	108		
Sachtofer	33	61	7.2
HCl-activated Sachtofer	22	62	11
Brazilian sand	79	107	5.3
HCl-activated Redmud	44	84	7.2

6.1.2 Surface characterization

In Figure 3, the SEM image of reference material CFH-12 from Kemira is shown. The surface is quite smooth with few lumps. This adsorbent is commercial product and it has large surface area, so the surface was assumed to be rougher than with others.

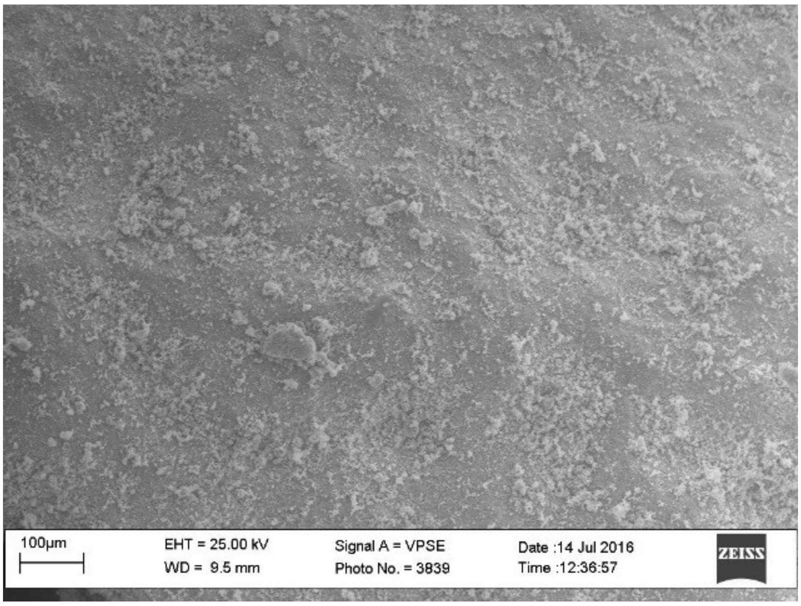

Figure 3. Overview of Kemira’s adsorbent CFH-12.

Figure 4 shows the SEM images for the Sachtofer samples. For Sachtofer there are two kinds of structures for granules, which can be seen with eyes. Figure 4 shows, untreated Sachtofer (a), washed Sachtofer (b) and HCl-activated Sachtofer (c) and (d) samples, all pictures are taken from the granules that have visually lumpier surface. In the figures it can be seen that the untreated Sachtofer surface is more uneven. In Figures 4(b) and 4(c) the washed Sachtofer and the HCl-activated Sachtofer, smoother surface is observed. Based on the BET-analysis, the untreated Sachtofer had a larger specific surface area than the HCl-activated sample. The structures observed in these SEM images are accordance with the BET results.

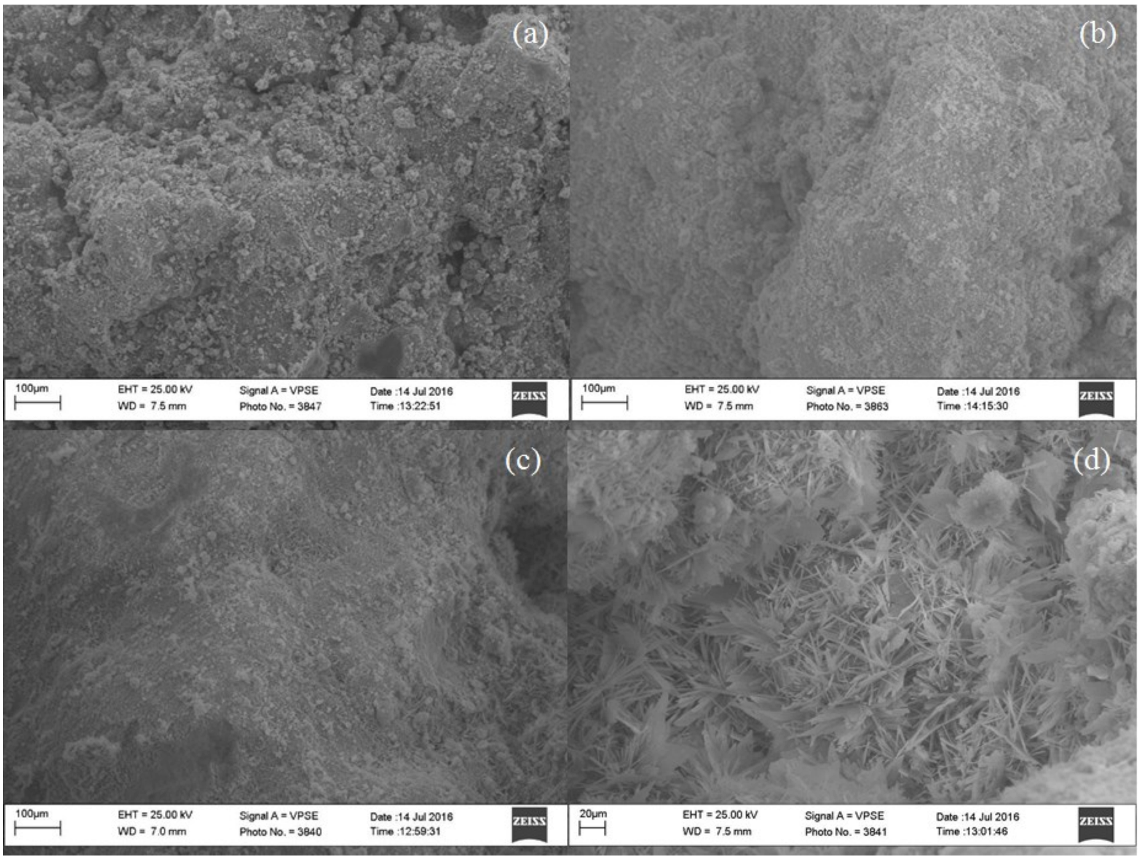

Figure 4. Overview images of (a) Sachtofer, (b) Washed Sachtofer, (c) HCl-activated Sachtofer and detailed image of (d) HCl-activated Sachtofer.

In all Sachtofer overview pictures presented in Figure 4, some deep cavities can be observed. For closer overview the untreated and the washed Sachtofer's cavities were quite solid. Figure 4(d) is a detailed picture from the HCl-activated Sachtofer. It can be seen that sharp shape edges and needle shape surface was found from cavities. Figure 5 shows the SEM images of Red mud and the Brazilian sand.

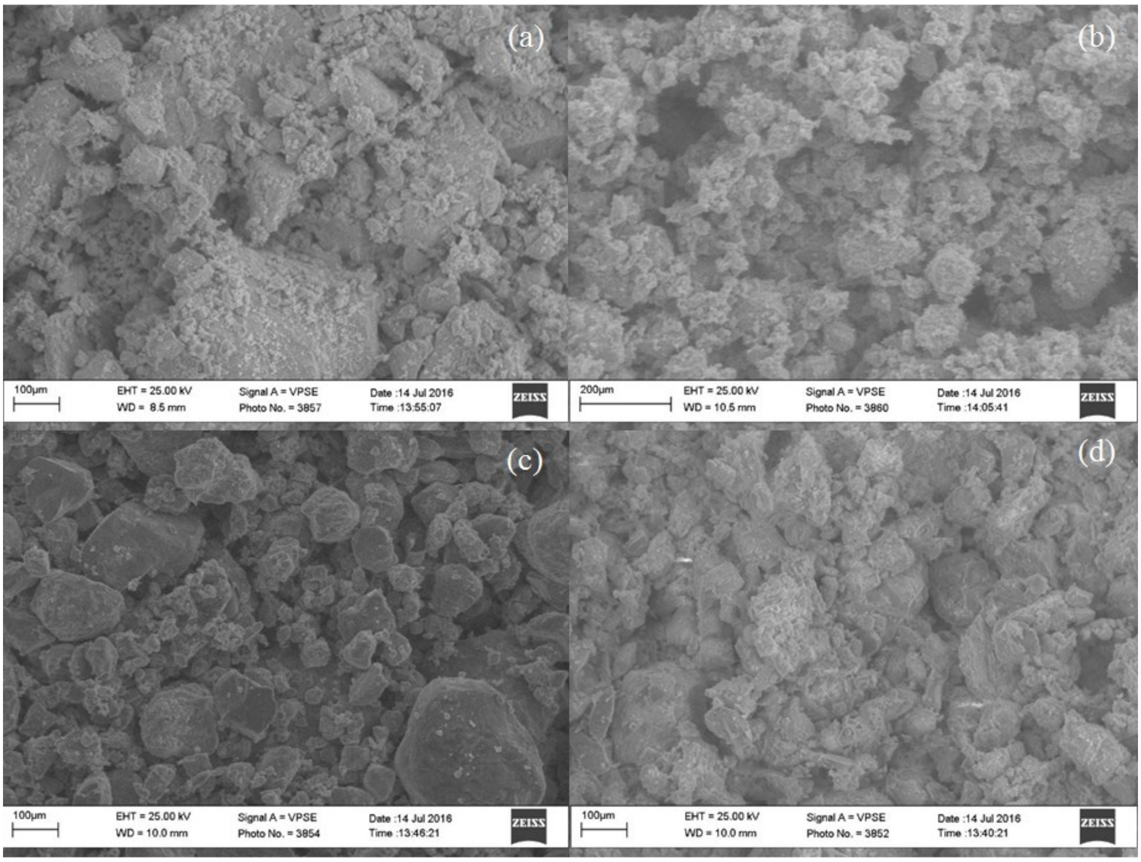

Figure 5. Overview images of (a) Washed Red mud, (b) HCl-activated Red Mud, (c) Washed Brazilian sand, (d) HCl-activated Brazilian sand.

Figure 5 gives the overview images from Washed Red mud 5(a) and the HCl-activated Red Mud 5(b). For washed Red Mud the particle size distribution is wide. There are particles from nanometer to millimeter. For the HCl-activated Red mud the particle size distribution is more even and there are only certain sizes of particles. In Figure 5(c) an overview from the washed Brazilian sand is presented. It has also wide range of size of particles, but not as wide as Red mud has. The surface seems to be more solid than for the HCl-activated Brazilian sand presented in Figure 5(d). For the HCl-activated Brazilian sand, the particle size is higher than for other samples.

Figure 6 shows detailed images for Red mud and the Brazilian sand. In Figure 6(a) the Red mud sample seems to has more porous structure than the Brazilian sand has. The 6(b) HCl-activated Red mud has also porous structure, but not as porous as washed Red mud. In 6(c) the washed Brazilian sand has some small particles on the surface. The smallest particles are charged and moving quite much, which makes the SEM imaging of them very difficult even after multiple coating of the sample. On the surface of the HCl-activated Brazilian sand 6(d) smaller particles were not detected anymore. Unfortunately we did not have possibility for the Energy-dispersive X-ray spectroscopy (EDS) analysis, so the quality of the particles remained unknown.

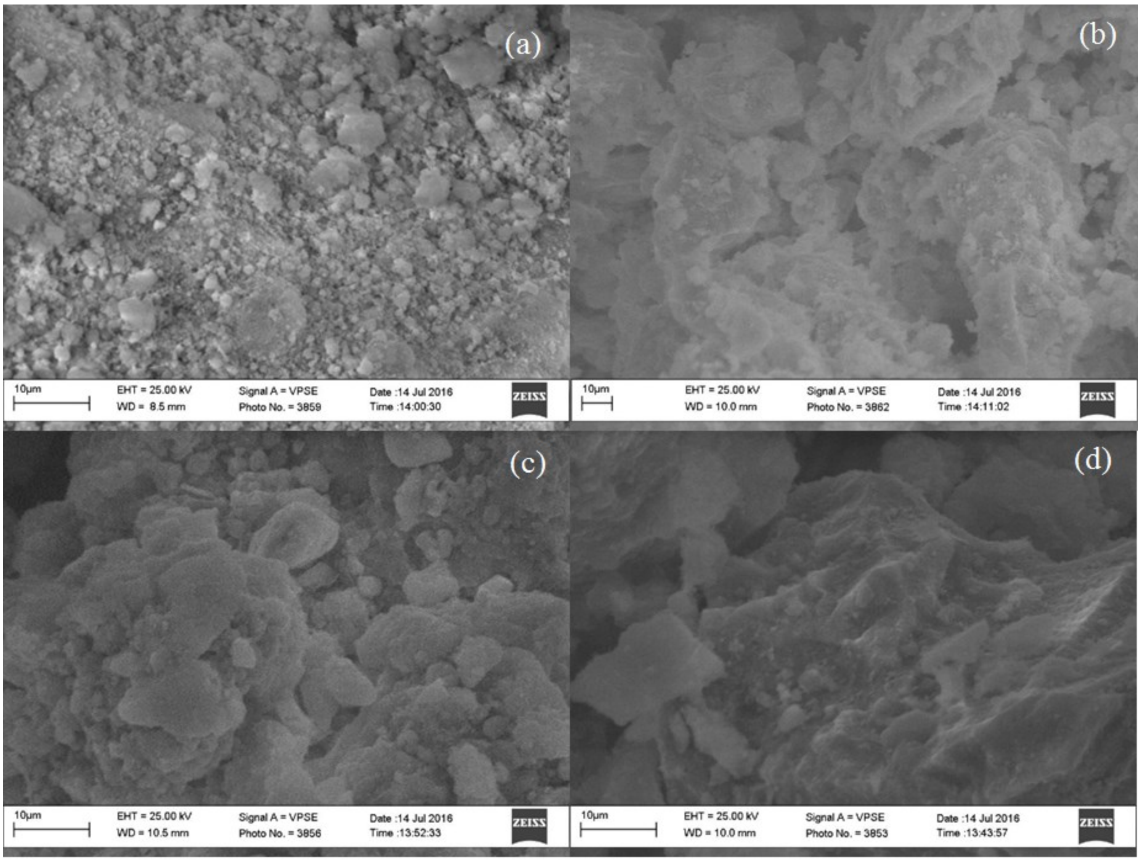

Figure 6. Detailed images of (a) Washed Red mud, (b) HCl-activated Red Mud, (c) Washed Brazilian sand, (d) HCl-activated Brazilian sand.

Based on the BET-analysis, the surface area was decreasing for Sachtofer, but also for Brazilian sand, when they were treated with HCl. With the SEM analysis it was observed for washed Brazilian sand that originally included small charged particles were probably removed with the HCl treatment, since they were not anymore observed, and also the observed specific surface area was smaller.

6.1.3 Point of zero charge determination

Adsorption is more efficient when the pH in the solution is on the certain level. The point of zero charge was measured for Kemira's adsorbent CFH-12, untreated Sachtofer, HCl-activated Red mud and HCl-activated Brazilian sand. These adsorbents worked the best according to preliminary tests. Determination of the point of zero charge was difficult and there were problems to determine it for certain adsorbents. This is why only for these four adsorbents the point of zero charge was measured.

pH$_{PZC}$ is calculated from interception between the curves pH$_{Final}$ vs. pH$_{Final}$ and pH$_{Initial}$ vs. pH$_{Initial}$. In Figure 7 one can observe these determinations for all four adsorbents. It can be assessed that the pH should be below these values to have efficient adsorption. This is because when pH < pH$_{PZC}$ the net surface of adsorbent have positive charge and it has tractive power for anionic adsorbate. If the pH > pH$_{PZC}$ the net surface would be negatively charge and between adsorbent and anionic adsorbate would have repulsive forces.

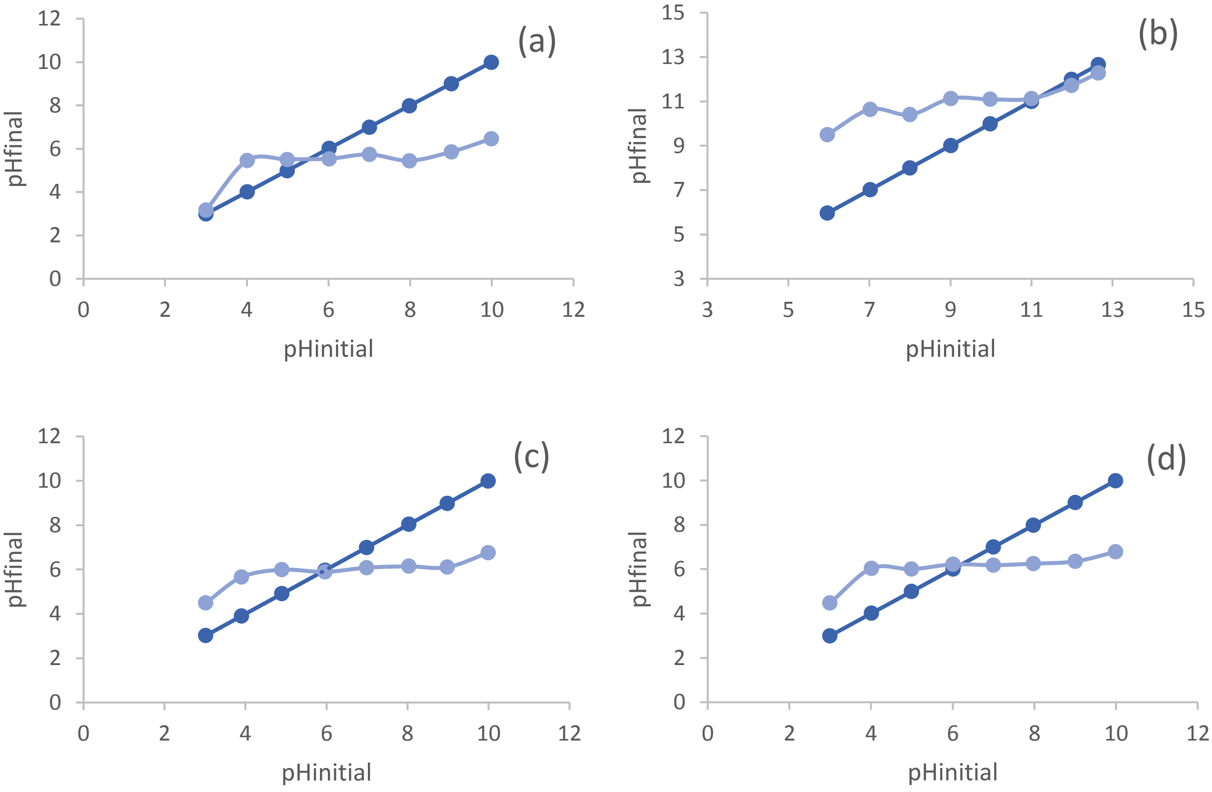

Figure 7. pH$_{PZC}$ for (a) CFH-12, (b) Sachtofer, (c) HCl-activated Red mud and (d) HCl-activated Brazilian sand.

The results are presented in Table 5. The lowest pH_{PZC} was for Kemira's adsorbent CFH-12. The highest value was for seen with Sachtofer. For Red mud and for the Brazilian sand the pH_{PZC} values were very close to each other. As the materials, they seemed to be quite similar and it was assumed that the pH_{PZC} might be close to each other.

Table 5. pH_{PZC} for selected adsorbents.

Adsorbent	CFH-12	Sachtofer	HCl-activated Red mud	HCl-activated Brazilian sand
pH_{PZC}	5.5	11.25	6.23	6.2

The problem in pH_{PZC} determination was that pH_{Final} varied very much. The results varied and the line of pH_{Final} was curly. It did not create straight line were the point of zero charge could be determined exactly. The reason why the experiment did not succeed every time was not clear. The pH meter was changed and the pH was tried to be measured with two different pH meters. There was no logical explanation at which time the experiment failed. For untreated Sachtofer for example the pH_{PZC} was determined two times, because the first experiment failed. Determination for the HCl-activated Sachtofer failed also, but for the HCl-activated Brazilian sand it was managed to be determined.

6.1.4 Elemental analysis

For some adsorbents elemental analysis was done to find out the elemental composition of the materials. The elemental analysis was done for the untreated, washed and HCl-activated Sachtofer and for the washed and HCl-activated Brazilian sand. During the earlier studies elemental analysis was done for the calcined HCl and H_3PO_4-activated Red muds. In Table 6 there are the results from elemental analysis for Sachtofer.

Table 6. Elemental analysis for the Sachtofer samples.

	Major elements (wt-%)		
	Sachtofer	Washed Sachtofer	HCl-activated Sachtofer
H	2.0	0.9	0.3
C	1.1	1.2	1.5
O	45.0	45.0	43.0
Na	0.4	0.1	0.1
Mg	1,4	1.7	1.7
Al	0.5	0.6	0.6
Si	0.7	0.9	0.9
S	9.5	10.4	11.3
Cl	0.1	0.1	0.1
K	0.1	-	-
Ca	22.6	25.7	25.6
Ti	1.6	1.9	2.2
V	0.3	0.3	0.3
Cr	0.1	0.2	0.1
Mn	0.6	0.7	0.8
Fe	8.9	10.3	11.3

It seems that the samples contain mostly O, Ca, Fe and S. There is also minor content of C, Mg and Ti. Iron could be in different oxidation stages. Calcium sulfate can be anhydrous or hemihydrate, but most probably gypsum. It is noticed that Sachtofer material is hard granular shape and composition between grains could vary. For elemental analysis, the sample amount was 1 g and it could be that it is not representative to the real content. It can be seen that there are two kinds of granules of Sachtofer. First one has more solid surface and from inside it seems to be more like a pellet with layers of different kind. The second one's surface is lumpier and the granular containing is more constant.

In Table 7 there are results from elemental analysis for Red mud. The main components in the Red mud samples are Na, Al, Si, Ca, Ti and Fe. The highest content are for aluminum and iron. In calcined Red mud there was content of sodium and calcium, but in activated samples the content was decreased.

Table 7. Elemental analysis for the Red mud samples.

	Major elements (wt-%)		
	Calcined Red mud	HCl-activated Red mud	Orthophosporic acid -activated Red mud
Na	3.3	0.1	0.1
Mg	0.4	0.1	0.1
Al	11.7	13.0	12.1
Si	3.1	3.2	2.9
P	0.3	0.4	4.3
S	0.2	0.1	-
Cl	0.2	0.4	0.2
Ca	3.4	0.3	1.4
Ti	4.1	4.4	4.0
V	0.1	0.1	0.1
Cr	0.2	0.2	0.2
Mn	0.9	0.8	0.8
Fe	43.5	47.4	42.5

The elemental analysis was done for the washed and HCl-activated sand. It was decided that the elemental analysis is not done for untreated sand, because it is the soil material straight from ground. As can be seen from Table 8 the main components for the washed Brazilian sand are O, Fe, Si, Al and Ti. For the HCl-activated Brazilian sand the main components are the same. The amount of silica and oxygen are increased and the iron content is decreased in the HCl-activated sand.

Table 8. Elemental analysis for the Brazilian sand samples.

	Major elements (wt-%)	
	Washed Brazilian sand	HCl-activated Brazilian sand
O	39.0	45.7
Mg	0.1	0.1
Al	8.5	6.6
Si	17.2	27.0
P	0.2	0.2
Cl	0.1	0.2
Ca	0.2	-
Ti	2.9	3.1
Cr	0.1	0.1
Mn	0.1	0.1
Fe	21.9	15.4
Zr	-	0.1

6.2 Diclofenac adsorption

Diclofenac adsorption tests were done with Kemira’s commercial adsorbent CFH-12, with three Sachtofer and Brazilian sand samples and with all four different ways treated Red mud samples. The pH adjustment was done with HCl and H_2SO_4 for the untreated Sachtofer and HCl-activated samples, but the results are not presented because the diclofenac decomposed after adding the acids.

For diclofenac adsorption the Kemira’s commercial adsorbent was the only one that reached diclofenac removal of 100%. The ferrous reference product from Kemira was a commercial product and it was assumed to work well. Figure 8 presents the pH conditions for diclofenac adsorption with CFH-12.

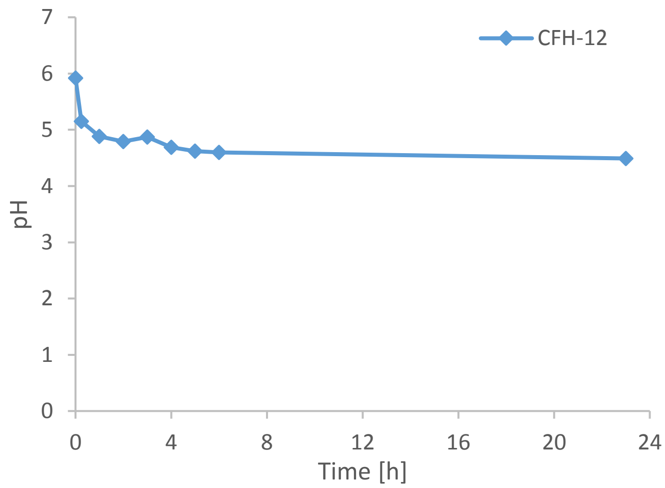

Figure 8. The pH conditions for diclofenac adsorption with the CFH-12 sample.

From Figure 8 it can be seen that the pH during the test was mostly under 5. The pKa for diclofenac is 4.15. In this test, we did not adjust the pH. Figure 9 shows the diclofenac removal efficiency with CFH-12.

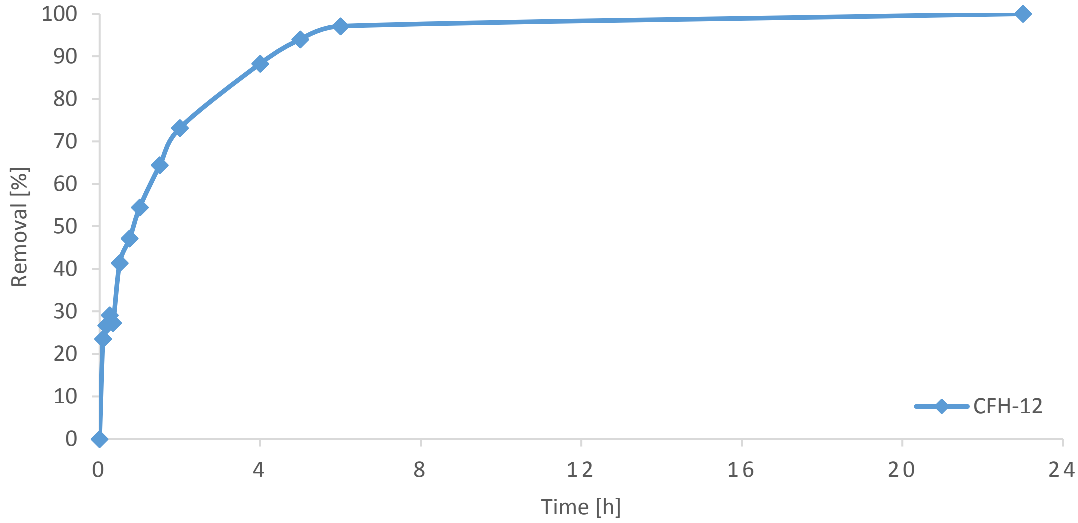

Figure 9. Diclofenac removal efficiency with the CFH-12 sample.

The samples taken during the adsorption tests were analyzed with spectrophotometry, but also HPLC analysis was used, to be sure that spectrophotometry is giving the right results. The observed results were close to each other. Based on those results it could be assumed that diclofenac samples can be analyzed with spectrophotometry. From Figure 9 it can be seen that the 100% removal was reached almost after five hours. This result was very good and based on this it can be proposed that the diclofenac adsorption can be done with the tested material. The efficiency could be higher and the adsorption time could be less if the pH would be closer pKa, but this result was satisfied enough. Figure 10 presents the pH conditions for diclofenac adsorption with Sachtofer.

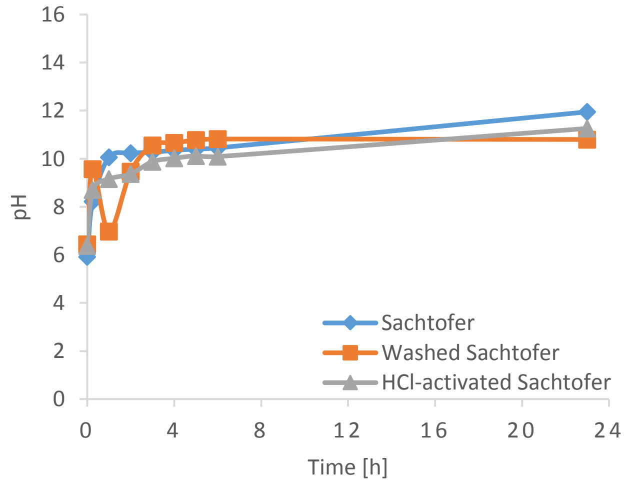

Figure 10. The pH conditions for diclofenac adsorption with the Sachtofer samples.

From Figure 10 it can be seen that the pH conditions with Sachtofer were rather high. The pH_{PZC} for untreated Sachtofer is 11.25. Sachtofer is a very basic material and this was a problem with diclofenac adsorption, when it changed the pH in the solution to be alkaline. Washing Sachtofer with distilled water and activation with HCl did not have remarkable effect on the material's alkalinity. When Sachtofer was washed with distilled water, the pH was decreased to around 7. After the third time of changing the water the pH came back to around 10. With HCl-activation, the pH was directly after the treatment 1.98, but after washing the activated adsorbent couple of times with the distilled water the pH was increased to 8.74. As it can be seen from Figure 10 the pH during the experiments were 10 or higher in all three cases. Figure 11 shows the removal efficiency of diclofenac with Sachtofer.

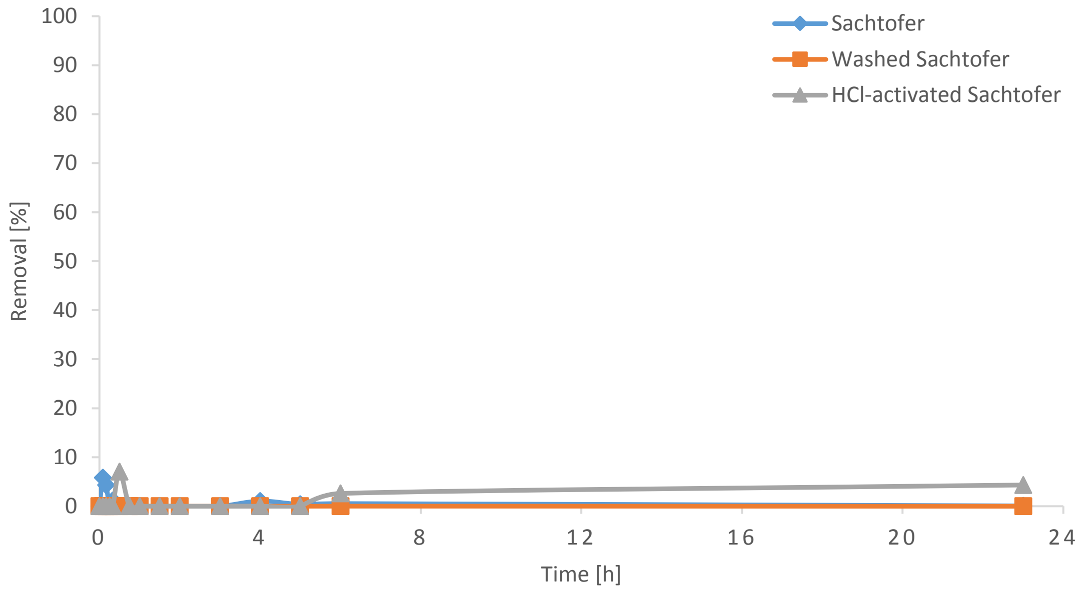

Figure 11. Diclofenac removal efficiency with the Sachtofer samples.

From Figure 11 it can be seen that Sachtofer did not work as an adsorbent for diclofenac. Samples from the Sachtofer experiments were analyzed with spectrophotometry. Only with the HCl-activated Sachtofer the removal after 23 hours was 4%. These bad results was mainly because the high pH. It was assumed that the removal efficiency might be lower, when the adsorbent will most likely increase the pH of solution. The diclofenac will stay as hydrophilic stage and does not adsorb onto adsorbent. Figure 12 presents the pH conditions for diclofenac adsorption efficiency with Red muds.

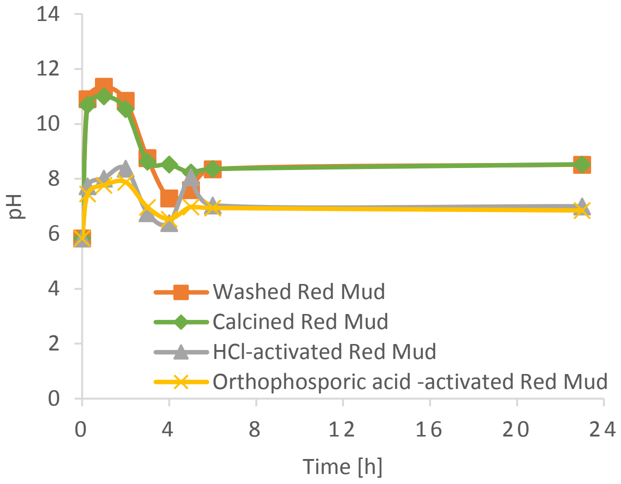

Figure 12. The pH conditions for diclofenac adsorption with the Red Mud samples.

In adsorption with washed and calcined Red Mud the pH conditions were higher than with the HCl and orthophosporic acid -activated adsorbents as it can be seen from Figure 12. With washed and calcined Red mud the pH was momentarily over 11, but it stabilized at approximately pH of 8. These conditions were too basic concerning also the pKa of diclofenac. With the HCl and orthophosporic acid -activated Red muds the pH was at the highest point over 8, but it stabilized in the level of pH 7. Diclofenac will stay in this neutral pH in acidic form and be more hydrophilic and do not adsorb onto adsorbent. Figure 13 presents diclofenac adsorption efficiency with Red muds.

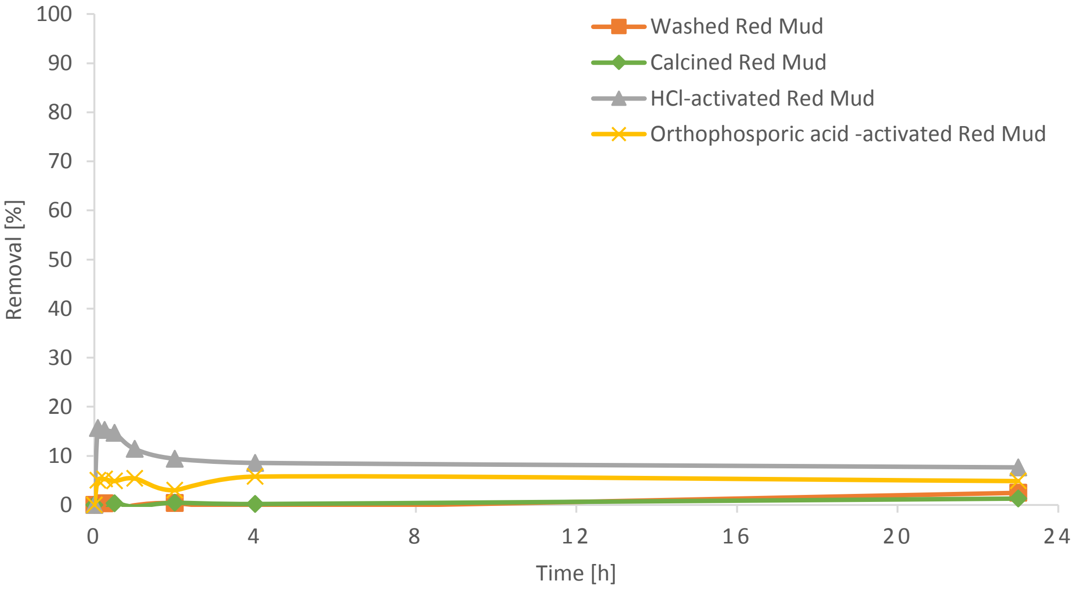

Figure 13. Diclofenac removal efficiency with the Red mud samples.

From Figure 13 it can be seen that in diclofenac adsorption the best adsorbent was the HCl-activated sample. The diclofenac samples during the experiments were analyzed first with spectrophotometry. The results showed increasing of diclofenac concentration over 15 mg/dm^3 with washed and calcined Red muds. Because the starting level was every time 15 mg/dm^3 it was assumed that something is leaching from the Red mud that will interfere the measurements and cause the increasing of concentration. Secondly, the samples were analyzed with HPLC, and it showed that calcined and washed Red muds did not adsorb any diclofenac and the concentration stayed at level of 15 mg/dm^3.

With the HCl and orthophosporic acid -activated Red mud the results were similar when analyzing with spectrophotometry or HPLC. With the HCl-activated Red mud the observed removal was 8%. With the orthophosporic acid -activated Red mud the removal was 5%. In the cases of washed and calcined Red muds the removal was 1−2%. The pH conditions were higher with those adsorbents and it is explaining why the adsorption efficiency was lower. The pH with the HCl and orthophosporic acid -activated Red muds was also very high explaining the low adsorption of diclofenac. Figure 14 shows the pH conditions for diclofenac removal efficiency with the Brazilian sand.

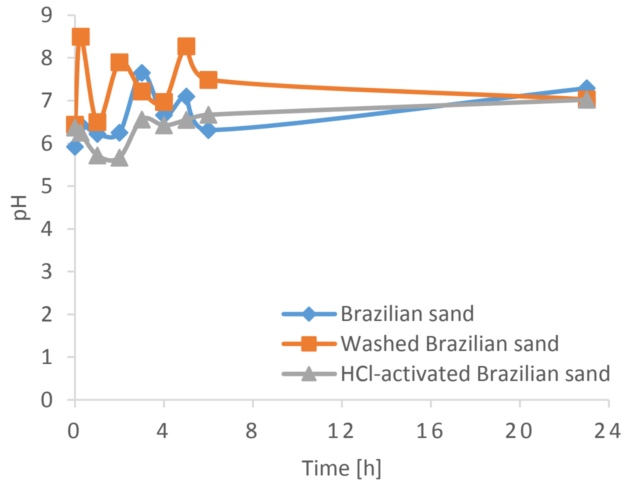

Figure 14. The pH conditions for diclofenac adsorption with the Brazilian sand samples.

All pH levels are quite at the same level. Washing and HCl-activation did not have any significant effect on the pH conditions in diclofenac adsorption in the case of the Brazilian sand. With the HCl-activated Brazilian sand, the pH is staying at the lowest level but after six hours the pH is stabilized at a level of around pH 7. The pH conditions are too high considering the pKa of diclofenac. Figure 15 shows the diclofenac adsorption efficiency with the Brazilian sand.

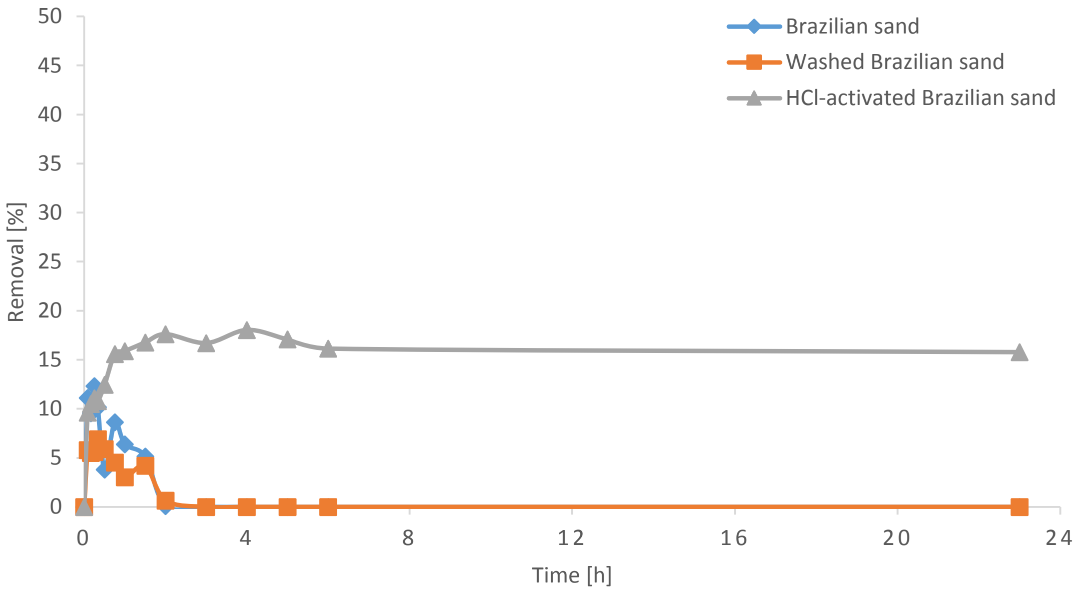

Figure 15. Diclofenac removal efficiency with the Brazilian sand samples.

The diclofenac adsorption results with the Brazilian sand, presented in Figure 15, show that the only adsorbent that worked was the HCl-activated Brazilian sand with the removal of 16%. Spectrophotometry was used in the analysis in connection to these experiments. The diclofenac removal was known to be difficult and this was an acceptable result considering the high pH level compared to the diclofenac's pKa level. When pH was on neutral or alkaline level in most of the experiments the diclofenac was staying in an acidic phase. In these cases it did not have any hydrophobicity and that is why it stays in the solution.

The untreated and washed Brazilian sand results seem to increase over 15 mg/dm^3. This is assumed to originate from the same phenomenon as with washed and calcined Red mud. There is something that is dissolved to the solution that will absorb the same wavelength of light than that used for diclofenac analysis. These samples were not analyzed with HPLC, because it was quite sure that there is no any significant removal of diclofenac. From Figure 15 it can be seen that during first hours diclofenac concentration is decreasing approximately 5−10%. If there is some components that are dissolved in the solution it could cause an error to the results. If the results were analyzed with HPLC the removal efficiency might be approximately 5−10% instead of 0%.

During the first hours, the diclofenac concentration did decrease slightly. This would need a repeated test to make it sure if there was some removal or if is just a coincidence. Time frequency of taking samples was short at the beginning of the experiment and sometimes the pH determination was taking over 15 minutes. During this operation the shaker was stopped. If the sample was taken when the shaker was not running the diclofenac might not be mixed properly and this could cause the decreased concentration in the analysis as well. Table 9 summarizes the observed diclofenac removal efficiencies.

Table 9. The diclofenac removal efficiency with the different secondary adsorbents.

	Removal		Removal		Removal		Removal
Kemira CFH-12	100%	Sachtofer	0%	Washed Red Mud	2%	Brazilian sand	0%
		Washed Sachtofer	0%	Calcined Red Mud	1%	Washed Brazilian sand	0%
		HCl-activated Sachtofer	4%	HCl-activated Red Mud	8%	HCl-activated Brazilian sand	16%
				Orthophosporic acid -activated Red Mud	5%		

The commercial CFH-12 was the only one that adsorbed 100% of diclofenac. The high pH levels were probably the reason why the diclofenac removal was not efficient enough. The diclofenac stays in acidic form and it is more hydrophilic and does not adsorb onto the adsorbent.

For diclofenac adsorption, the pH adjustment was tried to do with hydrochloric acid and with sulphuric acid for Sachtofer and the HCl-activated Brazilian sand. With both the acids the diclofenac was decomposed after acid adding. The results show concentration of 0 mg/dm^3 for starting zero samples. The samples were analyzed with spectrophotometry and HPLC. With Sachtofer, acids were reacting somehow and after 45 minutes diclofenac content seems to rise up approximately to the level 12–13 mg/dm^3.

6.3 Arsenic adsorption

Arsenic adsorption tests were done with Kemira's commercial adsorbent CFH-12, with three Sachtofer and Brazilian sand samples and with all four different ways treated Red mud samples. Arsenic concentration in experiments was 100 µg/dm^3 and it was diluted from a stock solution. Because the nitric acid that was added into the stock solution to preserve the sample, the pH conditions in the arsenic removal experiments were lower than in the diclofenac experiments.

In aerobic conditions when the pH is between 2 and 7, the dominant form of arsenic is arsenate $H_2AsO_4^-$ (Yang et al. 2007). The pH conditions for arsenic removal with Kemira's reference material CFH-12 are presented in Figure 16.

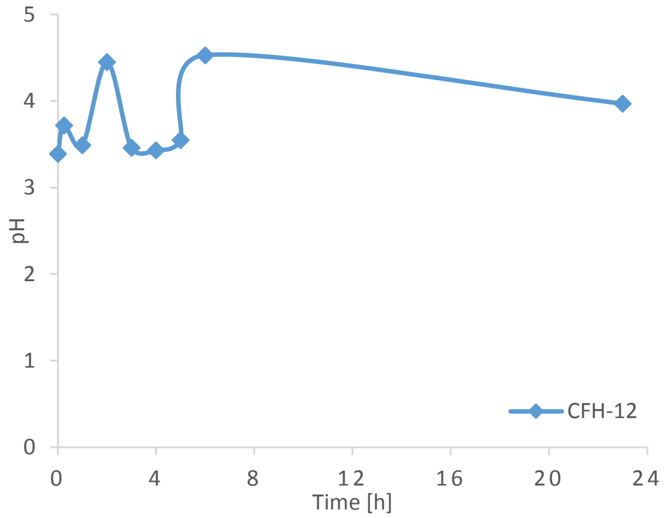

Figure 16. The pH conditions for arsenic adsorption with the CFH-12 sample.

During the experiment the pH stays in between 3.5–4.5. The pH$_{ZPC}$ for CFH-12 was 5.5, so the pH conditions were promising for arsenic removal when the net surface of the adsorbent was positively charge and the adsorbate is in an anionic phase. From Figure 17 it can be seen that in four hours almost all arsenic is removed. The removal conditions were optimal and the adsorption was efficient, which was assumed.

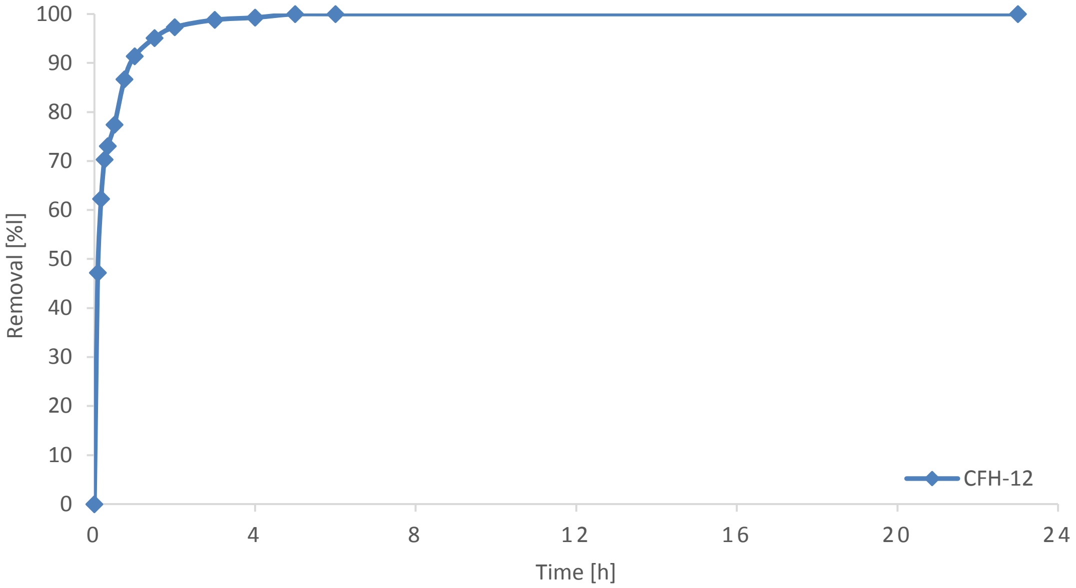

Figure 17. Arsenic removal efficiency with the CFH-12 sample.

Figure 18 shows the pH conditions for arsenic adsorption with the Sachtofer samples. This adsorbent material is a very alkaline one. According to Figure 18, the pH was raised above the value of 10 after one hour. Washing the Sachtofer did not have any significant effect on the pH conditions. The HCl-activation did have some effect on the pH increase. The pH was raised to the level of 8–9, but after 23 hours the pH was also higher than ten. When the pH is between 7 and 11.5 in aerobic conditions the dominant form of arsenic is arsenate $H_2AsO_4^{2-}$ (Yang et al. 2007).

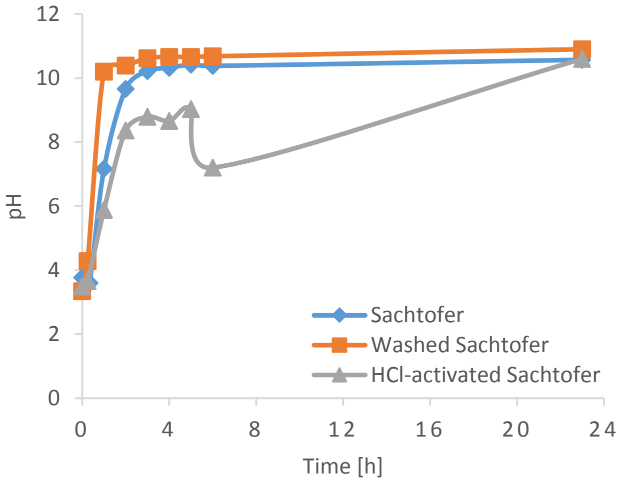

Figure 18. The pH conditions for arsenic adsorption with the Sachtofer samples.

Figure 19 shows the removal efficiency of arsenic with the Sachtofer adsorbents. Removal of arsenic with Sachtofer was very efficient as it can be seen. With all three adsorbents, the removal efficiency was 100%. The removal time varied when it was washed and activated with HCl, but the variation was very small and it might be due to an experimental error. It was assumed that the pH would have more effect on the removal efficiency, but in this case it did not have any influence.

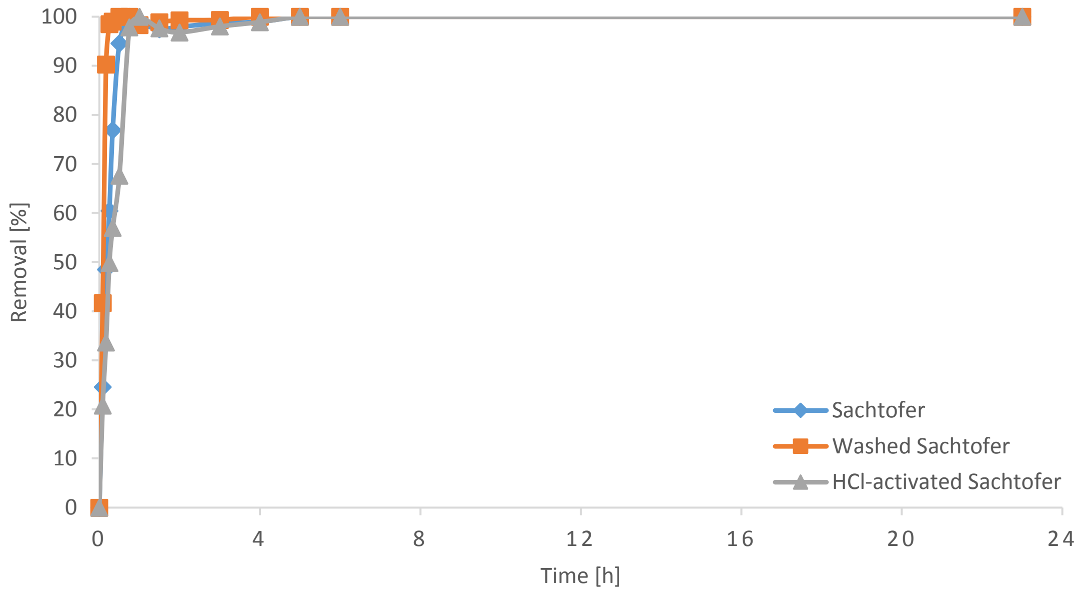

Figure 19. Arsenic removal efficiency with the Sachtofer samples.

The pH conditions in arsenic adsorption with Red muds treated in different ways are shown in Figure 20. Clearly the pH was higher with the washed and calcined Red Muds, at the level of pH 7–8. With the HCl and orthophosporic acid -activated Red muds the pH stayed between 3.5–4.5.

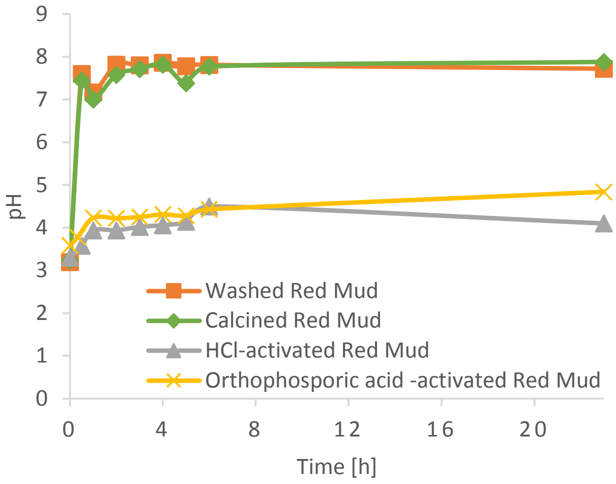

Figure 20. The pH conditions for arsenic adsorption with the Red mud samples.

The pH_{PZC} for the HCl-activated Red mud is 6.25 and the pH stays under that during the adsorption. The pH_{PZC} was not determined for the washed and calcined Red muds, but it might be possible that the pH_{PZC} of those samples is close to the same level than pH_{PZC} for the HCl-activated Red mud. In that case the pH conditions with the washed and calcined adsorbents were too high, when they are over 7. Figure 21 presents the removal efficiency of arsenic with the Red mud samples.

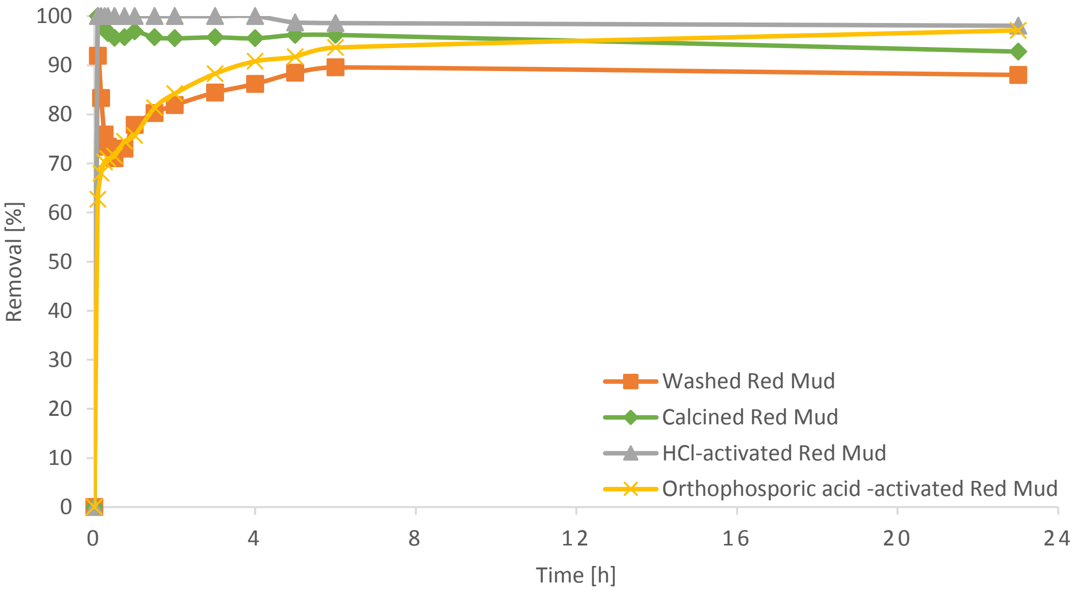

Figure 21. Arsenic removal efficiency with the Red mud samples.

It can be observed that arsenic removal was the most efficient with the HCl-activated Red mud. This was also the most efficient adsorption observed in these experiments. The time for the 100% removal was only 5 minutes. After 23 hours all the treated Red muds worked as adsorbents. The best result was observed with the HCl-activated Red mud with 98% removal efficiency. The second one was orthophosporic acid -activated with 97% removal efficiency. With the washed Red mud, the removal efficiency was 88% and with the calcined Red mud 92%. These results were very good. With the washed, calcined and HCl-activated red muds the concentration of arsenic had a minor increase in 23 hours. This result could be a coincidence and would require more studies to be verified.

The pH conditions were assumed to be more relevant for removal with washed and calcined Red muds. If the pH_{PZC} for these adsorbents would be assumed to be near 6.25, which is pH_{PZC} for the HCl-activated Red mud, the net surface would be negatively charged because of $pH > pH_{PZC}$. The arsenic would be in the anionic phase when pH is between 7 and 8, then it should have repulsive forces between the adsorbent that have the negatively charged surface. The results showed that the adsorption efficiency was quite high for the washed and calcined Red muds 88% and 92%, respectively. Based on these results it could be assumed that the pH_{PZC} for the washed and calcined Red muds might be higher than approximately 8. Figure 22 presents the pH conditions for arsenic adsorption with the Brazilian sand.

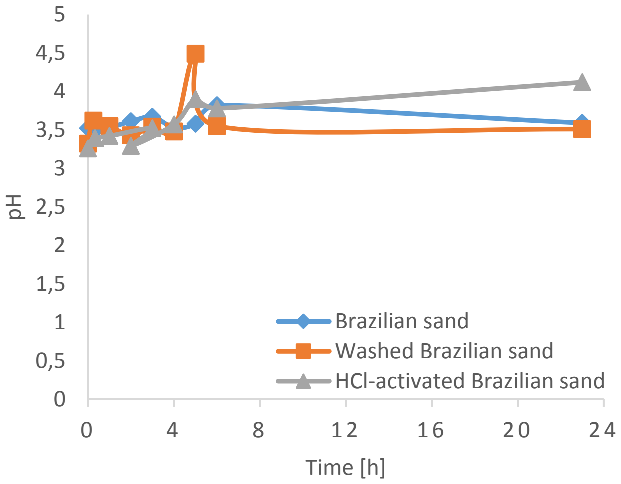

Figure 22. The pH conditions for arsenic adsorption with the Brazilian sand samples.

In Figure 22 it can be seen that for all the three Brazilian sand adsorbents, pH remains quite stable during the experiment. It should be noticed that with the HCl-activated

Brazilian sand the pH is higher than with untreated or washed sand. However, the difference is not that large and it could be caused by experimental error. If we compare the pH conditions of the Brazilian sand and Red mud, the difference is that with the washed Red mud the pH raised at higher level, but with the washed Brazilian sand the pH remained in the level 3.5–4.5. The pH was under the pH point of the zero charge for the HCl-activated Brazilian sand in arsenic adsorption. Figure 23 shows the arsenic removal efficiency with the Brazilian sand adsorbents.

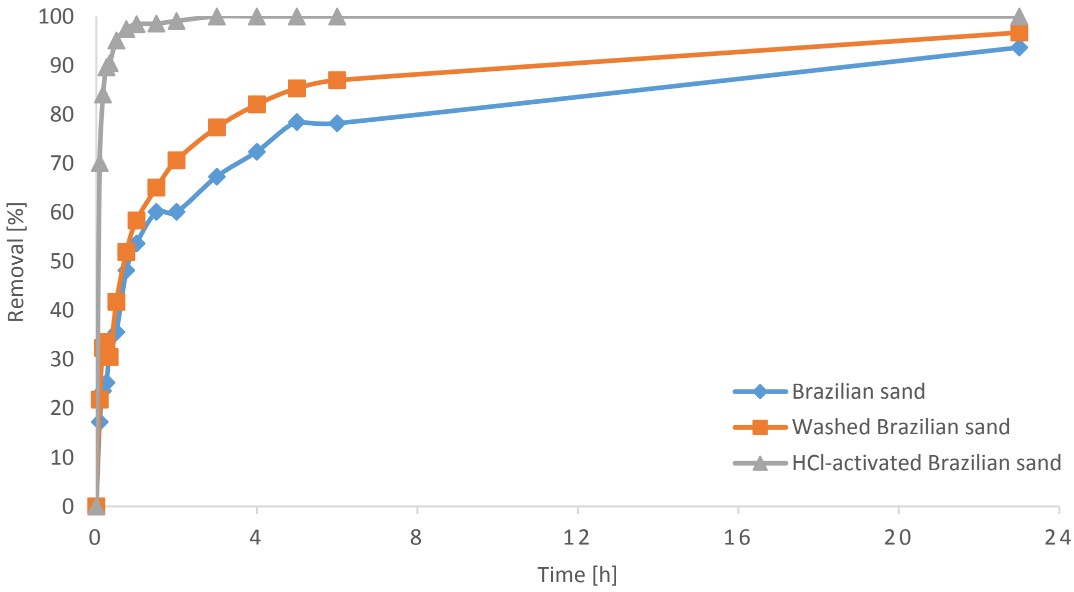

Figure 23. Arsenic removal efficiency with the Brazilian sand samples.

The HCl-activated Brazilian sand worked as the best in arsenic adsorption and the 100% removal efficiency was achieved after one hour as it can be seen from Figure 23. With the washed Brazilian, sand the removal was 97%, which is also a very good result. It is also remarkable that when the Brazilian sand was used as adsorbent without any pre-treatment the removal of arsenic was 94%. This should be noticed because the adsorbent material was normal ground soil.

Table 10 summarizes the arsenic efficiency removal results. All four materials worked well in arsenic removal. With Sachtofer all the three adsorbent managed to remove 100% of arsenic. With Red mud and the Brazilian sand the removal was successful with all four adsorbents, but with the HCl-activated adsorbents the removal was the best. Overall the HCl-activated adsorbents were the most efficient adsorbents in the arsenic removal.

Table 10. The arsenic removal efficiency with the different secondary adsorbents.

	Removal		Removal		Removal		Removal
Kemira CFH-12	100%	Sachtofer	100%	Washed Red Mud	88%	Brazilian sand	94%
		Washed Sachtofer	100%	Calcined Red Mud	92%	Washed Brazilian sand	97%
		HCl-activated Sachtofer	100%	HCl-activated Red Mud	98%	HCl-activated Brazilian sand	100%
				Orthophosporic acid -activated Red Mud	97%		

6.4 Secondary materials as adsorbents

With Kemira's commercial adsorbent CFH-12, the results showed how effective the industrial product could be. In this thesis diclofenac and arsenic adsorption with Kemira's adsorbent, was 100%. For the diclofenac removal the process was a little slower, and the 100% removal efficiency was reached after six hours. The 100% efficiency for arsenic removal was reached after four hours. In diclofenac removal with CFH-12, the pH stayed at the lowest level of all the tests, between 4.5 and 5. This is not below the diclofenac's pKa value 4.15, but it is clearly better than with other adsorbents.

With Sachtofer the best diclofenac removal was achieved with the HCl-activated adsorbent and it was 5%. The pH was clearly a problem when it rose over 10. The arsenic removal was 100% with all different ways treated Sachtofers. This is a very good result. Sachtofer is produced during the production of TiO_2, but it is modified to work as an adsorption material for water treatment. Therefore it should work without any pre-treatment. In this thesis Sachtofer samples were washed and activated with HCl because the pH conditions were too alkaline and it was assumed that the pre-treatment would decrease the alkalinity of the material. For the diclofenac removal washing and activation did not lower the pH significantly, but with the activated adsorbent diclofenac concentration was reduced a little. For arsenic removal with activated Sachtofer the pH was staying at lower level a little longer than with untreated or washed Sachtofer. Still, the removal was quite the same with all three adsorbents.

Only the Red mud was activated also with orthophosporic acid. It was noticed that the HCl-activated Red mud was the most efficient in diclofenac and arsenic removal. With Red mud the diclofenac removal was the best with the HCl-activated adsorbent and reached 8%. The removal with the orthophosporic acid -activated Red mud was 5%, so the difference was quite small. In arsenic adsorption the removal efficiency was 97% with the orthophosporic acid -activated Red mud and 98% with the HCl-activated sample. The removal efficiency was also very good with washed and calcined Red muds, 88% and 92%, respectively. The adsorption efficiency reached with Sachtofer and Red mud are confirming that waste and by products from industry could be considered as adsorbent materials in water treatment.

In diclofenac removal, the best result was with the HCl-activated Brazilian sand 16%. The diclofenac removal was assumed to be quite difficult, so this result was quite satisfied. The arsenic removal efficiency observed was 100% also with the HCl-activated sand, but even with untreated sand the removal was 94%. These results should be noticed, since arsenic contamination was managed to be removed with untreated soil material is a very good and interesting result. The sand was soil material that had very large surface area even for untreated sample. In the BET-analysis approximately 80 m^2/g specific surface area was observed. Though the surface area was decreased during HCl-activation, the arsenic removal was more efficient with activated adsorbents. The soil is environmentally friendly and cost effective source for adsorbent, and based on these results the Brazilian sand should be investigated more. There could also be larger interest to use soil material in water purification applications.

Based on the results of this thesis, secondary materials should be considered as viable adsorption materials in water treatment. There might be a huge potential in utilizing industrial waste materials for these applications or benefitting from soil properties of nature origin. At least in the inorganic heavy metals removal, secondary materials could be a cheap and environmental friendly solution.

7 CONCLUSIONS

This thesis shows very promising results and the investigation should be continued. Based on these results the secondary materials originating from nature and waste or by-products from industry can be utilized as adsorbent materials. However, more detailed studies are needed to fully understand the exploitability of the tested materials. With these secondary adsorbents, the arsenic removal was significantly more efficient than diclofenac removal. Arsenic is an inorganic component and diclofenac is an organic component, this could explain the difference.

The different pH values in arsenic removal were not tested, because the removal efficiency was good. For the next experiment, the pH conditions could be adjusted to be sure, what the level would be the most efficient for arsenic removal. With diclofenac, the higher pH value was most likely the reason why the removal efficiency was low. The conditions should be more acidic so diclofenac would be in neutral (non-ionized) and more hydrophobic form and could be removed from water onto the surface of the adsorbent more easily. The different adsorbent amounts could be also tested to find out the right dosage for the most efficient removal for both the cases of arsenic and diclofenac.

Based on the elemental analysis all adsorbents contained iron. From secondary materials Red mud contains approximately 40 wt-% of iron, the Brazilian sand contained approximately 20 wt-% or less and Sachtofer approximately 10 wt-% or less. The Brazilian sand contained more silicon than the other secondary adsorbents. Sachtofer contains calcium approximately 25 wt-% when the others have only the 0−3 wt-% calcium content. The differences in elemental analysis could explain the differences in the removal efficiencies, too.

The diclofenac removal was the most efficient with the HCl-activated Brazilian sand, and it was 16%. These results from the diclofenac removal could be better if pH is managed to be adjusted to lower level. The Sachtofer samples had a smaller pore volume and specific surface area than for the Brazilian sand samples and it might have an effect on the poor removal percent with Sachtofer. The electrostatic forces have a huge impact on the removal efficiency of pharmaceuticals. Thus samples used in these experiments might be to basic components for the use in pharmaceuticals removal from a water basin. Especially Sachtofer that had the high value of pH_{ZPC}.

The adjustment of pH done with HCl and H_2SO_4 acids for a solution containing diclofenac was not successful. When the acid was introduced to the diclofenac solution, diclofenac was decomposed. The adjustment was tried to do four different times for two different adsorbents and every time the result was the same. Based on the earlier published research, both HCl and H_2SO_4 have been used to adjust the pH level of a diclofenac solution, however we did not manage to do it. This could be one line that would require more investigation. The research question could be why the diclofenac decomposed and how the pH could be adjusted at the lower level. If the pH adjustment would be successful, perhaps the diclofenac removal would be more efficient with these adsorbents.

From arsenic removal, the results were very promising. Almost 100% removal efficiency with all the adsorbents is showing that secondary materials could be utilized more in water treatment applications. It is significant that the untreated adsorbents in arsenic removal were almost as good as the adsorbents which were pre-treated. When the materials do not require any pre-treatment before the use, it is better, since it lowers the costs of the adsorbent. Also if there is no need for pre-treatment, less energy and chemicals for activation are required. Though, the removal of arsenic was effective with these secondary materials, the adsorption of other inorganic heavy metals could be tested with these samples.

The determination of pH_{PZC} was giving the information, to which level the pH should be adjusted. The pH_{PZC} measure was failed for several types of adsorbents. It might be possible that the pH conditions for example with washed and calcined Red muds were too high and over the point of zero charge level of them. This is one investigation line that could be continued. First, to study why the pH_{PZC} determination failed with certain adsorbents. Secondly, to determine the pH_{PZC} level for all adsorbents and analyze if it has an effect on the adsorption efficiency with certain adsorbents.

To conclude, this thesis showed that secondary materials can be very efficient in water purification even without any pre-treatment in certain cases. This was approved with high arsenic removal efficiency with untreated, washed and calcined Red mud and Brazilian sand samples. This is an economically interesting application area of secondary materials should be studied more especially due to the possibility of improving the water treatment in developing countries.

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