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Sari Tuomikoski

UTILISATION OF GASIFICATION CARBON RESIDUES

ACTIVATION, CHARACTERISATION AND USE AS AN ADSORBENT

UNIVERSITY OF OULU GRADUATE SCHOOL;
UNIVERSITY OF OULU,
FACULTY OF SCIENCE,
DEPARTMENT OF PHYSICS AND CHEMISTRY;
KOKKOLA UNIVERSITY CONSORTIUM CHYDENIUS

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SARI TUOMIKOSKI

UTILISATION OF GASIFICATION CARBON RESIDUES

Activation, characterisation and use as an adsorbent

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Abstract

Gasification is an energy conversion method for the utilisation of biomass for obtaining energy (heat and power). In the gasification process carbon residue is formed as a waste. For improving the cost-effectiveness of the gasification process the utilisation of this waste is important and the present legislation also creates requirements for the utilisation of waste material.

Activated carbon is typically used for purification of water, for example, wastewaters as well as gaseous emissions. Consequently, commercial activated carbon is fairly expensive and its preparation is energy consuming. However, this inhibits sometimes its widespread use in wastewater treatment and therefore there is a need to develop cost-effective adsorbents from alternative biomass-based low-cost raw materials to remove harmful substances from aqueous solutions.

The first aim of this thesis was to determine physical and chemical properties of carbon residues from wood gasification, and fly ashes from burning processes were used as reference samples. The properties are essential to known when evaluating the potential utilisation applications for unknown carbon residue samples. Properties of carbon residue indicate that it would be suitable adsorbent due to the high carbon content but its activation or modification is needed. The second aim was to modify this industrial carbonaceous by-product by physical and chemical activation and chemical modification methods to maximise the adsorption capacity of material. Based on our results, adsorption properties can be enhanced by using zinc chloride as a chemical activating agent, carbon dioxide as a physical activating agent and ferric chloride in the chemical modification and adsorbents with specific surface areas 285, 590 and 52 m^2 g^{-1} were produced, respectively. The third aim was to test produced adsorbents to anions removal. Chemically activated carbon residue removes phosphate well and physically activated carbon residue removes phosphates and nitrates. Chemically modified carbon residue was observed to be suitable sorbent for sulphate removal. Optimal initial pH and concentration were determined and effect of time was studied and kinetic calculations and isotherm analysis was done for studied adsorbents.

Keywords: activated carbon, activation, adsorption, biomass, carbon residue, nitrate, phosphate, sulphate, utilisation, wood gasification

Tuomikoski, Sari, Kaasutuksessa muodostuvien hiilijäännösten hyödyntäminen. Aktivointi, karakterisointi ja käyttö adsorbenttinä
Oulun yliopiston tutkijakoulu; Oulun yliopisto, Luonnontieteellinen tiedekunta, Fysiikan ja kemian laitos; Kokkolan yliopistokeskus Chydenius
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Tiivistelmä

Kaasutus on tehokas tapa hyödyntää biomassaa sähkön- ja lämmöntuotannossa. Kaasutuksessa muodostuu jätteenä hiilijäännöstä, jonka hyödyntäminen on tärkeää kaasutusprosessin kustannustehokkuuden parantamiseksi. Myös nykyinen lainsäädäntö asettaa vaatimuksia jätemateriaalien hyödyntämiselle.

Aktiivihiiltä on tyypillisesti käytetty mm. jäteveden sekä kaasujen puhdistukseen. Aktiivihiili on kuitenkin kallista ja sen valmistaminen on energiaa kuluttava prosessi, mikä rajoittaa sen käyttöä. Tämän vuoksi tarvitaan uutta tietoa myös kustannustehokkaampien adsorbenttien valmistamiseen soveltuvista vaihtoehtoisista biomassapohjaisista raaka-aineista.

Tutkimuksen tavoitteena oli aluksi määrittää puun kaasutuksessa muodostuneen hiilijäännöksen fysikaalisia ja kemiallisia ominaisuuksia, joiden tunteminen on tärkeää arvioitaessa soveltuvia hyödyntämiskohteita kyseiselle tuntemattomalle jätemateriaalille. Referenssinäytteinä käytettiin polttolaitoksilla muodostunutta lentotuhkaa. Hiilijäännöksen ominaisuuksien perusteella se voisi olla soveltuva adsorbentti, mutta aktivointi tai modifiointi on välttämätöntä hiilijäännöksen adsorptiokapasiteetin parantamiseksi. Työn toinen tavoite oli parantaa hiilijäännöksen adsorptio-ominaisuuksia fysikaalisesti ja kemiallisesti aktivoimalla tai kemiallisesti modifioimalla. Tulosten perusteella adsorptio-ominaisuuksia voidaan parantaa parhaiten käyttämällä sinkkikloridia kemiallisessa aktivoinnissa, hiilidioksidia fysikaalisessa aktivoinnissa ja rautakloridia kemiallisessa modifioinnissa, jolloin valmistettujen adsorbenttien ominaispinta-alat olivat 285, 590 ja 52 $m^2\ g^{-1}$. Työn kolmas tavoite oli tutkia valmistettujen adsorbenttien adsorptiokykyä anionien poistossa laboratoriomittakaavassa. Kemiallisesti aktivoitu hiilijäännös poistaa tehokkaasti fosfaattia, fysikaalisesti aktivoitu fosfaattia ja nitraattia ja kemiallisesti modifioitu hiilijäännös on hyvä sorbentti sulfaatinpoistossa. Adsorptiokokeissa määritettiin optimaalinen alku pH ja alkukonsentraatio ja lisäksi tutkittiin ajan vaikutusta adsorptioon. Tulosten perusteella tehtiin kinetiikkamallinnusta sekä isotermianalyysi.

Asiasanat: adsorptio, aktiivihiili, aktivointi, biomassa, fosfaatti, hiilijäännös, hyödyntäminen, nitraatti, puun kaasutus, sulfaatti

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List of original publications

This thesis is based on the following scientific publications and manuscript, which are referred to in the text as roman numerals from I to VI:

I Kilpimaa (Tuomikoski) S, Kuokkanen T & Lassi U (2011) Physical and chemical properties of wood ash from burning and gasification processes. The Journal of Solid Waste Technology and Management, Proceedings in ICSW 2011: 879-887

II Kilpimaa (Tuomikoski) S, Kuokkanen T & Lassi U (2013) Characterization and Utilization Potential of Wood Ash from Combustion Process and Carbon Residue from Gasification Process. Bioresources 8(1): 1011-1027.

III Kilpimaa (Tuomikoski) S, Runtti H, Lassi U & Kuokkanen T (2012) Chemical activation of gasification carbon residue for phosphate removal. Porous Media and its applications in Science, Engineering and Industry, AIP Conference Proceedings 2012: 293-298.

IV Kilpimaa (Tuomikoski) S, Runtti H, Kangas T, Lassi U & Kuokkanen T (2014) Removal of phosphate and nitrate over a modified carbon residue from biomass gasification. Chemical Engineering Research and Design 92(10): 1923-1933.

V Kilpimaa (Tuomikoski) S, Runtti H, Kangas T, Lassi U & Kuokkanen T (2014) Physical activation of carbon residue from biomass gasification: Novel sorbent for the removal of phosphates and nitrates from aqueous solution, In press, Journal of Industrial and Engineering Chemistry.

VI Runtti H, Tuomikoski S, Kangas T, Lassi U, Kuokkanen T & Rämö J (2014) Sulphate removal over carbon residue from biomass gasification: Effect of chemical modification methods on sulphate removal efficiency, submitted.

The present author was the primary author of publications I–V and she has planned and performed mainly all these experiments. She has also written publications I–V. Sari Tuomikoski (neé Kilpimaa) is the second author in publication VI in which she has participated to the research plan, laboratory experiments and writing process. Hanna Runtti has been the principal investigator of this paper.

Contents

1 Introduction

1.1 Background

In recent years, energy generated from biomass-based heat and power production has become more established. The use of wood for energy production has many advantages since it is renewable, local, and creates jobs, especially in rural areas. Energy can be generated in different ways, for example, by wood combustion or gasification. Climate change is one of the most serious environmental problems in the world today and the use of biomass as an energy source will only increase in the future (Berndes *et al.* 2003). However, energy generated from biomass produces a considerable amount of solid residue that must be utilised economically. Utilisation of solid residue (e.g. ash from combustion process or carbon residue from gasification process) is a part of sustainable power generation from biomass and contributes to a green energy image (Knoef 2005, Kumar *et al.* 2009, Pan & Eberhardt 2011).

Combustion and gasification are thermochemical conversion methods that are used to convert biomass to energy. Gasification is a process which converts carbonaceous materials such as biomass to gas. In the combustion process the oxidation is substantially complete in one-step process, but in the gasification process the chemical energy of carbon is converted into a combustible gas in two stages. Biomass can be converted at either high temperatures to syngas, which mainly contains CO and H_2, or at low temperatures into a product gas which contains CO, H_2, CO_2, H_2O, CH_4, other hydrocarbons (C_xH_y), benzene, toluene, tars and inorganic impurities (mainly H_2S, NH_3, HCl). Syngas produced via gasification can be used directly as an internal combustion engine fuel or used as a chemical feedstock to produce liquid fuels. Biosyngas and product gas after purification can also be used as a one raw material in catalytic processes to synthesise different products such as methanol, oils and ammonia, as seen in Figure 1. Biomass is a variable feedstock and the use of gasification can convert low or even negative value feedstock, for example wet materials or waste materials from public gardens, into fuels and chemicals. (Knoef 2005, Kumar *et al.* 2009, McKendry 2002).

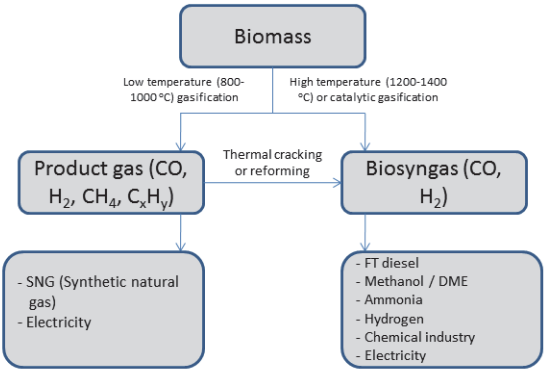

Fig. 1. Difference of syngas and product gas and their typical utilisation applications (Knoef 2005) (II, published by permission of BioResources).

In Finland, the national environmental legislation is based on EU directives and regulations, but there are, in some cases, stricter standards and limits compared with EU legislation. There are lots of laws which affect to the utilisation of waste materials. The most important pieces of Finnish environmental legislation concerning waste recovery and reuse are Finnish Environmental Protection Act (86/2000), Finnish Environmental Protection Decree (169/2000), Waste Act (646/2011) and Waste Decree (179/2012). Industrial residues are regarded as wastes according to Waste Decree and Environmental Protection Act (2012, 2000). According to the Waste Act (2011), waste may also be regarded as a by-product if the End-Of-Waste criteria given in the legislation are fulfilled. Government Decree (591/2006) regulates the utilisation of waste materials in earth construction. Ministry of Agriculture and Forestry Decree on Fertiliser Products 24/11 (In Finnish) determines the maximum concentration values of heavy metals that are allowed to exist in fertilisers for forestry and agricultural use and one objective in Fertiliser Product Act (539/2006) is the utilisation of by-products suitable to be used as a fertiliser. Government Decree (331/2013) regulates about the waste disposal in landfills.

Based on Finnish legislation, the properties of solid waste have to be known when it is either transferred to a landfill site or utilised in other ways, because heavy metals or other harmful contaminants could be dissolved to the environment (Kuokkanen *et al.* 2006). According to the Finnish strategy on waste materials, in accordance with the corresponding European strategy, the different options available for dealing with waste can be described by a waste hierarchy which is derived from five categories; i.e prevention, reuse and preparation for reuse, recycling, recovery (e.g. as energy) and disposal. (Directive 2008/98/EC of the European parliament and of the council).

Commercial activated carbon is widely used adsorbent in water purification processes. Commercial activated carbon is typically produced by activating various carbonaceous materials, e.g. coal and cellulosic materials (Ahmadpour & Do 1996). Price of activated carbon is depending e.g. on its producing process, quality and purchasing amount, but commercial activated carbon is expensive and preparation of it is energy consuming process. Therefore other substitutive adsorbents must be investigated. (Bart & von Gemmingen 2005, Guo *et al.* 2009, Marsh & Rodríquez-Reinoso 2006). Wastes may be a better choice in some places because of their availability and cheapness, and the use of waste materials for producing adsorbents is also very attractive from the point of view of their contribution to decrease the costs of waste disposal and for helping environmental protection. In fact, many materials have been studied to prepare cheaper activated carbons, for example agricultural wastes such as rice hulls (Teker *et al.* 1997) and palm-tree cobs (Avom *et al.* 1997). Also walnut shells (Martínez *et al.* 2006), corn cobs (Chang *et al.* 2000) and cherry stones (Lussier *et al.* 1994) have been used as a raw material for activated carbon production. There is still need to study locally available waste materials to produce inexpensive adsorbent for example wastewater purification processes.

1.2 Scope and objectives

The main objective of this study was to determine physical and chemical properties for the carbon residues formed in wood gasification processes and based on these results, develop suitable utilisation applications for that waste material. The first part of this thesis is focused to characterisation of carbon residues from wood gasification processes and ashes from burning process whilst comparing the results between these two types of solid residues. These properties are essential to know when evaluating the potential utilisation applications of carbon residue or combustion ashes. In literature, there are a lot of suitable utilisation applications available for burning fly and bottom ashes; however, only few exist for carbon residues formed during the gasification processes. The first research questions are: Which are the physical and chemical properties of carbon residue formed in wood gasification process? Does carbon residue have potential to be used in some utilisation applications and if yes, where? These research questions are discussed in Papers I and II.

Results presented in Papers I and II indicate that carbon residue from wood gasification process would be suitable adsorbent but some treatment is needed. Therefore, the second research question: Can the adsorption properties of carbon residue be modified, and if, how? This was studied by activating carbon residue chemically and physically and by chemical modification. Chemical activation was studied in Papers III and IV and physical activation in Paper V. Chemical modification was studied in Paper VI. During chemical activation, the different chemical activating agents were examined and the conditions during activation were optimised (Paper III and IV). Also in the physical activation, different physical activating agents were evaluated and activation parameters were optimised (Paper V). In Paper VI, the different chemical activation and modification methods were studied.

The third research question of this thesis is: Can activated or modified carbon residue be used as an adsorbent for anion removal? This was studied by batch adsorption experiments in laboratory scale and during adsorption test, the influence of initial pH, initial concentration and adsorption time was determined. Results were fitted to pseudo-first-order and pseudo-second-order kinetic models to identify the rate of adsorption. Isotherm analysis was done by Freundlich and Langmuir model and later also by using Temkin and Dubinin-Radushkevich (D-R) isotherm models. Carbon residue without pre-treatment process was used as a reference sample to evaluating the influence of activation or modification to the samples adsorption capacity. Commercial activated carbon was also used as a reference material.

2 Materials and characterisation methods

2.1 Materials and sampling

In this thesis, carbon residue from biomass gasification processes was studied. According to Pan & Eberhardt (2011), the solid residues obtained from the thermochemical processing of biomass (gasification) are typically mixtures of char and ash, and therefore referred to as biochar. The term biochar is not used in this case, because biochar is formed in a limited supply of oxygen, and our samples are obtained from gasifiers where gasification is done by air (Wang *et al*. 2013). In this thesis, solid residue formed in wood gasification process is called a carbon residue. In Paper I, carbon residue is called a biogasification ash.

The carbon residue mentioned in Papers II─VI was obtained from the pilot-scale biomass gasification process (Sievi, Finland) which involved a 150 kW air-blown downdraft gasifier operating at a temperature of about 1000 ^{o}C. Finnish wood chips (pine and spruce) were used as fuel for the gasifier at a feeding rate of 50 kg h^{-1}. The gas produced in the gasifier was washed by a wet scrubber and the carbon residue formed in the process was collected from a water container. In this summary, carbon residue samples A, B and C are from the same gasifier but different process. This was done because the durability of carbon residue samples is not well. Sample A is carbon residue 2 in Paper II. Sample B is the carbon residue in Papers III and IV. Sample C is the carbon residue in Papers V and VI.

The second carbon residue sample obtained from different gasifier was marked as biogasification ash 1 (Paper I) and carbon residue 1 (Paper II) and in this summary, it is marked as Carbon residue D. It was produced from a 1 MW gasifier at around 900 ^{o}C, which possessed an updraft and downdraft gasifier combination. 100% Finnish wood was used as the raw material at a fuel consumption rate of 333 kg h^{-1}. Both gasifiers from which carbon residue samples were collected for this thesis was classified as low temperature gasifiers as presented in Figure 1.

In addition, fly ashes from burning process were studied as a reference samples in Papers I and II. Ashes from burning process were collected in the form of fly ash from a thermal power plant involving a bubbling fluidised-bed boiler. Each fly ash was sampled from an electric filter, however, the ratio of raw material used and the boiler properties employed were different. A combination of 75% Finnish wood and 25% peat was used to produce ash A (ash 2 in the Paper I and ash 3 in paper II) whilst a 50/50 ratio was used for ash B (ash 4 in Paper II). The total power output of the boiler was 24 MW (6 MW electricity and 18 MW heat) at a pressure of 60 bar for ash A and 70 MW (20 MW electricity and 50 MW heat) at a pressure of 80 bar for ash B. The temperature and fuel consumption was 510 ^{o}C and 8 kg s^{-1} for ash A, and 482 ^{o}C and 27 kg s^{-1} for ash B.

Commercial activated carbon (pro analysis quality) provided by Merck was used as a reference sample in Papers III and IV (activated carbon A) and another commercial activated carbon (Norit GCN 1240) produced from coconut shells by steam activation in Papers V and VI (activated carbon B).

2.2 Determination of physical and chemical properties

pH and electrical conductivity values were determined by a Hach Lange HQ40d pH electrode and a conductivity electrode, respectively. This was achieved by dissolving sample into distilled water so that a liquid to solid ratio L/S was 10 (w/w). Analysis of the dry matter content was performed in accordance to the European standard SFS-EN 12880 (SFS-EN 2000a), where the sample was dried overnight to a constant mass in an oven at 105 ^{o}C. The organic matter content, measured by observing the loss-on-ignition value (LOI), was determined according to the European standard SFS-EN 12879 (SFS-EN 2000b), where the previously at 105 ^{o}C dried sample is heated in a muffle furnace overnight at 550 ^{o}C.

Determination of the dissolved organic carbon (DOC) concentration was carried out in accordance to the European standard SFS-EN 1484 (SFS-EN 1997) using a Sievers 900 Portable TOC analyser that implements the oxidation method. Organic compounds are oxidised to carbon dioxide using UV radiation and ammonium persulfate which is used as a chemical oxidising agent. Carbon dioxide is measured using a sensitive, selective membrane-based conductometric detection technique. (Sievers 900 Portable Total Organic Carbon Analyser 2006).

Carbon content was determined by elementary analysis using a Perkin Elmer CHNS analyser or Flash 2000 whose method is based on combustion where the sample element is converted to simple gas (CO_2) in a pure oxygen atmosphere. Formed gas is separated and detected. (Perkin-Elmer 1991). Oxygen content was determined by Flash 2000 analyser. Carbon content results of modified carbon residue samples presented in Paper VI was analysed by using SKALAR Formacs HT TOC Analyzer. TC is determined by catalytic oxidation at 1100 ^{o}C.

Neutralising value and reactivity of the samples were measured according to the European standards SFS-EN 12945 (SFS-EN 2002) and SFS-EN 13971 (SFS-EN 2003), respectively. The principle behind measuring the neutralising value is to dissolve the dried sample in a specific quantity of hydrochloric acid. The excess acid is then titrated with a standard sodium hydroxide solution. Reactivity is the determination of the speed and effectiveness of the neutralising potential of sample whose reaction is generated by potentiometric titration with hydrochloric acid. Analysis of the reactivity value is based on the following reaction:

$$MeCO_3 + 2\ H^+ \rightarrow Me^{2+} + H_2O + CO_2 \qquad (1)$$

where metal carbonates decompose with acid. The consumption of hydrochloric acid in titration is a direct measure of the reaction rate of the sample being tested.

The heat value of a sample under specific conditions was measured by IKA Calorimeter system C200 using benzoic acid as calibrating compound. This was achieved by placing a solid fuel sample in a decomposition vessel and then measuring the increase in temperature through combustion. In addition, the decomposition vessel is filled with pure oxygen to a pressure of 30 bar to ensure the total combustion.

The specific surface area of samples was determined from nitrogen adsorption-desorption isotherms at the same temperature of liquid nitrogen (-196 ^{o}C) by using a Micromeritics ASAP 2020. The same equipment was also used for the determination of pore size and pore volume. Microscopic analysis was performed using a field emission scanning electron microscope (FESEM, Zeiss Ultra Plus Gemini) whilst density of sample was calculated by measuring the mass of a sample under compression using a 7.7 g cm^{-3} weight on top of the sample layer for three minutes. Zeta potential measurements were done by using Delsa™Nano Submicron Particle Size and Zeta Potential analyser. Sample was placed in a 50 cm^3 plastic vessel, into which 40 cm^3 of a 10 mM NaCl solution was added. The contents were centrifuged for 10 minutes by using 230 rpm. pH values were adjusted by using 0.1 M NaOH or HCl solutions before measurement.

2.3 Determination of nutrient concentration and the total element concentration

Determination of easily soluble nutrient concentrations in the samples was carried out according to the procedure of Yli-Halla & Palko (1987). In this procedure, the easily soluble forms of Ca, Na, K and Mg are extracted into a mixture of 0.5 M acetic acid and 0.5 M ammonium acetate (pH 5.0). In the extraction of Cu and Zn, the ammonium acetate extract contains 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na_2EDTA) and the pH of solution was 4.7. In both extraction procedures, the liquid-to-solid ratio between sample and the extraction solution was set to 10 (w/w), whilst the extraction time was 1 h. Before the analysis, the extract was separated from the solid residue by filtration using a 0.45 μm filter. The concentration of the elements was determined with ICP-OES (Thermo Elemental) and the deviation of measuring was 5%.

Acid decomposition was performed in order to determine the total element concentration in samples. A dried sample was decomposed with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a microwave oven with Teflon vessels using the US EPA method 3051. After decomposing the cooled solutions were transferred in to 100 mL volumetric flasks and diluted with ultrapure water generated with Elgastat Prisma reverse osmosis and an Elgastat Maxima ion exchange water purification system. Except for Hg, total element concentrations in the solutions were measured with a Thermo Elemental IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer. (USEPA 3051A (revision 1) 2007). Finally, the concentration of Hg was determined by Perkin-Elmer Aanalyst cold-vapour atomic absorption spectrometry (Norwalk, USA). Analysis were done at Suomen Ympäristöpalvelu Oy, a FINAS accredited test laboratory (T231). Uncertainty is included in the analysis results as extended measuring ambiquity (U=2u, 95%) in which the confidence level is depending on the element to be determined and on its content.

3 Activation and modification of carbon residue

Commercial activated carbon is widely used adsorbent in water purification processes because of its good adsorption properties. It has typically well-developed pore structure, high internal surface area and good mechanical characteristics. (Guo *et al.* 2009). Activated carbon can be prepared from a variety of raw materials with high carbon content, for example coal and lignocellulosic materials are common used as a precursor (Ahmadpour & Do 1996). Various novel materials such as coconut husk (Tan *et al.* 2008), agricultural residues (Ioannidou & Zabaniotou 2007), macadamia nutshell (Ahmadpour & Do 1997) and coffee endocarp (Nabais *et al.* 2008), are studied as precursor for activated carbon production. However, abundance and local availability of by-products and waste materials make them good sources of raw materials for activated carbon production.

Basically, there are two different processes for the preparation of activated carbon: chemical and physical activation. Both methods include carbonisation and activation steps. (Ahmadpour & Do 1996). The porosity formed in carbonisation step is typically not enough for most applications which is the reason to develop porosity further (Marsh & Rodríquez-Reinoso 2006). In this study, only activation step is needed because carbonisation took place already during the gasification process. There are several advantages and disadvantages of chemical activation compared to physical activation. The main advantages typically are among others lower temperature of activation, shorter activation time and higher development of porosity. Disadvantage for the use of chemical activation process is the pollution generated by the activation chemical, and also chemical consumption and price must be considered. Chemical activation needs also washing stage and therefore, physical activation could be more environmental friendly and effective method to produce an adsorbent from waste material. (Marsh & Rodríquez-Reinoso 2006). The raw material used, activation method and activation conditions play an important role in the characteristics of activated carbon including e.g. porosity and shapes of pores. (Guo *et al.* 2009).

Chemical modification is also possible surface modification method. Vinke *et al.* (1994), for example, have done chemical modification of activated samples to increase larger amount of surface functional groups (Menéndez *et al.* 1996). Suitable surface functional groups and the great amount of them are important properties of adsorbent because adsorption is not based only to the surface porosity.

3.1 Chemical activation

Chemical activation is a single-step process in which carbonisation and activation are carried out simultaneously. Common used chemical activating agents are alkali and alkaline earth metal containing substances and some general acids. Typically used chemical are KOH, NaOH, $ZnCl_2$, H_3PO_4, for example. (Ahmadpour & Do 1996).

In this study, chemical activation was performed using a wet impregnation method. Firstly, carbon residue was dried at 110 °C overnight and then washed with 1 N solution of HCl : H_2SO_4 (1:1) for 24 hours in order to reduce the ash content. After that, the sample was washed with distilled water, dried at 110 °C overnight before being crushed and sieved to achieve particles under 150 µm with uniform quality. The dried sample was mixed with a chemical activating agent for five minutes (contact time). The carbon residue used in this experiment was treated with 0.1 M HCl, 0.1 M H_2SO_4, 5 M $ZnCl_2$, 5 M KOH, HCl or HNO_3 by using a liquid-to-solid ratio L/S of 10 (w/w). The mixture of carbon residue and chemical activating agent was dried at 110 °C overnight and activated at 500 °C in an air atmosphere for one hour. The resulting products were washed sequentially with 0.5 M HCl for ten minutes by using a liquid-to-solid ratio L/S of 10, hot distilled water and finally cold distilled water to remove any remaining residual chemicals and organic and mineral matters. Finally, products were dried at 110 °C overnight and crushed and sieved again to ensure particle size < 150 µm. Success of the activation was evaluated by measuring specific surface area of samples. This chemical activation is presented in Papers III and IV.

3.2 Physical activation

In the physical activation, a raw material is first carbonised and secondly activated by physical activating agent; however, steam, carbon dioxide, air or their mixtures are typically used. Activation temperature varied typically between 600 °C and 900 °C. (Guo *et al.* 2009). Activation time depends strongly on used raw material, for example Guo *et al.* (2009) have used 2–6 h activation time for studies in which raw material was coconut shell.

Physical activation in this study was carried out by using two different activation agents, CO and CO_2. In addition, reference samples were prepared by thermal treatment without activating agent under nitrogen atmosphere. Carbonisation step was not done in this study because it can be assumed to taken place already during the gasification. Literature survey has shown that carbon monoxide is not a typical physical activating agent but preliminary experiments have shown that it might be suitable activating agent for gasification carbon residue. Temperature and duration of activation were the two parameters investigated in addition to activating agent. Temperatures 600 °C and 800 °C were tested and duration of activation was 1 or 3 h. Activation conditions in detail during physical activation are presented in Paper V. Success of the activation was evaluated by measuring e.g. specific surface area and pore volume for produced adsorbents.

3.3 Chemical modification

Chemical modification (or impregnation) was done with chemicals $FeCl_2$, $FeCl_3$, $BaCl_2$ and $CaCl_2$ by using different methods. Chemical modification methods are presented in detail in Paper VI. By different methods modified carbon residue samples were tested as an adsorbent for sulphate removal and the highest sulphate removal efficiency was obtained by using following methods: At first, carbon residue was dried overnight at 110 °C and after that it was washed with 1 N solution of HCl : H_2SO_4 (1:1) for 24–29 hours in order to reduce the ash content by using liquid-to-solid (L/S) ratio of 10 (w/w). After that, the sample was washed with distilled water. Sample was dried at 110 °C overnight before being crushed and sieved to achieve particles under 150 µm with uniform quality. The carbon residue was mixed with 1.0 M ferric chloride L/S ratio 10 (w/w) and the mixture was shaked with magnetic stirrer at room temperature for 24 h. After that the solution was dried at 110 °C for 24 hours and then it was washed with one liter of distilled water. Finally sample was dried at 110 °C and crushed and sieved again to ensure particle size < 150 µm.

Iron and calcium dissolution from chemically modified adsorbents were studied by dissolving 0.25 g of adsorbent into 50 mL of distilled water. The pH of the solution was adjusted by adding HCl and/or NaOH. Bottles were then shaken by a laboratory shaker using an orbital movement to mimic shaking at room temperature for 24 hours. pH values were also measured after 24 h experiments. Samples were filtered through 0.45 µm filter paper (Sartorius stedim biotech) and the amount of soluble iron and calcium were measured by an AAS PerkinElmer AAnalyst 200 at maximum absorption wavelengths (λ_{max}) of Fe(248.3 nm) and Ca(422.67 nm), respectively.

4 Activated and modified carbon residue as an adsorbent

Adsorption is commonly used method for the removal of different pollutants from an aqueous solution due to its high efficiency, cost-efficient technique and simple operation. Adsorption processes using commercial activated carbon are widely used to remove pollutants from wastewaters. However, the high cost of activated carbon inhibits sometimes its widespread use in wastewater treatments and therefore there is a need to develop other adsorbents from alternative low-cost raw materials. In this study, phosphate, nitrate and sulphate adsorption onto carbon-based adsorbents has been studied.

4.1 Phosphate and nitrate removal

Excess nutrients in water are identified one of the major factors leading to eutrophication and deterioration of water bodies. Eutrophication may occur when the concentration of phosphate is higher than 0.02 mg L^{-1}. Wastewaters possess harmful levels of phosphates and its removal before discharge is paramount (Huang *et al.* 2009, Lau *et al.* 1997). Biological, chemical and physical treatment methods have been developed as a phosphate removal technology (Huang *et al.* 2009, Yao *et al.* 2011, Yeoman *et al.* 1988). Chemical precipitation with e.g. iron salt is simple phosphate removal technique but the problems are especially costs and the sludge formation in this process which are also problems in the biological treatment (Huang *et al*. 2009, Li *et al.* 2006, Yao *et al.* 2011).

There are also various physical methods developed for phosphate removal such as electrodialysis, reverse osmosis and ion exchange (Biswas *et al.* 2008, Momberg & Oellermann 1992, Yeomann *et al.* 1988). Most of those methods are expensive as well as inefficient (Yao *et al.* 2011). Phosphate removal by electo-coagulation is also possible method (Vasudevan *et al.* 2009). Adsorption onto porous materials such as zeolites is suitable way to remove phosphates from aqueous solution (Biswas *et al.* 2008, Bolan *et al.* 2004).

In addition to phosphate, also nitrate stimulates eutrophication. Nitrate has been linked outbreaks of infectious diseases and excess nitrate in drinking water may cause methemoglobinaemia, also called a blue baby syndrome, in newborn infants. (Feleke & Sakakibara 2002). According to the World Health Organisation (2011), the recommended maximum concentration for nitrate in drinking water is 50 mg L^{-1}. Nitrate can be removed in many ways such as by biological denitrification (Soares 2000), reverse osmosis (Schoeman & Steyn 2003), electrodialysis (Hell *et al.* 1998), ion exchange (Chabani *et al.* 2006) and catalytic denitrification (Pintar *et al.* 2001). Reverse osmosis and ion exchange process, for example, forms second pollution which must be treated and therefore increase the overall costs of the process. Biological processes requires biomass waste disposal. Adsorption is often used nitrate removal process because it is simple and attractive method in terms of cost and post-treatment is not often required (Bhatnagar & Sillanpää 2011, Katal *et al.* 2012).

4.2 Sulphate removal

Sulphate is a major anion occurring in both natural waters and industrial effluents, such as inorganic chemical industry wastewater and acid mine drainage (Cao *et al.* 2011). The main natural source of sulphate is the processes of chemical weathering and dissolution of sulphur-containing minerals. Also the oxidation of sulphides and sulphur are natural sources of sulphate. (Cao *et al.* 2011, Dong *et al.* 2011). If a sample contains organic material, the bacteria can reduce sulphate (SO_4^{2-}) to sulphide (S^{2-}) (Rayner-Canham 1999). Sulphate ions are common also in drinking water (Dong *et al.* 2011) but many countries have not set guidelines for sulphate because it is only mildly hazardous comparing with toxic metals (Silva *et al.* 2012). On the other hand, sulphate is also necessary for many kind of organism (Dong *et al.* 2011). Excess sulphate can cause an imbalance of the natural sulphur cycle, endanger human health and it is also corrosive to reinforced steel (Dong *et al.* 2011, Namasivayam & Sureshkumar 2007). Concentrations higher than 600 mg L^{-1} can affect laxative effects and taste for water (Silva *et al.* 2012). In Finland, the sulphate limit in drinking water is set to 250 mg L^{-1} but it is recommended that concentration is not higher than 150 mg L^{-1} that it won´t damage water pipes (Decree 461/2000). Environmental agencies in many countries have set maximum values varying between 250 and 500 mg L^{-1} in both mine drainages and industrial effluents (Silva *et al.* 2012). Sulphate is typically present in high concentrations especially in industrial wastewaters which may contain several thousands of mg L^{-1} sulphate. Domestic sewage contains typically sulphate less than 500 mg L^{-1} and therefore, removal sulphate with a large concentration range is a considerable task (Namasivayam & Sureshkumar 2007, Silva *et al.* 2012).

Established methods for removal of sulphate ions are for example chemical precipitation, biological treatment, ion exchange, reverse osmosis, electrodialysis and adsorption. Precipitation can be done for example by barium or calcium salts or by lime but it produces large amount of sludge in solution. (Silva *et al.* 2012). Sulphate removal e.g. by lime precipitation is also problematic because of the high solubility of the produced $CaSO_4$ (Hartinger 1994). The main advantages of biological sulfate reduction are the low volume of sludge produced and the recovery of base metals as sulfides. Despite such advantages, sulphate reduction is yet to be widely adopted by the mining industry as a strategy to remove sulphate to levels that comply with environmental regulations. (Silva *et al.* 2012). On the other hand, biological treatment and ion exchange are expensive. Due to the high cost associated with chemical treatment technologies and long residence time requirement for biological treatment, there has been a concerted effort towards developing other sulphate removal technologies. Adsorption may be preferred for sulphate removal because it is rapid and selectivity is high. During adsorption process sulphate can also be recovered. The commonly used adsorbents include chemicals such as $BaCl_2$, $ZrO(OH)_2$, and $CaCl_2$, but $BaCl_2$ and $ZrO(OH)_2$ are expensive. $BaCl_2$ will also pollute the environment. (Dong *et al.* 2011, Madzivire *et al.* 2010, Namasivayam & Sureshkumar 2007).

4.3 Adsorption experiments

Laboratory experiments were carried out in order to examine the effects of different variables on the adsorption efficiency of phosphates, nitrates and sulphates on the adsorbents surface. Used adsorbents were carbon residue from wood gasification process, physically or chemically activated carbon residue, chemically modified carbon residue and commercial activated carbon. The studied variables were initial pH, initial concentration of adsorbate in solution and adsorption time. The experimental data of the adsorption properties were obtained using a batch type process which is presented in Papers III‒VI. The effect of initial pH on adsorption was studied over a pH range of 4‒8 in case of phosphate and nitrate removal and in case of sulphate removal, used pH range was 2‒8. pH optimisation experiments were done by using a solution whose concentration was 75 mg L^{-1} (Papers III and IV), 80 mg L^{-1} (Paper V) or 100 mg L^{-1} (Paper VI). The effect of initial solution concentration was studied at optimum pH with range 25‒125 mg L^{-1} (Papers III and IV), 10‒140 mg L^{-1} (Paper V) and 50–1000 mg L^{-1} (Paper VI). The model solution of phosphate was prepared by adding solid KH_2PO_4 to distilled water whilst the nitrate test solution was prepared from solid $NaNO_3$. Sulphate solutions were prepared by using $NaSO_4{\cdot}7H_2O$. During adsorption tests, each type of adsorbent was weighed so that the adsorbent dose was 5 g L^{-1} in all experiments.

The optimum initial pH and effect of initial concentrations were determined by using 250 mL polyethylene flasks, in which a solution of adsorbate and adsorbent was mixed together and its pH was adjusted by HCl or NaOH. This was done after adding the adsorbent to adsorbate solution to ensure that the solution had the correct pH because the carbon residue from the gasification process is clearly alkaline (pH ≈ 9) and carbon residue has some buffer capacity which have been studied in Paper II. It means that carbon residue is able to retain an almost constant pH when a small amount of acid is added to the solution, and therefore, it possesses ions that have the ability to neutralise the added hydrogen ions. These ions are similar to hydrogen carbonates, carbonates, and hydroxides. The solution was shaken by a laboratory shaker using a reciprocating motion to mimic shaking (Papers III and IV) or by a laboratory shaker using an orbital movement at a speed 230 rpm (Papers V and VI) at room temperature for 24 hours.

Effect of adsorption time was studied at optimum initial pH and initial solution concentration. The rate of adsorption was determined at following time intervals: 1 min, 2 min, 5 min, 30 min, 2 h, 4 h and 24 h (Papers III and IV) and 1 min, 2 min, 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 12 h and 24 h (Papers V and VI). Kinetic studies were carried out by using a 500 mL (Papers III and IV) or 1000 mL (Papers V and VI) sample volume in a Erlenmeyer flask whilst at the same time shaking was taking place by a magnetic stirrer with an agitation speed of 1000 rpm. All samples including the initial samples were filtered through a 0.45 μm filter so that the phosphate, nitrate or sulphate concentrations could be analysed by ion chromatography (Metrohm 761 Compact IC). Some sulphate analysis were done by using vacu vials test (CHEMetrics Sulfate Vacu-vials® Kit). The amount of anions adsorbed (q_e in mg g^{-1}) was determined as follows:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of phosphate, nitrate or sulphate in a solution (mg L^{-1}), respectively, V is the volume of solution (L) and m is the mass of the adsorbent (g). (Bhatnagar *et al.* 2010a, 2010b).

5 Results and discussion

5.1 Characterisation of samples

Some important chemical and physical properties for the characterised samples are summarised on Table 1, and were originally presented in Papers I and II. For quality control purposes all analyses from samples were carried out as duplicate determinations. Carbon residues A and D were obtained from different gasifiers, and ashes A and B obtained from burning processes were used as reference samples because properties and utilisation applications for burning ashes are studied a lot. Only few studies about characterisation of carbon residue samples exist in literature. Commercial activated carbon was also used as a reference sample. Characterisation was done to obtain basic knowledge of studied carbon residue samples so that the potential utilisation applications or needed treatment could be evaluated.

Table 1. Physical and chemical properties of studied samples.

Parameter	Unit	CR A[a]	CR D[b]	Ash A	Ash B	AC[c]
pH (1:10)		9.0	10.7	12.4	12.4	4.4
Electrical conductivity (1:10)	mS cm^{-1}	0.46	1.0	7.9	10.1	0.32
Dry matter content	%	16.4	18.7	99.8	99.9	96.3
Loss on ignition	%	68.4	94.8	8.7	1.5	98.0
DOC	mg kg^{-1}	565	649	0.84	0.46	n.d.
TC	%	60.9	89.4	6.5	1.3	77.6
Neutralising value	% Ca	8.0	3.8	13.3	11.3	1.0
Reactivity value	% Ca	6.6	1.6	10.0	5.1	0.95
Liming capacity	t t^{-1}	4.8	10	2.9	3.4	38
Combustion heat	MJ kg^{-1}	20.0	29.7	1.44	0.035	n.d.
Specific surface area	m^2 g^{-1}	15	100	29.8	5.9	603
Pore size (average)	nm	15.9	3.9	3.2	4.8	3.00
Pore volume (total)	cm^3 g^{-1}	0.056	0.098	0.024	0.007	0.45
Density	g cm^{-3}	0.274	0.178	0.544	0.674	n.d.

[a]CR A: carbon residue (from 150 kW gasifier, sample A), [b]CR D: carbon residue (1 MW gasifier), [c]AC: commercial activated carbon (sample A). n.d. not determined

The results presented in Table 1 indicate that all studied samples are clearly alkaline with ashes from the burning process possessing a notably higher pH comparing with carbon residue samples. A similar trend is observed for the results obtained for electrical conductivity value, an index of the total dissolved electrolyte concentration, whose value was quite high for ash produced by the burning process. A high electrical conductivity value indicates that parts of the dissolved metals may occur as dissolved basic metal salts, e.g. oxides and hydroxides (Nurmesniemi *et al*. 2005). Dry matter content was found to be very low in carbon residues which indicate that moisture was present. This is a consequence due to the fact that in the gasifiers where samples were collected, there is no separate carbon residue collector. The gas produced in the gasifier is washed by a water scrubber and the carbon residue formed in the process is collected from the water container. Further evidence of this is provided by the lack of dust problems during handling compared to burning ashes which exhibited high dry matter content and a significant increase in the amount of dust during handling. Loss-on-ignition values (LOI) were high for carbon residues A and D, which indicates that they contain organic matter. This is further supported by high DOC values; however, it should be noted that the determination of LOI values is not an accurate measuring method for the amount of residual carbon in sample that was not burned (Brown & Dykstra 1995, Kuokkanen *et al*. 2006). Carbon contents and combustion heats are very high for both carbon residues and therefore, they have potential to be used as a fuel. Ashes A and B from the combustion process have a low carbon content, which indicates that the burning of organic matter in the boiler has been completed (Kuokkanen *et al.* 2006).

The neutralising value is one of the most important indicators when evaluating the utilisation potential of sample as a liming agent in acidic soil. The capacity of the liming agent to neutralise soil acidity depends on its content of soluble and hydrolysable bases (oxides, hydroxides, carbonates and silicates). The liming effect of commercial limestone produced by SMA Saxo Mineral Ltd. is known to be 38% (Ca equivalents; d.w.); however, the neutralising values for the investigated samples were much lower than those for commercial limestone. Low neutralising values indicate that the ash or carbon residue must be used in large quantities to replace the commercial limestone. Out of the four investigated samples, ash A had the greatest liming capacity; it required 2.9 tonnes to replace 1 tonne of commercial limestone produced by SMA Saxo Mineral Ltd. (Nurmesniemi *et al*. 2005). Combustion ashes contain a great amount of calcium carbonate, but gasification carbon residues do not, which could explain this difference in liming effects.

Specific surface area, pore size and pore volume are important physical properties that determine the quality and utilisation potential of ashes or carbon residues, e.g. as a sorbent. Differences in the surface area and porosity of particles within a material can affect its performance characteristics. Both gasification carbon residues have high carbon contents, and the specific surface area of carbon residue D was also quite high. To put this into context, commercial activated carbon has typically specific surface area 600–1100 m^2 g^{-1}. For the other three samples, their specific surface areas are quite low. The adsorption properties of samples would be better suited if the specific surface area was larger, since pore size affects the type of molecules that can be adsorbed by the surface (Dias *et al.* 2007). Total pore volumes were higher for carbon residues A and D comparing with ashes A and B. The average pore size is notably high for carbon residue A which can cause the quite high total pore volume even the specific surface area is not very large. The densities for combustion ashes were higher than carbon residues formed through gasification, which indicates that combustion ashes were heavier.

The concentrations of soluble nutrients measured in the two carbon residue samples and two ashes are presented in Table 2 to evaluating the samples suitability as fertilisers. Results were originally presented in Paper II. As a reference point, the typical values of K, Mg, and Ca in arable land in Central Finland are 100, 200, and 1600 mg kg^{-1}, respectively. Therefore, the relatively high soluble concentration of K measured in all four investigated samples may contribute to improving soil fertility. Elevated Ca concentrations in ashes A and B and in carbon residue A indicated that these samples may also have a potential to act as a soil conditioning agent. Thus our results for ashes agree with the findings of other researches (Kuokkanen *et al.* 2006, Pöykiö *et al.* 2005).

Table 2. Concentrations of soluble nutrients measured in the four samples.

Nutrient	Unit[a]	CR A[b]	CR D[c]	Ash A	Ash B
K	g kg^{-1} (d.w.)	2.3	3.1	11.4	2.9
Mg	g kg^{-1} (d.w.)	3.2	1.6	4.1	2.1
Ca	g kg^{-1} (d.w.)	42.3	8.5	46.5	26.7
Na	mg kg^{-1} (d.w.)	71	<101	1484	891
Cu	mg kg^{-1} (d.w.)	<10.1	<10.1	11.8	14.8
Zn	mg kg^{-1} (d.w.)	66.1	15.2	52.3	86.8

[a]Concentrations are expressed on dry weight (d.w.) basis, [b]CR A: carbon residue (sample A), [c]CR D: carbon residue (1 MW gasifier)

Table 3 presents the heavy metal concentrations for studied samples and also the limit values for forest fertiliser and in agricultural use given in the current Finnish decree (24/11) and in the previous Decree (12/07) (Ministry of Agriculture and Forestry). The heavy metal concentration results presented in the original Papers (I and II) were compared with this earlier Decree limit values. New legislation relating to the total heavy metal concentrations for biomass-derived ashes used as a forest fertiliser or in agricultural use came into force in 2011 and in Papers I and II lower emission limits for Cd and As were used but it has no effect to the interpretation of the results.

Table 3. Total heavy metal concentrations (mg kg^{-1}; d.w.) in the four investigated samples together with the previous (Decree 12/07) and current (Decree 24/11) limit values for Finnish forest fertilisers or for agricultural use (Ministry of Agriculture and Forestry). Unit in all cases are mg kg^{-1}.

Element	Previous limit value (FF[a])	Previous limit value (AU[b])	Current limit value (FF[a])	Current limit value (AU[b])	CR A[c]	CR D[d]	Ash A	Ash B
Cd	17.5	1.5	25	1.5	6.3	<0.3	5.0	3.0
Cu	700	600	700	600	130	15	83	81
Pb	150	100	150	100	25	<3	27	72
Cr	300	300	300	300	210	7	82	60
Zn	4500	1500	4500	1500	134	85	380	530
As	30	25	40	25	< 3	<3	19	28
Ni	150	100	150	100	110	3	36	37
Hg	1.0	1.0	1.0	1.0	0.04	<0.04	0.56	0.47

[a]FF: forest fertiliser, [b]AU: agricultural use, [c]CR A: carbon residue (sample A), [d]CR D: carbon residue (1 MW gasifier)

Based on the results presented in the Table 3, the total heavy metal concentrations in studied samples were lower than the current Finnish maximum limit allowed in forest fertiliser. As a result, these samples can be utilised as a forest fertiliser in terms of heavy metals. In terms of agriculture, results in Table 3 shows that the concentrations of cadmium in carbon residue A and ashes A and B were higher than the current maximum limit allowed for agricultural use. The concentration of nickel in carbon residue A was also calculated to be higher than the current acceptable limit whilst a similar scenario was observed for arsenic in ash B. However, this is not the case for ash A which could therefore be utilised entirely as a potential source for a forest fertiliser or in agricultural use in terms of heavy metals. For example Cd, Zn and Pb will concentrate to fly ash because combustion process is like a thermodynamic separation process for the different inorganic materials in the fuel. The most notable effect is temperature, because bottom ash leaves the combustion chamber at high temperatures, bottom ash is free of volatile heavy metals. Instead metals with low volatility, like nickel and chromium, will concentrate in the bottom ash. Hg concentration was measured to be very low in all the investigated ashes which are typical for wood-based ash. This is a consequence to the fact that mercury is volatilised during the thermal treatment due to its high vapour pressure. (Kuokkanen *et al.* 2006, Narodoslawsky & Obernberger 1996, Pöykiö *et al*. 2009). Past studies have also shown that pH has a strong effect on the mobility of heavy metals. As such, when the alkalinity of the ash decreases, metals will become more mobile. (Kuokkanen *et al*. 2006, Steenari & Lindqvist 1997).

Finnish legislation (Decree 24/11) creates also other requirements than metal limit values for wastes or by-products before they can be utilised as a forest fertiliser or in agricultural use. Neutralising value, for example, have to be at minimum 10.0% (Ca, d.w) and the total amount of phosphorus and potassium should be 2.0% (d.w). In addition, calcium content has to be at least 6.0% (d.w).

Results presented in this section indicate that the properties of carbon residue samples from gasification processes and ashes from burning processes are totally different. The strength of carbon residue samples is their high carbon content and specific surface area which can be increased by activation or modification methods.

5.2 Chemical activation

It is well known that the most important property of activated carbons and other adsorbents is their adsorption capacity which is related e.g. to the specific surface area. Typically adsorption capacity is higher when specific surface area is larger so there is a great importance to investigate the parameters which affect to the activation process and enlarge specific surface area. (Guo *et al*. 2009). Specific surface areas of chemically activated carbon residues were determined in order to evaluate the success of the activation with different activation agents. The highest specific surface area was obtained by using 5 M $ZnCl_2$ as a chemical activating agent; results shown in Table 4 which are originally presented in Paper IV. Any chemical activation increases specific surface area but the highest was obtained by using zinc chloride as a chemical activating agent.

Table 4. Specific surface areas for carbon residue samples which were activated by different chemical activating agents.

Sample	Specific surface area of sample [m^2 g^{-1}]
CR[a] activated by 0.1 M HCl	194
CR[a] activated by 0.1 M H_2SO_4	157
CR[a] activated by 5 M $ZnCl_2$	285
CR[a] activated by 5 M KOH	117
CR[a] activated by HCl	171
CR[a] activated by HNO_3	259
Carbon residue	14.4
Commercial activated carbon (sample A)	603

[a] CR: Carbon residue (sample B)

There are many experimental variables which have influence on the surface area and the porosity of the material and therefore, the next step was to examine the effect of activation parameters: liquid-to-solid ratio to the carbon residue and chemical activating agent, the concentration of impregnation solution and contact time between the activating agent and carbon residue by using zinc chloride as the activating agent. These parameters varied in the ranges L/S 4─10, concentration 2─5 M and time 10 min─6 h. The highest specific surface area was obtained by using 5 M zinc chloride solution with a liquid-to-solid ratio L/S of 10 and a contact time of 1 hour for the chemical activation. The adsorbent prepared in that way was considered further. Activation time at 500 °C was constant (one hour) in all experiments. Chemically activated carbon residue was sieved again to ensure all particles had a diameter less than 150 µm.

In the Figure 2 is presented FESEM-images for chemically activated carbon residue, carbon residue and commercial activated carbon which illustrate pores and crystals on the adsorbent´s surface. Activated carbon and activated carbon residue seem to be clearly more porous compared to carbon residue whilst the porosity is quite similar in the samples. The values of specific surface areas also support this argument.

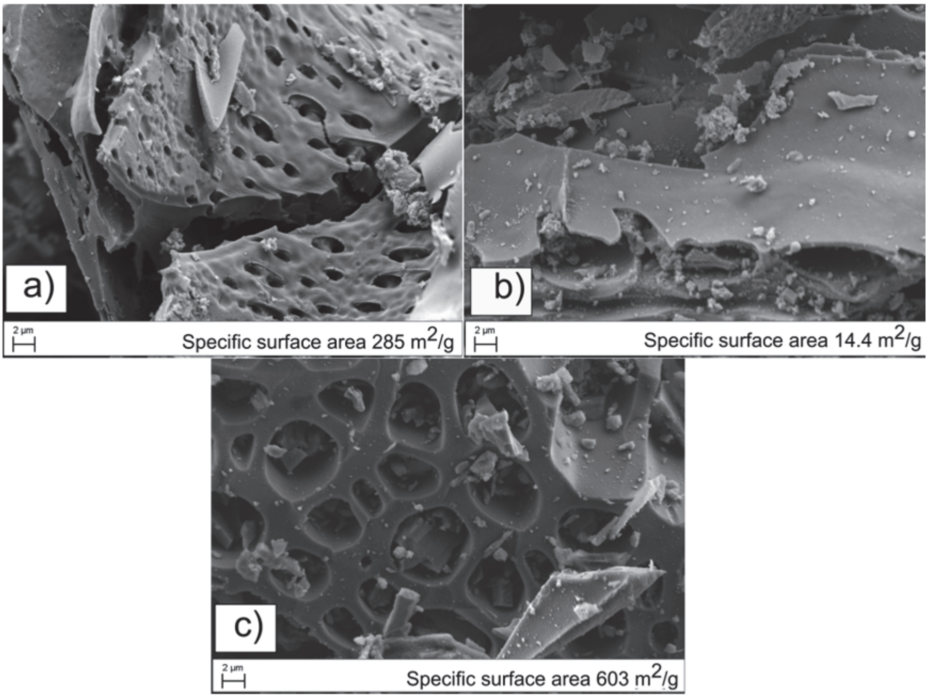

Fig. 2. FESEM images for a) $ZnCl_2$ activated carbon residue b) carbon residue, c) commercial activated carbon, magnification x7000 (IV, published by permission of Elsevier).

5.3 Physical activation

The activation conditions, burn-offs during the activation procedure as well as the properties of physically activated samples, including the specific surface areas, pore sizes, total pore volumes, micropore volumes and macro-mesopore volumes are summarised on Table 5, and were originally presented in Paper V. According to these results, activating agent and activation temperature had an important role of developing porosity but duration of activation has significant role only when carbon dioxide was used as an activating agent. Burn-offs increased clearly when temperature and duration of activation increased. The highest surface area obtained in our studies was 590 m^2 g^{-1} and it was obtained by using carbon dioxide as a physical activating agent, duration of activation 3 hours and temperature 800 ^oC. Burn-off of that sample was also quite high compared with other conditions but specific surface area was notable high and therefore, this sample was chosen to further consideration. Mechanism of physical activation by carbon dioxide is presented in equations 3–6 which was originally presented in Paper V.

The mechanism involved in the activation of a carbonaceous material is not clear but it is known that during physical activation with CO_2 the following reaction occurs:

$$C + CO_2 = 2\,CO \tag{3}$$

The chemical mechanism of physical activation is not as simple as presented in reaction 3, but the following mechanism is postulated to be:

$$C + CO_2 \leftrightarrow CO + C(O) \tag{4}$$

In reaction 4 surface oxygen complex C(O) is initially formed. It became stable under the reaction conditions and acting as a retardant by blocking reaction sites as presented in reaction 5:

$$C(O) \leftrightarrow C\text{–}O \tag{5}$$

However, it may decompose leaving the surface as CO

$$C(O) \rightarrow CO \tag{6}$$

in which the “free” surface carbon atom stays available for reaction. (Marsh & Rodríquez-Reinoso 2006).

Table 5. Properties of various physically activated carbon residues and reference samples.

Sample	Burn-off [%]	BET [$m^2\,g^{-1}$]	Pore size [nm]	Total pore volume [$cm^3\,g^{-1}$]	Micropore volume [$cm^3\,g^{-1}$]	Macro-mesopore volume [$cm^3\,g^{-1}$]
CO 600 °C 1 h	15.6	117	6.04	0.176	0.050	0.126
CO 600 °C 3 h	16.6	126	5.83	0.183	0.064	0.119
CO 800 °C 1 h	20.5	135	6.02	0.204	0.056	0.148
CO 800 °C 3 h	25.6	133	6.16	0.205	0.052	0.156
CO_2 600 °C 1 h	15.0	150	5.25	0.196	0.062	0.134
CO_2 600 °C 3 h	16.3	152	5.20	0.197	0.075	0.122
CO_2 800 °C 1 h	40.1	353	3.86	0.340	0.172	0.168
CO_2 800 °C 3 h	55.2	590	3.44	0.335	0.175	0.160
N_2 600 °C 1 h	17.8	136	5.61	0.191	0.052	0.139
N_2 600 °C 3 h	18.2	145	6.08	0.220	0.050	0.170
N_2 800 °C 1 h	15.7	156	5.52	0.215	0.069	0146
N_2 800 °C 3 h	30.9	160	5.98	0.240	0.058	0.182
CR[a]	-	52.4	8.16	0.107	0.024	0.083
AC[b]	-	786	2.21	0.435	0.394	0.041

[a]CR: carbon residue (sample C), [b]AC: activated carbon (sample B)

In physical activation, the development of pore structure can happen by opening the previously inaccessible pores, creation of new pores by selective activation or widening of the existing pores (Guo *et al.* 2009). For carbon residue samples, physical activation by carbon dioxide work very well.

5.4 Chemical modification

Carbon residues were chemically activated or modified (impregnated) by several ways and the results of all modification methods are presented in Paper VI. Produced adsorbents were tested for sulphate removal in pH range of 2–8. Based on those adsorption experiments (presented in details in Paper VI), the adsorbent with the highest removal efficiency towards sulphate was selected for further studies (modified by $FeCl_3$). In the Table 6 is presented properties for chemically modified carbon residue, carbon residue and activated carbon samples.

Table 6. Comparison of properties of chemically modified carbon residue, carbon residue and activated carbon.

Sample	BET [$m^2 g^{-1}$]	Pore size [nm]	Total pore volume [$cm^3 g^{-1}$]	Micropore volume [$cm^3 g^{-1}$]	Macro-mesopore volume [$cm^3 g^{-1}$]	TC [%]
MCR[a]	52.4	7.56	0.12	0.02	0.10	61.0
CR[b]	52.4	8.16	0.11	0.02	0.10	69.5
AC[c]	786	2.21	0.44	0.39	0.04	91.9

[a]MCR: chemically modified ($FeCl_3$) carbon residue, [b]CR: carbon residue (sample C), [c]AC: commercial activated carbon (sample B)

It is known that calcium and iron can precipitate with sulphate ions and form iron or calcium sulphate. Since carbon residue includes a notable amount of calcium as mentioned in Paper II and produced adsorbent was modified by iron, it makes sense to study iron and calcium dissolution from modified adsorbent since the object of this study was to investigate adsorption. Results of iron and calcium dissolution studies are presented in Table 7 for carbon residue and modified carbon residue. In the case of carbon residue, dissolution of Ca is quite high at pH 2, but sulphate removal was very low at this pH as mentioned in Paper VI. Therefore, dissolved calcium from carbon residue does not precipitates all sulphate in the solution but it can be assumed that sulphate removal is based on precipitation in addition to adsorption. In the case of iron modified carbon residue, calcium is not dissolved in acidic conditions. This is due to carbon residue being acid-washed before iron modification. Since the main idea of this research is to study adsorption phenomena, conditions in adsorption tests were selected so that precipitation should not occur.

Table 7. Dissolution of calcium for unmodified carbon residue in addition to calcium and iron from iron modified carbon residue. Mass of adsorbent: 0.25 g, V(distilled water): 0.050 L.

Adsorbent	Conditions		Dissolution of Fe	Dissolution of Ca
	Initial pH	Final pH	[mg L^{-1}]	[mg L^{-1}]
CR	2.0	2.4	6.4	254
	4.1	6.5	*	183
	6.1	7.2	*	38
	8.1	8.3	*	2.3
MCR	2.2	2.2	59.4	0.4
	4.0	2.9	21.6	0.3
	6.0	3.3	0.5	0.4
	7.9	3.4	0.3	0.3

* Below detection limit (0.02 mg L^{-1}). CR: Carbon residue (sample C), MCR: Iron modified carbon residue.

5.5 Utilisation application as an adsorbent

The main goal of adsorption experiments was to evaluate previously produced materials as an adsorbent for phosphate, nitrate or sulphate removal. Chemically activated carbon residue sample was studied as an adsorbent for phosphate, nitrate and sulphate removal. Physically activated carbon residue was tested for phosphate and nitrate removal experiments whilst chemically modified carbon residue was studied as an adsorbent only for sulphate removal. During the adsorption experiments, the optimum initial pH and initial concentration were determined and the effect of adsorption time was studied. In addition, isotherm analysis and kinetic calculations were done. In Papers III and IV, the amount of experimental points in concentration optimisation experiments was quite low and therefore, in Papers V and VI this amount has been increased. In Papers V and VI the amount of experimental points in studies for effect of time for removal efficiency was also increased. Error analysis for isotherm analysis and kinetic calculations was also presented in Papers V and VI.

5.5.1 Adsorption experiments

Effect of initial pH

When carbon-based adsorbents and adsorbates are in contact in aqueous solution, there are electrostatic or non-electrostatic interactions. Electrostatic interactions occur when adsorbate is an electrolyte that dissociates in aqueous solution and interactions can be attractive or repulsive which depend on e.g. charge density of the carbon surface, chemical characteristics of adsorbate or ionic strength of the solution. When interactions are non-electrostatic, they are always attractive and can include van der Waals forces, hydrophobic interactions and hydrogen bonding. (Dias *et al.* 2007). Therefore, pH is one of the most important parameters controlling the uptake of ions from an aqueous solution because it controls the electrostatic interactions between the adsorbent and the adsorbate. The surface of the adsorbent became positively charged in acidic conditions and negatively charged in alkaline conditions. Our studied anions are negatively charged and it appears that there are repulsion forces between ions and the negatively charged adsorbent surface in alkaline conditions. This occurs because at active sites OH^- ions and other negatively charged anions give the appearance that they are in competition with each other. (Bhatnagar *et al.* 2010a). pH is also an essential variable in case of phosphate because depending on the pH of the system, phosphorus can exist as H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-}.

However, results presented in Paper III, in which phosphate removal was studied by chemically activated carbon residue, did not support this claim and the reason for that is that industrial wastes such as the carbon residue formed in the gasification process never include a single element and therefore many compounds can affect the adsorption capacity. For example, carbon residue includes a notable amount of calcium (42.3 g kg^{-1}) determined by ammonium acetate extraction as presented in Paper II. High pH and high calcium concentration are advantageous for calcium phosphate precipitation (Ferguson *et al.* 1973). However, precipitation is not such a significant mechanism for phosphate removal because of the solution´s pH and if calcium could not be released into the solution. Adsorption depends also on e.g. the competitive adsorption of ions, ionic size and the stability of the bonds between adsorbent and different ions. (Ahmaruzzaman 2011, Grubb *et al.* 2000, Kumar *et al.* 2010, Kumar *et al.* 2011, Yao *et al.* 2011). Precipitation reactions often co-occur with the adsorption process and thus it is difficult to distinguish these individual processes (Prasad & Mortimer 2010). In paper III is presented phosphate removal by chemically activated carbon residue and highest removal efficiency was obtained at pH 8. The purpose was to investigate the adsorption, so in later studies we chose the conditions in such a way that precipitation should not occur, and therefore pH 8 was eliminated in Papers IV and V in case of phosphate removal studies. The optimum pH for phosphate removal over different adsorbents is presented in Table 8.

Commercial activated carbon can include also variable amounts of heteroatoms such as oxygen, hydrogen, nitrogen and sulphur which have originally in raw material or they have added to the carbon surface during its production step. Those heteroatoms can have influence to the charge, hydrophobicity and electronic density of the adsorbents surface. Heteroatoms have great influence on electrostatic and non-electrostatic interactions. (Dias *et al.* 2007).

In the case of nitrate ions, it occurs naturally in nitrogen cycles and resided in a stable form in oxygenated nitrogen systems. Nitrate can be reduced to nitrite (NO_2^-) by a microbial action under reducing conditions; however, nitrite is unstable and can be oxidised back to nitrate. Chemical and biological processes can also reduce nitrite into various compounds. (Bhatnagar & Sillanpää 2011). Nitrate ions are also negative and as in the case of phosphate, repulsion forces exist between these ions and adsorbent in alkaline conditions. The poor removal efficiency of anions in alkaline conditions was most likely due to the increasing competition for sites between OH^- and anions (Bhatnagar *et al.* 2010a). Typically carbon based adsorbents show poor adsorption towards anions whilst published results on the sorption of nitrates by activated carbon are limited (Bhatnagar & Sillanpää, 2011). Afkhami *et al.* (2007) discovered that the acid treatment of carbon-based adsorbent increases its adsorbent capacity towards nitrate and nitrite. They assumed that the acid treatment produces positive sites on the carbon surface by protonating the OH^--groups located there. This increases the electrostatic adsorption of anions which may also explain why the optimal pH for nitrate adsorption is found in acidic conditions. Optimal pH values for nitrate adsorption over different adsorbents are presented in Table 8.

Sulphate (SO_4^{2-}) can be reduced to sulphide (S^{2-}) by bacteria. (Rayner-Canham 1999). In Paper VI sulphate removal was studied by iron-modified carbon residue. Iron could precipitate with sulphate and also calcium sulphate may precipitate due to the fact that carbon residue includes calcium. The pH value was selected so that iron should not dissolve from modified carbon sample and therefore, iron sulphate precipitation should not occur. Because iron dissolution was low at pH 4, that pH value was selected for further studies. In case of carbon residue sample, the highest sulphate removal efficiency was obtained at pH value of 2 and that was selected for optimum pH value for further studies. Sulphate removal over commercial activated carbon varied between 13.2–21% at the pH range of 2–8. The sulphate removal is highest in acidic conditions but there were no high differences between sulphate removal at pH 2 and 4. Corresponding preliminary studies showed also same phenomena. Therefore, pH 2 was selected as the optimum initial pH value. Optimal pH values for sulphate removal are presented also in Table 9.

However, pH changes during the adsorption process when alkaline carbon residue or activated or modified carbon residues were used as an adsorbent which can cause precipitation and therefore precipitation cannot be totally neglected in present adsorption experiments. From an utilisation point of view it is insignificant how phosphate removal occurs, i.e if the mechanism is by adsorption or precipitation.

Effect of initial concentration

The effect of initial phosphate or nitrate concentration on the removal efficiency of anions between the concentration levels of 25 to 125 mg L^{-1} by using chemically activated carbon residue or 10 to 140 mg L^{-1} by using physically activated carbon residue are presented in Figure 3. Carbon residue and commercial activated carbon were used as a reference sample. Sulphate removal over chemically modified carbon residue, carbon residue and activated carbon was studied in the concentration range of 50 to 1000 mg L^{-1} and results are presented in Figure 4. The optimum initial pH and initial phosphate and nitrate concentrations for removal are presented in Table 8 and in the Table 9 is presented results for sulphate removal. Removal efficiency over the adsorbents decreased typically when the initial concentration was increased. This can be explained to be due to the fact that optimal adsorption sites are occupied first at low concentrations. This is not the fact in all cases, e.g. phosphate removal over carbon residue samples is not optimum with the lowest concentration. This can be explained due to the fact that some driving forces exist when the concentration increases.

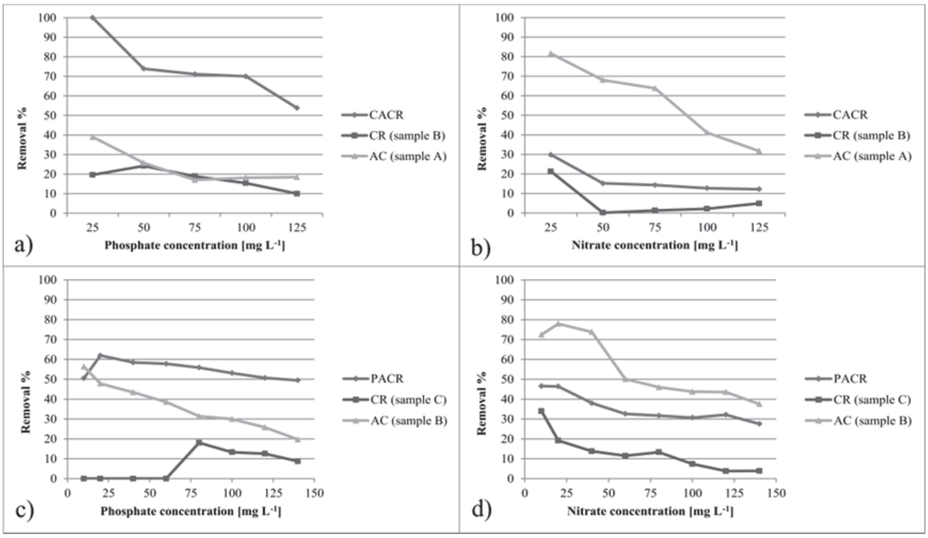

Fig. 3. Removal efficiency as a function of different initial concentrations for chemically and physically activated carbon residues, carbon residues and commercial activated carbons. CACR: chemically activated carbon residue, PACR: physically activated carbon residue, CR: carbon residue, AC: activated carbon.

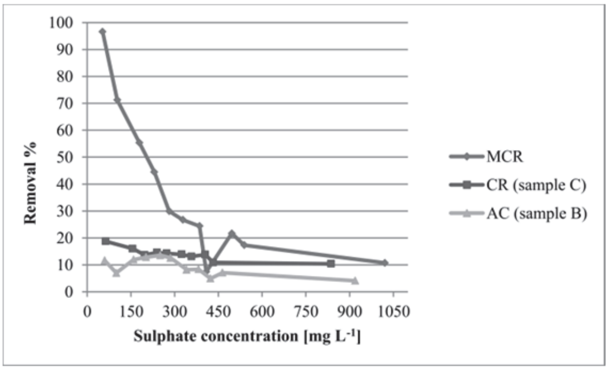

Fig. 4. Sulphate removal efficiency as a function of initial sulphate concentrations for chemically modified carbon residue (MCR), carbon residue (CR) and commercial activated carbon (AC).

Table 8. Optimum pH and concentration values for different adsorbents in the case of phosphate and nitrate removal studies.

Adsorbent	Phosphate		Nitrate	
	pH	Concentration [mg L^{-1}]	pH	Concentration [mg L^{-1}]
CACR[a]	6	25	6	25
PACR[b]	6	20	4	10
CR[c] (sample B)	4	50	6	25
CR[c] (sample C)	6	80	4	10
AC[d] (sample A)	6	25	4	25
AC[d] (sample B)	6	10	4	20

[a]CACR: chemically activated carbon residue, [b]PACR: physically activated carbon residue, [c]CR: carbon residue, [d]AC: activated carbon

Table 9. Optimum pH and concentration values for different adsorbents in sulphate removal studies.

Adsorbent	Sulphate	
	pH	Concentration [mg L^{-1}]
MCR[a]	4	50
CR[b]	2	50
AC[c]	2	200

[a]MCR: iron modified carbon residue, [b]CR: carbon residue (sample C), [c]AC: activated carbon (sample B)

Effect of adsorption time

The adsorption of phosphate, nitrate and sulphate over different adsorbents was investigated as a function of adsorption time (1 min–24 h) using the optimum initial pH and optimum initial concentration. Removal efficiencies as a function of time are presented in Figures 5 and 6, which clearly shows that mainly removal efficiencies increase rapidly with time especially when activated carbon residue was used as the adsorbent. Results show that in cases of phosphate, the removal efficiencies are notably higher for chemically or physically activated carbon residues compared with commercial activated carbon. The same effect was observed in case of sulphate removal in which removal efficiency was notable higher comparing with commercial activated carbon. On the other hand, removal efficiency is higher for activated and modified carbon residues compared with unactivated carbon residue in all adsorbates and therefore, activation and modification can enhance the adsorption capacity. Typically pH increases during adsorption reaction when using alkaline carbon residue as an adsorbent and therefore, it can be assumed that after 24 h reaction time some removal efficiency is based on chemical precipitation in case of phosphate and sulphate removal experiments.

In case of nitrate removal, commercial activated carbon shows good adsorption capacity and physically activated carbon residue also. The best removal efficiency was achieved in the beginning of experiments when physically activated carbon residue was used as an adsorbent but after that the removal efficiency starts to decrease gradually. This can be explained by its pH value: in the beginning of experiments the pH was optimum but then it starts to increase and therefore, it is not optimum anymore.

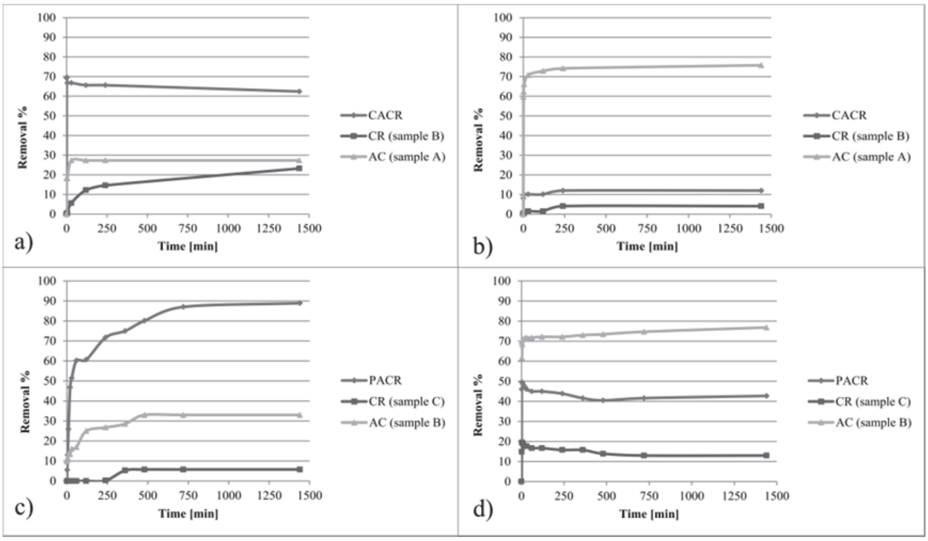

Fig. 5. The removal efficiency of phosphate (a and c) and nitrate (b and d) as a function of time for different adsorbents. Experiments were performed at room temperature using the optimum initial pH values and initial concentration of phosphate or nitrate solution presented in Table 8. CACR: chemically activated carbon residue, PACR: physically activated carbon residue, CR: carbon residue, AC: activated carbon.

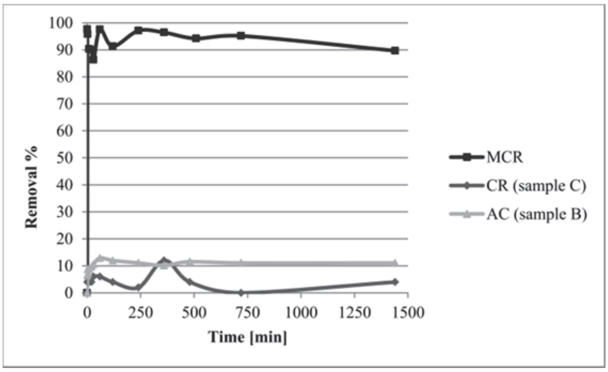

Fig. 6. The effect of time for sulphate removal over modified carbon residue (MCR), carbon residue (CR) and commercial activated carbon (AC) samples.

5.5.2 Adsorption mechanism

Adsorption mechanism for phosphate, nitrate and sulphate over different adsorbents is quite difficult to evaluate because studied adsorbents includes many metals and compounds which can affect on adsorption process. According to Ahmaruzzaman (2011) in the case of the various industrial adsorbents the adsorption mechanisms can be very complicated and appear attributable to electrostatic attraction, ion-exchange, adsorption-precipitation, hydrogen bonding, and chemical interaction between ions and the surface functional groups of the various industrial adsorbents.

According to Dias *et al.* (2007), typically there may be, for example, following mechanisms by which ions are removed from an aqueous solution:

- Process is based on electrostatic adsorbate-adsorbent interaction which is dependent on the existence of adsorbents´s surface functionality
- Enhanced adsorption potential which typically occurs in the narrowest microporosity, may be strong enough to adsorb ions

Physically activated carbon residue removes nitrate better compared with chemically activated carbon residue and the same effect was observed also in case of phosphate. The reason for that may be that specific surface area is larger for physically activated sample. Therefore adsorption may occur due to the porosity of sample.

The pH-dependent charging of adsorbents governs the adsorption of ions. Point of zero charge describes the pH value in which the electrical charge density in the surface is zero. pH (ZPC) was found in acidic conditions for all studied adsorbents as presented in Table 10 and therefore, it can be assumed that optimal conditions for anions removal can also be found in acidic conditions. pH optimisation experiments were done in range 4–8 in Papers III–V for practical reasons because those pH values were realistic in real wastewaters. In the last Paper (VI), the studied pH range was widened to 2–8.

Table 10. Point of zero charges (pH (ZPC)) for the studied adsorbents.

Sample	pH (ZPC)
CACR[a]	4
PACR[b]	3
MCR[c]	5.4
CR (Sample B)[d]	2.2
CR (Sample C)[d]	2.1
AC (Sample A)[e]	2.1
AC (Sample B)[e]	2.1

[a]CACR: chemically activated carbon residue, [b]PACR: physically activated carbon residue, [c]MCR: chemically modified carbon residue, [d]CR: carbon residue, [e]AC: activated carbon

5.5.3 Isotherm studies

Adsorption isotherms are generally used for the design of an adsorption system since they represent the amount of species adsorbed versus the amount of species left in the solution phase at equilibrium. Therefore isotherm analysis was performed for studied adsorbents. The Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) equations are by far the most commonly used equations for describing the adsorption isotherm. The Langmuir isotherm assumes that adsorption occurs at specific homogeneous sites within the adsorbent without any interactions between the adsorbed substances. The Freundlich model is empirical in nature and assumes that the uptake of ions occurs on a heterogeneous surface. The linear form of the Langmuir and Freundlich isotherm models are given by Equations (7) and (8), respectively, as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \tag{7}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

where q_e (mg g^{-1}) is the amount of species adsorbed per unit mass of adsorbent, C_e (mg L^{-1}) is the solution concentration at equilibrium while q_m (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the capacity and energy of adsorption, respectively. K_f (L g^{-1}) and n (dimensionless) are Freundlich constants related to the adsorption capacity and intensity of adsorption, respectively. Furthermore, the constants of Langmuir and Freundlich were obtained from the linear plots of $1/q_e$ versus $1/C_e$, and log qe versus log C_e, respectively.

In addition to Langmuir and Freundlich isotherm models, Temkin and Dubinin-Radushkevich (D-R) isotherm models have commonly been applied in linear form. The heat of the adsorption and the adsorbent-adsorbate interaction were evaluated by using Temkin isotherm model (Roosta *et al.* 2014a, 2014b). The D-R model was also applied to estimate e.g. the characteristics of adsorption (Roosta *et al.* 2014c). That model does not assume a homogeneous surface or constant adsorption potential. Linear forms of isotherms are presented in Equations (9) and (10) (Temkin & Pyzhev 1940, Zheng *et al.* 2009):

$$q_e = B \ln A + B \ln C_e \tag{9}$$

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{10}$$

where B = (RT)/b is the Temkin constant related to heat of the adsorption (J mol^{-1}), R is the gas constant (J mol^{-1} K^{-1}), T is temperature (K), b is Temkin isotherm constant and A is the Temkin isotherm equilibrium binding constant (L g^{-1}). In the D-R isotherm, q_e is the amount of ion adsorbed to adsorbent per unit dosage (mg g^{-1}), β (mol^2 $(J^2)^{-1}$) is a constant related to the adsorption energy, q_m (mg g^{-1}) is the theoretical saturation capacity, ε is Polanyi potential, which is described in Equation (11). (Dada *et al.* 2012, Ghaedi *et al.* 2014, Zheng *et al.* 2009).

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{11}$$

The slope of the plot of ln q_e versus ε^2 gives β and the intercept yields the adsorption capacity. The mean free energy of adsorption E (kJ mol^{-1}) describes free energy change when one mole of ion is transferred from the solution to the surface of the sorbent and it can be calculated as follows (Zheng *et al.* 2009):

$$E = \frac{1}{\sqrt{-2\beta}} \tag{12}$$

In the Table 11 is presented the best fit adsorption isotherm results for studied adsorbents. Chemically activated carbon residue and physically activated sample shows high Langmuir adsorption capacity towards phosphate. In those cases, there are differences between experimental and calculated values. RMSE is very small for phosphate adsorption onto physically activated carbon residue and therefore, experimental equilibrium point differ a lot of calculated value but other values differ not so much. Nitrate adsorption onto physically activated carbon residue is also well and also sulphate adsorption onto chemically modified carbon residue. In the case of sulphate removal by activated carbon there is notable difference between maximum sorption capacities compared with experimental value. This may be a consequence of the fact that sulphate removal is very low at whole concentration range used. In the Tables 12–14 Langmuir adsorption capacities obtained in literature over different adsorbents for phosphate, nitrate and sulphate removal are presented. Based on those values, Langmuir adsorption capacities obtained in this study are in the same order of magnitude.

Table 11. Langmuir isotherm constants for the adsorption of phosphate, nitrate and sulphate onto studied adsorbents at room temperature.

	Langmuir				
	q_m [mg g^{-1}]	q_{exp} [mg g^{-1}]	b [L mg^{-1}]	R^2	RMSE
Phosphate/CACR[a]	20.5	14.3	0.046	0.848	n.d.
Nitrate/CACR[a]	7.97	3.06	0.0056	0.997	n.d.
Phosphate/PACR[b]	30.2	15.1	0.012	0.998	0.0973
Nitrate/PACR[b]	11.2	8.2	0.017	0.992	0.318
Sulphate/MCR[c]	19.5	21.9	0.6119	0.918	1.65
Phosphate/AC[d]	4.43	4.46	0.0478	0.851	n.d.
Phosphate/AC[e]	8.70	6.44	0.0275	0.992	0.0715
Nitrate/AC[d]	10.0	10.0	0.14298	0.948	n.d.
Nitrate/AC[e]	14.6	11.4	0.0444	0.9407	1.09
Sulphate/AC[e]	15.0	7.59	0.0012	0.957	2.48

[a]CACR: chemically activated carbon residue, [b]PACR: physically activated carbon residue, [c]MCR: iron modified carbon residue, [d]AC: activated carbon (sample A), [e]AC: activated carbon (sample B), n.d.: not determined

Table 12. Langmuir adsorption capacities for phosphate removal over different adsorbents.

Adsorbent	Adsorption capacity [mg g^{-1}]	pH	Concentration [mg L^{-1}]	Contact time	Reference
Iron-hydroxide eggshell[a]	14.5	7	27	30 min	Mezenner & Bensmaili 2009
Goethite	6.42	-	-	3–28 days	Borggaard *et al.* 2005
Iron oxide tailings	8.21	6.6–6.8	-	-	Zeng *et al*. 2004
Na-natural zeolite	2.19	-	0.5–1000	24 h	Wu *et al*. 2006
Chemically ($ZnCl_2$) activated carbon residue	20.5	6	25	24 h	This study
Physically (CO_2) activated carbon residue	30.2	6	20	24 h	This study

[a] Temperature 45 °C

Table 13. Langmuir adsorption capacities for nitrate removal over different adsorbents.

Adsorbent	Adsorption capacity [mg g^{-1}]	pH	Concentration [mg L^{-1}]	Contact time	Reference
Chemically modified sugar beet bagasse	9.14–27.55	6.58	10–200	-	Demiral & Gündüzoğlu 2010
Sepiolite activated by HCl	38.16	-	100	5 min	Öztürk & Bekta 2004
Impregnated almond shell activated carbon	16–17	6.2	10–50	120 min	Rezaee *et al.* 2008
$ZnCl_2$ treated coconut granular activated carbon	10.2	5.5	5–200	2 h	Bhatnagar *et al.* 2008
Zr(IV)-loaded sugar beet pulp	63	6.0	-	24 h	Hassan *et al.* 2010
Chemically ($ZnCl_2$) activated carbon residue	7.97	6	25	24 h	This study
Physically (CO_2) activated carbon residue	11.2	4	10	24 h	This study

Table 14. Langmuir adsorption capacities for sulphate removal over different adsorbents.

Adsorbent	Adsorption capacity [mg g^{-1}]	pH	Concentration [mg L^{-1}]	Contact time	Reference
γ-Al_2O_3	7.7	5.7	-	-	Wu *et al.* 2002
Chitin-based scrimp shells	156.0	4.5	1540	15 min	Moret & Rubio 2003
Coir pith carbon	0.06	4.0	-	-	Navasivayam & Sangeetha 2008
$ZnCl_2$ activated coir pith carbon	4.9	4.0	-	-	Navasivayam & Sangeetha 2008
Carbon residue	17.6	2	50	24 h	This study
Iron modified carbon residue	21.5	4	50	24 h	This study
Commercial activated carbon	9.4	2	200	24 h	This study

5.5.4 Rates of adsorption

The kinetic study of adsorption processes provides useful information regarding the efficiency of the adsorption and the feasibility for large scale operations. The kinetics of phosphate, nitrate and sulphate ions adsorption on different adsorbent surfaces was studied by using pseudo-first-order and pseudo-second-order kinetic models to identify the dynamics of the adsorption process (Ho & McKay 1999, Lagergren 1898). The Lagergren´s equation (Lagergren 1898) is widely used for liquid adsorption studies and the linear form of pseudo-first-order rate expression is given as follows (Bhatnagar *et al.* 2010b):

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \qquad (13)$$

where q_e and q_t are the amounts of phosphates, nitrates or sulphates adsorbed (mg g^{-1}) at equilibrium (1440 minutes in this study) and at time t, respectively. The pseudo-first-order rate constant is marked as k_f [min^{-1}].

Pseudo-second-order process can be expressed in a linear form (Bhatnagar *et al.* 2010b):

$$\frac{t}{q_t} = \frac{1}{k_s {q_e}^2} + \frac{1}{q_e} t \qquad (14)$$

where k_s [g mg^{-1} min^{-1}] is the rate constant of pseudo-second-order kinetics.

The rate constants, linear correlation coefficients (R^2) and both experimental values of q_e(exp) and theoretical q_e(cal) uptakes for all studied adsorbates for different adsorbents are given in Tables 15–17. Pseudo-second-order model gave a good fit for all adsorbents and for all adsorbates. The values of q_e(exp) and q_e(cal) indicate that the theoretical values agree well with the experimental uptake values in the case of pseudo-second-order kinetic model for phosphate, nitrate and sulphate adsorption for all adsorbents studied in this thesis. Values presented to chemically activated carbon residue in phosphate removal were obtained by modified test points which are the reason why R^2 value is 1.00. However, for nitrate adsorption over a carbon residue surface, the k_s value was negative and is not included in Table 16 and the same situation was in the results presented in the Table 15 for phosphate removal over chemically activated carbon residue. The negative rate constant can be explained to be due to the fact that the maximal nitrate removal efficiency was achieved at the beginning of experiments but then removal percentage starts to decrease with time. Results show poor adsorption capacity towards nitrate in case of carbon residue which also explains the negative rate constant.

Table 15. Pseudo-second-order model parameters, calculated q_e(cal) and experimental q_e(exp) values for different adsorbents in phosphate removal experiments.

Adsorbent	$q_{e(exp)}$ [mg g^{-1}]	$q_{e(cal)}$ [mg g^{-1}]	k_s [g mg^{-1} min^{-1}]	R^2	RMSE
CACR[a]	3.48	3.48	-	1.00	n.d.
PACR[b]	3.84	3.88	0.0075	0.997	0.0836
CR[c]	5.36	6.03	1.008	0.945	n.d.
CR[d]	0.97	0.96	0.0966	0.999	n.d.
AC[e]	1.20	1.20	2.355	0.999	n.d.
AC[f]	0.74	0.75	0.0526	0.997	0.0057

[a]CACR: chemically activated carbon residue, [b]PACR: physically activated carbon residue, [c]CR: carbon residue (sample B), [d]CR: carbon residue (sample C), [e]AC: activated carbon (sample A), [f]AC: activated carbon (sample B), q_e: amount of phosphate adsorbed on the adsorbent (mg g^{-1}) at equilibrium calculated or experimental value, k_s: rate constant for pseudo-second-order kinetics, R^2: linear correlation coefficient. Number of test points was 7 for CACR, CR (sample B) and AC (sample A) and 14 for PACR and AC (sample B). Only 5 test points were used for CR (sample C) because adsorption started quite late (after 360 minutes) and therefore the calculations before that point cannot be made. n.d.: not determined.

Table 16. Pseudo-second-order model parameters, calculated qe(cal) and experimental qe(exp) values for different adsorbents in nitrate removal experiments.

Adsorbent	$q_{e(exp)}$ [mg g^{-1}]	$q_{e(cal)}$ [mg g^{-1}]	k_s [g mg^{-1} min^{-1}]	R^2	RMSE
CACR[a]	0.62	0.622	0.046	0.999	n.d.
PACR[b]	0.76	0.75	5.619	0.999	0.0329
CR[c]	0.22	0.231	0.00017	0.981	n.d.
CR[d]	0.28	0.28	-	0.998	n.d.
AC[e]	3.58	3.584	20.32	0.999	n.d.
AC[f]	3.64	3.62	0.0537	0.999	0.6019

[a]CACR: chemically activated carbon residue, [b]PACR: physically activated carbon residue, [c]CR: carbon residue (sample B), [d]CR: carbon residue (sample C), [e]AC: activated carbon (sample A), [f]AC: activated carbon (sample B), q_e: amount of nitrate adsorbed on the adsorbent (mg g^{-1}) at equilibrium calculated or experimental value, k_s: rate constant for pseudo-second-order kinetics, R^2: linear correlation coefficient. Number of test points was 7 for CACR, CR (sample B) and AC (sample A) and 14 for PACR, CR (sample C) and AC (sample B). n.d: not determined.

Table 17. Pseudo-second-order model parameters and error for chemically modified carbon residue, carbon residue (sample C) and commercial activated carbon (sample B) in sulphate removal experiments.

Adsorbent	$q_{e(exp)}$ [mg g^{-1}]	$q_{e(cal)}$ [mg g^{-1}]	k_s [g mg^{-1} min^{-1}]	R^2	RMSE
MCR[a]	9.5	9.6	-	0.999	3.125
CR[b]	0.4	0.4	6.4	0.941	0.933
AC[c]	4.8	4.8	0.208	0.999	0.167

[a]MCR: chemically modified carbon residue, [b]CR: carbon residue (sample C), [c]AC: activated carbon (sample B), q_e: amount of sulphate adsorbed on the adsorbent (mg g^{-1}) at equilibrium, calculated or experimental value, k_s: rate constant for pseudo-second-order kinetics, R^2: linear correlation coefficient. Number of test points 12 for MCR and CR, and 13 for AC.

All studied adsorbents and adsorbates followed well pseudo-second-order kinetic model. In the Table 18 is presented results obtained in literature which indicates that most of adsorption of phosphates, nitrates and all sulphates pseudo-second-order kinetic model was found to fit well with the data.

Table 18. Kinetic studies of phosphate, nitrate and sulphate on different adsorbents obtained in literature.

Adsorbent	Adsorbate	Applicable kinetic model	Reference
H_2SO_4-treated activated carbon	Phosphate	First-order	Kumar *et al.* 2010
Iron hydroxide-eggshell waste	Phosphate	Pseudo-second-order	Mezenner & Bensamaili 2009
Chemically modified sugar beet bagasse	Nitrate	Pseudo-second-order	Demiral & Gündüzoğlu 2010
Modified wheat residue	Nitrate	Pseudo-second-order	Wang *et al.* 2007
$ZnCl_2$ treated coconut granular activated carbon	Nitrate	Pseudo-second-order	Bhatnagar *et al*. 2008
Zr(IV)-loaded sugar beet pulp	Nitrate	Pseudo-first-order	Hassan *et al*. 2010
Surfactant-modified palygorskite	Sulphate	Pseudo-second-order	Dong *et al.* 2011
Surfactant-modified coir pith	Sulphate	Pseudo-second-order	Namasivayam & Sureshkumar 2007
$ZnCl_2$ activated coconut coir pith	Sulphate	Pseudo-second-order	Namasivayam & Sangeetha 2008

6 Conclusions

6.1 Summary of the results

The first research question in this thesis was related to the physical and chemical properties of carbon residue and burning ashes and their potential utilisation applications. Properties of carbon residues from gasification processes and fly ash samples from burning processes are totally different and therefore, they will be best suited in opposite utilisation applications. Based on results presented in Papers I and II, carbon residues from biomass gasification have potential to be used as a fuel or carbon residues may be potential adsorbents if their adsorption properties can be enhanced by some chemical or physical treatment methods.

The second research question was that could the adsorption properties for carbon residue be enhanced by activation or modification methods. This was studied by activating carbon residue chemically (Papers III and IV) and physically (Paper V) or by chemical modification of carbon residue (Paper VI). In chemical activation studies, the highest specific surface area for carbon residue was obtained using $ZnCl_2$ as a chemical activating agent. In the physical activation procedure, the highest surface area was obtained using carbon dioxide as a physical activating agent. In Paper VI, the different chemical activation and modification methods were studied and the highest removal efficiency for sulphate removal was obtained using ferric chloride. In the Table 19 crucial properties for modified and activated carbon residue samples, unmodified carbon residues and commercial activated carbons are presented.

Table 19. Summary of the critical properties of studied adsorbents.

Parameter	Unit	CR 1[1]	CR 2[2]	PACR[3]	CACR[4]	MCR[5]	AC 1[6]	AC 2[7]
Carbon content	%	63.8	69.5	52.1	61.8	61.0	77.6	91.9
BET	$m^2 g^{-1}$	14.4	52.4	590	285	52.4	603	786
Pore size	nm	8.38	8.16	3.44	3.94	7.56	3.00	2.21
Pore volume	$cm^3 g^{-1}$	0.03	0.107	0.335	0.26	0.12	0.45	0.435

[1]CR 1: carbon residue (sample B), [2]CR 2: carbon residue (sample C), [3]PACR: physically activated carbon residue, [4]CACR: chemically activated carbon residue, [5]MCR: iron modified carbon residue, [6]AC 1: activated carbon (sample A), [7]AC 2: activated carbon (sample B).

The third research question in this thesis was that are those activated or modified carbon residues applicable adsorbents for phosphate, nitrate and sulphate removal. Chemically activated carbon residue was studied for phosphate, nitrate and sulphate removal, physically activated for phosphate and nitrate removal and chemically modified for sulphate removal. That was studied by batch adsorption experiments in which the effect of initial pH and initial concentration of anions were studied. The effect of adsorption time was studied at optimum initial pH and initial concentrations and those results were fitted to pseudo-first-order and pseudo-second-order kinetic models. Isotherm analysis was done by Freundlich and Langmuir model and later also by using Temkin and Dubinin-Radushkevich (D-R) isotherm models. The best fit for all studied adsorbents and adsorbates was obtained by using Langmuir model, and adsorption capacities are presented in Table 20. In that Table is also presented best fit kinetic model for the anion adsorption onto produced adsorbents which was in all cases pseudo-second-order. Carbon residue without pre-treatment process was used as a reference sample to evaluate the influence of activation or modification to the samples adsorption capacity and commercial activated carbon was also used as a reference sample. Based on these results, adsorption capacity can be clearly enhanced by chemical and physical activation or chemical modification methods. Chemically and physically activated carbon residue samples adsorb phosphate better comparing with commercial activated carbon whilst chemically modified carbon residue is better adsorbent for sulphate removal than activated carbon.

Table 20. Langmuir isotherm constants and the best fit kinetic model for the adsorption of phosphate, nitrate and sulphate onto produced adsorbents at room temperature.

Adsorbent/adsorbate	q_m [mg g^{-1}]	Kinetic model
Phosphate/CACR[a]	20.5	Pseudo-second-order
Nitrate/CACR[a]	7.97	Pseudo-second-order
Phosphate/PACR[b]	30.2	Pseudo-second-order
Nitrate/PACR[b]	11.2	Pseudo-second-order
Sulphate/MCR[c]	19.5	Pseudo-second-order
Phosphate/AC[d]	4.43	Pseudo-second-order
Phosphate/AC[e]	8.70	Pseudo-second-order
Nitrate/AC[d]	10.0	Pseudo-second-order
Nitrate/AC[e]	14.6	Pseudo-second-order
Sulphate/AC[e]	15.0	Pseudo-second-order

[a]CACR: chemically activated carbon residue, [b]PACR: physically activated carbon residue, [c]MCR: iron modified carbon residue, [d]AC: activated carbon (sample A), [e]AC: activated carbon (sample B)

6.2 Implications of the results

In the future, applications of thermo-chemical or hydro-thermal conversion of biomass will significantly increase. Carbon residue waste and some other residues with high carbon content are formed during these processes. Therefore, some reuse would be needed. Based on the results presented in this thesis, activation of carbon residue from thermo-chemical process is possible, and it can be used as an adsorbent for nitrate and phosphate removal. Maybe after that it would be suitable to be used as phosphorus and nitrogen rich forest fertiliser.

Based on results presented in this thesis, carbon residue can also be modified and after that it would be suitable adsorbent for sulphate removal. In the case of sulphate, removal challenges are different. Sustainable solutions for sulphate removal are needed e.g. in closed mines, where biodegradable adsorbents or biopolymers are needed for the continuous on-site sulphate removal for several years. However, above-mentioned ideas are not studied in this thesis.

6.3 Reliability and validity

The sampling of ashes and carbon residues was done every time in the same way. The sampling in combustion and gasification plants was done during normal process operating conditions. Two burning plants and one gasifier were in commercial use and one gasifier was pilot-plant. Samples from pilot plant were obtained in three different processes because durability is not well for carbon residue samples. This may cause small variations to results.

During the laboratory experiments, replication tests were done. During adsorption experiments, pH is an essential variable and therefore, pH was adjusted in the beginning of experiment and measured after experiments and based on those results, precipitation cannot be totally neglected and it may occur in addition to adsorption. In adsorption isotherm and kinetic calculations error analysis were done in two last Papers, V and VI.

Further, it should be kept in mind that the environmental authorities will finally decide on the allowable utilisation of the carbon residue waste studied in this thesis. One target of the research is to get information about unknown samples so that they could be utilised or their status could be changed from waste to by-product. That target is in compliance with European Union waste strategy, waste hierarchy and Finnish legislation.

6.4 Future work

In this thesis have been presented different techniques to characterise produced adsorbents, but in future also other characterisation techniques, e.g. methylene blue number, iodine number, analysis of surface functional groups, would be used. During adsorption experiments, the effect of temperature and effect of co-existing ions will also be studied and therefore, thermodynamic calculations will be done. The adsorption properties of samples in this study have been studied by a batch test, which is not practical on a large scale. The development of different adsorption tests like a flow-through test, where a solution contain a certain amount impurities is running through the adsorbent bed, would meet the industrial needs. This is already in preparation in our research group. Also the study with actual wastewaters will belong to the studies of the future.

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