Minna Pirilä

ADSORPTION AND PHOTOCATALYSIS IN WATER TREATMENT

ACTIVE, ABUNDANT AND INEXPENSIVE MATERIALS AND METHODS
MINNA PIRILÄ

ADSORPTION AND PHOTOCATALYSIS IN WATER TREATMENT
Active, abundant and inexpensive materials and methods

Academic dissertation to be presented with the assent of the Doctoral Training Committee of Technology and Natural Sciences of the University of Oulu for public defence in the Arina auditorium (TA105), Linnanmaa, on 8 May 2015, at 12 noon

UNIVERSITY OF OULU, OULU 2015
Abstract

Water contamination is a global problem and the growing utilization of limited water resources creates a need for efficient purification methods. Industrial effluents are polluting the natural waters, e.g., uncontrolled mining activities in developing countries have created numerous environmental hazards and different types of pollutants. This study focuses on novel adsorbents and photocatalytic materials in order to reach the aim of more efficient and affordable water treatment.

This thesis aimed at making active, efficient, and viable adsorbents out of waste materials, as well as using photocatalysis in water treatment for organic pollutants originating from different types of industries. Local Peruvian agro-waste was used as a precursor for activated carbon that was used in adsorption studies for single (As(V) and methylene blue, MB), and multicomponent mixtures (As(V)/Pb/Cd), and real polluted river water. An industrial intermediate product, hydrous TiO₂, was used for As(III)/As(V) removal. Photocatalytic materials included a commercial photoactive TiO₂ (P25), and tailor-made TiO₂ based nanofibers (NF) decorated with Pt/Pd.

The results show that the agro-waste based activated carbons show high potential as adsorbents (e.g., ~100% As(V) removal in 2 h). With the multicomponent solution there is evidently competition for the adsorption sites; Pb was removed most efficiently. The specific surface area and pore size distribution play an important role in MB adsorption, as with As(V) the ash content is the most influential parameter. The industrial intermediate product has a high adsorption capacity towards both As(III) and As(V) (over 96% removals in 4 h), and is promising for use in natural and wastewater treatment due to its adsorption properties, availability, low cost, and nontoxicity. Photocatalysis was found to be an efficient removal method for the pollutants tested, also in the diluted industrial wastewater matrix, e.g., diuron was removed 99% in 1 h. The NFs are promising for the efficient photocatalytic degradation of organic effluents in aqueous streams such as wastewaters originating from e.g., biofuel production or fine chemicals and pharmaceutical industry. This study provides new and valuable knowledge for the purification of waters, especially when aiming at developing inexpensive water treatment materials and methods for different applications.

Keywords: activated carbon, adsorption, arsenic, heavy metals, organic pollutants, photocatalytic degradation, photocatalytic oxidation, titanium dioxide, wastewater
Puhtaan veden puute on maailman laajuinen ongelma, ja raskasmetallien ja orgaanisten haittaaineiden päättymistä ympäristöön ja luonnovesiin voidaan vähentää hyvällä ja tehokkaalla teollisuuden jätevesien käsittelyllä. Uusia ja tehokkaita, ympäristön kannalta aina soveltuvia ja kestäviä vedenpuhdistustekniikoita tarvitaan erityisesti kehitysmaissa, joissa esim. kontrolloimaton kai- 
vosto aiheuttaa ympäristö- ja terveyshaittoja.

Työn kokeellisessa osassa valmistettiin perulaisesta maatalous jätteistä aktiivihiiltä kemiallisella aktivoinnilla, ja seurattiin niiden kykyä adsorboida haitta-aineita (As(V), Pb, Cd, metyleeninisini) yksi- ja monikomponenttiluoksista ja saastuneesta luonnovesestä (Puyango-Tumbesjo-
ti, Peru). Lisäksi tutkittiin teollisuuden välittömällä (TiO₂) aktiivisuutta arseeniin, As(III) ja As(V), adsorptiossa. Viimeisessä osiossa tutkittiin valokatalyyysiä organisten haitta-aineiden poistossa vesiliuoksista sekä kaupallisella TiO₂ P25-katalyytille että kokeellisilla Pd/Pt-dopatuilla TiO₂-nanokuiduilla.

Tulokset osoittavat, että paikallisesta raaka-aineesta valmistetut aktiivihiilet ovat hyvin potentiaalisia vedenpuhdistusmateriaaleja saavuttaen jopa 100% As(V) poistuman (2h). Adsor- 
boitavien ionien välillä on nähtävissä kilpailua monikomponenttiluoksissa; liyyn havaittiin poistuvan tehokkaimmin tutkittuissa olosuhteissa. Adsorbentin ominaispinta-ala ja huokosko- jakauma ovat tärkeitä tekijöitä metyleeninisiniin adsorptiossa, kun taas tuhkapitoisuudella on arse-
nin adsorptioon suurempi vaikutus. Teollisuuden TiO₂-välittömällä havaittiin olevan korkea adsorptiokapasiteetti sekä As(III)- että As(V)-spekseksii kohtaan saavuttaen yli 96% poistumatt (4h). Se on luopaava materiaali edelleen kehitettäväksi ja käytettäväksi esimerkiksi luonnoves- 
en ja jätteisten puhdistuksessa johtuen sen hyvistä adsorptio-ominaisuuksista, saatavuudesta, 
edullisuudesta ja myrkytömyydestä. Valokatalyyysiin havaittiin olevan toimiva menetelmä orga-
nisten molekyylin hajottamiseen, myös laimeasta teollisuuden jätteematriisista, esim. diuron 
poistui 99% tunnissa. Nanokuitujen tapauksessa aktiivinen metalli vaikutti merkittävämmin 
reaktion tehokkuuteen kuin ominaispinta-ala.

Tämä työ tarjoaa uutta ja tärkeää tietoa vesien puhdistukseen kun tavoitteena on löytää tehokas ja edullinen menetelmä erityyppisiin sovelluksiin.

Asiasanat: adsorptio, aktiivihiili, arseeni, jätteesi, orgaaniset haitta-aineet, raskasmetallit, titaanidioksidi, valokatalyyttinen hapetus
To my beloved
Acknowledgements

The research reported in this thesis was conducted at the University of Oulu, Faculty of Technology, Environmental and Chemical Engineering. First, I would like to sincerely thank my principal supervisor Professor Riitta Keiski who gave me the opportunity to work in her research group. Her guidance during these many years has been extremely valuable. I would like to express my gratitude to her for giving me the possibility to learn more by having responsibilities beyond my PhD thesis. I would also like to thank my supervisor Adjunct Professor Toivo Kuokkanen for introducing me to the interesting world of research and for advising me along the way. Official reviewers of this thesis, Professor Simo Pehkonen from the University of Eastern Finland and Professor Lucie Obalová from the Institute of Environmental Technology, VŠB-Technical University of Ostrava, are greatly appreciated for their efforts and valuable comments on this thesis.

I am truly grateful to Dr. Pentti Pekonen, Senior Manager at Kemira Oyj, who encouraged me to continue my studies by saying that true research work and careers often begin only after gaining a Ph.D. degree. In addition, I would like to thank my co-author Mika Martikainen, Business Development Manager at Outotec Oyj, for giving me valuable advice already during my Master’s thesis, from which my enthusiasm for research started.

I am thankful to my co-authors Dr. Satu Ojala, Dr. Mika Huuhtanen, Dr. Lenka Matejová, Dr. Gerardo Cruz, Dr. Mohammed Saouabe, Ritva Lenkkeri, Lic.Sc., and Prof. Krisztian Kordás who have given me advice and helped me with the writing process of some of the articles. My special thanks go to Dr. Junkal Landaburu, Dr. Satu Ojala, and Kaisu Ainassaari, Lic.Sc., for reading some parts of my thesis and providing valuable comments.

I would like to thank my colleagues, co-authors and friends Dr. Kati Oravisjärvi, Paula Saavalainen (my dear office-mate for five years), Marja Kärkkäinen, Dr. Timo Kulju, Dr. Prem Seelam, Bouchra Darif, Dr. Satu Pitkäaho, Kaisu Ainassaari, Piia Häyrynen, Anna Valtanen, Khawer Shafqat, and many others. You have worked with me and helped me in the laboratory, we have spent time together in conferences, meetings, and above all in the coffee-room and during the lunch hours. The working would be really hard and difficult without nice colleagues to have discussions and lunch with, and above all to take nice coffee breaks with, e.g. in Humus-kuppila. In addition, I am thankful to Ms. Kirsi Ahtinen and Mr. Jorma Pentinnen for helping a lot with the laboratory experiments and analyses. It has been a pleasure to work with all of you, and I thank you for all your help during
my studies. Above all, I warmly thank the whole Environmental and Chemical Engineering personnel for the nice working environment.

I would have not been able to conduct this work without financial support. First, I would like to acknowledge the Finnish Doctoral Programme in Environmental Science and Technology (EnSTe) for giving me a four year scholarship. I thank the Finnish Funding Agency for Innovation (Tekes), Academy of Finland and the Council of Oulu Region from the European Regional Development Fund as well as several industries and companies for financing the research projects I have been working for. In addition, I would like to thank Tauno Tönning Foundation, Maa- ja Vesiteknikan Tuki ry, KAUTE Foundation and Erkki Paasikivi Foundation for the highly appreciated financial support.

In addition to the work environment, I would like to thank Kati, Marja, Paula, Junkal, Veronica and Mari for nice moments also outside the University. Thank you for being such a good friends. I also want to thank my dear friends in Raase – Jenni, Johanna and Nina. Thank you for being who you are and sharing with me many great moments. Jenni has the power of always cheering me up when we talk. Thank you! In addition, I thank my dear friends in my neighbourhood Anne-Mari and Mervi. With you it is always so nice to spend time, and do some relaxing sports (that I aim to continue later this year!). Anne-Mari deserves a special thanks for taking our children to football training so many times allowing me to write this thesis during those valuable hours, thank you!

I wish to express my heartfelt gratitude to all my friends and relatives for their nice and relaxing company and for taking my mind of the work. Especially, I want to thank my sisters Marja and Maarit, you are important to me. And thank you my dear cousin Terhi for improving my press release! Without the support of my parents Marianna and Hannu Laine and parents-in-law Kaija and Mauri Pirilä this work would not have been possible. They have always been there for taking care of our children when needed. And thank you Kaija for your valuable help with the abbreviations and reference lists!

Without a family there would be no reason to achieve these goals. I want to thank my precious children Eemil and Pekko for bringing joy and happiness to our lives, and especially our third child who was the driving force to complete this thesis. My beloved husband Teemu has supported and encouraged me during all these years. He has told me that everything is possible as long as you decide so. Thank you!

Oulu, 10th of April, 2015

Minna Pirilä
# List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>at%</td>
<td>Atomic percent</td>
</tr>
<tr>
<td>b</td>
<td>Langmuir adsorption coefficient, related to the binding energy of the sorption system [l/mg]</td>
</tr>
<tr>
<td>c</td>
<td>Concentration [mg/l] or [μg/l] or [mol/l]</td>
</tr>
<tr>
<td>c&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Equilibrium concentration [mg/l] or [μg/l]</td>
</tr>
<tr>
<td>e⁻</td>
<td>Electron</td>
</tr>
<tr>
<td>E&lt;sup&gt;°&lt;/sup&gt;</td>
<td>Oxidation-reduction (redox) potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;AE&lt;/sub&gt;</td>
<td>Applied energy [kWh]</td>
</tr>
<tr>
<td>E&lt;sub&gt;EO&lt;/sub&gt;</td>
<td>Electric energy per order [kW min/l] or [kWh/l]</td>
</tr>
<tr>
<td>E&lt;sub&gt;SAE&lt;/sub&gt;</td>
<td>Specific applied energy [kWh /mol]</td>
</tr>
<tr>
<td>h</td>
<td>Initial adsorption rate [mg/(g·min)]</td>
</tr>
<tr>
<td>h&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Photogenerated hole</td>
</tr>
<tr>
<td>h&lt;sub&gt;v&lt;/sub&gt;</td>
<td>Irradiation energy in photocatalysis</td>
</tr>
<tr>
<td>k</td>
<td>Langmuir-Hinshelwood reaction rate constant</td>
</tr>
<tr>
<td>k&lt;sub&gt;F&lt;/sub&gt;</td>
<td>Freundlich adsorption constant, indicator of adsorption capacity</td>
</tr>
<tr>
<td>k&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Power-law kinetic model rate constant [µg/(mg&lt;sub&gt;ads&lt;/sub&gt;·min&lt;sup&gt;3&lt;/sup&gt;)]</td>
</tr>
<tr>
<td>k&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Pseudo-first order rate constant [1/h] or [1/min]</td>
</tr>
<tr>
<td>k&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Pseudo-second order rate constant [g/(mg·min)] or [g/(mg·h)]</td>
</tr>
<tr>
<td>K&lt;sub&gt;L&lt;/sub&gt;</td>
<td>Langmuir-Hinshelwood reaction equilibrium constant</td>
</tr>
<tr>
<td>K&lt;sub&gt;H&lt;/sub&gt;</td>
<td>Henry’s law adsorption equilibrium constant [l/mg]</td>
</tr>
<tr>
<td>k&lt;sub&gt;app&lt;/sub&gt;</td>
<td>Apparent pseudo-first order rate constant [1/h] or [1/min]</td>
</tr>
<tr>
<td>m</td>
<td>Mass [g]</td>
</tr>
<tr>
<td>M</td>
<td>Molar mass [g/mol]</td>
</tr>
<tr>
<td>M&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Metal ion</td>
</tr>
<tr>
<td>n</td>
<td>Mole [mol]</td>
</tr>
<tr>
<td>n&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Freundlich exponent, indicator of adsorption intensity</td>
</tr>
<tr>
<td>p</td>
<td>Partial pressure</td>
</tr>
<tr>
<td>P</td>
<td>Power [kW]</td>
</tr>
<tr>
<td>p&lt;sub&gt;r&lt;/sub&gt;/p&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Relative pressure</td>
</tr>
<tr>
<td>p&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Saturation vapour pressure</td>
</tr>
<tr>
<td>q&lt;sub&gt;t&lt;/sub&gt;</td>
<td>Loading/adsorption density at time t [mg/g] or [μg/mg]</td>
</tr>
<tr>
<td>q&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Adsorption density at equilibrium [mg/g] or [μg/mg]</td>
</tr>
<tr>
<td>q&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Adsorption capacity [μg/mg] or [mg/g]</td>
</tr>
<tr>
<td>r</td>
<td>Rate [1/h]</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant [J/(mol·K)]</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Correlation coefficient</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface</td>
</tr>
<tr>
<td>$S_{BET}$</td>
<td>Specific surface area [m$^2$/g]</td>
</tr>
<tr>
<td>$S_{meso}$</td>
<td>Mesopore surface area [m$^2$/g]</td>
</tr>
<tr>
<td>$t$</td>
<td>Time [s], [min] or [h]</td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>Half-life of a reaction [s] or [min] or [h]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature [K] or [$^\circ$C]</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume [l]</td>
</tr>
<tr>
<td>$V_{intruse}$</td>
<td>Intrusion pore volume [cm$^3$/g]</td>
</tr>
<tr>
<td>$V_{net}$</td>
<td>Net pore volume</td>
</tr>
<tr>
<td>$V_{micro}$</td>
<td>Volume of micropores [mm$^3$/g]</td>
</tr>
<tr>
<td>$V_p$</td>
<td>Total pore volume [cm$^3$/g]</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percent</td>
</tr>
<tr>
<td>$x$</td>
<td>Kinetic order of a reaction following the power-law kinetic model</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Porosity [%]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength [nm]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density [kg/l]</td>
</tr>
<tr>
<td>$\rho_{Hg}$</td>
<td>Bulk density [g/cm$^3$]</td>
</tr>
<tr>
<td>$\rho_{He}$</td>
<td>Skeletal density [g/cm$^3$]</td>
</tr>
</tbody>
</table>
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>Annual average</td>
</tr>
<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>AMD</td>
<td>Acid mine drainage</td>
</tr>
<tr>
<td>AOP</td>
<td>Advanced oxidation process</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BAT</td>
<td>Best available technique</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller, a multilayer adsorption isotherm model</td>
</tr>
<tr>
<td>BJH</td>
<td>Barret-Joyner-Halenda method</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
</tr>
<tr>
<td>BP</td>
<td>Bisphosphonates</td>
</tr>
<tr>
<td>BPA</td>
<td>Bisphenol A</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>CPH</td>
<td>Cocoa pod husk</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection by-product</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>EDC</td>
<td>Endocrine disrupting chemical</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectrometer</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>EQS</td>
<td>Environmental quality standard</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>GFH</td>
<td>Granular ferric hydroxide</td>
</tr>
<tr>
<td>GF-AAS</td>
<td>Graphite Furnace Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>GS</td>
<td>Ice-cream bean seeds</td>
</tr>
<tr>
<td>GS-AC</td>
<td>Ice-cream bean seeds based activated carbon</td>
</tr>
<tr>
<td>GS-RM</td>
<td>Ice-cream bean seeds raw material</td>
</tr>
<tr>
<td>IARC</td>
<td>International Agency for Research on Cancer</td>
</tr>
<tr>
<td>ICPF</td>
<td>Institute of Chemical Process Fundamentals</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometer</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International union of pure and applied chemistry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>MAC</td>
<td>Maximum allowable concentration</td>
</tr>
<tr>
<td>MB</td>
<td>Methylene blue</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiber</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>NTP</td>
<td>Normal temperature and pressure; 20 °C (293 K), 1 atm (101,325 kPa)</td>
</tr>
<tr>
<td>PAH</td>
<td>Polyaromatic hydrocarbon</td>
</tr>
<tr>
<td>PCOU</td>
<td>$p$-Coumaric acid</td>
</tr>
<tr>
<td>pH$_{PZC}$</td>
<td>pH of the point of the zero charge</td>
</tr>
<tr>
<td>PHA</td>
<td>Phthalic anhydride</td>
</tr>
<tr>
<td>POP</td>
<td>Persistent organic pollutant</td>
</tr>
<tr>
<td>POE</td>
<td>Point of entry</td>
</tr>
<tr>
<td>POU</td>
<td>Point of use</td>
</tr>
<tr>
<td>PSi</td>
<td>Nanostructured silicon</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of the zero charge</td>
</tr>
<tr>
<td>RMS</td>
<td>Red mombin seeds</td>
</tr>
<tr>
<td>RMS-AC</td>
<td>Red mombin seeds based activated carbon</td>
</tr>
<tr>
<td>RMS-RM</td>
<td>Red mombin seeds raw material</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>RX$_{ads}$</td>
<td>Adsorbed substrate</td>
</tr>
<tr>
<td>SEM-EDX</td>
<td>Scanning electron microscopy coupled with energy dispersive X-ray</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>UV-A</td>
<td>Ultra violet A</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra violet visible</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZVI</td>
<td>Zero valent iron</td>
</tr>
</tbody>
</table>
List of original papers

This thesis is based on the following publications, which are referred throughout the text by their Roman numerals:


II Pirilä M, Cruz GJF, Ainassari K, Gomez MM, Matějová L & Keiski RL. Removal of As(V), Cd(II) and Pb(II) from multicomponent aqueous systems using activated carbons. Manuscript.


Pirilä was the corresponding author of papers II, IV, V and VI. In papers I and III, Pirilä’s contribution was planning the contents of the publication together with the first author, conducting the experimental work related to material preparations together with the first author and designing and conducting the adsorption experiments with both arsenic and methylene blue. In addition, Pirilä wrote the sections related to adsorption and edited the articles together with the first author.
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Tiivistelmä

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1 Introduction and aims

Water contamination is today a major problem globally and the growing utilization of limited water resources creates a need for efficient purification methods. Water resources can be divided into renewable and non-renewable resources. Renewable water resources represent the long-term average annual flow of rivers (surface water) and groundwater, whereas non-renewable water resources are groundwater bodies (deep aquifers) that have a negligible rate of recharge on the human time-scale and therefore can be considered non-renewable (FAO 2003). The European Union has launched a thematic strategy on the sustainable use of natural resources, such as water, with the aim of reducing their depletion and their pollution. The overall objective of the strategy is to reduce the negative environmental impacts generated by the use of natural resources in a growing economy (European Commission 2005).

Water has a major role in the wellbeing of all human beings. In western countries people use over 300 litres of fresh water per person per day, on average (Data 360 2014). However, 768 million people do not have access to safe, clean drinking water (Unicef 2014). In addition, 2.5 billion people lack improved sanitation facilities. The effects of water scarcity or water shortage are very severe and therefore, producing clean water is one of the main needs worldwide.

More than 600 organic and inorganic pollutants have been reported in water along with biological pollutants (Gupta & Ali 2013). Among these pollutants, toxic heavy metals and metalloids as well as organic pollutants are a serious concern for human health and the environment. Moreover, metal ions are not biodegradable or bio-transformable and, hence, exist in the environment for long time. These contaminants are present, for example, in drinking water sources as well as in industrial waste streams, and must be controlled to an acceptable level according to environmental regulations worldwide.

Arsenic in particular is a global problem since over 130 million people are exposed to arsenic in drinking water (Ravenscroft et al. 2009) above the World Health Organization’s drinking water standard of 10 µg/l (WHO 2011). In addition, it has been estimated that over 220 million people are exposed to arsenic contamination from drinking water or food (Murcott 2012). Naturally occurring arsenic contamination of groundwater has been found in at least 70 countries worldwide, however, most of the people at risk of arsenic exposure live in Asia (Unicef 2013).
Industrial water treatment is important, since industrial effluents are often discharged straight into nature and the contaminants may end up into fresh water sources such as rivers, lakes and ground water. In rural areas, people are consuming these waters without any purification. For example, uncontrolled and illegal mining activities in developing countries have created numerous environmental hazards and different types of pollutants. In an abandoned mine area of Mkpuma Akpatakpa, South-East Nigeria, arsenic concentrations are high (0.1 to 0.492 mg/l) in both surface and groundwater, nevertheless the people of this area are continuously using the water (Wazoh et al. 2014). In addition, mercury is a serious and increasing environmental and public health problem in the gold mining region of Madre de Dios, Southeast of Peru. E.g. 78% of adults in Puerto Maldonado had hair mercury concentrations above the international mercury reference limit of 1.1 µg/g for human hair (Carnegie Institution for Science 2013, Nielsen & Grandjean 2000).

Thus, new, economically feasible, more efficient methods for pollution control and prevention as well as for drinking water treatment are needed for environmental protection, and the discharge of effluents into the environment must not affect human health, natural resources or the biosphere.

1.1 Metals and metalloids in aqueous solutions

Metallic elements are found in all living organisms and some of them are essential for humans, e.g. as stabilizers of biological structures, components of control mechanisms and activators or components of redox systems. However, these essential elements might be toxic when present in excess and some of the heavy metals and metalloids are already highly dangerous due to their effects on human health in low quantities (Nordberg et al. 2008). Table 1 presents the drinking water guidelines and the toxicity to humans of selected heavy metals and metalloids and their inorganic compounds.

<table>
<thead>
<tr>
<th>Metal / metalloid</th>
<th>Characteristics</th>
<th>Drinking water guideline</th>
<th>Toxic symptoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>Neurotoxicant Carcinogenic (group 1) occupational exposures during aluminium production</td>
<td>200 µg/l&lt;sup&gt;2,3&lt;/sup&gt;</td>
<td>Neurotoxic effects, lung fibrosis (pulmonary fibrosis also called aluminosis), Gastrointestinal symptoms, bone remodeling inhibition by high doses of aluminium, occupational exposures during aluminium production cause cancer of bladder, and of the lung.</td>
</tr>
<tr>
<td>Antimony</td>
<td>SbO₃ possibly carcinogenic (Group 2B)</td>
<td>20 µg/l&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Symptoms of irritation in the respiratory tract (industrial exposure). Long-term exposure: pneumoconiosis, occasionally in combination with obstructive lung changes. Effects on the heart, even fatal, have been related to long-term industrial exposure to antimony trioxide. Acute antimony poisoning: vomiting, nausea, and diarrhoea. Skin eruptions.</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Carcinogenic (group 1)</td>
<td>10 µg/l</td>
<td>Skin lesions such as dermatoses, hyperpigmentation, hypopigmentation that may ultimately lead to skin cancer. Effects on the nervous system, e.g. peripheral nervous disturbance, and on the heart and circulatory system e.g. abnormal electrocardiograms, peripheral vascular disease. Haematological changes such as anaemia and leukopenia. Internal cancers of lung, bladder, kidneys and liver.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Carcinogenic (group 1)</td>
<td>3 µg/l&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Acute gastrointestinal effects with concomitant diarrhoea and vomiting. Disturbance of calcium metabolism, bone injuries such as osteoporosis and osteomalacia. Cancer of the lungs and might also cause cancers of the kidney and the prostate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 µg/l&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Chromium (III)</td>
<td>Essential nutrient</td>
<td>Moderate toxicity from oral exposure: respiratory tract is the major target organ for Cr (III) toxicity.</td>
<td></td>
</tr>
<tr>
<td>Chromium (VI)</td>
<td>Carcinogenic (group 1)</td>
<td>50 µg/l (for total Cr)</td>
<td>Allergic skin reactions. Induced mutations, chromosomal aberrations, DNA damage. Cancer of the lungs, and might cause cancer of the nose and nasal sinuses and cancers of the skin and muscles.</td>
</tr>
<tr>
<td>Metal / metalloid</td>
<td>Characteristics</td>
<td>Drinking water guideline</td>
<td>Toxic symptoms</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Possibly carcinogenic (group 2B)</td>
<td>-</td>
<td>Affects the respiratory system (asthma and lung cancer together with tungsten carbide), hematopoietic system (increases blood volume and total erythrocyte number), the myocardium, and possibly the reproductive system (mutagenic effects).</td>
</tr>
<tr>
<td>Copper</td>
<td>Essential nutrient</td>
<td>2.0 mg/l</td>
<td>High doses cause stomach and intestinal distress, nausea, liver and kidney damage and anaemia.</td>
</tr>
<tr>
<td>Iron</td>
<td>Essential nutrient</td>
<td>200 µg/l&lt;sup&gt;2,3&lt;/sup&gt;</td>
<td>Chronic overload damages organs such as the heart and liver, and without treatment leads to death.</td>
</tr>
<tr>
<td>Lead</td>
<td>Probably carcinogenic (group 2A)</td>
<td>10 µg/l</td>
<td>Accumulates in the teeth and skeleton. Toxic effects to central and peripheral nervous system, blood, kidney, cardiovascular, endocrine and immune systems, gastrointestinal tract, and male reproduction system. Genetic toxicity (passes through the placenta). Might cause cancers of the lungs, stomach and the kidneys.</td>
</tr>
<tr>
<td>Manganese</td>
<td>Essential nutrient</td>
<td>50 µg/l&lt;sup&gt;2,3&lt;/sup&gt;</td>
<td>Long-term exposure to increased concentrations causes neurological and neurobehavioral effects.</td>
</tr>
<tr>
<td>Mercury</td>
<td>Highly toxic</td>
<td>6.0 µg/l&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Accumulates in the brain causing neurological signs (unspecific psychoasthenic and vegetative syndrome), behavioural and personality changes, loss of memory, insomnia. Damages kidneys.</td>
</tr>
<tr>
<td>Nickel</td>
<td>Carcinogenic (group 1)</td>
<td>70 µg/l&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Acute poisoning causes headache, vertigo, nausea, vomiting, nephrotoxic effects, pneumonia, and pulmonary fibrosis. Chronic effects include rhinitis, sinusitis, nasal septum perforations, and asthma. Nickel has the potential to cause heart and liver damage and inflammation of the skin. Causes cancers of the lung and of the nasal cavity and paranasal sinuses.</td>
</tr>
<tr>
<td>Palladium</td>
<td>Catalyst</td>
<td>-</td>
<td>Swelling of the lips and cheeks, stomatitis, oral lichen planus, itching, dizziness, asthma, and chronic urticaria.</td>
</tr>
<tr>
<td>Platinum</td>
<td>Catalyst</td>
<td>-</td>
<td>Irritation of the eyes and upper respiratory tract, asthma.</td>
</tr>
</tbody>
</table>
Selenium | Essential nutrient | 40 µg/l\(^1\) | 10 µg/l\(^2\) | In excess concentrations may cause hair and fingernail loss, skin lesion and depigmentation. Damages the central nervous system, liver, heart, and lungs.

Zinc | Essential nutrient | - | Ingestion of high concentrations cause nausea, abdominal cramps, vomiting, tenesmus, and diarrhoea. Very high levels of zinc can damage the pancreas and disturb the protein metabolism and cause arteriosclerosis.

\(^1\)WHO, 2011; \(^2\)European Commission DIRECTIVE 98/83/EC; \(^3\)Quality recommendation, \(^4\)WHO 2003

Among different industrial sectors, mining and metallurgical industries are generating wastewaters and effluents with heavy metals and metalloids that have the tendency to accumulate in nature. Arsenic (As), cadmium (Cd) and lead (Pb) are especially detrimental from the environmental point of view due to their presence in several fresh water sources worldwide.

Long-term exposure of arsenic causes pigmentation changes and then skin lesions, hard patches on the palms of the hands and soles of the feet. Arsenic can also cause cancers of the skin, bladder and lungs, as well as kidney, liver and prostate gland (WHO 2012). Arsenic and its inorganic compounds have been classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Group 1), dimethylarsinic acid and monomethylarsonic acid are possibly carcinogenic to humans (Group 2B), and arsenobetaine and other organic arsenic compounds not metabolized in humans, are not classifiable as to their carcinogenicity to humans (Group 3) (IARC 2012).

Arsenic occurs in the environment both in organic and inorganic compounds in two different oxidation states of trivalent, arsenite As(III), or pentavalent, arsenate As(V), and their relative distributions are influenced by pH and redox conditions. The As(V) species predominates in oxidizing environments. At pH from 4 to 9, As(V) exists as two oxyanions of arsenic acid (H\(_2\)AsO\(_4^-\) or HAsO\(_4^{2-}\)), the first one dominating in acidic and the second one in basic conditions. Under moderately reducing conditions, As(III) is thermodynamically stable, and exists mainly as a non-ionized arsenous acid (H\(_3\)AsO\(_3\)) at pH below 9. At above pH 7 anionic species (H\(_2\)AsO\(_3^-\)) also exist (Smedley & Kinniburgh 2002). As(III) is significantly more toxic and more mobile than As(V). It is also more difficult to
remove by conventional treatment methods. Therefore, most purification techniques require pre-oxidation of As(III) to As(V) for effective arsenic removal, causing added complexity.

Cadmium exists only in +2 oxidation state in aqueous solutions (Baes & Mesmer 1976) and the concentrations in unpolluted water are usually below 1 µg/l. Cadmium occurs in the earth’s crust at levels of 0.1–0.5 ppm and is commonly associated with zinc, lead, and copper ores (Morrow 2001). Naturally cadmium can be released to the environment from volcanic eruptions, forest fires, generation of sea salt aerosols, or other natural phenomena (EPA 1985, Morrow 2001, Shevchenko et al. 2003). The main anthropogenic sources of cadmium in the environment include mining and refining of nonferrous metals, manufacture and application of phosphate fertilizers, fossil fuel combustion, and waste incineration and disposal (ATSDR 2012).

Cadmium exposes human health to severe risks and it has been classified by the IARC as carcinogenic to humans (Group 1) (IARC 1993). It is highly toxic, possibly because it forms a strong bond with sulphur and hence can displace essential metal ions i.e. Zn$^{2+}$ and Ca$^{2+}$ from the binding sites of certain enzymes (Klaassen 2001 in Memon et al. 2007). Chronic exposure of cadmium results in kidney dysfunction and high levels of exposure will result in death (WHO 2010a). In addition, long-term exposure to cadmium has the potential to cause damage to the liver, bone and blood (Nordberg et al. 2008). The drinking water guideline for cadmium set by WHO is 3 µg/l (WHO, 2011), whereas in Finland the drinking water guideline is a bit higher, 5 µg/l, set by the Ministry of Social Affairs and Health, Finland (2000).

Lead occurs naturally in the environment, and its minerals are found in association with zinc, copper, and iron sulphides as well as gold, silver, bismuth, and antimony minerals. Naturally occurring lead is found to have the oxidation states 0, +2 and +4. Pb$^{2+}$ is the most common one and it has the most complex hydrolysis behaviour in aqueous solutions (Baes & Mesmer 1976). Lead released from natural sources, such as volcanoes, windblown dust, and erosion, are minor compared with releases from human activities, which have increased the environmental levels of lead more than 1000-fold over the past three centuries. Industrial sources responsible for putting lead into the environment can result from the effluents from mining lead and other metals, and from factories that make or use lead, lead alloys, or lead compounds. (ATSDR 2007)

Lead in the human body is distributed to the brain, liver, kidney and bones. It is stored in the bones and teeth, where it accumulates over time. Lead can cause
central nervous system damage and it can also damage the kidneys, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms of lead are anaemia, insomnia, headache, dizziness, irritability, weakness of the muscles, hallucinations, and renal damage (WHO 2010b). The IARC has classified inorganic lead compounds as probably carcinogenic to humans (Group 2A) (IARC 2006). The drinking water guideline for lead is 10 µg/l (WHO 2011).

1.2 Organic contaminants in aqueous solutions

Organic pollutants in water are defined as agents that degrade water quality, and form threats to human health and aquatic life. Organic water contaminants mainly include food processing waste, disinfection by-products (DBPs) found in chemically disinfected drinking water, volatile organic compounds (VOCs), pesticides including insecticides and herbicides, tree and bush debris from logging operations, polyaromatic hydrocarbons (PAHs), dyes, phenols, and detergents. Persistent organic pollutants (POPs) are resistant to environmental degradation and have been observed to persist in the environment, to be capable of long-range transport, bioaccumulation in human and animal tissue and biomagnification in food chains and to have potential significant impacts on human health and the environment. Many POPs are currently used as pesticides. Others are used in industrial processes and in the production of a range of goods such as solvents, polyvinyl chloride, and pharmaceuticals. (Gupta & Ali 2013)

Diuron is a commonly used herbicide in agriculture (Rosas et al. 2014), however the use of it leads to contamination of the aquatic environment through soil leaching, and it is persistent when applied in high dosages to the soil. Diuron is considered a Priority Substance by the European Commission (2008) DIRECTIVE 2008/105/EC among 33 substances of priority concern at Community level, due to their widespread use and their high concentrations in rivers, lakes and coastal waters. The maximum allowable concentration in surface waters has been set to 1.8 µg/l. Most of the commercial products containing diuron are classified as harmful chemicals, as they are generally considered dangerous for aquatic life, flora, and for humans. For example, it may damage developing foetuses and congenital malformations have been reported. Diuron is toxic to photosynthetic organisms, therefore, it is important to eliminate diuron from wastewater. (Pohanish 2012, Tomlin 1997 in Oturan et al. 2008, Vieno et al. 2007, Viltanen 2010, Wintgens et al. 2008)
$p$-Coumaric acid (PCOU) is a phenolic compound typically found in agro-industrial effluents, such as olive pressing and wine distillery wastewaters. PCOU is especially a problem in southern Europe in the Mediterranean region (Minh Pham et al. 2008). PCOU belongs to a range of phenolic components such as gallic, caffeic and vanillic acids which are known to strongly inhibit the conventional biological treatment of wastewaters (Mantzavinos et al. 1996). Due to the high chemical oxygen demand (COD) ranging from 80 to 200 g/l these effluents cause serious environmental threats with inadequate treatment (Baransi et al. 2012). Phenolic compounds are potential contributors of the toxicity and antibacterial activity of agricultural wastewaters, and thus their removal is of high importance.

Phthalic anhydride (PHA) is released into the environment from the chemicals industry, mainly from the manufacturing of PHA or from the production of plasticizers, surfactants and pesticides, which all use phthalic acid esters. Phthalic acid esters have been identified as environmental pollutants that are refractory to microorganisms and also considered as endocrine disrupting chemicals (EDC) (EPA 1994, Abdel daiem et al. 2012). PHA is also used to make polyesters, alkyl resins, halogenated anhydrides, phthalocyanine pigments, dyes, perfumes, pharmaceuticals, tanning and curing agents, solvents, insect repellents and various chemical intermediates (Sin et al. 2011). The major sources of these releases are process off-gases and industrial effluents (EPA 1994). In addition, the plasticizer might migrate from a plastic item to the medium (gas, liquid or solid) that it is in contact with (Abdel daiem et al. 2012). It is known, that exposure to phthalic anhydride produces irritation of the eyes, skin and respiratory tract, and lung sensitization in humans and animals (EPA 1994). In addition, repeated or prolonged skin contact may cause dermatitis, skin sensitization, and allergies. In animals PHA causes liver and kidney damages (Pohanish 2012).

Bisphenol A (BPA) is one of the most studied high production volume chemicals used for the manufacture of various polycarbonate and epoxy resins and as a stabilizing material or antioxidant for many types of plastics such as polyvinyl chloride (Makris et al. 2013, Miyakoda et al. 2000). BPA is found in compact disks, food can linings, thermal papers, adhesives, plastic drink bottles and containers, composite dental fillings, sheathing of electrical parts and numerous personal care products including, body and face lotions, shampoos, conditioners etc. (Chiang et al. 2004, Dodson et al. 2012). Leaching of BPA into the environment into surface waters, for example, is possible during manufacturing processes, but also by migration from the end products (Jia et al. 2012). The annual global production of BPA has reached over 4.6 million tonnes in 2012 (Merchant Research & Consulting
BPA is widely used, even though it is known to be an endocrine disrupting chemical due to its estrogenicity. The EDCs exert physiological effects by resembling the natural hormone or by interfering with the hormone's production, release, metabolism and elimination (Selvaraj et al. 2014). In addition, BPA produces a typical contact dermatitis, i.e. inflammation of the skin including redness and edema, followed by crusting and scaling. Furthermore, probable symptoms might include nausea, burning of mouth, throat, and stomach, vision disturbances, irregular breathing and pulse, dizziness, fainting, coma, and possible death. (Pohanish 2012)

VOCs, such as butanol, are commonly used in the chemicals industry, for example, in the manufacturing of a wide variety of products such as fuels, pharmaceuticals and adhesives. A strict definition for VOCs determined by Derwent (1995) is that they refer to compounds present in the atmosphere as vapours but under normal temperature and pressure conditions (NTP) would be liquids or solids. VOCs have been proven to be toxic and some of them carcinogenic, mutagenic and teratogenic (García et al. 2013, Ojala et al. 2011, Hussain et al. 2011). Furthermore, VOCs contribute to global warming, the formation of ground level ozone and photochemical smog, as well as the depletion of the ozone layer (Komilis et al. 2004). Butanol, for example, has been widely studied in the gas phase, however only a few studies are reported for aqueous phase reactions, although it is a common effluent in wastewaters. However, the reclamation of butanol has been studied e.g. by García (2009) via pervaporation from aqueous solutions.

Among other organic contaminants, effluents containing colouring agents cause significant environmental harm. The major sources of dyes in the environment are various dyestuff manufacturing and the industries which use them, such as textile, leather, printing, petroleum, cosmetics, paints, pesticide and pharmaceutical industries. Usually, the dyes are not entirely used, and it is estimated that approximately 10-60% of reactive dyes are lost during textile dyeing, and the dye house wastewater can contain even 2 g/l of the reactive dye (Alinsafi et al. 2007, Allègre et al. 2006, Rosa et al. 2015). The dye-containing wastewaters discharged into the aquatic environment can cause environmental problems because when the dyes give the water an undesirable colour, they might inhibit the light penetration and consequently prevent the photosynthesis of aqueous flora (Al-Degs et al. 2008, Cardoso et al. 2011a, Cardoso et al. 2011b, Wang et al. 2005). Thus, textile wastewaters are considered as the most polluting among all industrial sectors when considering both wastewater compositions and the discharge volumes.
(Tehrani-Bagha et al. 2010). In addition, many dyes are toxic/carcinogenic and thus harmful for humans and for the environment, e.g. methylene blue, used extensively for dying of cotton, wool and silk, causes burning effects on the eyes, nausea, vomiting and diarrhoea (El-Sharkawy et al. 2007). The treatment of the effluents from the textile and dyestuff industries is challenging because the conventional wastewater treatment techniques are inadequate for the complete decolourization and removal of dye residues. This is due to the fact that dyes have complex aromatic molecular structures and thus they are stable and extremely resistant towards biological or chemical processing. (Tehrani-Bagha et al. 2010, Nguyen & Juang 2013)

1.3 Objectives and scope

There is a substantial need for innovative environmental technologies, and clean, cost-effective and sustainable industrial processes to meet the global efforts on combating pollution. New cost effective and easily usable techniques for water treatment are needed especially in the developing countries. Therefore, this study has focused on studying adsorbents and photocatalysts for the removal of both inorganic and organic pollutants from water in order to reach the aim of more efficient water treatment with the following main objectives:

1. To study the applicability of waste materials, e.g. abundant rural local agricultural waste and industrial side products, as precursors for activated carbon and as adsorption materials, with the aim of making valuable products out of waste.

2. To study the utilization of those materials in more sustainable water treatment, with the aim of overcoming the need for extra chemicals (as is the case with the traditional methods e.g. coagulation/precipitation).

3. To study the use of photocatalysis in water treatment with the aim of degrading and even mineralizing organic pollutants.

Different tasks have been performed in order to reach the aims of the thesis. The water treatment methods selected for this research are adsorption and photocatalysis. Both these techniques are used in ambient conditions (temperature and pressure), and no extra chemicals are needed. The results of the thesis have been published in the refereed scientific journal articles shown in Figure 1.
Papers I-IV are related to adsorption as a water treatment method for removing both inorganic and organic contaminants from polluted waters, both synthetic and real natural waters. In papers I-III biomass based activated carbons are developed and used as adsorption materials, and in Paper IV TiO$_2$ based adsorption material is studied. In papers V and VI the abatement method studied is photocatalysis, which is used to remove organic pollutants from both synthetic and industrial wastewaters, by using TiO$_2$ as the photocatalyst.

Papers I-III study the production and use of activated carbon made from different raw materials, namely carbonaceous biomass originating from agriculture. The adsorption material development research is done in close collaboration with the National University of Tumbe, and National University of Engineering, Lima, Peru. There are serious drinking water problems in Peru, e.g. the Rimac river that runs through Lima has arsenic in excess of the WHO recommended limit (George et al. 2014), and the Tumbes River is polluted by different metals and metalloids, mainly arsenic, cadmium and lead, originating from illegal mining activities in

Fig. 1. Scope and contribution of the refereed articles to the thesis.
Ecuador, north of Peru. These pollutants cause serious problems to the local people in rural areas where they consume the river water without any treatment at all. Therefore, it is important to find inexpensive and eco-efficient treatment methods for the polluted water both in the urban and rural areas. When planning the production of activated carbon from biomass there are a lot of variables to be taken into account, including e.g. how much of the biomass is available, how it is grown, whether it needs to be fertilized, how easy it is to handle and activate, the activation costs, etc. In addition, the nature of the raw material is important, since it might have catalytic properties due to its acidity or basicity or other inherently existing property (such as a metal/surface group that may act as an active site).

In papers I and II, cocoa pod husk (Theobroma cacao) was chosen as the raw material for activated carbon due to its availability in Peru. The raw material was activated with different chemical activation agents including zinc oxide, potassium hydroxide and potassium carbonate. After activation, the materials were characterized for physico-chemical properties as well as for removal of inorganic (arsenic, lead and cadmium) contaminants from aqueous solutions both in synthetic and real polluted river water by means of short term batch kinetic experiments.

For the final use for water treatment in rural areas, it is important to select the best possible raw materials from the wide variety of different biomass available. Therefore, in Paper III, two different raw materials, red mombin (Spondias purpurea L.) and ice-cream bean (Inga edulis) seeds, were studied in order to find out the effect of the raw material on the activity of the activated carbon. Here, only the best method from the previous chemical activation methods was selected, i.e. the ZnCl₂ activation. The produced activated carbons were again characterized and tested for both inorganic (arsenic) and organic (methylene blue) adsorption from aqueous solutions.

The purpose of Paper IV was to study the applicability of an industrial intermediate product, a mixture of titanium hydroxide and titanium dioxide for the removal of aqueous arsenic. Dissolved arsenic in drinking water is a global concern as it causes serious health problems especially in highly populated areas including e.g. Bangladesh. The titanium dioxide material is common, inexpensive, and nontoxic, making it an attractive choice for drinking water purification. The kinetics and equilibrium of removing both primary inorganic arsenic forms, As(III) and As(V), were studied.

Paper V aimed to study the photocatalytic degradation of four organic pollutants originating from different types of industry both in synthetic solutions and in diluted industrial wastewater matrix. The wastewater was collected from a
pharmaceutical industry and diluted before the experiments in order to represent wastewater that has been discharged into natural waters. The pollutants were diuron (pesticide), \( p \)-coumaric acid (agro-industrial wastewaters), bisphenol A and phthalic anhydride (plasticizers), which all are widely used and cause significant health and environmental problems. The commercial photocatalyst Aerioxide P25 (formerly Degussa) was selected as the catalyst due to its known activity and properties.

The aim of Paper VI was to study the photocatalytic performance of novel tailor-made TiO\(_2\) nanofiber catalysts on water purification by photocatalytic degradation of butanol, a typical solvent in fine chemicals/pharmaceuticals industry. The activities were compared to a commercial TiO\(_2\) photocatalyst Degussa P25. Butanol is widely studied in the gas phase, however it is a common pollutant in wastewaters, and therefore also the aqueous phase studies are important.

To conclude, ensuring reliable access to clean and affordable water is a worldwide challenge that needs new water resource management approaches and technological improvements. It is extremely important to find low-cost water treatment methods especially for developing countries, where the economic benefits are usually more important than the environmental and health issues. Therefore, if a local low-cost material can be utilized in the water treatment, it will not only bring economic benefits but also decrease the environmental load and improve people’s health and well-being.
2 Water treatment

Various methods for water treatment have been developed and can be classified on the basis of physical, chemical, electrical, thermal and biological principles. These methods include screening, centrifugation and filtration, membrane techniques (micro-, ultra-, and nanofiltration, reverse osmosis), sedimentation, crystallization, and gravity separation, precipitation, flotation, oxidation, evaporation, coagulation, solvent extraction, distillation, ion exchange, electrolysis, adsorption, electrodialysis, etc. (Gupta & Ali 2013)

2.1 Drinking water treatment in rural areas

The WHO has suggested that one potential solution to poor-quality household drinking water is treatment at the point of use (POU), which typically describes the treatment procedures that can be implemented at the household-level. These procedures include e.g. disinfection with chlorine or other chemical disinfectants, sunlight or ultra-violet (UV) lamps, various filters, or flocculation-disinfection formulations. (WHO 2007)

Sobsey et al. (2008) have reviewed some of the POU technologies that have proven to be effective in microbiological efficacy and diarrhoeal disease reduction, including chlorination with safe storage, combined coagulant-chlorine disinfection systems, solar disinfection, ceramic filters, and biosand filters. In addition, Ehdai et al. (2014) have developed a silver-infused ceramic tablet for long-term water disinfection as a new POU technology. The tablet is made of clay, water, sawdust, and silver nitrate, and when dropped into a household water storage container, it releases silver ions that disinfect microbial pathogens. The above mentioned methods are designed primarily to prevent diarrhoea and other water borne deceases. Thus, for water contaminated with heavy metals and metalloids, these methods might not be adequate enough and more specific treatment is needed. For example, reverse osmosis (RO) is a common POU technique for removing heavy metals and metalloids. Ion exchange and adsorption are also other potential techniques.

Techniques for removing arsenic from water either at the point of use (i.e. at a single tap) or at the point of entry (POE, i.e. the whole house) include adsorptive media, reverse osmosis, distillation, and anion exchange. E.g. 86% of total arsenic can be removed by RO (Bufa-Dörr et al. 2012). AdEdge Technologies Inc. (2009) provides water treatment products to remove arsenic from drinking water in
individual households. The system uses Bayoxide® E33 adsorption media which is one of the best media for removing both As(III) and As(V) according to several United States Environmental Protection Agency (EPA) demonstration sites, third-party comparison tests, and successful residential and community water systems across the U.S.A. (AdEdge Technologies Inc. 2009).

Mansoor Ahammed and Meera (2010) have studied a dual media filter consisting of manganese oxide-coated and iron hydroxide-coated sand for the simultaneous removal of heavy metals and bacteria from water with encouraging results; bacteria and zinc with the removal greater than 99% and 96%, respectively.

However, more research is needed, and inexpensive, effective small scale treatment units for developing countries and rural areas need to be further developed in order to develop the technology to be able to treat several types of pollutants simultaneously. In addition, the process should be simple to use, effective for the long-term, reduce risk of recontamination, and also it should be socially acceptable, scalable, and affordable, meaning local materials and possibly labor (Ehdaie et al. 2014).

2.2 Industrial wastewater treatment

The amount and environmental hazard of the waste that industrial companies produce are nowadays strictly monitored and targeted by international environmental legislation. For example, in the European Commission (2010) Directive 2010/75/EU on industrial emissions (integrated pollution prevention and control), the polluting substances for water are listed. Among others, the environmental water pollutants of industrial origin include substances and mixtures which have been proven to possess carcinogenic or mutagenic properties or properties which may affect reproduction in or via the aquatic environment, persistent hydrocarbons and persistent and bioaccumulative organic toxic substances, cyanides, metals and their compounds, arsenic and its compounds, biocides and plant protection products, just to mention a few.

Table 2 presents the European Union environmental legislation related to selected metals, metalloids and organic pollutants in industrial effluents. In Table 2, the Helcom (2002) recommendations for the requirements for discharging wastewater from the chemicals industry, are shown for those compounds found in the document. However, before discharging, there are (1) general requirements to be carried out, i.e. wastewater should only be discharged if the wastewater volume and pollutant load are minimised by the use of best available technologies (BATs),
and (2) requirements for the effluent of the plant, i.e. the mixing or diluting of different wastewaters (e.g. mixing of treated process water with cooling water) for the purpose of reaching the limit values established for the effluent should not be allowed, and there are separate requirements for different types of pollutants (2–24 h values).

Table 2. European Union legislation regarding selected metals, metalloids and organic pollutants (European Commission 2013, 2008, 2006a, Helcom 2002).

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<td></td>
<td>Priority substance</td>
<td>Priority hazardous substance</td>
<td>EQS¹</td>
<td>Dangerous substance for aquatic environment</td>
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<tr>
<td>Arsenic</td>
<td>X</td>
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<tr>
<td>Cadmium</td>
<td>X</td>
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<td>0.2</td>
<td>0.45-1.5</td>
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<tr>
<td>Chromium</td>
<td>X</td>
<td>X</td>
<td>0.5 Cr,</td>
<td>0.1 Cr(VI)</td>
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<td>Cobalt</td>
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<td>Copper</td>
<td>X</td>
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<td>Lead</td>
<td>X</td>
<td>1.3</td>
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<td>Mercury</td>
<td>X</td>
<td>X</td>
<td>0.07</td>
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<tr>
<td>Nickel</td>
<td>X</td>
<td>8.6</td>
<td>34</td>
<td>X</td>
</tr>
<tr>
<td>Selenium</td>
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<td>Zinc</td>
<td>X</td>
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<td>Benzene</td>
<td>X</td>
<td>8</td>
<td>50</td>
<td>X</td>
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<tr>
<td>Dichloromethane</td>
<td>X</td>
<td>20</td>
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<td>X</td>
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<td>Diuron</td>
<td>X</td>
<td>0.2</td>
<td>1.8</td>
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<tr>
<td>Polyaromatic hydrocarbons</td>
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¹Environmental quality standard, ²Annual average concentration in other surface waters ³Maximum allowable concentration in other surface waters

The European Union has set guidelines on how to treat wastewaters from different industrial sectors in the form of the BATs. For example, in the mining industry the acid mine drainage (AMD) should be treated to prevent emissions into water by the BAT methods including (European Commission 2009):
– re-using of process water
– mixing process water with other effluents containing dissolved metals
– installing sedimentation ponds to capture eroded fines
– removing suspended solids and dissolved metals prior to discharge of the effluent to receiving watercourses
– neutralising alkaline effluents with sulphuric acid or carbon dioxide
– removing arsenic from mining effluents by the addition of ferric salts.

The European Commission (2006b) has also defined BATs for the manufacture of organic fine chemicals with a separate section for managing and treating waste streams. For refractory organic compounds containing wastewaters the BAT is to separate and pretreat those streams if the refractory organic loading is relevant. The relevance is classified with the following criteria: (1) not relevant if the wastewater stream shows a bio-elimination of greater than about 80–90%, (2) not relevant if the refractory organic loading is lower than the range of about 7.5–40 kg TOC per batch or per day, even if the bioeliminality is lower than 80%. Accordingly, for the segregated wastewater containing relevant refractory organic load, the BAT is to achieve over 95% overall COD elimination by the combination of pre-treatment and biological treatment. In addition, according to the BATs, solvents should be removed from the wastewaters for on-site or off-site reuse by e.g. stripping, distillation/rectification, extraction or combinations of such techniques, if the costs for recovery and purification are lower than the costs for biological treatment and purchase of fresh solvents. (European Commission 2006b)

In addition to the legislative reasons, the purification of wastewaters has several advantages for industrial companies, for example the wastewater volumes are minimized, the harm towards the environment by eliminating the discharges of harmful compounds is reduced, the resource efficiency of valuable compounds is improved, and water re-use is promoted, thus reducing freshwater consumption.

In developing countries, agricultural and industrial operations, such as mining, smelting of metal containing ores, secondary smelting of batteries and electronic waste products, are often conducted without proper environmental or safety regulations, even though the international community tries to promote sustainable development. Poverty and lack of resources are the main reasons that the environmental standards are not implemented, since the economy often highly depends on these operations, and thus, tighter regulations of ongoing practices are not the priority. In addition, significant quantities of both toxic and precious metals are mined in a number of developing and newly industrialized countries in various
regions of the world. For example, almost half of the world’s arsenic production is in China, followed by Chile, Morocco, and Peru. (Fowler et al. 2015)

Artisanal gold mining, a small scale industry, is estimated to involve approximately 20 million people worldwide, and it is evaluated as the second largest source of mercury released into the atmosphere after coal-fired power plants. In the process, metallic mercury is used to form gold-mercury amalgams by running river water containing sedimentary gold particles through channels coated with mercury and then recovering the gold by burning off the mercury with propane torches. This causes environmental pollution as well as clear adverse health effects in both local and global levels due to the movement of mercury in the atmosphere and its accumulation in fishery products. In spite of this, it brings important financial resources to impoverished people in developing countries. (Fowler et al. 2015)

Pharmaceutical industry wastewaters are another emerging problem, especially in Asia, where several global pharmaceutical manufacturers have relocated their production facilities. Most of these manufacturing units do not have a treatment process for their highly contaminated wastewaters, and discharge them straight into natural water bodies (rivers/streams) or into municipal sewer systems, thus increasing the health risks for the entire ecosystem (Rehman et al. in press). Both the conventional drinking water treatment processes and the conventional wastewater treatment plants are often inefficient to remove these types of contaminants.

A lot of research is published with the aim of achieving more efficient industrial water treatment, e.g. Landaburu-Aguirre (2012) studied micellar-enhanced ultrafiltration for the removal of heavy metals from phosphorous-rich wastewaters and concluded it to be a feasible technique for simultaneous removal of harmful compounds and recovery of the valuable compounds, e.g. phosphorous for further use.

Relatively low cost, innovative methods for the removal of toxic metal ions or organic pollutants from both wastewater and ground water have also been developed for use in developing countries. These methods include e.g. adsorption/biosorption materials and constructed wetlands (Akunwa et al. 2014, Ali et al. 2012, Zhang et al. 2014a). Bech et al. (2012) studied lead and zinc accumulation in two native plant species at a polymetallic mine in Peru and noted their potential application for phytoremediation.

Kim et al. (2007) found incomplete removal of 25 micropollutants such as pharmaceuticals and hormones from South Korean surface, drinking and
wastewaters by conventional methods, i.e. coagulation and sand filtration in drinking water purification and activated sludge in the wastewater treatment. They suggest the use of granular activated carbon and membrane filtration (reverse osmosis, RO/nanofiltration, NF) or membrane bioreactor followed by RO or NF to achieve the efficient removal of microcontaminants.

To conclude, wastewater treatment should not just improve the quality of water being discharged into the environment, but it should enhance the recycling, effective reuse, and the recovery of valuable compounds such as chemicals, bioenergy, and biomaterials, from the wastewater (Ranade & Bhandari 2014). Thus, a combination of innovative recycling methods and low-cost purifications methods are needed now and in the future.
3 Adsorption

The adsorption technique for the treatment of water is considered an effective, efficient, and economic method for water purification (Qu 2008) due to its wide range of applications, efficiency and ease of operation. This technique is also considered as universal water treatment and reclamation technique as it can be applicable for the removal of organics, inorganic and biological pollutants which are soluble and insoluble in water, and has a potential of 99% removal efficiency. (Gupta & Ali 2013)

Adsorption is a process where molecules from an ambient fluid phase are adhered to a solid surface (Ruthven 2001). The substance to be adsorbed, before it is on the surface, is called the adsorptive substance, and when it is in an adsorbed state it is called the adsorbate, and the material that adsorbs the molecules is the adsorbent. (Butt et al. 2003)

Adsorption depends on the nature of the surface forces, which can be either chemical (chemisorption) or physical (physisorption). In chemisorption, the forces between the adsorbate and adsorbent are equivalent to the formation of a chemical bond due to electron transfer, and the bond may be characterized as ionic, metallic or covalent. The interaction is stronger and more specific than the forces of physisorption, and chemisorption is limited to a monolayer. (Ruthven 2001)

In physical adsorption the adsorbate is held by physical forces that are relatively weak, mainly involving van der Waals interactions (Ruthven 2001). In physisorption, the equilibrium between the solid surface and the adsorbed molecules is usually achieved quickly and it is easily reversible since the energy requirements are small. Multilayer formation is also possible in physisorption. (Smith 1970)

Adsorption processes might also contain surface diffusion, and diffusion on metal surfaces is often described as the movement of atoms jumping between the nearest adsorption sites (Antczak et al. 2004). For example, activated carbon and silica gel have been reported to show surface diffusion if the relative humidity is higher than 40% (Bart & Gemmingen 2005).

Adsorption processes are often described for solid-gas systems, where the partial pressure $p$ of the molecules is the most important parameter to determine the amount adsorbed. For solid-liquid systems pressure $p$ has to be replaced with concentration $c$ in order to be able to use the same models. Multilayer formation is less common in solid-liquid adsorption than in the gas phase due to the fact that the
adsorbent is surrounded with solvent and the adsorbing molecules have also alternative partners. (Butt et al. 2003)

The advantages of adsorption are that it allows the separation of selected compounds from dilute solutions, its design, operation and scale up are relatively simple, it demonstrates high capacity and favourable rate, and it is insensitive to toxic substances (Soto et al. 2011). In addition, the adsorbed compounds may be recovered by desorbing agents, leaching by means of chemical reagents, biological processes and thermal treatment (Kikuchi & Tanaka 2012).

3.1 Adsorption equilibrium

The adsorption equilibrium, i.e. the distribution of a sorbate between fluid and adsorbed phases, follows the principles of thermodynamics. Equilibrium data is commonly reported in the form of an isotherm, which at constant temperature relates the amount of material in the adsorbed phase to the amount of material in the solution at equilibrium (Ruthven 1997). The isotherm’s shape reflects the adsorption intensity and the attraction between the adsorptive and adsorbent (Ullmann’s 2004). Isotherms can give qualitative information about the adsorption process and also indicate the fraction of the surface coverage (Schweitzer 1979).

Generally with low concentrations, the isotherm of the physical adsorption on a homogenous surface should approach a linear form since there are no changes in the molecular state on adsorption, meaning there is no association or dissociation. A Henry’s law constant can be used to represent the low concentration region (Ruthven 1984):

\[
q_e = Kc_e
\]  

where \( q_e \) is the adsorption density at equilibrium (\( \mu g \) adsorbate/mg adsorbent), \( c_e \) is the equilibrium concentration (\( \mu g/l \)) and \( K \) is the adsorption equilibrium constant (l/mg) referred to as the Henry’s law constant. Physically Henry’s law corresponds to a situation with no competition for surface sites and no significant interaction between the adsorbed molecules. At higher concentrations both of these effects become important and the isotherms become more complex. (Ruthven 1997)

There are six recognized adsorption isotherm types classified by the International union of pure and applied chemistry (IUPAC) (Sing et al. 1985), shown in Fig. 2.
Fig. 2. The six types of adsorption isotherms according to the IUPAC classification. Picture modified from Sing et al. (1985).

The type I isotherm is typical for microporous adsorbents with the pore width less than 2 nm. It appears in saturated monolayer adsorption. Types II and III are typical of nonporous or macroporous (pore width > 50 nm) materials with strong (type II) or weak (type III) adsorbate-adsorbent interactions (Balbuena & Gubbins 1993). Type IV isotherm with a hysteresis loop is commonly associated with mesoporous
adsorbents (pore widths from 2 to 50 nm) and the shape is unique to each adsorption system. Type V isotherms indicate weak adsorbate-adsorbent interactions and are applied for microporous or mesoporous solids. Type VI isotherm is primarily introduced as a hypothetical isotherm. The shape comes from the complete formation of monomolecular layers before progression to a subsequent layer. (Ruthven 1984) It may occur for some materials with relatively strong attractive forces, usually when the temperature is near the melting point for the adsorbed gas (Balbuena & Gubbins 1993).

The Langmuir isotherm model (Langmuir 1918), seen in Eq.(2), is the simplest theoretical model for monolayer adsorption, and it assumes monolayer sorption onto a homogenous surface with a finite number of identical sites. The Langmuir model is based on four basic assumptions: (1) molecules are adsorbed at a fixed number of well-defined localized sites, (2) each site can hold one adsorbate molecule, (3) all sites are energetically equivalent, and (4) there is no interaction between molecules adsorbed on the neighbouring sites. (Ruthven 1984)

\[
q_e = \frac{bc_e}{1+bc_e}q_{max} \leftrightarrow \frac{1}{q_e} = \frac{1}{bq_{max}c_e} + \frac{1}{q_{max}}
\]

where, \(q_e\) (µg/mg) is the adsorption density at equilibrium, \(c_e\) (mg/l) is the liquid-phase equilibrium concentration. The factor \(q_{max}\) (µg/mg) in the Langmuir model is the saturated monolayer adsorption capacity i.e. maximum solid-phase concentration, and \(b\) is the Langmuir adsorption coefficient, related to the binding energy of the sorption system. The slope and intercept of the linear plot of \(1/q_e\) versus \(1/c_e\) gives the values of the Langmuir isotherm parameters \(b\) and \(q_{max}\). The Langmuir isotherm constant \(b\) can be used to indicate the affinity i.e. combining capacity of adsorbent toward the ions to be adsorbed. High value of \(b\) indicates for a strong affinity of adsorption. (Lv et al. 2004, Shaw 1994).

The isotherm usually follows the Freundlich equation, Eq.(3), when the concentrations are really low or high

\[
q_e = kc_e^n \leftrightarrow \log q_e = \log k + n \log c_e
\]

where \(k\) is the Freundlich adsorption coefficient representing the adsorption capacity and \(n\) is the Freundlich exponent related to the adsorption intensity and surface heterogeneity. It gives an indication of how favourable the adsorption processes. The Freundlich model is empirical in nature and assumes that the uptake of ions occurs on a heterogeneous surface. The slope and intercept of the linear plot of \(\log q_e\) versus \(\log c_e\) give the values of the Freundlich isotherm parameters \(n\) and \(k\), respectively. If the values of \(n\) are from 0.1 to 0.5 adsorption is favourable, if the
values are between 0.5 and 1.0 the adsorption is quite difficult and if n is greater than 1, adsorption is difficult. (Reunanen 1992)

The surface area is a key parameter for charactering an adsorbent since almost all practically important adsorbents are porous solids. Brunauer, Emmet & Teller (1938) developed a simple model isotherm (Brunauer–Emmet–Teller, BET), seen in Eq.(4), to describe multilayer adsorption and used this model to extract the monolayer capacity and the specific surface area. (Ruthven 1984). The BET theory assumes a Langmuir adsorption for each of the layers (Butt et al. 2003). Numerous variations of the BET method are developed but the basic BET method remains the most widely used technique for the measurement of the specific surface area.

\[ \frac{q}{q_{\text{max}}} = \frac{b(p/p_s)}{(1-p/p_s)(1-p/p_s+bp/p_s)} \]  

where \( p_s \) represents the saturation vapour pressure of the saturated liquid sorbate at the relevant temperature. This expression is found to provide a good representation of experimental physical adsorption. (Ruthven 1984).

### 3.2 Kinetics

The rate at which thermodynamic equilibrium is attained in a system that is not in equilibrium is generally described by kinetics. The adsorption process continues until the equilibrium is reached. The reverse process occurs during desorption which also continues until the equilibrium is attained. (Bart & Gemmingen 2005). Adsorption, either physical or chemical, includes the mass transfer of the adsorptive from the solution to the surface of the adsorbent. The adsorption takes place in four basic steps in the presence of a porous adsorbent (Ullmann’s 2004):

1. **Bulk solution transport** – The adsorptive is first transported to the hydrodynamic boundary layer surrounding the adsorbent. This transport occurs either by diffusion or turbulent mixing.
2. **External film diffusion** – The adsorptive is then transported through the hydrodynamic boundary layer to the surface of the adsorbent by the assistance of molecular diffusion. The thickness of the boundary layer affects the rate of transport and depends on the velocity of the bulk solution.
3. **Internal (pore) transport** – The adsorptive is next transported through the pores of adsorbent to the adsorption sites via intraparticle diffusion i.e. either molecular diffusion through the solution in the pores (pore diffusion) or by the
diffusion along the adsorbent surface (surface diffusion) after adsorption has taken place.

4. Adsorption – The final step is the adsorption in which the adsorptive adheres to the adsorbent surface on the available sites. This step is very rapid and therefore one of the previous diffusion steps will control the rate of mass transfer.

Desorption, occurs in the reverse manner; it begins with desorption and ends with transport from the concentration boundary layer around the adsorbent into the solution.

The pseudo-first order kinetic model, Eq.(5), was developed by Lagergren (1898) and it is widely applied to describe the rates of adsorption processes (Ho & McKay 1999).

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]

where \(q_e\) and \(q_t\) are the amounts adsorbed (mg/g) at equilibrium and at time \(t\), \(k_1\) is the pseudo-first order rate constant (1/h). Equation (5) can be linearized to the form of Equation (6) and the rate constant \(k_1\) can be calculated from the plot of \(\log(q_e/(q_e - q))\) versus time.

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

The first-order equation does not always fit well with the whole range of contact time and usually it is applicable only over the initial stage of the adsorption processes (Hameed et al. 2007).

The pseudo-second order kinetic model based on sorption equilibrium capacity, Eq.(7), is also widely used since it is a good representation of the experimental data. The model can be used to predict the behaviour over the whole range of adsorption. (Ho & McKay 1999, Liu 2008)

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]

where \(k_2\) is the rate constant for the pseudo-second order adsorption [g/(mg min)]. An integrated and rearranged form of the pseudo-second order model is presented in Eq.(8). If the model is applicable the plot of \(t/q\) versus \(t\) should give a linear relationship and values of \(q_{eq}\) and \(k_2\) can be then calculated from the slope and intercept (Ho & McKay 1999).

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]
where \( k_2 q^2 \) equals to the initial adsorption rate \( h \) (mg of adsorbate/(g of adsorbent·min)).

### 3.3 Materials

In water treatment, adsorbents could be used in the form of spherical pellets, rods, mouldings, or monoliths. The specific composition and structure of the adsorbent influences its sorption capacity. The most important characteristics affecting the sorption capacity of an adsorbent are a high surface area, high surface charge (positive or negative), and high thermal and chemical stability (Barrot & Ersoz 2012). The pore size and the pore size distribution as well as the characteristics of the solid material such as the crystal structure, morphology, defects, surface impurities and modifiers also affect the adsorption properties (Ruthven 1997, Liang et al. 2000). The most important characteristic of an adsorption material is its high specific internal surface area, which is related to the mean pore diameter. Accordingly, the minimal pore diameter accessible for penetration is determined by the molecular size of the adsorptive. The mass transfer, pressure drop, and operability are influenced by the particle size of adsorbent; with small particles the intraparticle diffusion path is shorter, and thus diffusion and mass transfer are endorsed, but they result in a higher pressure loss than with the bigger particles. Generally, particle sizes for gas-phase processes are between 1 and 10 mm, whereas in liquid-phase applications smaller diameters are used due to lower liquid diffusivities. (Bart & Gemmingen 2005)

Polar adsorbents such as most zeolites, silica gel, or activated alumina adsorb water more strongly than they adsorb organic species and are commonly called hydrophilic. In contrast, on a nonpolar surface water is held only very weakly and is easily displaced by organic molecules. Such adsorbents are termed hydrophobic. Adsorbents such as silica gel and activated alumina are made by the precipitation of colloidal particles. Carbon adsorbents are prepared by a controlled burn-out of carbonaceous materials. (Ruthven 2001)

Alternative, inexpensive, performance abundant and more environmentally friendly raw materials are needed for absorbent material production. Of particular interest for improving the environmental performance of heavy metal removal by means of adsorption is the use of waste or industrial side products as the adsorbent.
3.3.1 Activated carbon

Activated carbon (AC) is the common name for carbonaceous adsorbents which are generally non-hazardous having a porous structure and a large internal surface area, able to adsorb a wide variety of substances (Henning & Kienle 2012). Activated carbon is widely used in the treatment of both drinking water and industrial wastewater due to its high micro- and meso-porosity and large surface area from 300 to 4000 m²/g (Fu & Wang 2011, Ruthven 2011). However, AC is traditionally manufactured from non-renewable coal or peat which increases the price as well as the environmental impact. Relatively high production costs of activated carbon may limit its use especially in developing countries, which has led to a search for new low cost production methods and precursors.

Activated carbon is commercially available in shaped (cylindrical pellets), granular, or powdered form, and it can be produced by chemical or physical activation. The most commonly used activation chemicals are ZnCl₂, H₃PO₄, H₂SO₄, KOH, K₂S and KCNS (Gupta & Ali 2013), and temperature of 400–1000 ºC is usually used. The physical activation is typically done by using either steam or carbon dioxide at temperatures of 800–1000 ºC (Henning & Kienle 2012).

In the activation by zinc chloride, ZnCl₂ is mixed as a concentrated solution with the carbonaceous materials, in a ratio of (0.4–5.0):1, respectively. The mixture is then dried and heated to 600–700 ºC, washed with acid and water, and sometimes, steam activation is carried out after the chemical activation to obtain additional fine pores (Henning & Kienle 2012).

Phosphoric acid activation is used to produce commercially available activated carbons by e.g. Ceca (France), Hooker (Mexico), and Norit (United Kingdom and United States). In the process, the finely ground raw material is mixed with a phosphoric acid solution, forming a pulp, which is dried and heated to 400–600 ºC. Phosphoric acid is then extracted, and the material is dried, resulting usually in activated carbon with finer pores than the zinc chloride product. In addition, a combination of phosphoric acid and steam can be used in the activation. (Henning & Kienle 2012)

In drinking water treatment, activated carbon is used to remove unpleasant odours, tastes, and compounds constituting a health hazard (pesticides, chlorinated hydrocarbons, etc.) (Henning & Kienle 2012).

The removal efficiency of activated carbon is influenced by many factors, such as particle size, the chemical nature of the AC, adsorbent modification procedure, type and concentration of the metal ions, temperature and pH of water, and the flow
rate or time exposure of water to the AC (Barrot & Ersoz 2012). There is a wide variety of research going on for using different types of low-cost precursors for activated arbon production. For example, Tuomikoski (2014) has studied carbon residues from wood gasification processes as adsorption materials after chemical activation. In addition, among other waste derived activated carbons, mahogany fruit husk (Njoku et al. 2014), waste potato residue (Zhang et al. In press), eggshells (Giraldo & Moreno-Piraján 2014), palm stems and lubricating oil waste (AlOthman et al. 2014), and scrap tyres (Acevedo et al. 2015) have all been studied as raw materials for activated carbon with good adsorption results in aqueous phase experiments. To conclude, the origin of the activated carbon precursor can be generally whatever widely available carbon containing material that is easy to handle, and above all, the acquisition costs must be minimal.

3.3.2 Hydrous metal oxides

Hydrous metal oxides are commonly used as adsorbents in industrial wastewater treatment as they are inexpensive and common in nature. Titanium dioxide consists of nanoparticles that are clusters of atoms, or molecules of metal and oxide, with size ranging from 1 to 100 nm. Nanoparticles consist mostly of surface atoms, which are unsaturated and can easily bind with other atoms and possess high chemical activity. Thus, nanometre sized material has a very high adsorption capacity and can adsorb metal ions selectively. (Liang et al. 2000)

Activated alumina is widely used in water purification and wastewater treatment, e.g. for the removal of arsine (AsH₃), phosphate, chloride and fluoride (Bart & Gemmingen 2005). The activated aluminas are porous high surface area solids made by thermal treatment from aluminium hydroxide, and they contain a series of nonequilibrium forms of partially hydroxylated aluminium oxide, Al₂O₃. (Ruthven 1997)

Iron oxides, including oxyhydroxides and hydroxides are effective adsorbents for both As(III) and As(V) (Zhang et al. 2003). Granular ferric hydroxide (GFH) is a typical porous iron adsorbent with a BET surface area of approximately 235 m²/g (Badruzzaman et al. 2004), and it is an efficient adsorbent e.g. for arsenic (Thirunavukkarasu et al. 2003). Zero valent iron (ZVI) is the most commonly used reagent in permeable reactive barriers. ZVI has been proven to be an effective sorbent material for multiple contaminants including heavy metals and arsenic. (Kanel at al. 2005, Lien & Wilkin 2005)
3.3.3 Clay materials

Zeolites are naturally occurring structured minerals with high cation exchange and ion adsorption capacity (Barrot & Ersoz 2012). Zeolitic molecular sieves are a group of porous crystalline aluminium silicates that release water at high temperature (Ullmann's 2004). They have a solid microporous structure with approximately 50% of intrinsic void space with the surface up to 1500 m²/g. The most important properties of zeolites include differing adsorption capacities for a number of compounds (including metal-ions, vapours and gases); high chemical-, temperature- and radiation stability; low density and large void volume of dehydrated samples; reversible water absorption. (Barrot & Ersoz 2012) Aluminosilicates can be used for metals and metalloids (e.g. As, Cu, Pb, Ni) removal from water. Thus, a large majority of applications for zeolites are purification processes where zeolite is used as a selective adsorbent for the removal of e.g. water (Ruthven 1984). Synthetic zeolites have controlled and known physico-chemical properties, which make them more useful compared to natural zeolites (Shevade & Ford 2004).

Bentonite is a clay formed from weathering of volcanic ash and it consists mostly of montmorillonite. Sodium bentonite and calcium bentonite are the two types of recognized bentonites. Sodium bentonites can absorb large quantities of water, swelling to many times their original volume. Calcium bentonites are nonswelling, and break down to a finely granular aggregate that is widely used as an adsorbent clay sometimes called fuller's earth. (Bentonite 2014)

3.3.4 Biosorbents

Biosorption refers to the removal of heavy metals and other hazardous substances by the passive binding to non-living micro-organisms, such as algae, fungi and bacteria, and other biomass like peat, rice hull, wheat shell, fruit peel, leaves, saw dust, tree bark, macro fungus etc. from aqueous solutions. Different from synthetic sorbents, biosorbents are bio-renewable, biodegradable and cost-effective. Generally, biosorbents are distinguished for their high sorption selectivity for heavy metals. Alkaline and alkaline earth metals are not removed from water by biosorbents. Therefore, biosorbents are highly suitable for the treatment of drinking water, since they remove the hazardous substances but meanwhile the essential minerals (calcium, magnesium) remain in water. However, the sorption ability of
biosorbents is usually low and their regeneration in many cases still remains to be solved. (Barrot & Ersoz 2012)

Biosorbents such as algae, fungi and bacteria are examples of tested biomass for biosorption of several metal species with very encouraging results (Gome-da-Costa et al. 2005). For example fungal, a non-living biomass and an industrial waste, with trade name Mycan has been found to be a good adsorbent for removing Zn, Cu, Ni and As from an aqueous mixture (Loukidou et al. 2003).

### 3.3.5 Regeneration of the adsorption materials

The used adsorption materials can be regenerated by different methods including thermal regeneration, chemical regeneration, regeneration by changing the pressure, and microbial regeneration (Ullmann’s 2004, Salvador et al. 2015a, Salvador et al. 2015b). Thermal and chemical regeneration are the most important types for the regeneration of carbonaceous adsorbents. Thermal regeneration involves heating of the spent adsorbent. Chemical regeneration uses an extensive variety of reagents to remove adsorbates. Regeneration by changing the pressure shifts the adsorption equilibrium towards desorption through pressure changes in adsorption-regeneration cycles. In the microbiological regeneration microorganisms are used as the regeneration agents. (Salvador et al. 2015b)

Thermal regeneration consists of heating the saturated adsorbent to provide the amount of energy needed for the removal the retained adsorbate from the surface of the adsorbent by breaking the adsorbent–adsorbate interactions across all the adsorption sites. Three techniques can be distinguished within the thermal desorption methods, depending on the heat source; (1) temperature swing process (TSA), (2) low-temperature steam (Steaming), or (3) application of an electrical current (ESA). (Salvador et al. 2015) Thermal regeneration costs are determined primarily by the course of the adsorption isotherms and the temperature difference between adsorption and desorption (Ullmann’s 2004).

Chemical regeneration can be done using different methods such as solvent extraction, pH change, wet air and thermal oxidative regeneration, electrochemical and supercritical regeneration (Salvador et al. 2015b). Displacement is also one of the chemical regeneration methods, and the adsorbate is removed from the adsorbent by displacing the active sites with adsorption of a third material (the displacing agent). A known example is the removal of organic substances from activated carbon by steam. The choice of suitable displacement agent depends both on the equilibrium of the system and on the kinetics of adsorption and desorption.
In regeneration by extraction an extracting agent (solvent) is brought in contact with the loaded adsorbent and the adsorbate is removed from the adsorbent into the solvent. For example adsorbent loaded with sulphuric acid can be regenerated by extraction with water or ammonia. (Ullmann’s 2004) However, the use of organic solvents increases the costs, and these chemicals are often environmental pollutants and usually highly toxic. The supercritical regeneration is also carried out through an extractive mechanism but has significant advantages, since it employs supercritical CO2 and water which are more environmentally friendly than organic solvents, and a final step to remove the retained solvent is not necessary. (Salvador et al. 2015b)

Regeneration of the used adsorbent can be done by changing the pressure with a pressure-swing adsorption (PSA) process which is carried out at the congruent temperature of the adsorption step but at lower pressure. The course of the adsorption isotherms and the pressure difference during adsorption and desorption determine the costs of regeneration by the pressure-swing process. (Ullmann’s 2004)

Reactivation of the adsorption material is necessary if the pores of an adsorbent become blocked up e.g. if the adsorbate is not volatile or soluble enough to be desorbed by increasing the temperature, reducing the concentration or extracting with solvents. Reactivation can be carried out e.g. by gas activation, atomization or thermooxidative regeneration. (Ullmann’s 2004)
4 Photocatalysis

Advanced oxidation processes (AOPs) based on ozonation, UV irradiation, Fenton reaction, catalytic peroxide oxidation etc. have been suggested as potential treatment alternatives for wastewaters containing organic pollutants by oxidizing and mineralizing them into less harmful inorganic substances – preferably into carbon dioxide and water. These processes are of particular interest for the treatment of effluents for which biological processes might not be applicable e.g. for highly toxic organic compounds. The main objective of most AOPs is the generation of powerful oxidizing agents, such as the highly reactive hydroxyl radical, (OH• with the oxidation potential 2.8 V), that reacts rapidly (the rate depends on the contaminant molecules) (Saïen & Nejati 2007) and relatively non-selectively with practically any organic compounds by hydrogen abstraction, by addition to unsaturated bonds and aromatic rings, or by electron transfer (Daneshvar et al. 2005, Machulek et al. 2013).

Heterogeneous photocatalysis is one of the AOPs, and it uses titanium dioxide or other semiconductor materials as a catalysts activated by UV irradiation. Photocatalysis has been studied widely in the degradation of organic compounds in both liquid and gas phase processes (Fujishima et al. 2008, Hernández-Alonso et al. 2009, Herrmann et al. 2007, Kanakaraju et al. 2014, Lazar et al. 2012, Malato et al. 2009, Rauf et al. 2011, Zhao et al. 2011). It has the potential to reduce the toxicity of the contaminants and even mineralize target compounds (Bianco Prevot et al. 2004, Chung & Chen 1998, Kirchnerova et al. 2005). Due to the non-selective nature of the photocatalytic processes, photocatalysis can be used for the simultaneous abatement of several different organic pollutants via converting them into less harmful compounds. The process is typically operated at ambient temperatures and pressures, and can be applied to environmental remediation by following the principles of green chemistry (Herrmann et al. 2007, Richter & Caillol 2011). In addition, photocatalysis can be used for the production of energy/fuels such as hydrogen (Izumi 2013, Wu et al. 2011b) or for selective conversion reactions in organic chemistry (Palmisano et al. 2010), giving the technique a definite role in the future as a more sustainable purification and a production process.
4.1 Photocatalysis mechanism and kinetics

The energy needed to produce the reactive radicals in photocatalysis is provided, when a semiconductor is irradiated with the energy \((hv)\) equal or superior to the band gap energy of the semiconductor (e.g. for TiO\(_2\): \(hv \geq 3.2\) eV). Electrons (e\(^-\)) of the valence band are excited to the conduction band forming an electron-hole pair (Fig. 3). (Herrmann 1999)

![Energy band diagram of a spherical titanium dioxide particle. Picture modified from Herrmann (1999).](image)

The photo-generated holes (h\(^+\)) in the valence band diffuse to the surface of the photocatalyst and react with adsorbed water molecules, creating hydroxyl radicals. The nearby organic molecules can be oxidized by these radicals and the holes on the surface of the semiconductor. The electrons in the conduction band participate in reduction processes e.g. in the formation of superoxide radical anions (O\(_2^-\)) with the molecular oxygen of the environment. (Nakata & Fujishima 2012, Carp \textit{et al.} 2004)
The above described process can be expressed via the following equations by Alinsafi et al. (2007) and Lasa et al. (2005).

\[ TiO_2 + hv \rightarrow h^+ + e^- \] (9)

An electron can now transfer from an adsorbed substrate, \( RX_{ad} \), adsorbed water or \( OH_{ad}^- \) ion, to the electron-hole creating \( OH^• \) radicals

\[ h^+ + RX_{ad} \rightarrow RX_{ad}^+ \] (10)
\[ h^+ + H_2O_{ad} \rightarrow OH_{ad}^\bullet + H^+ \] (11)
\[ h^+ + OH_{ad}^- \rightarrow OH_{ad}^\bullet \] (12)

On the conductor band molecular oxygen acts as an acceptor and generates reactive superoxide anions \( O_2\bullet^- \)

\[ O_2 + e^- \rightarrow O_2\bullet^- \] (13)

and the following reactions can occur

\[ O_2\bullet^- + H^+ \rightarrow HO_2\bullet \] (14)
\[ H^+ + O_2\bullet^- + HO_2\bullet \rightarrow H_2O_2 + O_2 \] (15)

Further, hydrogen peroxide gives more \( OH^• \) radicals

\[ H_2O_2 + hv \rightarrow 2OH^• \] (16)

Finally, \( OH^• \) radicals oxidize adsorbed organic compounds \( RX_{ad} \) on the surface of the photocatalyst

\[ OH_{ad}^• + RX_{ad} \rightarrow \text{degradation intermediates} \] (17)

The \( OH^• \) radicals generated in the process are very reactive and degrade the pollutant molecule finally into mineral acids including carbon dioxide and water if the treatment time is adequate. However, the photo-efficiency can be reduced by the electron-hole recombination, which corresponds to the conversion of the photoelectronic energy to heat. (Herrmann 1999)

Generally, for low pollutant concentrations, the photocatalytic reaction kinetics follow the first-order and can be modelled by the Langmuir-Hinshelwood (L-H) equation (pseudo-first order kinetics) (Houas et al. 2001)

\[ r = \frac{dc}{dt} = \frac{kkc}{1+Kc} \] (18)

where \( r \) is the oxidation rate of the pollutant, \( c \) the pollutant concentration, \( k \) is the L-H reaction rate constant, and \( K \) the equilibrium constant. At small concentrations \( (c<<1) \), the equation can be simplified to the form of the apparent first order rate equation
where $k_{app}$ is the apparent pseudo-first order rate constant (1/h), $c$ and $c_0$ are final and initial pollutant concentrations (mg/l) and $t$ is the reaction time (h).

4.2 Materials

The catalyst material in photocatalysis is a semiconductor with a favourable band gap energy, primarily metal oxides or sulphides i.e., TiO$_2$, ZnO, ZrO$_2$, SnO$_2$, WO$_3$, CeO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, ZnS and CdS (Hoffmann et al. 1995). The energy of the electrons and holes (potential) determines the photocatalytic activity and usefulness for a particular reaction. The activity of a photocatalyst is influenced by structure, particle size, surface properties, preparation method, spectral activation, and resistance to mechanical stress. Teichner et al. (in Mo et al. 2009) explored the photoactivity of numerous oxides for hydrocarbon partial oxidation in the gas phase, finding that the active catalysts involving titania, zinc, and tungsten ranked in the activity sequence: TiO$_2$ (anatase) > ZnO > WO$_3$.

Ideally, a semiconductor photocatalyst should be chemically and biologically inert, photocatalytically stable, easy to produce and to use, efficiently activated by sunlight, able to efficiently catalyze reactions, inexpensive, and without risks for the environment or humans (Carp et al. 2004). The Degussa P25 TiO$_2$ catalyst is the most widely applied photocatalyst in water treatment research to date. This catalyst has been on the market for a relatively long time, and thus is used typically as a standard reference for comparisons of photoactivity under different treatment conditions (Serpone et al. 1996, Hoffmann et al. 1995).

4.2.1 Titanium dioxide

Titanium dioxide (TiO$_2$), also known as titanium(IV) oxide or titania, is the most commonly used catalyst material in photocatalysis. It can have sizes ranging from clusters to colloids to powders and large single crystals, and it is close to being an ideal photocatalyst, displaying almost all the properties mentioned above. The advantages of TiO$_2$ are its good activity (the photogenerated holes are highly oxidizing), high physical and chemical stability both in acidic and basic conditions, nontoxicity, resistance to corrosion, commercial availability and inexpensiveness (Fujishima et al. 2000, Carp et al. 2004, Hung et al. 2006). Further, it can be utilized as a photocatalyst itself or it can be combined e.g. with noble metals (Pd,Pt,….) or
carbon nanotubes to achieve higher activity in certain reactions (Rosseler et al. 2010, Ye et al. 2012).

TiO$_2$ exists in different allotropic forms including natural anatase, rutile and brookite, and an artificial form (TiO$_2$–B, TiO$_2$–H), for example the commercially available Aeroxide (former Degussa) P25 is a mixture of anatase and rutile. Anatase shows a greater photocatalytic activity for most reactions. The energy band-gaps of anatase and rutile are 3.23 and 3.02 eV, respectively. Anatase is thermodynamically less stable than rutile, but it has a higher surface area, and a higher surface density of active sites for adsorption and for catalysis. (Herrmann 1999)

### 4.2.2 Zinc oxide

The nanoscale form of zinc oxide (ZnO) can be considered as one of the most important semiconductor oxides at present (Ischenco et al. 2005). ZnO is a wide-gap semiconductor with a direct band gap around 3.4 eV (i.e. in the near-UV) (Klingshirn 2007). The potential use of ZnO in photocatalysis has particularly arisen great interest, as there have been several examples of ZnO displaying more impressive photocatalytic activity in solar light than widely studied titanium dioxide due to the higher quantum efficiency (Sakthivel et al. 2003). Also it has been shown that ZnO is more efficient in the degradation of industrial effluents at neutral pH than TiO$_2$ (Chen et al. 2010).

Zinc oxide (ZnO) exists with three types of crystal structure; hexagonal wurtzite, cubic zinc blende, and cubic rock salt. Wurtzite is the most stable structure and is abundantly available, unlike the other two structures (Klingshirn 2007).

### 4.2.3 Other metal oxides

Other metal oxide photocatalysts, such as iron, vanadium, tungsten, and copper oxides, have been used to treat wastewaters based on their photocatalytic properties. For example, tungsten oxide (WO$_3$) has a narrower band gap (2.5 eV) than TiO$_2$, allowing it to be activated by visible light (<500 nm) (Kominami et al. 2001). Iron(III) (hydr)oxides can absorb light up to 600 nm, and most of them have semiconductor properties, thus electron/hole recombination generally takes place efficiently (Paola et al. 2012). For example, Fe$_2$O$_3$ is an n-type semiconducting material and can be used for photodegradation under visible light conditions. Iron oxide nanomaterials can even achieve better photocatalytic performance when
compared to TiO\textsubscript{2} due to significant generation of electron–hole pairs through a narrow band-gap illumination. (Xu \textit{et al.} 2012)

Metal vanadates, such as bismuth vanadate, BiVO\textsubscript{4}, have recently been considered as potential photocatalysts in the treatment of dye wastewaters (Chan \textit{et al.} 2011). Cu\textsubscript{2}O is a p-type semiconductor with a direct band gap of ca. 2.0–2.2 eV that has been studied for organic dye degradation (Huang \textit{et al.} 2011, Paola \textit{et al.} 2012).

4.2.4 Photocatalyst modifications

The commercially available photocatalysts tend to have poor degradation efficiency and low utilization rate of visible light. Rehman \textit{et al.} (2009) have published a comprehensive survey of making TiO\textsubscript{2} and ZnO active in visible light. A few methods that could improve the activity of photocatalysts (Yu \textit{et al.} 2009, Kamat & Meisel 2002) include surface modifications, band gap modifications, and using composite materials.

Surface modification can be done via coupling organic materials and semiconductors e.g. by dye sensitization; surface-complex assisted sensitization where the adsorption of photoexcited sensitizers (e.g., ruthenium based complexes) on the surface of photocatalysts can extend the photoresponse of TiO\textsubscript{2} into the visible region (Cho \textit{et al.} 2001); polymer sensitization; and semiconductor coupling.

Band gap modification can be done via different methods including the creation of oxygen vacancies and oxygen sub-stoichiometry: TiO\textsubscript{2} is reported to absorb visible light via artificially created oxygen vacancies in its crystal structure (Rehman \textit{et al.} 2009). It can also be done by transition metal doping, i.e. the addition of transition metal ions (Pt\textsuperscript{4+}, Ir\textsuperscript{4+}, Rh\textsuperscript{3+}, Au\textsuperscript{3+}, Ag\textsuperscript{+}, Pd\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Fe\textsuperscript{3+}, Mo\textsuperscript{5+}, Ru\textsuperscript{2+}, V\textsuperscript{5+} or Rh\textsuperscript{2+}) can improve the activity of photocatalysts by prolonging the recombination time of electron-hole pairs, widening the available wavelength range, and increasing the utilization rate of visible light (Yu \textit{et al.} 2009). Further, band gap modification can be done through nonmetal doping and co-doping of nitrogen, halogen, sulphur, boron, or carbon. For example, doping nitrogen into substitutional sites of TiO\textsubscript{2} narrows the bandgap and induces photocatalytic activity in the visible light region (Asahi \textit{et al.} 2001). In addition, TiO\textsubscript{2} improved with carbon doping possesses more micro-pores, and its degradation capability is two times higher than that of the ordinary TiO\textsubscript{2} (Yu \textit{et al.} 2009).
The use of composite materials is a method to improve the activity of a catalyst since composite materials can have higher specific surface areas, improve the reaction conditions, and widen the response range to light (Yu et al. 2009).

4.2.5 Morphology of photocatalysts

The ability to control particle morphology is an important objective in nanocrystal synthesis, as size and shape can significantly influence various properties (Ischenco et al. 2005, McLaren et al. 2009). For example, the photocatalytic properties of Cu$_2$O depend strongly on the shape of the crystals, and Cu$_2$O octahedra have shown higher photocatalytic activity than the Cu$_2$O cubes (Ho & Huang 2009, Xu et al. 2006).

The Degussa P25 as well as several others finely powdered photocatalyst particles suspended in contaminated waters in slurry systems are widely utilized (Marugán et al. 2009, Nishio et al. 2006), however the powder form catalyst has to be removed after the photocatalytic treatment. The post-treatment removal of the photocatalyst may be a time-consuming and expensive process, and in addition, can significantly reduce other benefits gained via the photocatalytic mineralization process (Mahmoodi & Arami 2006). In order to eliminate this solid-liquid separation stage the catalyst should be immobilized onto a suitable solid support, e.g. glass tubes or plates, glass fibre filters, activated carbon filters, textile or steel fibres (Hosseini et al. 2007, Chong et al. 2010). The immobilization can result in a significant reduction in system efficiency, since the fixation of catalysts into a large inert substrate can inherently reduce the surface area available for the reaction, the number of catalyst active sites and also the mass transfer limitations may enlarge (Chong et al. 2010). However, in some studies the catalyst has been reported to inherit a high surface area from a specially prepared nanostructured support since the mass transfer limitation can be resolved by a thin longitudinal morphology of the nanofibers, nanowires or nanorods (Doh et al. 2008, Turkevych et al. 2008, Chong et al. 2010).

4.2.6 Deactivation and regeneration of photocatalysts

Poisoning and deactivation of photocatalysts, i.e. the loss of the photocatalytic performance during operation, are mainly resulted from crystallite aggregation and intermediate products and/or inorganic ions adhering to the surface of photocatalyst more strongly than the reactants themselves (Li et al. 2009, Miranda-Garcia et al. 2009).
Deactivation is an important issue for practical applications of photocatalysts. A comparative study of literature data reveals that photocatalyst deactivation is generally found in single-pass fixed photocatalytic reactors (Sauer & Ollis 1996). Depending on the nature of the organic compound both reversible and irreversible deactivation are observed (Carp et al. 2004). The regeneration treatment of the catalyst depends on the causes of the deactivation. Thus, finding a suitable regeneration method to recover the initial photocatalytic activity of a specific application is a major challenge to be faced. There are different regeneration methods for photocatalysts, and a few them are mentioned below.

- Thermal regeneration achieved by heating at temperatures high enough to decompose the intermediates (Carp et al. 2004).
- Photocatalytical regeneration using simultaneous UV illumination and exposure to humidified air. However, since the surface intermediates leading to activity loss are probably recalcitrant to photocatalytic regeneration, it requires longer regeneration times than thermal regeneration (Carp et al. 2004).
- Flowing humid air over the catalyst (Carp et al. 2004).
- Washing with alkaline solutions, e.g. NaOH or NH₄OH (Carp et al. 2004, Miranda-García et al. 2014).
- soft-mechano-chemical ion exchange method: Activity of nano-ZnO suspending solution photocatalyst can be regenerated and no pollutants are produced under the process (Li et al. 2009).
- Oxidation with H₂O₂ combined or without UV irradiation (Kanna et al. 2010).
5 Hybrid techniques

The increased demands for both drinking water quality and industrial effluents encourage the development of effective and low cost water treatment technologies. One possibility for achieving this aim is to combine existing methods into a so-called hybrid process. Generally, hybrid processes have been described as processes where one or more processes are coupled with other unit processes and are integrated into a single system. Several different physical, chemical and/or biological processes can be combined so that they complement each other well, thus forming a hybrid process. This way, the disadvantages of each separated process can be overcome and the advantages can be further enhanced and hence the sustainability and process efficiency can be improved.

Hybrid separations and technologies are required mainly for the following: (1) to increase process efficiency along with cost effectiveness, (2) to comply with stringent pollution control norms, (3) to take advantage of various new developments in the separations area including new devices/processes. For example, hybrid process can be done in combination with individual processes including coagulation, adsorption/ion exchange, membrane techniques, cavitation, biological methods, and advanced oxidation processes. The hybrid technologies can substantially improve the treatment and e.g. biological process combined with AOPs can reduce the toxicity of the pollutants to the needed level. (Ranade & Bhandari 2014)

There are several hybrid material development research published related to adsorption and photocatalysis for water treatment. For example, Vimonses (2011) published a doctoral thesis titled Development of Multifunctional Nanomaterials and Adsorption-Photocatalysis Hybrid System for Wastewater Reclamation. In the thesis, low-cost, local Australian materials (clay minerals) were investigated in dye adsorption and further impregnated with TiO₂ to get a hybrid material to be used in an annular slurry photoreactor. The chemical removal efficiency was notably enhanced. (Vimonses 2011)

Li et al. (2006) studied TiO₂-coated activated carbon for the photodegradation of methyl orange with several benefits compared to only adsorption or photocatalysis; (1) the adsorbent support provides a high concentration environment for the target organic molecules near the loaded TiO₂ particles by adsorption, thus enhancing the rate of photooxidation; (2) the possible toxic intermediates are also adsorbed and oxidized instead of being released into the atmosphere or solution phase, thus secondary pollution by the intermediates is
prevented; (3) the high adsorption ability of the hybrid photocatalysts for the organic substances is maintained for a long time because the adsorbed molecules are finally mineralized to produce CO₂.

Lim et al. (2011) reviewed the synergistic adsorption-photon catalysis processes with TiO₂/AC for organic pollutants degradation. They reported advantages compared to the systems with bare TiO₂ to be: (1) TiO₂/AC is more versatile and provides more reliable pollutant removal; (2) TiO₂/AC might be more resistant to deactivation; (3) TiO₂/AC provides better mineralization results; and (4) micron-size TiO₂/AC is more easily recovered than the nanoparticulate TiO₂. However, they have also considered numerous practical issues to be taken into account before the TiO₂/AC can be utilized commercially or in industrial applications, including:

- Dispersibility and recovery from aqueous phase.
- UV intensity and its attenuation.
- Photostability under prolonged UV irradiation.
- Mechanical stability.
- Effect of the solution matrix.
- Assessment of the photoysis products for their toxicity, degree of mineralization, hydrophobicity/hydrophilicity, trihalomethane formation potential, biochemical oxygen demand (BOD).
- Potential microbial fouling of the TiO₂/AC.
- Regeneration.

In addition to published research results, there are ongoing research projects related to this field. For example, The Finnish Funding Agency for Innovation (Tekes) has funded a project called Nanostructured hybrid materials for removal of heavy metals from waste waters. In the project, the approach is to combine microcrystalline bisphosphonates (BP) with nanostructured silicon (PSi). The stable hybrid material of BP and PSi can make the adsorption of metal ions faster and more effective. (Lehto 2014)

Nanocomposite materials for photocatalytic degradation of pollutants is an ongoing project funded by the European Commission 7th Framework Programme, FP7-NMP 'Cooperation', 'Nanosciences, nanotechnologies, materials and new production technologies'. The project aims at developing materials and technologies based on the synergic combination of different types of nanoparticles (NPs) into a polymer host in order to generate innovative nanocomposites for the catalytic degradation of pollutants and bacteria, both in gaseous and aqueous phases. (European Commission 2014)
6 Materials and methods

6.1 Adsorption materials

6.1.1 Activated carbons

Three different agro-waste raw materials were used for activated carbon preparation, cocoa pod husk (CPH, *Theobroma cacao*), in Papers I and II, and red mombin seeds (RMS, *Spondias purpurae* L.) and ice-cream bean seeds (GS, *Inga edulis*) in Paper III. All the raw material samples were collected from different agricultural areas in Tumbes, Northwest Peru, and they were chemically activated and the produced activated carbons were used for the adsorption experiments. In addition to cocoa pod husk based activated carbons in Paper II, a commercial activated carbon Chemviron (by CalgonCarbon) was used as a reference material. It has a BET surface area of 775 m$^2$/g, which is at the same level as both the studied CPH ACs. The Chemviron material was used as such with its original particle size of around 1–2 mm, and in addition it was ground and sieved to a particle size fraction less than 0.25 mm in order to study similar particle size with the CPH ACs.

The CPH raw material was dried at 80 °C to obtain a constant weight, and was ground and sieved to two fractions: 0.25–0.5 mm and 0.5–1 mm. The activation chemicals potassium carbonate (K$_2$CO$_3$), potassium hydroxide (KOH) and zinc chloride (ZnCl$_2$) were used in a weight proportion of 1:1. The ratio 1:1 of raw material:ZnCl$_2$ has been reported as an effective ratio for agro-waste based activated carbon production (Kalderis *et al.* 2008), and higher ratios could cause problems during the activation and wash phases, and affect the final quality of activated carbons (Ahmadpour & Do 1997).

With K$_2$CO$_3$ and KOH, water was added to the samples before the carbonization in the ratio of 1:1 (water:mixture of CPH and activation chemical), and dried at 100 °C overnight. All the materials were carbonized for two hours at three different temperatures (500, 650 and 800 °C) reached at the heating rate of 10 °C/min, and then cooled down to room temperature. The carbonization process was done under a nitrogen atmosphere (150 ml/min). After carbonization, the samples activated with KOH and ZnCl$_2$ were washed with dilute HCl (0.5 N) solution and room temperature distilled water. The samples activated with K$_2$CO$_3$ were washed first with boiled distilled water and then with room temperature
distilled water. Finally, all samples were dried at 100 °C overnight, ground and sieved to less than 0.25 mm particles.

The RMS raw material was washed repeatedly in order to remove the fruit pulp residues and to avoid undesirable reactions during activation and pyrolysis. Samples of GS were used without washing. Both raw materials were dried at 100 °C until a constant weight was achieved, and ground and sieved to obtain a particle size between 0.5–1 mm. ZnCl₂ was mixed with the sieved raw materials in a 1:1 weight proportion under dry conditions. It is important to notice that during the mixing, water from the surrounding air and from the raw material was adsorbed by the chemical activation agent. It might occur because of the hydrophilic character of ZnCl₂ and/or the occurrence of osmotic dehydration phenomenon. The mixture was carbonized under a nitrogen gas flow (150 ml/min) at 600 °C for two hours, using a heating rate of 10 °C/min. An indirect air flow was used to cool the samples down to room temperature. After the carbonization, the samples were washed with dilute HCl (0.5 M) and then repeatedly with distilled water at room temperature until the pH of the washed solution was 6–6.5. Finally, all samples were dried at 100 °C overnight, ground and sieved (< 0.25 mm).

6.1.2 Hydrous titanium dioxide

Paper IV studied a nanocrystalline hydrous titanium dioxide (TiO₂) containing a mixture of titanium hydroxide and anatase titanium dioxide. This finely divided high surface area powder was an intermediate from the TiO₂ manufacturing process. The material was not thermally treated (i.e. calcined) so the surface area remained high. Kemira, an international chemicals company, provided the material for this study.

6.2 Photocatalytic materials

All the studied photocatalysts were TiO₂ based materials. In Paper V, the commercial photocatalyst Aeroxide P25 (formerly Degussa) was used. Paper VI studied tailor-made nanofibers (NF) and a commercial TiO₂ product Degussa P25. The P25 catalyst has a phase composition of 75% anatase and 25% rutile, its specific surface area was 56 m²/g, average pore size 9 nm, and total pore volume 0.13 cm³/g.

The nanofibers were nitrogen doped and decorated with palladium (Pd) or platinum (Pt). The preparation method for the studied catalysts is reported more
detailed by Wu et al. (2011a and 2011b). In the catalyst preparation process, titanate NFs were synthesized in alkaline media (10 M NaOH) by the hydrothermal route from anatase TiO2 nanoparticles. The obtained sodium titanate was washed with 0.1 M HCl to exchange Na+ ions for protons in the nanofibers. Finally, the product was washed with deionized water to reach pH ∼ 7 and finally filtered and dried in air at 70 °C. In the next step, the titanate NFs were calcined in air to obtain TiO2 NFs and/or in ammonia to produce N-doped TiO2 NFs, referred as N-TiO2(A) NF (annealed only in ammonia) and N-TiO2(B) NF (annealed in air and subsequently in ammonia). Pd(II) and Pt(II) acetyl acetonates were impregnated and decomposed on the surfaces of the nanofibers to obtain the active metal sites on the catalyst. The metal loading of the catalysts obtained from the impregnation was approximately 1 wt% (Wu et al. 2011a, Wu et al. 2011b). The TiO2 nanofibers were prepared in the Microelectronics and Materials Physics Laboratories, Faculty of Information Technology and Electrical Engineering, University of Oulu.

6.3 Material characterization

Different characterization methods including proximate, elemental, textural, and structural analyses, were carried out in order to characterize the studied adsorption and photocatalytic materials, as well as some of the raw materials.

6.3.1 Proximate analysis

Proximate analysis is a thermal analysis technique. It provides an approach to estimating the content of moisture, volatile matter, fixed carbon, and ash (Durán-Valle 2012). In papers I to III, proximate analysis consisted of moisture (wt%), dry matter (wt%), and ash (wt%) contents analyses. Moisture was determined using the ASTM D2867-04 method, consisting of the oven-drying method at 150 °C, until a constant weight was achieved. The dry matter content (%) was obtained from the difference between 100% and the moisture content (%). The ash content was calculated using the ASTM D2866-94 (reapproved 2004) method at 650 °C in a muffle furnace until a constant weight was achieved. The proximate analyses for paper I and II were completed in the Environmental and Chemical Engineering research group in the Faculty of Technology, University of Oulu. For Paper III, the analyses were conducted in the National University of Tumbes, Peru.
6.3.2 Elemental analysis

In papers I and II, elemental analysis included the determination of different elements (wt%) such as carbon (C), oxygen (O), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K), calcium (Ca), iron (Fe) and zinc (Zn), etc. These were analysed using an inductively coupled plasma optical emission spectrometer (ICP-OES) Perkin Elmer Optima 5300 DV. Before the analysis, a microwave-assisted sample digestion including dissolving with a mixture of HNO₃, H₂O₂, HF and HCl was performed. The ICP-OES analyses were conducted in the Trace Element Laboratory in the Department of Chemistry at the University of Oulu.

6.3.3 Textural characterization

Nitrogen physisorption was used in order to determine the textural parameters of the studied materials. In papers I-III, the nitrogen physisorption measurements at 77K were performed on a Gemini VII 2390 Surface Area Analyzer (Micromeritics, USA) and by ASAP2020 (Micromeritics). The specific surface area, \( S_{\text{BET}} \), was calculated according to the classical BET theory. The mesopore-size distribution was evaluated from the desorption branch of the nitrogen adsorption-desorption isotherm by the Barrett–Joyner–Halenda (BJH) method (Barret et al. 1951) via the Roberts algorithm (Roberts, 1967), using the carbon standard isotherm and the assumption of slit-pore geometry. The physisorption analyses for papers I to III were partly performed in the National University of Engineering, Lima, Peru and partly in the Institute of Chemical Process Fundamentals (ICPF) of the CAS, v. v. i., Prague, Czech Republic.

In addition, in Paper III, the bulk density (\( \rho_{\text{Hg}} \)), the skeletal density (\( \rho_{\text{He}} \)), the porosity (\( \varepsilon \)), and the intrusion pore volume (\( V_{\text{intruse}} \)) of the processed raw agro-materials were determined by high-pressure mercury porosimetry and helium pycnometry measurements. Those measurements were conducted on an AutoPoreIII mercury porosimeter (Micromeritics, USA) and an AccuPycII1340 pycnometer (Micromeritics, USA), respectively, also in the ICPF. The mercury porosimetry technique consists of measuring the extent of mercury penetration into the pores of a solid as a function of the applied pressure (Durán-Valle 2012). The gas pycnometry is recognized as one of the most reliable techniques for obtaining skeletal (true) volume and density by using a gas displacement method (Micromeritics 2015). Before the measurements, the raw materials received as non-
crushed seeds were dried in an oven at 105 °C for several days to remove the physisorbed moisture. For each precursor the high-pressure mercury porosimetry measurement was carried out at least twice in order to evaluate the average value of porosity because of the inhomogeneity in the pore structure of the raw materials. Porosity, \( \varepsilon \) (%), was calculated according to the following equation

\[
\varepsilon = \left( 1 - \frac{\rho_{He}}{\rho} \right) \cdot 100
\]

(20)

In papers IV-VI, the nitrogen physisorption measurements at -196 °C were performed with an automated volumetric apparatus Micromeritics ASAP2020. \( S_{BET} \) (m\(^2\)/g), determined for all the catalysts, was evaluated from the adsorption data according to the classical BET method. The total pore volume (\( V_p \)) and the average pore width were evaluated using the BJH-method. The physisorption analyses for papers IV-VI were completed in the Environmental and Chemical Engineering research group in the Faculty of Technology, University of Oulu.

6.3.4 Structural analysis

The Fourier Transform Infrared Spectroscopy (FTIR) is one of the most powerful tools for identifying different types of chemical bonds, and thus functional groups on the surface of the material. The absorbed wavelength is characteristic for the chemical bond, and when the infrared absorption spectrum is interpreted, the chemical bonds in a molecule can be determined (Coates 2000). In Paper II, FTIR analyses were carried out for the CPH ACs, obtained by Shimadzu Spectrophometer IRPrestige-21. Pressed potassium bromide (KBr) pellets were prepared and the spectra were evaluated between 4000–400 cm\(^{-1}\). The FTIR measurements were completed in the National University of Engineering, Lima, Peru.

Raman spectroscopy is a standard nondestructive tool for the characterization of crystalline, nanocrystalline, and amorphous carbons (Ferrari & Robertson 2000). Raman spectroscopy can be used to study vibrational and rotational modes in a system, and for most of the activated carbons, Raman spectra gives two peaks generally at 1360 and 1580 cm\(^{-1}\), corresponding to disordered carbons structure and graphite structure, respectively (Durán-Valle 2012). The presence and position of D- and G-peaks, their intensity ratio (I_D/I_G) and full width at half maximum (FWHM) can be used to extract structural information of the materials (Ferrari & Robertson 2000). In Paper III, Raman spectra were collected in order to reveal the
structure order of the produced activated carbons using a dispersive Nicolet Almega XR spectrometer equipped with an Olympus BX 51 microscope. An excitation laser source (473 nm) with an incident power of 5 mW with 256 expositions with 0.5 s duration was used for collecting the spectra. The laser beam was focused to a spot of 0.6 mm in diameter. The incident energy was minimized to avoid thermal effects as a consequence of the laser irradiation. Spectral resolution of the instrument was 1.93 cm\(^{-1}\) and the spectrometer was calibrated using a crystalline silicon standard with line at 520 cm\(^{-1}\). The samples during analysis were placed on an aluminium substrate. Raman spectra were taken from several different places within each sample. The Raman spectroscopy measurements were conducted at the ICPF, in the Czech Republic.

6.3.5 High magnification imaging and elemental mapping

In all the papers, pore shape and pore distribution of the prepared materials were studied using FESEM images from a Field Emission Scanning Electron Microscopy Zeiss Ultra plus equipped with Oxford Instruments INCA-X-act Energy Dispersive X-ray Spectrometer (EDS) detector. The combination of these two techniques allows a point elemental analysis of the surface, and can be used to study the content and dispersion of metals on surfaces (Durán-Valle 2012).

Prior to the imaging, the TiO\(_2\) samples and the raw materials were coated with a carbon layer to avoid the accumulation of charge. The activated carbon samples were studied without the additional carbon layer. The FESEM imaging was completed at the University of Oulu in the centre of Microscopy and Nanotechnology.

The elemental analysis was done with a Tescan Indusem Scanning Electron Microscope with an EDX probe Bruker Quantax 125eV, performed at the ICPF, Czech Republic. For each produced activated carbon, a representative sample (0.25 mm particle size) was taken from the stock and the EDX analyses were carried out on three different areas of the sample. The averages of the results are reported.

6.3.6 Surface charge analysis

The pH is one of the most important variables in the adsorption in solution, since this parameter affects the surface charge of the adsorbate. The predominant charge (positive or negative) depends on the acidic or basic character of the adsorbent.
Therefore, it is important to study the presence of acidic or basic functional groups on the adsorbents (Durán-Valle 2012).

In Paper II, the pH of the point of zero charge ($\text{pH}_{\text{PZC}}$) was determined for both CPH ACs (CPH-21 and CPH-22) and for commercial Chemviron by using an acid-base titration method. Aliquots with 50 ml of 0.01 M NaCl solution were prepared in separate flasks. The pH was adjusted with an addition of 0.01 M solutions of NaOH or HCl. When the pH value was constant, 0.15 g of the activated carbon sample was added to each flask and shaken for 24 h with a mechanical shaker. The $\text{pH}_{\text{PZC}}$ value is the point where the curve $\text{pH}_{\text{final}}$ versus $\text{pH}_{\text{initial}}$ crosses the line $\text{pH}_{\text{initial}}=\text{pH}_{\text{final}}$.

In Paper IV, the zeta potential (isoelectric point) of the material was determined using a Coulter Delsa 440SX zeta potential analyser. Before the analysis, a 135 mg/l suspension of the TiO$_2$ sample in 0.1 M NaNO$_3$ solution was done to obtain the desired ionic strength. The suspensions were measured for the zeta potential (or surface charge density) at different pH values varying from 2 to 8, and the zeta potential curve as a function of the pH was possible to determine from the measured points. The point, in which the surface charge equals zero is the zero point of charge of the studied material. Z potential is the level of pH which the zero charge is reached but considering only the charge of the material surface.

All the $\text{pH}_{\text{PZC}}$ analyses were completed in the Environmental and Chemical Engineering research group, Faculty of Technology at the University of Oulu.

6.3.7 Phase composition and crystallite size

X-ray diffraction (XRD) was used to identify the phase composition and crystallite size of the hydrous titanium dioxide (Paper IV and V) using a Siemens D500 diffractometer employing nickel filtered Cu Kα radiation ($\lambda = 1.5406 \text{ Å}$). The XRD patterns were acquired in the diffraction angle range of $10^\circ \leq 2\theta \leq 75^\circ$. The XRD analysis was performed at the University of Oulu. XRD peak broadening can be used to evaluate the crystallite size (a large peak means small particles and vice versa) by different theories using the full width height medium (Scherrer equation), integrated width (Williamson-Hall formula) and the Fourier transform (Warren- Averbach theory) (Scherrer 1918, Williamson & Hall 1953, Warren & Averbach 1950). Here, the Scherrer’s formula has been used.
6.4 Adsorption experiments

6.4.1 Agro-waste based activated carbons as adsorbents

In Paper I, batch adsorption experiments were carried out to test the arsenic adsorption capability of the five best activated carbons obtained. The experiments were conducted at room temperature. The initial arsenic concentration of 100 µg/l in the 200 ml batches was achieved by diluting the As stock solution with Milli-Q water. The initial pH of the arsenic solution was between 6 and 7 and the experiments were conducted without adjusting the solution pH during the test. The activated carbon loadings were 0.5 g/l and 1.0 g/l. The solutions were shaken with a Certomat mechanical shaker at 175 rpm for six hours. Samples were taken periodically as a function of time, filtered through 0.45 µm syringe filters and acidified with p.a. nitric acid in order to maintain the preservability of the samples. The arsenic concentration of the samples was analysed using a Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) Perkin Elmer A Analyst 600 at the University of Oulu, Finland.

In Paper II, kinetic adsorption experiments with synthetic multicomponent solutions were carried out. An aqueous solution of As(V), Cd(II) and Pb(II) was prepared with the initial concentrations of 210, 190 and 140 µg/l, respectively. The initial concentrations were based on the real concentrations found from the Puyango-Tumbes river water in the dry season (ANA 2014). CPH-21 and CPH-22 were used with particle size <0.25 mm, Chemviron activated carbon was used with two particles sizes: <0.25 mm and between 1 and 2 mm. The synthetic multicomponent solutions were studied in 200 ml batches with an activated carbon dosage of 0.5 g/l, and the initial pH close to 7 in order to be close to most of the natural waters. Finally, the solutions were shaken with a Certomat mechanical shaker at 175 rpm for 4 hours. The samples taken at certain time intervals until 240 minutes were filtered through 0.45 µm syringe filters and acidified with p.a. nitric acid. As, Cd and Pb concentrations in the aliquots were analysed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS), Thermo Fisher Scientific, XSeries II Q ICP-MS with a detection limit of 0.25 µg/l.

Adsorption kinetic experiments with the Puyango-Tumbes River water (Paper II) were carried out in order to test the ability of the CPH ACs to adsorb As, Cd and Pb from real polluted natural water. The water was collected from the Puyango-Tumbes River approximately 2 weeks before the adsorption experiments were conducted at the University of Oulu, Finland. The River water was acidified
(pH < 2) with p.a. concentrated nitric acid in order to maintain the preservability of the water and to prevent microbial growth in it. The sampling time was not during the dry season (28th January, 2014), so the concentrations of the metals and metalloids were lower than with the synthetic multicomponent water. The pH level of the sample of Puyango-Tumbes river water was re-adjusted before the experiments by adding diluted NaOH (0.1–1 M) to reach a pH level of 6.8. Because of the conditions of redox potential (50–100 mV), the pH level (close to 7) of the river water samples is supposed that As is present predominantly with the valence of +5 and Cd and Pb with the valence of +2. The particle size of the studied ACs (CPH-21, CPH-22, and Chemviron) was less than 0.25 mm.

The sample of the Puyango-Tumbes River water was divided in 150 ml batches and put into separate flasks. A dose of 0.5 g/l of ACs was added. The aliquots taken at different time intervals (0–6 h) were filtered through 0.45 μm syringe filters and acidified with p.a. nitric acid before the analysis. In addition, extra aliquots were taken during the experiments after 22 hours in order to determine further information about the content of other heavy metals and elements from the river water and/or activated carbon impurities that could interfere with the adsorption of the three studied ions (As, Cd, Pb). As, Cd, Pb and other element concentrations in the aliquots were analysed using an Inductively Coupled Plasma Mass Spectrometer, Thermo Fisher Scientific, XSeries II Q ICP-MS with a detection limit of 0.25 µg/l. The analyses for Paper II were done in the accredited laboratory Suomen ympäristöpalvelu (Ahma Insinöörit Oy), Oulu, Finland.

In Paper III, batch adsorption experiments were carried out to test the methylene blue (MB) and arsenic (As) adsorption capacities of the prepared activated carbons at room temperature. The MB experiments were conducted without a pH adjustment (the pH level directly measured was between 5.5 and 6.5) and at room temperature between 20 and 25 °C. The As experiments included a pH adjustment from the initial pH 3.3 to pH 6.

In the case of MB, the activated carbon concentration was 0.5 g/l and the initial MB concentration was 50 mg/l (prepared from the 1000 mg/l stock solution), in a 250 ml erlenmeyer flask. The solutions were shaken in a magnetic stirrer during the experiments. Aliquots were extracted at the beginning and at different times between 5 and 150 min. In order to determine the MB concentration a UV-Vis spectrophotometer Spectroquant Pharo 300 by Merck was used at the wavelength of 660 nm. In order to obtain the calibration curve, solutions of MB were prepared with different concentration between 5 and 50 mg/l. The MB adsorption
experiments and analyses were conducted at the National University of Tumbes, in Peru.

In the case of arsenic adsorption, the initial arsenic concentration was 100 µg/l in 200 ml batches and the activated carbon loading was 0.5 g/l. The solutions were shaken with a Certomat mechanical shaker at 175 rpm for four hours. Samples were taken periodically at certain time intervals until 240 minutes, filtered through 0.2 µm syringe filters and acidified with p.a. nitric acid in order to maintain the preservability of the samples. The arsenic adsorption experiments were conducted in the Environmental and Chemical Engineering research group, at the University of Oulu. The arsenic concentration of the samples was analysed using an Inductively Coupled Plasma Mass Spectrometer, Thermo Fisher Scientific, XSeries II Q ICP-MS with a detection limit of 0.25 µg/l in the Suomenympäristöpalvelu laboratory.

The reproducibility of the adsorption experiments was confirmed by repeating selected experiments.

6.4.2 Hydrous titanium dioxide as an adsorbent

In Paper IV, two different experimental series were conducted, one for the kinetic analysis and another one for the equilibrium analysis. In the kinetic analysis, the effect of pH, adsorption time, and adsorbent dose on arsenic removal was evaluated by separate batch experiments. Adsorption experiments were carried out at room temperature. De-ionized water was used to prepare all the solutions into in 5 l glass beakers. The initial concentration of both As(III) and As(V) was 1 mg/l (i.e. 13 µmol/l) in all cases. The pH of the solution was adjusted to 4, 6, or 8 with dilute hydrochloric acid or sodium hydroxide, and the required amount of TiO2 was added. The solutions were stirred with a mechanical propeller mixer (150–200 rpm) for 22 h, and the pH was maintained at the initial value throughout the experiments by the addition of acid or base solutions. The samples were taken as a function of time, filtered through 0.2 µm syringe filters and acidified with p.a. HCl or HNO3 in order to maintain the preservability of the samples. The arsenic concentration of the samples was analysed with a combination of a spectrophotometer (Perkin Elmer 5100) and a Flow Injection Analysis System (Perkin Elmer FIAS 400) using the mercury hydride method.

The adsorption equilibrium was examined by isotherm experiments at room temperature at pH values of 4, 5, and 6. As(III) and As(V) containing solutions (800 ml each) in a concentration range from 0.2 to 8.5 mg/l were prepared in
de-ionized water. The pH was adjusted with dilute HCl or NaOH. The required amounts of adsorbent, from 25 mg/l to 100 mg/l, were added to obtain the desired suspensions. The equilibrium was let to settle for 28 days before the equilibrium samples were withdrawn, filtered through 0.2 µm syringe filters and analysed for arsenic concentrations as described earlier. The equilibrium time was quite long in order to see the longer time viability of the adsorbent, i.e. to affirm that the arsenic was not starting to be desorbed over a longer term. The equilibrium adsorption capacity \( q_e, \mu g/mg \) was calculated using the following equation:

\[
q_e = \frac{(c_0 - c_e)V}{m_{ads}}
\]

where \( c_0 \) and \( c_e \) are the initial and equilibrium concentrations (µg/l) of arsenic in solution, respectively. \( V \) is the total volume of the solution. The reproducibility of the adsorption experiments was confirmed by repeating selected experiments.

### 6.5 Photocatalytic experiments

Photocatalytic experiments were carried out in two different self constructed laboratory scale reactors, one made of quartz (1.0 l) (Fig. 4.) and the other made of Teflon with an inner glass cylinder for the test solution (0.5 l) (Fig. 5).

![Fig. 4. The photocatalytic Quartz reactor setup with 1 air flow inlet, 2 mass flow controller, 3 photoreactor, 4 gas outlet, 5 cooling circulation, 6 hose pump, 7 sampling, 8 heat exchanger, 9 cooling water in/out, 10 six UV-A lamps.](image)

The quartz reactor was used to study the effects of pH and catalyst dose, on the degradation of the pollutants. The Teflon reactor was used for the experiments with the industrial wastewater solution. The quartz reactor was a vertical tubular reactor with a circulation loop. The circulation of the slurry was maintained by a peristaltic
pump operating at a speed of 60 l/h. The circulation had two functions: firstly, to maintain good agitation and secondly, to control the temperature. The circulation loop contained a heat exchanger through which the slurry was passed. The loop also contained the sampling port through which the samples were drawn for analysis after pre-defined sampling times. A synthetic air feed (6.5 cm$^3$s$^{-1}$) to the reactor was accomplished with a sintered glass tube to improve the dissolution of gas in the reaction suspension. The compartment contained six UV-A lamps with the maximum radiation at the wavelength of 365 nm (Philips, 15 W) which were placed outside the reactor hexagonally. The average light irradiance measured with a Delta Ohm Photo-Radiometer HD2302.0 was 15 W/m$^2$.

In the experiments, the solutions with initial concentration of 15 mg/l of the organic compounds with different amounts of the catalyst was introduced into the reactor. Before the photocatalytic experiment, a 30 min. dark period was used to establish the adsorption/desorption equilibrium between the solid and liquid materials in the reactor. After the dark period, the UV-A lamps were switched on and the photocatalytic experiment was continued for 3 hours. The temperature of the test solution was adjusted to room temperature during the experiment and followed with a thermocouple (Delta OHM HD2128.1). Samples were drawn at certain time intervals and filtered through a 0.2 µm filter (Millipore) to remove suspended TiO$_2$. The concentration of the pollutants, pH and TOC were measured from the filtered samples.

The Teflon reactor (Fig. 5) was an annular type vertical batch photoreactor. Synthetic air was bubbled into the reactor with a flow rate of 2.5 cm$^3$s$^{-1}$ before starting and during the experiments. The reactor had a plunging tube made of quartz and fixed in the middle of the reactor cell for the UV-A lamp (Philips Cleo PL-L 36 W with maximum radiation at a wavelength of 350–360 nm). The irradiance in the annulus of the reactor was measured to be 52 W/m$^2$ using Delta Ohm Photo-Radiometer HD2302.0. The experiments were adjusted to room temperature (25±1 ºC) by cooling water circulation in a steel coil inside the reactor, the flow controlled using a flow-meter. The temperature was monitored using a Delta OHM HD2128.1 thermocouple. Constant agitation of the test solution was provided by a Heidolph MR3000 magnetic stirrer with approximately 250 rpm. The pH of the solution was measured using a HACH H170 pH meter.
The experiments were done with the initial concentration of 15 mg/l of the pollutants and with a catalyst dose of 200 mg/l in Paper V. In addition, in Paper V the photocatalysis was also studied in a diluted pharmaceutical wastewater matrix. It contained different organic compounds, mainly ethanol and smaller amounts of other alcohols and ketones. The wastewater was highly alkaline with a pH above 12. The total organic compound (TOC) content was 7600 mg l⁻¹. The actual test water was prepared by mixing 15 ml of the industrial wastewater with 15 mg of each of the model compounds and by diluting the solution into 1000 ml with distilled water. Diluted NaOH and HCl were used for adjusting the initial pH of the solutions. In Paper VI the initial butanol concentration was 0.25 vol% (i.e. 27.3 mmol/l) and the catalyst loadings were 50 and 100 mg/l.

The dark equilibrium conditions were reached after 30 min. mixing, and the lamp was switched on. The progress of the reactions was followed by taking samples from the suspension at certain time intervals and by analysing the pollutant concentrations. Prior to the analysis the aqueous samples were filtered through 0.45 µm syringe filters in order to remove the suspended TiO₂ catalysts. The reproducibility of the photocatalytic experiments was confirmed by repeating selected experiments.

The influence of direct photolysis in the absence of TiO₂ under the UV-A irradiation was studied with both the reactors in separate experiments at similar conditions as the photocatalytic test runs.

In Paper V, the concentration of the model pollutants were followed by a spectrophotometer (Beckman DU-640i) at the wavelengths of 228, 230, 248 and 283 nm for bisphenol A (BPA), phthalic anhydride (PHA), diuron and p-coumaric acid (PCOU), respectively. Calibration curves were prepared for all the studied...
compounds by dissolving desired amounts of the reagents into Milli-Q ultrapure water (MQ). The total organic carbon present in the samples was determined by a TOC analyser (Shimadzu TOC-5000A). The necessary dilutions of the samples were prepared in MQ-water.

In Paper VI, the quantification of butanol in the samples was carried out with a Gas Chromatograph Agilent Technologies 6890N Network GC System utilizing an Agilent DB-ALC1 capillary column of 320 µm in diameter, and 1.8 µm film thickness. Helium was utilized as the carrier gas in the inlet at 2.0 cm³/min and the make-up gas in the flame ionization detector at 25 cm³/min., air as utility gas at 250 cm³/min, and hydrogen as the combustible gas at 60 cm³/min. The oven temperature was kept at 50 ºC for 2 minutes, then raised with a constant rate of 50 ºC/min. to 100 ºC, held for 2 min. and then raised again with 50 ºC/min. to 150 ºC, where it was held for 2 min. The injector and detector temperatures were both 250 ºC; the split ratio for injection was 1:1. The injection volume was 2 µl. A multi-point calibration curve enabled the calculation of the liquid phase concentrations of the studied alcohol.
7 Results and discussion

7.1 Water treatment by adsorption

7.1.1 Development of agro-waste based activated carbons and their adsorption properties

In Paper I, the activated carbons were prepared from cocoa pod husks using three different activation chemicals (KOH, K_2CO_3 and ZnCl_2) at three different temperatures, shown in Table 3.

<table>
<thead>
<tr>
<th>Carbonization temperature (ºC)</th>
<th>KOH</th>
<th>K_2CO_3</th>
<th>ZnCl_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (mm)</td>
<td>0.25-0.5</td>
<td>0.5-1</td>
<td>0.25-0.5</td>
</tr>
<tr>
<td>500 CPH-10</td>
<td>CPH-10</td>
<td>CPH-12</td>
<td>CPH-18</td>
</tr>
<tr>
<td>650 CPH-08</td>
<td>CPH-08</td>
<td>CPH-11</td>
<td>CPH-16</td>
</tr>
<tr>
<td>800 CPH-07</td>
<td>CPH-07</td>
<td>CPH-09</td>
<td>CPH-13</td>
</tr>
</tbody>
</table>

All together 18 activated carbon samples were prepared from the CPH raw material. However, with three of them (CPH-07, CPH-08 and CPH-10), the yield was really low and practically only an insignificant amount of the product was recovered. This might be due to the following reasons: (1) the CPH particles of 0.25–0.5 mm were digested by KOH, (2) high volatilization took place during the carbonization stage, (3) material loss during the washing step. The rest of the produced ACs were characterized for their properties using various methods, shown in Table 4.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>T (ºC)</th>
<th>Act. agent</th>
<th>Particle size (mm)</th>
<th>Final yield (%)</th>
<th>Bulk density (kg/l)</th>
<th>Ash (%)</th>
<th>Moisture (%)</th>
<th>Dry matter (%)</th>
<th>S_{BET} (m^2/g)</th>
<th>V_p (cm^3/g)</th>
<th>Av. pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPH-09</td>
<td>800</td>
<td>KOH</td>
<td>0.5-1</td>
<td>13.5</td>
<td>0.1</td>
<td>22.3</td>
<td>6.8</td>
<td>93.2</td>
<td>490</td>
<td>0.24</td>
<td>2.0</td>
</tr>
<tr>
<td>CPH-11</td>
<td>650</td>
<td>KOH</td>
<td>0.5-1</td>
<td>20.7</td>
<td>0.23</td>
<td>53.0</td>
<td>9.0</td>
<td>91.0</td>
<td>8</td>
<td>0.02</td>
<td>7.9</td>
</tr>
<tr>
<td>CPH-12</td>
<td>500</td>
<td>KOH</td>
<td>0.5-1</td>
<td>21.0</td>
<td>0.22</td>
<td>51.5</td>
<td>8.7</td>
<td>91.3</td>
<td>7</td>
<td>0.01</td>
<td>7.0</td>
</tr>
<tr>
<td>CPH-13</td>
<td>800</td>
<td>K_2CO_3</td>
<td>0.25-0.5</td>
<td>24.2</td>
<td>0.12</td>
<td>20.5</td>
<td>6.9</td>
<td>93.1</td>
<td>615</td>
<td>0.31</td>
<td>2.0</td>
</tr>
<tr>
<td>CPH-14</td>
<td>800</td>
<td>K_2CO_3</td>
<td>0.5-1</td>
<td>19.9</td>
<td>0.1</td>
<td>11.4</td>
<td>6.0</td>
<td>94.0</td>
<td>614</td>
<td>0.31</td>
<td>2.0</td>
</tr>
<tr>
<td>CPH-15</td>
<td>500</td>
<td>K_2CO_3</td>
<td>0.5-1</td>
<td>28.5</td>
<td>0.21</td>
<td>20.2</td>
<td>6.8</td>
<td>93.3</td>
<td>8</td>
<td>0.01</td>
<td>5.2</td>
</tr>
<tr>
<td>CPH-16</td>
<td>650</td>
<td>K_2CO_3</td>
<td>0.25-0.5</td>
<td>14.8</td>
<td>0.15</td>
<td>13.2</td>
<td>8.9</td>
<td>91.1</td>
<td>320</td>
<td>0.17</td>
<td>2.1</td>
</tr>
<tr>
<td>Sample Code</td>
<td>T (°C)</td>
<td>Act. agent</td>
<td>Particle size (mm)</td>
<td>Final yield (%)</td>
<td>Bulk density (kg/l)</td>
<td>Ash (%)</td>
<td>Moisture (%)</td>
<td>Dry matter (%)</td>
<td>SBET (m²/g)</td>
<td>Vₚ (cm³/g)</td>
<td>Ave. pore size (nm)</td>
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<tr>
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<td>-------</td>
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<td>-------------------</td>
<td>-----------------</td>
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<td>---------------</td>
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<td>------------------</td>
</tr>
<tr>
<td>CPH-17</td>
<td>650</td>
<td>K₂CO₃</td>
<td>0.5-1</td>
<td>31.3</td>
<td>0.15</td>
<td>17.7</td>
<td>7.0</td>
<td>93.0</td>
<td>8</td>
<td>0.02</td>
<td>7.3</td>
</tr>
<tr>
<td>CPH-18</td>
<td>500</td>
<td>K₂CO₃</td>
<td>0.25-0.5</td>
<td>21.7</td>
<td>0.13</td>
<td>10.7</td>
<td>5.8</td>
<td>94.2</td>
<td>12</td>
<td>0.02</td>
<td>6.4</td>
</tr>
<tr>
<td>CPH-19</td>
<td>800</td>
<td>ZnCl₂</td>
<td>0.5-1</td>
<td>36.6</td>
<td>0.41</td>
<td>8.8</td>
<td>4.3</td>
<td>95.7</td>
<td>562</td>
<td>0.42</td>
<td>3.0</td>
</tr>
<tr>
<td>CPH-20</td>
<td>800</td>
<td>ZnCl₂</td>
<td>0.25-0.5</td>
<td>35.3</td>
<td>0.36</td>
<td>6.4</td>
<td>4.3</td>
<td>95.7</td>
<td>574</td>
<td>0.38</td>
<td>2.6</td>
</tr>
<tr>
<td>CPH-21</td>
<td>500</td>
<td>ZnCl₂</td>
<td>0.5-1</td>
<td>42.5</td>
<td>0.28</td>
<td>6.1</td>
<td>3.3</td>
<td>96.7</td>
<td>724</td>
<td>0.53</td>
<td>2.9</td>
</tr>
<tr>
<td>CPH-22</td>
<td>650</td>
<td>ZnCl₂</td>
<td>0.25-0.5</td>
<td>37.3</td>
<td>0.32</td>
<td>11.9</td>
<td>3.0</td>
<td>97.0</td>
<td>780</td>
<td>0.58</td>
<td>2.9</td>
</tr>
<tr>
<td>CPH-23</td>
<td>650</td>
<td>ZnCl₂</td>
<td>0.5-1</td>
<td>44.9</td>
<td>0.33</td>
<td>11.5</td>
<td>4.5</td>
<td>95.5</td>
<td>663</td>
<td>0.57</td>
<td>3.4</td>
</tr>
<tr>
<td>CPH-24</td>
<td>500</td>
<td>ZnCl₂</td>
<td>0.25-1</td>
<td>47.2</td>
<td>0.32</td>
<td>12.8</td>
<td>4.4</td>
<td>95.6</td>
<td>599</td>
<td>0.43</td>
<td>2.9</td>
</tr>
</tbody>
</table>

ZnCl₂ was the most effective activation chemical for the cocoa pod husk raw-material, giving the highest BET surface areas for the activated carbon (780 m²/g in the best case), the highest pore volumes (0.58 m³/g in the best case) and the lowest ash content (6.14% in the best case). The properties of the ACs prepared with ZnCl₂ at 800 °C did not achieve as high quality as those prepared at 500 °C and 650 °C, possibly due to ZnCl₂ evaporation during carbonization at 800 °C.

With KOH as the activation agent, the best results of surface area, pore volume and ash content were obtained at the highest temperature applied, 800°C, because the activation mechanism with KOH (in order to create high porosity) requires high temperatures. Ahmadpour & Do (1997) made similar observations in the preparation of activated carbon from macadia nutshell.

When K₂CO₃ was used as the activator, the quality of the activated carbons improves with an increase in the studied carbonization temperatures from 500 °C to 800 °C. Hayashi et al. (2002) have reported similar results with various nutshells, however, noting that at carbonization temperatures above 900 °C this trend changes.

The highest final yield was obtained with ZnCl₂, due to the difference between activation methods and mechanisms. The impregnation with the ZnCl₂ activation was only for a few minutes in dry conditions at room temperature, while with K₂CO₃ and KOH, the impregnation was in wet conditions overnight at 100 °C. According to Ahmadpour (1997) ZnCl₂ (a Lewis acid) promotes the aromatic condensation reactions, producing an increase in the yield; while KOH (a strong base) catalyses the oxidation reactions, resulting in further carbon gasification. The reaction mechanism of K₂CO₃ at temperatures above 600 °C involves its conversion to CO (Hayashi et al. 2002) and thus results in significant yield loss.

The best activated carbon using KOH and two best with K₂CO₃ and ZnCl₂ were selected for further characterizations. The selection criteria included the BET
surface area, pore volume, and ash content resulting in samples: CPH-09, CPH-13, CPH-14, CPH-21, and CPH-22. These five samples were analysed for chemical impurities with ICP-OES and the results are shown in Table 5 together with the carbon contents of the samples. CPH-09, CPH-13 and CPH-14 have high potassium levels, as CPH-21 and CPH-22 show high levels of zinc, both because of the activation agents used. Further washing steps are needed in order to reduce the amount of these impurities in the final product (Lozano et al. 2001a and 2001b). Some of the impurities shown in Table 5 originate from the natural composition of the cocoa pod husk.

Table 5. The impurities and carbon content of the selected five most potential ACs (Paper I).

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>CPH-09</th>
<th>CPH-13</th>
<th>CPH-14</th>
<th>CPH-21</th>
<th>CPH-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>mg/kg</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/kg</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/kg</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/kg</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>32</td>
<td>31</td>
</tr>
<tr>
<td>Mo</td>
<td>mg/kg</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/kg</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
<td>&lt; 25</td>
</tr>
<tr>
<td>Ca</td>
<td>g/kg</td>
<td>12</td>
<td>10</td>
<td>9</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Mg</td>
<td>g/kg</td>
<td>12.0</td>
<td>10.0</td>
<td>10.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>K</td>
<td>g/kg</td>
<td>110</td>
<td>100</td>
<td>80</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>P</td>
<td>g/kg</td>
<td>1.9</td>
<td>2.8</td>
<td>2.3</td>
<td>1.9</td>
<td>2.4</td>
</tr>
<tr>
<td>S</td>
<td>g/kg</td>
<td>1.3</td>
<td>0.6</td>
<td>1.1</td>
<td>2.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Si</td>
<td>g/kg</td>
<td>3.0</td>
<td>1.0</td>
<td>2.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>C</td>
<td>%</td>
<td>72.0</td>
<td>76.6</td>
<td>69.6</td>
<td>86.1</td>
<td>82.9</td>
</tr>
</tbody>
</table>

1semiquantitative result

Samples activated by ZnCl₂ had the highest carbon content (86.1% in the best case), which is an important quality of activated carbon in order to adsorb pollutants.

FESEM micrographs (Fig. 6) confirm that the structure and the pore size vary depending on the activation agent. Also, the average pore sizes are low due to the predominance of a microporous structure. The ACs activated by KOH and K₂CO₃ have slightly smaller pores (2 nm in average) than the ACs activated by ZnCl₂ (3 nm in average). The reason for the predominantly microporous structure might
be partly explained by the fact that cocoa pod husk has high cellulose and low lignin contents (Ioannidou & Zabaniotou 2007). It has been stated that the differences in the lignin and cellulose contents of the raw material might affect the porous structure of the activated carbon (Savova et al. 2001). However, also contrary results are published, showing that the porous structure of the activated carbon obtained by the two-step process (carbonization followed by activation) depends mainly on the experimental conditions during the activation and only partly on the lignocellulosic material and the used carbonization process (Gonzalez et al. 1995).

Fig. 6. FESEM micrographs of a) CPH-09, b) CPH – 13, c) sample CPH-14, d) CPH-21, e) CPH-22, and f) CPH raw material (modified from Paper I).
From the FESEM images (Fig. 6) it can be seen that the pore size distribution of activated carbons activated by ZnCl$_2$, shows a well-developed mesoporous structure. It is possible to find micropores inside these mesopores. The mesoporous structure allows water or wastewater to enter inside the pores of the activated carbon and to come in contact with the micropores in order to permit the adsorption of the desired molecules, such as heavy metals and organic compounds. In addition, the CPH raw material surface (Fig. 6f) is smooth with no visible porosity except some occasional cracks, confirming the observation that the porosity is formed during the activation/carbonization process.

The five best activated carbons were tested for their arsenic adsorption ability in neutral pH and in oxidizing conditions because of the river water conditions in the north of Peru, where the materials are planned to be utilized later on. In these experimental conditions, the aqueous speciation of arsenic is dominated by As(V), in the forms of oxyanions $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$ and $\text{AsO}_4^{3-}$ (Gross et al. 1997). The ZnCl$_2$-activated cocoa pod husks were the only ACs capable of adsorbing arsenic over 50% in the experimental conditions (activated carbon concentration 0.5 g/l, initial As(V) concentration 100 µg/l). The KOH activated ACs achieved only 10% removal, as the K$_2$CO$_3$ activated ACs had no removal at all. In order to see, if the KOH and ZnCl$_2$ activated ACs were able of also adsorbing organic pollutants, two preliminary experiments were conducted with methylene blue. The results (not shown here) indicate that the ZnCl$_2$ activated AC was again superior when compared to the AC prepared with KOH, giving removal percentages of 99% and 34%, respectively.

Fig. 7 shows that the rate of As(V) adsorption with CPH-21 and CPH-22 is high at the initial state (between 0–50 min.), achieving removal levels of 80%, then the rate decreases rapidly. This might be possibly due to availability of active sites in the initial period of the reaction after which the amount of available active sites decreases (Jameel & Hussain 2009).
The pseudo-second order kinetic model, which assumes that the rate-limiting step is a chemical sorption between the adsorbate and adsorbent, was applied for the experimental results obtained with CPH-21 and CPH-22 with good correlations (Fig. 8). The values of $q_e$ and the second order adsorption rate constant ($k_2$) were obtained from the slopes and the intercepts, respectively and are presented in Table 6.

Fig. 7. As removal with activated carbons CPH–21 and CPH–22 and CPH-09.

Fig. 8. Pseudo-second order kinetic fitting for the adsorption of As(V) with activated carbons CPH–21 and CPH–22.
Table 6. Pseudo-second-order kinetic constants for As(V) adsorption with two ACs (modified from Paper I).

<table>
<thead>
<tr>
<th>AC</th>
<th>Dose [g/l]</th>
<th>k_2 [g/(mg·h)]</th>
<th>q_e [mg/g]</th>
<th>Initial rate h [mg/(g·min)]</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPH-21</td>
<td>0.5</td>
<td>104.3</td>
<td>0.146</td>
<td>2.22</td>
<td>0.998</td>
</tr>
<tr>
<td>CPH-22</td>
<td>0.5</td>
<td>931.4</td>
<td>0.114</td>
<td>12.10</td>
<td>0.992</td>
</tr>
</tbody>
</table>

Based on the adsorption results with the CPH ACs, it was decided to include the two materials (CPH-21 and CPH-22) activated with ZnCl₂ in further studies within Paper II. First, FTIR analysis was conducted on the materials and the resulting FTIR spectra were evaluated over the wavenumber range of 4000–400 cm⁻¹ and are presented in Fig. 9. Both the samples showed a broad peak between the wavelengths from 3300 cm⁻¹ to 2914, and it is assigned to the C-OH stretching vibration. However, the peak was more pronounced for sample CPH-21, carbonized at 500 °C, than for sample CPH-22, treated at 650 °C. A small broad peak at 1560 cm⁻¹ in the case of sample CPH-21 and at 1530 cm⁻¹ in sample CPH-22, could be attributed to two different kind of vibrations, the a C=O stretching mode or C=C aromatic vibration mode (Romanos et al. 2013). The broadness of these peaks could be also attributed to the overlap of a C-OH stretching mode, and the presence of the poly-aromatic rings can be supported by the high content of hemicellulose in the cocoa pod husk (Donkoh et al. 1991, Daud et al. 2013).

Fig. 9. FTIR spectra of activated carbon from cocoa pod husk a) CPH-21 and b) CPH-22 (Paper II).
There is a noticeable broad shoulder in the case of sample CPH-21 centered at 1247 cm\(^{-1}\) can be assigned to the overlapping of C-O-C stretching and vibration modes. While for sample CPH-22 this shoulder is mainly divided between the peak already seen at 1530 cm\(^{-1}\) and the small peak presented at 1050 cm\(^{-1}\) attributed to the C-O vibration (Heidari et al. 2014). This last observation could be related to the fact that at higher temperatures the C-O-C bond breaks down to form C-O (Paper II).

After FTIR studies, the materials were tested for their surface charge as a function of time in order to calculate the pH of the point of zero charge (pH\(\text{PZC}\)) i.e. the pH at which the surface has a net zero charge. The pH\(\text{PZC}\) was calculated twice for each material, and the results were 5±0.2 and 4.4±0.2 for CPH-21 and CPH-22, respectively. For the reference material, Chemviron activated carbon, the pH\(\text{PZC}\) was 7.6±0.1. At pH < pH\(\text{PZC}\) the material surface has a positive charge, and at pH > pH\(\text{PZC}\) the surface charge becomes negative, resulting in repulsive forces between the adsorbent and anionic adsorbate.

The aim with the adsorption materials was to use them for real polluted river water. However, before the real river water experiments, synthetic multicomponent experiments were conducted. In these experiments, the adsorption of As(V), Pb(II) and Cd(II) was studied at an initial pH of approximately 7. At this pH, there might be already hydrolysis of the metal cations, e.g. with lead, Pb\(^{2+}\) is the major species (88%), but the remaining (12%) is in a form of PbOH\(^+\). However, cadmium exist only as Cd\(^{2+}\) in the pH values between 0-8, after which small amounts of CdOH\(^+\) begins to be formed (Baes & Mesmer 1976). Hydrolysis is an important factor in sorption processes. Adsorption may be related directly to the loss of the outer hydration sphere that precedes the hydrolysis of metal ions (Horsfall & Spiiff 2005). Also, the stronger the tendency of the cation to hydrolyze, the more strongly it is sorbed (Smith 1999). As the ion is hydrolysed, its charge is reduced, thus giving dominance to the electrostatic attraction, and further making the adsorption favourable.

The surface of the CPH ACs showed more affinity for Pb(II) than for As(V) or Cd(II) in the experimental conditions. CPH-21 and CPH-22 (Fig. 10a,b) achieved removals levels of Pb of around 87% and 65%, respectively within 240 minutes of adsorption, as for As(V) and Cd(II) less than 20% removal was achieved.

The commercial AC Chemviron, ground and sieved to particle size < 0.25 mm, showed the best adsorption capacity for the tested metal ions (Fig. 10c). During the first 10 minutes, the Pb(II) adsorption reached equilibrium with approximately 89% removal. In the case of As(V) the intial removal rate was somewhat slower,
reaching the equilibrium with 92% removal only after 120 minutes. With Cd(II), the highest removal percentage of around 20% was achieved during the first 30 minutes with the ground and sieved Chemviron.

The adsorption of all the three studied ions onto Chemviron with the original particle size was remarkably slower than with the < 0.25 mm Chemviron (Fig. 10d). The Pb(II) removal reached the equilibrium (approximately 85% removal) in around 120 minutes, as for As(V) equilibrium was not reached within the studied experimental time, and the removal level stayed below 50%. Clearly the particle size of activated carbon significantly affects the adsorption process, and in general,
a smaller particle size results in a higher adsorption capacity, due to decreasing mass transfer limitations, i.e. the access of the adsorbate molecules to the pores of the ACs becomes easier.

The net surface charges of CPH-21 and CPH-22 were negative at the initial reaction conditions (pH 7) of the adsorption experiments, since their pH_{PZC} values were 5 and 4.4, respectively. The reason for the very low As(V) adsorption ability might lie in the repulsive forces between the anionic As(V) and the negatively charged surface of the AC. The pH level decreased slightly during the experiments with CPH-ACs possibly because of the reactions that occur between metal ions and the functional groups on the surface of the ACs, which can be explained by the following ion exchange model (Namasivayam & Kadirvelu 1997), on the AC surface (S), a carbon-oxygen (C-O) complex binds metal ions (M⁺) by displacing protons from the AC surface according to the following equations (Kadirvelu & Namasivayam 2003):

\[ 2S - COH + M^+ \leftrightarrow S - (CO)_{2}M^+ + 2H^+ \]  \hfill (22)

\[ S - COH_{2}^{2+} + M^+ \leftrightarrow S - COM^{2+} + 2H^+ \]  \hfill (23)

The FTIR spectra (Fig. 9) reveal that both CPH-21 and CPH-22 exhibit C-OH groups on their surface, suggesting that the Cd(II) and Pb(II) adsorption releases essential amount of H⁺ causing the reduction in the pH level.

In the case of adsorption experiments with Chemviron (< 0.25 mm), the pH level was very close to its pH_{PZC} in the first 50 minutes, and then decreased slightly until the end of the experiment. This indicates that the net surface charge of the carbon was possibly slightly positive at the beginning, and in addition, the negatively charged active sites existed on the AC surface, enabling the activated carbon to adsorb both cations and anions such as Pb(II) and As(V), respectively.

A pseudo-second order kinetic model, Eq.(7) (Ho & McKay 1999), was applied to the adsorption data to evaluate the kinetics of the reactions. According to kinetic parameters q_e, k_2 and R^2 (Table 7), for most of the cases the adsorption data followed the pseudo-second order kinetic model. This fact indicates that there is chemical monolayer adsorption involving interactions between ions and groups of the AC surface.
Table 7. Pseudo-second order kinetic parameters, $q_e$, $k_2$ and $R^2$ for the adsorption of the three ions by the tested activated carbons in synthetic multicomponent solutions (Paper II).

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>As(V)</th>
<th></th>
<th></th>
<th></th>
<th>Cd(II)</th>
<th></th>
<th></th>
<th></th>
<th>Pb(II)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ [mg/g]</td>
<td>$k_2$ [g/(mg·h)]</td>
<td>$R^2$</td>
<td>$q_e$ [mg/g]</td>
<td>$k_2$ [g/(mg·h)]</td>
<td>$R^2$</td>
<td>$q_e$ [mg/g]</td>
<td>$k_2$ [g/(mg·h)]</td>
<td>$R^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPH-21</td>
<td>0.063</td>
<td>72.59</td>
<td>0.9856</td>
<td>0.088</td>
<td>12.42</td>
<td>0.9406</td>
<td>0.288</td>
<td>4.062</td>
<td>0.9894</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPH-22</td>
<td>0.084</td>
<td>50.97</td>
<td>0.9952</td>
<td>0.042</td>
<td>70.16</td>
<td>0.8879</td>
<td>0.241</td>
<td>3.005</td>
<td>0.969</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemviron (&lt;0.25 mm)</td>
<td>0.398</td>
<td>16.12</td>
<td>0.9993</td>
<td>0.098</td>
<td>29.41</td>
<td>0.9978</td>
<td>0.243</td>
<td>16.91</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemviron (orig.size)</td>
<td>0.359</td>
<td>0.6458</td>
<td>0.3072</td>
<td>0.099</td>
<td>48.64</td>
<td>0.9755</td>
<td>0.319</td>
<td>3.32</td>
<td>0.9628</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is evident that the presence of the three ions simultaneously in the synthetic aqueous solution creates competition during the adsorption process. The difference in the adsorption of different metal ions is in relation to their ionic radius, their atomic weight, and the affinity of the metal ions for the active sites on the adsorbent (Zhang et al. 2014b, Abia & Igwe 2005).

According to the kinetic results of the multicomponent adsorption experiments, Pb(II) showed higher removal levels than Cd(II) by all the AC samples. The same behaviour was also found by Li et al. (2003) and Doyurum & Celik (2006) when they studied the competitive adsorption between Pb(II) and Cd(II). The adsorption of As(V) and Cd (II) was very low, except in the case of Chemviron (< 0.25 mm), which was able to remove over 95% arsenic in the synthetic multicomponent system. This could be partially explained by the ionic radii of the elements, 1.19 Å for Pb(II), 0.97 Å for Cd(II) and 0.47 Å for As(V) (Lide 2005). The larger the ionic radius (i.e. the smaller the hydrated radius) of an element is, the faster and more effective the adsorption occurs.

The Pyuango-Tumbes River water experiments with the CPH ACs, shown in Fig. 11, gave similar results as with the synthetic multicomponent water, i.e. Pb was the most efficiently removed with both CPH-21 and CPH-22. However, with CPH-21, the removal levels did not reach those achieved with the synthetic water, being only approximately 35%, 13%, and 2% for Pb, Cd, and As, in six hours, respectively, as with the synthetic water experiments the corresponding removals were 87%, 14% and 21% already after four hours of adsorption. With CPH-22, the removals of Pb, Cd, and As were 62%, 27%, 10% from the river water after 6 hours, and 65, 11, and 19% after 4 hours from the synthetic solution, respectively. Hence,
the Pb removal is somewhat the same, as the Cd removal has increased and As removal decreased when compared to the synthetic experiments.

The commercial AC Chemviron (< 0.25 mm) exhibited the highest removal levels at 180 minutes for all the followed ions, i.e. Pb, Cd, and As, being 82%, 33% and 89%, respectively. The corresponding values in the synthetic solution were a bit higher in the case of Pb and As (89% and 93%), and 10% lower with Cd after 4 hours. Indeed, it seems that Cd removal is enhanced in the river water conditions. However, the different initial concentrations of the synthetic and the River water need to be taken into account and therefore, the results are not straightforward comparable with each other.

![Graphs showing removal efficiency of As, Cd, and Pb](image)

**Fig. 11.** Removal efficiency of As, Cd, and Pb from Puyango-Tumbes river water by a) CPH-21, b) CPH-22, and c) Chemviron (all particle sizes < 0.25mm) (Paper II).
The presence of other interfering ions in the Puyango-Tumbes River water evidently affects the adsorption of As, Cd and Pb. Figure 12 shows the removal levels of the elements that were removed from the water during three hours of the adsorption experiments. The other interfering ions are shown in Table 25 in Appendix 1. According to Fig. 12, Al was totally removed from the water by all the studied activated carbons. In addition, Fe was also removed efficiently with the final removal with all the ACs above 46%, in fact the removal could also be near 100%, but due to the detection limit of the analysis, concentrations below 15 µg/l were not able to be detected. CPH-21 also adsorbed Sb 45% within 3 hours, and Chemviron adsorbed zinc from the water. The explanation for the adsorption of the other elements instead of the target ones could be based on the higher affinity between the functional groups of the activated carbon surface and the ions Al, Fe, Sb, and Zn.

Some impurities from the ACs were dissolved in the river water (shown in Table 25 in Appendix 1). In the case of CPH-21 and CPH-22, Zn was released from the
carbon and dissolved in the water sample, while in the case of Chemviron, Cr was released and dissolved. It is not clear if part of the impurities released in the water might be re-adsorbed by the surface of the activated carbon. It would be important to study the levels of organic matter, silica and other compounds in the water that can affect the adsorption of As, Cd and Pb.

In addition, some of the elements behaved inconsistently during the experiment with CPH-21, e.g. lead concentration first increased above the initial concentration (from 2.6 to 4.8 µg/l), and then decreased (to 1.6 µg/l in 3 h) and finally increased again (to 3 µg/l) within 22 hours. For Fig. 11, the initial increase in the concentration has been marked as 0% removal, however, these inconsistencies might just be due to analytical demands, since the total concentrations were rather low.

Based on the encouraging results gained with the CPH ACs, it was decided that more raw materials would be tested for activated carbon production. Therefore, two unconventional materials were selected for studies in Paper III; the *Spondia purpurae* L. (red mombin) seed (RMS-RM) and the *Inga edulis* (ice-cream bean) seed (GS-RM). First, the raw materials were characterized by the methods described in section 6.3. According to the proximate analysis (Table 8) the moisture and ash contents in RMS-RM are lower than in GS-RM.

Based on the elemental analysis (SEM-EDX) (Table 9) the most abundant elements on the surface of the raw materials were C, O and N, however, also minor amounts of elements such as Na, Mg, Al, Si, P, S, Cl, P, Ca and Fe, were present on the surface. C and O were present in more or less in the same weight proportion in both raw materials. Both of these elements are the main compounds of carbonaceous compounds (cellulose, hemicellulose and lignin) within the structure of vegetal products (Cagnon *et al.* 2009). The raw materials should especially have high carbon contents and low inorganic compound levels in order to obtain a better yield during the carbonization processes. This is valid for practically all lignocellulosic wastes (Peláez-Cid & Teutli-León 2012).

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Proximate analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture</td>
</tr>
<tr>
<td>RMS-RM</td>
<td>46.5</td>
</tr>
<tr>
<td>GS-RM</td>
<td>53.3</td>
</tr>
</tbody>
</table>

Table 8. Proximate analysis of the used raw materials (modified from Paper III).
Table 9. Elemental surface compositions of the used raw materials analysed by SEM-EDX (modified from Paper III).

<table>
<thead>
<tr>
<th>Raw material</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS-RM</td>
<td>46.3</td>
<td>2.3</td>
<td>46.4</td>
<td>0.19</td>
<td>0.52</td>
<td>1.15</td>
<td>1.36</td>
<td>0.05</td>
<td>0.15</td>
<td>0.05</td>
<td>0.32</td>
<td>1.14</td>
<td>0.62</td>
<td>---</td>
</tr>
<tr>
<td>GS-RM</td>
<td>47.1</td>
<td>3.3</td>
<td>48.8</td>
<td>---</td>
<td>0.04</td>
<td>---</td>
<td>0.03</td>
<td>0.05</td>
<td>0.09</td>
<td>0.05</td>
<td>0.38</td>
<td>0.46</td>
<td>0.04</td>
<td>---</td>
</tr>
</tbody>
</table>

Na and Al are present in RMS-RM, but not in GS-RM. Zn was not detected in RMS-RM or GS-RM. In both cases the ash content is low and the carbon content is high, which both are desirable properties for the precursor in order to produce high quality ACs (Lua & Yang 2004). Heschel & Klose (1995) studied different agricultural by-products (around 14) for the manufacture of granular activated carbon and found that all precursors exhibited a low ash content between 0.2 and 2.9 wt% and a high C content between 47.3 and 54.4 wt%, comparable to the findings in this study. Cagnon et al. (2009) studied 7 different lignocellulosic precursors originating from agriculture for AC production, and also found the carbon content to vary from 41.6 to 50.7 wt%, and the oxygen content between 41.1 and 47.2 wt%, and the ash amount ranging from 0.9 to 4.4 wt%, all of which are in good correlation with the results of this study.

Table 10. Densities and porosity of the raw materials (Paper III).

<table>
<thead>
<tr>
<th>Raw material</th>
<th>(\rho_{\text{dry}}) (g/cm³)</th>
<th>(\rho_{\text{He}}) (g/cm³)</th>
<th>(V_{\text{true}}) (cm³/g)</th>
<th>(\varepsilon) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS-RM</td>
<td>1.38</td>
<td>0.72</td>
<td>0.66</td>
<td>44 ± 5</td>
</tr>
<tr>
<td></td>
<td>0.84</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GS-RM</td>
<td>1.41</td>
<td>1.36</td>
<td>0.05</td>
<td>2.5 ± 1</td>
</tr>
<tr>
<td></td>
<td>1.39</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10 shows the results from the high-pressure mercury porosimetry and the helium pycnometry measurements for both raw materials. The porosity of GS-RM is very low, only about 2.5±1%, compared to RMS-RM with a porosity of ~44±5%. The higher porosity of RMS-RM could be more beneficial for the chemical activation, because the activation agent can more easily penetrate into the internal porous structure of the raw material particles during the activation step, leading after carbonization to a better established microporous-mesoporous structure of RMS-AC.
The FESEM images (Fig. 13) showing the morphology of both RMS-RM and GS-RM indicate that RMS-RM is formed of layers/slices, while the structure of GS-RM is compact with an irregular surface. Neither one of the raw materials have a highly porous structure based on the FESEM imaging.

Fig. 13. FESEM micrographs of both precursors RMS-RM (a,b) and GS-RM (c,d) (Paper III).

After chemical activation of the raw materials, the obtained activated carbons were further characterized for different properties. First, the final yields were calculated based on the mass balance giving approximately 26.6 and 25.3 wt% for RMS-AC and GS-AC, respectively. Then the elemental surface composition analysis was done for the produced activated carbons (Table 11), and showed that both the ACs have carbon as the main component, then oxygen and other minor elements. When comparing the raw materials and the produced ACs, the C/O proportion was different. The percentage of O decreases and the percentage of C increases during
the carbonization process due to the release of CO₂. The carbon content RMS-AC (85.1 wt%) and GS-AC (82.4 wt%) are at the same level as was those for the CPH-ACs activated with ZnCl₂, see Table 5 (86.1 and 82.9 wt% for CPH-21 and CPH-22, respectively). The amount of Cl is increased in both the ACs compared to the raw materials, and Zn is present in both the ACs as well, even though in the raw materials did not exist. Despite the exhaustive washing step and the high water solubility of ZnCl₂, both elements remain as residues in the prepared ACs. However, a more accurate method such as ICP-OES analysis should be performed for both the raw material and the prepared AC to determine the real elemental composition of the whole sample, and not just the surface.

Table 11. Elemental surface compositions of the produced activated carbons analysed by SEM-EDX (modified from Paper III).

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Elemental analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>RMS-AC</td>
<td>85.1</td>
</tr>
<tr>
<td>GS-AC</td>
<td>82.4</td>
</tr>
</tbody>
</table>

-- not detected.

The carbonization process causes the increases in the ash content in the ACs (Table 12) with respect to the raw materials (Table 8). Although the ash content in GS-RM (2.3 wt%) is higher than that of RMS-RM (1.3 wt%), the ash content in GS-AC (10.0 wt%) was significantly lower than in RMS-AC (38.8 wt%). The presence of the other elements Na, Mg, Al, Si, Ca and Fe in the RMS-RM, is one of the reasons for the high ash content in RMS-AC. The high ash content in activated carbons could block the pores and reduce the total specific surface area, and thus the adsorption capacity. However, a high ash content in activated carbons have also been reported earlier (Ioannidou et al. 2010, Kalderis et al. 2008).

Table 12. Proximate analysis of the produced ACs (modified from Paper III).

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Proximate analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture</td>
</tr>
<tr>
<td>RMS-AC</td>
<td>15.8</td>
</tr>
<tr>
<td>GS-AC</td>
<td>28.7</td>
</tr>
</tbody>
</table>
The nitrogen adsorption-desorption isotherms were measured for the produced ACs (Fig. 14a), and the evaluated pore-size distributions as well as textural parameters based on the isotherms are shown in Fig. 14b and summarized in Table 13.

Table 13. Textural properties of the produced activated carbons (modified from Paper III).

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)</th>
<th>S\textsubscript{meso} (m\textsuperscript{2}/g)</th>
<th>V\textsubscript{micro} (mm\textsuperscript{3}/g)</th>
<th>V\textsubscript{net} (mm\textsuperscript{3}/g)</th>
<th>V\textsubscript{micro}/V\textsubscript{net} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS-AC</td>
<td>1405</td>
<td>965</td>
<td>214</td>
<td>792</td>
<td>27</td>
</tr>
<tr>
<td>GS-AC</td>
<td>937</td>
<td>766</td>
<td>82</td>
<td>693</td>
<td>12</td>
</tr>
</tbody>
</table>

Both the produced adsorbents exhibit clearly a well-established microporous-mesoporous structure. The shapes of nitrogen adsorption-desorption isotherms (Fig. 14a) correspond to the type I isotherm according to the IUPAC classification, shown in Fig. 2, (Gregg & Sing 1982), which is typical for microporous materials. In addition, the isotherms comprise hysteresis loops at higher relative pressures, which are typical for the type IV IUPAC isotherm, indicating mesoporosity. The characteristics of the nitrogen adsorption-desorption isotherms correspond reasonably well to the evaluated pore-size distributions shown in Fig. 14b. However, RMS-AC shows significantly higher mesopore surface area (965 m\textsuperscript{2}/g) and micropore volume (214 mm\textsuperscript{3}/g) than GS-AC (766 m\textsuperscript{2}/g and 82 mm\textsuperscript{3}/g, respectively). Regarding the mesopore sizes, GS-AC includes slightly wider mesopores than RMS-AC. These features could partly provide the explanation for the sorption abilities of RMS-AC and GS-AC.
RMS-AC and GS-AC exhibited high $S_{BET}$, 1405 and 937 m$^2$/g, respectively, which are significantly higher than those of the ACs prepared similarly (by ZnCl$_2$ activation, carbonization at 600°C) having other types of seeds as the raw material. For example, Uçar et al. (2009) prepared activated carbon from pomegranate seeds, and were able to get $S_{BET}$ of 700 m$^2$/g.

Raman spectroscopy was used to evaluate the structure of the produced ACs. Raman spectra (Fig. 15) for GS-AC and RMS-AC have two broad bands centered at 1358 cm$^{-1}$ (D-band) and 1609 cm$^{-1}$ (G-band), and 1367 cm$^{-1}$ and 1607 cm$^{-1}$, respectively. The D-band is associated with the disordered carbon structure in amorphous and quasi-crystalline forms of carbon. The G-band corresponds to the E$_{2g}$ mode (stretching vibrations) in the basal plane of the crystalline graphite (Ferrari & Robertson 2000). Since both (G) and (D) bands were depicted, the crystallographic structure in both the ACs combines both ordered graphitic and disordered carbons.

Carbonization of both raw materials was performed at relatively low temperature (600 °C) and the amorphous character of the prepared carbon dominates above the nanocrystalline forms. The position of the G peak is determined by several factors and one of the most important is the hydrogen content. In both ACs, the G peak positions are above 1600 cm$^{-1}$, which is an evidence of a low hydrogen content (lower than 20 at%). (Ferrari & Robertson 2000). There is
no feature providing the presence of C-H bonds in the C-H bonding vibration region (above 3000 cm⁻¹) (Ristein et al. 1998).

Concerning the intensity ratio of bands D and G, I_D/I_G is a measure of the zone edges or border phonons of the clusters, which depends on the cluster sizes and distributions (Wagner et al. 1989). The G-bandwidths for RMS-AC and GS-AC are 69 and 77 cm⁻¹, respectively. The corresponding I_D/I_G ratios are 1.61 (RMS-AC) and 1.52 (GS-AC), which means that cluster sizes are smaller than 1 nm (Tuinstra & Koenig 1970). The Raman spectra interpretation is described in more detail in Paper III.

![Raman spectra of the produced activated carbons (Paper III).](image)

The prepared ACs possess a developed macroporous structure (Fig. 16) compared to the raw materials (Fig. 13). The macropores of both ACs have mostly an irregular shape and size (Fig. 16a,b for RMS-AC, and Fig. 16c,d for GS-AC). The macropores of the RMS-AC are neater and exhibit more regular distribution compared to the GS-AC sample. In addition, some impurities on the surface of the ACs were detected in the FESEM micrographs. These impurities might originate...
from the chemical activator (Zn and Cl) and different pyrolysis by-products or residues generated during the final grinding step.

Fig. 16. FESEM micrographs of the prepared activated carbons: RMS-AC (a,b) and GS (c,d) (Paper III).

After the characterization presented above, the prepared activated carbons were further examined for their adsorption ability towards methylene blue (MB) and As(V). Here, also an organic model compound was included into the experiments to determine the ability of the agro-waste based ACs to adsorb organic pollutants. Fig. 17 shows the removal of MB and As(V) as functions of time for both produced ACs. Both ACs are able to efficiently adsorb MB, reaching comparable levels of its removal (over 90%) after 1h. The As(V) adsorption performances of the two studied ACs are quite different, and are markedly higher for the RMS-AC.
In spite of the well-established porous structure in both the produced ACs, the wider mesopores in the GS-AC are more easily available for MB molecules in the initial phase of the adsorption and allow them to be transported and adsorbed more efficiently on the surface of micropores and mesopores than on the pores of the RMS-AC. During the first 30 minutes, the diffusion of the pollutant molecules into the AC porous structure plays a major role, and thus, the MB adsorption is higher for GS-AC, as its pores are more easily accessible. Nevertheless, after reaching the adsorption equilibrium, the RMS-AC exhibits higher adsorption efficiency mainly due to higher $S_{BET}$. Moreover, the molecular dimension of MB according to Umemura et al. (2009) is $1.7 \times 0.76 \times 0.33$ nm, thus it can be reasonably supposed that the adsorption of MB cannot occur on the whole micropore surface of the ACs. Hence, in the case of MB adsorption, the mesopore surface area is the determining parameter over microporosity.

![Graph showing adsorption efficiency over time for GS-AC and RMS-AC for methylene blue and As(V)](image1)

The As(V) removal by the RMS-AC reached almost 100% after 2 h, as with GS-AC the As(V) removal level is less than 60% after 2 h. At pH 6, the dominant form of As(V) is $\text{H}_2\text{AsO}_4^-$, and its molecular size is 0.38 nm on average (Urase et al. 1998), meaning that the AC porous structure (including micropores) should not limit the transport and subsequent adsorption of a pollutant with such a small molecular size to the whole surface area. In general, there are other factors (besides AC surface area and pore-size distribution) that may influence the adsorption of ions on ACs: (1) the chemistry of the metal ion (speciation) or metal ion complex, (2) the solution pH, (3) the point of the zero charge, and (4) the functional groups.
on the AC surface (Dias et al. 2007). However, it has been stated that carbons with a higher ash content are more suitable for adsorbing As(V), indicating the ash content to be even more important parameter than the specific surface area (Huang & Fu 1984, Diamadopoulos et al. 1992, Lorenzen et al. 1995). Here, a similar observation can be made, since RMS-AC with a higher ash content (38 wt%) had better As(V) adsorption performance, while GS-AC with a lower ash content (10 wt%) has lower As(V) adsorption capacity.

The results of the MB and As(V) adsorption experiments were fitted to the integrated pseudo-second order kinetic model, Eq.(8), and the $t/q_t$ as a function of time gave linear correlations in all the cases. This indicates that the adsorption of As(V) by the studied ACs is of chemical nature. The second-order adsorption rate constant ($k_2$) and equilibrium adsorption capacity ($q_e$) values were obtained from the slope and the intercept of the graphs and are presented in Table 14.

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Methylene blue adsorption</th>
<th>As(V) adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS-AC</td>
<td>$q_e$ [mg/g] $k_2$ [g/(mg min)] h [mg/(g min)] $R^2$</td>
<td>$q_e$ [mg/g] $k_2$ [g/(mg min)] h [mg/(g min)] $R^2$</td>
</tr>
<tr>
<td>RMS-AC</td>
<td>105.26 0.0013 14.86 0.997</td>
<td>0.22 0.405 0.0198 0.997</td>
</tr>
<tr>
<td>GS-AC</td>
<td>98.04 0.0020 20.96 0.986</td>
<td>0.15 0.591 0.0126 0.996</td>
</tr>
</tbody>
</table>

The calculated equilibrium adsorption capacity ($q_e$) for MB adsorption by RMS-AC (105.3 mg/g) was slightly higher than that for GS-AC (98.0 mg/g) corresponding to the higher surface area of the previous activated carbon. The higher pseudo-second order rate constant ($k_2$) of the GS-AC (0.0020 g/(mg-min)) than that of the RMS-AC (0.0013 g/(mg-min)), reveals that the GS-AC reached the adsorption equilibrium more quickly than RMS-AC, even though the $q_e$ of GS-AC is lower than that of RMS-AC.

The As(V) adsorption follows the pseudo-second order kinetic model well with both the ACs with correlation coefficients $R^2$ of 0.997 and 0.996 for the RMS-AC and GS-AC, respectively. While the RMS-AC exhibits higher $q_e$ (0.22 mg/g) than GS-AC (0.15 mg/g), it shows lower $k_2$ (0.405 g/(mg-min)) than the GS-AC (0.591 g/(mg-min)). According to those kinetic parameters, RMS-AC is the AC with better adsorption performance in As(V) uptake, however, in this case the microporosity, surface area and pore structure morphology might not be the
limiting factors for As(V) adsorption, but instead the higher ash content may be one of the parameters that have a strong influence on the As(V) adsorption.

The initial adsorption rate \((h)\) for MB uptake is higher for the GS-AC (20.96 mg/g·min) than for the RMS-AC (14.86 mg/g·min). This fact is in agreement with the better MB adsorption performance of the GS-AC during the first 30 minutes, because of the wider mesopores as discussed above. In the case of As(V) adsorption, the RMS-AC exhibited higher \(h\) (0.0198 mg/g·min) than the GS-AC (0.0126 mg/g·min), coinciding with a better initial adsorption performance in As(V) adsorption.

### 7.2 Water treatment by adsorption onto hydrous titanium dioxide

In Paper IV, adsorption of arsenic (both As(III) and As(V)) was studied using an industrial intermediate product hydrous titanium dioxide as the adsorbent. The properties of the studied material are shown in Table 15.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal form</td>
<td>Anatase</td>
</tr>
<tr>
<td>Crystallite size</td>
<td>10.8 nm</td>
</tr>
<tr>
<td>(S_{\text{BET}})</td>
<td>280 m(^2)/g</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.283 cm(^3)/g</td>
</tr>
<tr>
<td>Average pore width</td>
<td>4.1 nm</td>
</tr>
<tr>
<td>(pH_{\text{pzc}})</td>
<td>4.8</td>
</tr>
</tbody>
</table>

The \(S_{\text{BET}}\) and porosity information were obtained from the nitrogen adsorption-desorption isotherm (Fig 18), which shows that the shape of the isotherm corresponds well to the Type IV isotherm according to the IUPAC classification (Fig. 2). The type IV isotherm is typical for mesoporous materials.
The results of the kinetic experiments at different pH values, shown in Fig. 19, reveal rapid initial uptake of arsenic, followed by slower removal gradually approaching the equilibrium. The slower adsorption is probably due to the decrease in the concentration difference between the bulk solution and the surface, which slows down the transport of the arsenic species to the TiO$_2$ surface. The studied material is mesoporous, and the adsorption therefore most probably is determined by the pore diffusion, and thus it takes a relatively long time to reach the adsorption equilibrium. As seen from Fig. 19, the removal percentage also continues to increase after 4 hours in some of the experiments.
The pH$_{PZC}$ of the adsorbent is 4.8, meaning that at pH 4, the surface of the studied TiO$_2$ is more protonated giving a positive net surface charge. At pH $>$ pH$_{PZC}$ the surface charge becomes negative, indicating repulsive forces between the adsorbent and anionic adsorbate. As(V) adsorption especially was faster at the lower pH value than that at the higher pH value possibly due to these electrostatic reasons. From Fig. 19 it is clearly seen that the pH value affects the adsorption of both As(III) and As(V) more than the adsorbent amount, since the removal levels are higher at pH 4 with the smallest adsorbent amount than at pH 8 even if the adsorbent amount is tripled.

The power-law kinetic model (Sparks 1999) was selected from many kinetic equations to simulate the experimental data of arsenic adsorption on TiO$_2$, defined in Eq.(24).

$$ q_t = k t^x \leftrightarrow \log q_t = \log k + x \log t $$

where the adsorption density $q$ is the amount adsorbed per milligram of adsorbent ($\mu$g/mg) at time $t$, $k$ is the rate constant ($\mu$g/(mg$_{ads}$·min$^x$)) and $x$ is the kinetic order. The linearization of the curve can be achieved by plotting log $q$ as a function of log $t$. The values of the kinetic parameters $x$ and $k$ are obtained from the slope and the intercept, respectively, shown in Table 16 together with the arsenic reduction half-lives $t_{1/2}$, i.e. the time taken for the concentration of the reactant to fall to half of its initial value. The values of $t_{1/2}$ were calculated from the kinetic parameters for each reaction with Eq.(25).
The half-lives $t_{1/2}$ for the removal of arsenic confirm that arsenic removal is the most rapid at pH 4, which is seen most obviously with the smallest adsorbent dose; the half-lives decrease over 20-fold from pH 8 to pH 4. However, with the highest adsorbent dose the effect of the pH is not that clear anymore, and instead e.g. with As(III) the half-life is longer at pH 4 than at pH 8. With As(V) the half-live has the lowest value at pH 4 with all the adsorbent amounts. These observations indicate that electrostatic factors exist between the adsorbent surface and As(III) or As(V), since at pH 8 As(III) exists mainly as neutral species, and As(V) only as anionic species. Furthermore, as the amount of adsorbent increases the half-lives decrease radically. The rate constants for As(V) adsorption on TiO$_2$ are in line with the results of Dutta et al. (2004), who reported power-law kinetic model rate constants for As(V) adsorption on a Hombikat UV100 TiO$_2$ catalyst to be 3.96 and 3.39 $\mu$g/(mg-TiO$_2$)min$^{0.12}$ at pH 4 and 6, respectively.

The adsorption equilibrium experiments of As(III) and As(V) onto TiO$_2$ at pH 4, 5 and 6 were carried out in order to define the adsorption isotherms (Fig. 20), which are of high importance to represent how solutes interact with adsorbents, and in optimizing the use of adsorbents. The equilibrium adsorption densities of both As(III) and As(V) increase with a decreasing pH value as the equilibrium concentrations of arsenic are below 3000 $\mu$g/l. However, as the equilibrium concentration increases, the effect of the pH is not that clear anymore especially
with As(III), as its isotherm curves at different pH values seem to have more or less the same shape and positions. With As(V) the curves at pH 4 and 5 have somewhat similar paths at higher equilibrium concentrations, but at pH 6 the curve is clearly apart from the two others, and has a lower adsorption equilibrium density values. This can probably be explained again by the differences in the distributions between As(III) and As(V), as their predominant forms are neutral and anionic, respectively. The pHZC of the studied adsorbent is about 4.8, and therefore at pH 6 there might be some repulsive forces between anionic As(V) and the negatively charged adsorbent, as stated before.

The relationship between the amount of arsenic adsorbed onto TiO₂ and its equilibrium concentration in solution was studied by fitting the experimental results from the adsorption equilibrium experiments to the Langmuir, Eq.(2), and Freundlich, Eq.(3), isotherm models. The saturated monolayer adsorption capacity \( q_{\text{max}} \) i.e. the maximum solid-phase concentration, and the Langmuir adsorption coefficient \( b \) were obtained from the intercept and the slope, respectively, of the linear plot of the Langmuir equation. From the linearization of the Freundlich equation, the slope and intercept give the values of the Freundlich isotherm parameters \( n \) and \( k \), respectively. The parameters of the adsorption isotherms calculated from the linear fittings of the Langmuir and Freundlich equations are presented in Table 17.
Table 17. The parameters of Langmuir and Freundlich isotherms for adsorption of As(III) and As(V) on TiO₂ at different pH values (Paper IV, © Elsevier).

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>pH</th>
<th>q max [µg/mg]</th>
<th>b [l/mg]</th>
<th>R²</th>
<th>k [l/mg]⁻¹</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>4</td>
<td>31.8</td>
<td>0.054</td>
<td>0.910</td>
<td>12.10</td>
<td>0.130</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>32.1</td>
<td>0.013</td>
<td>0.835</td>
<td>7.13</td>
<td>0.194</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>25.8</td>
<td>0.034</td>
<td>0.830</td>
<td>4.42</td>
<td>0.255</td>
<td>0.985</td>
</tr>
<tr>
<td>As(V)</td>
<td>4</td>
<td>33.4</td>
<td>0.045</td>
<td>0.935</td>
<td>11.89</td>
<td>0.137</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>22.0</td>
<td>0.298</td>
<td>0.862</td>
<td>8.09</td>
<td>0.176</td>
<td>0.974</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>26.8</td>
<td>0.010</td>
<td>0.936</td>
<td>3.57</td>
<td>0.270</td>
<td>0.989</td>
</tr>
</tbody>
</table>

The Freundlich equation gives better correlations for both As(III) and As(V) at all the studied pH values, which indicates heterogeneity of the surface due to involvement of stronger and weaker binding sites for adsorption, and hence resulting in multisite adsorption processes of the adsorbate ions. The Langmuir monolayer adsorption capacity of 31.8 mg/g for As(III) at pH 4 is well in line with the result of Manna et al. (2004), who reported this capacity to be 31.7 mg/g. However, these results should be considered as apparent, not as absolute. For As(V) the calculated Langmuir q max value was 34.4 mg/g.

Possibly, due to the high surface area (280 m²/g) and the presence of high affinity surface hydroxyl groups, this hydrous titanium dioxide material has a high adsorption capacity for both As(III) and As(V). The conducted adsorption experiments on As(III) suggested that As(III) can be directly removed with the studied TiO₂ without pre-oxidation.

7.3 Water treatment by photocatalysis

7.3.1 Photocatalytic degradation of organic pollutants originating from different types of industry

In Paper V, the photocatalytic degradation of four organic pollutants originating from different types of industry was studied both in synthetic solutions and in a diluted industrial wastewater matrix. The degradation of the pollutants was studied using two different reactors, first the photocatalytic quartz reactor (Fig. 4) and then the photocatalytic Teflon reactor (Fig. 5). The pollutants were diuron (pesticide), p-coumaric acid (PCOU) (agro-industrial wastewaters), bisphenol A (BPA) and
phthalic anhydride (PHA) (plasticizers) (Fig. 21), which all are widely used and cause significant health and environmental problems.

![Molecular structures of the model compounds](image)

Fig. 21. Molecular structures of the model compounds a) BPA, b) PCOU, c) PHA and d) diuron (Paper V).

The studied photocatalyst was a commercial photoactive titanium dioxide, Aeroxide P25, and its characterized properties are shown in Table 18. The studied TiO₂ catalyst consist of mesoporous particles with an average pore size of approximately 7 nm and has a combination of both anatase and rutile phases.

**Table 18. Properties of the studied commercial Aeroxide P25.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal form</td>
<td>Anatase 82 wt%, rutile 18 wt%</td>
</tr>
<tr>
<td>S BET</td>
<td>50 m²/g</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.096 cm³/g</td>
</tr>
<tr>
<td>Average pore width</td>
<td>7.2 nm</td>
</tr>
</tbody>
</table>

The pH PZC of the TiO₂ (Aeroxide P25) is widely studied and reported to be approximately at pH 6.25 (Bahnemann et al. 2007), i.e. its surface is positively charged in acidic medium (pH < 6.25) and negatively charged in an alkaline medium (pH > 6.25). This most probably affects not only its adsorption properties but also the catalytic properties, depending on the ionic form of the organic compound to be treated.

First, the adsorption of the organic pollutants was studied in dark conditions. The pH was not adjusted for these adsorption experiments, and the initial pH values were 6.4 for BPA, 4.7 for PCOU, 5.9 for PHA and 8.1 for diuron. The increasing adsorption efficiencies in a two hour experiment were as follows diuron (4%) < PCOU (8%) ≈ PHA (9%) < BPA (20%). In all the cases the observed adsorption occurred within the first 10 minutes, confirming that the 30 minutes dark period is sufficient to establish the adsorption/desorption equilibrium between the organic
compounds and the photocatalyst surface before the photocatalytic experiment. Generally, the adsorption of the organic compounds on the surface of the catalyst might increase the reaction rates in photocatalysis.

The first set of experiments was done using the quartz reactor. The photolysis in the absence of the photocatalyst was studied for the model pollutants during three hours of UV-A irradiation. The results showed that the removal percentages of the studied pollutants by photolysis increased in the order of BPA = PHA (~7%) < diuron (~10%) < PCOU (22%). Diuron and PHA had less than 10% removal by both adsorption and photolysis. BPA had higher adsorption than photocatalysis and with PCOU the behaviour was the opposite. Thus, it can be concluded that the type of the molecule has a remarkable influence on the adsorption and photolysis activity.

The effect of the amount of catalyst (from 0.1 to 1 g/l) was studied with BPA to find out the optimum dosage to be used in all the other experiments. It was observed that the removal percentage of BPA improved from 50% to almost 90% by increasing the catalyst amount from 0.1 to 0.2 g/l, and then stayed at the same level in the rest of the experiments until 1 g/l. Hence, it was concluded that 200 mg/l was the optimum photocatalyst amount to be used in the experiments.

The effect of the initial pH of the solutions was studied by conducting experiments at different pH values. The removal results at 75 minutes of UV-A irradiation time at different pH values were compared. It was found that bisphenol A was most effectively removed at alkaline conditions (pH 9), but p-coumaric acid, phthalic anhydride and diuron had the best removal levels at neutral pH. However, after three hours of the experiments, the removal percentages at neutral pH increased up to 100% in all the cases exceeding the performances at other pH values. The data from the experiments done at different pH values was inserted into the apparent first order rate model, and the kinetic parameters are shown in Table 19. It is interesting to notice that even though the BPA removal level after 75 minutes of the photocatalytic experiment is higher at pH 9, its reaction half-life is slightly lower at neutral pH. The lowest half-life was found to be with diuron at neutral pH (17 minutes), but when the pH was changed to acidic, the half-life increased over 6-fold.
Table 19. Kinetic constant and removal percentages, removal (%) after 75 minutes of pollutants degradation with an initial pollutant concentration of 15 mg/l and the catalyst dose of 200 mg/l under UV-A irradiation (Paper V).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Initial pH</th>
<th>Removal (%)</th>
<th>Removal (%) after 75 minutes</th>
<th>( k_{app} ) (1/min)</th>
<th>( t_{1/2} ) (min)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
<td>3</td>
<td>36</td>
<td>99</td>
<td>0.007</td>
<td>99</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>56</td>
<td>62</td>
<td>0.0111</td>
<td>62</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>70</td>
<td>38</td>
<td>0.0182</td>
<td>38</td>
<td>0.978</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>76</td>
<td>40</td>
<td>0.0175</td>
<td>40</td>
<td>0.987</td>
</tr>
<tr>
<td>PCOU</td>
<td>4.8</td>
<td>74</td>
<td>38</td>
<td>0.0181</td>
<td>38</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>6.9</td>
<td>85</td>
<td>25</td>
<td>0.0273</td>
<td>25</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>50</td>
<td>86</td>
<td>0.0081</td>
<td>86</td>
<td>0.995</td>
</tr>
<tr>
<td>PHA</td>
<td>3</td>
<td>50</td>
<td>76</td>
<td>0.0091</td>
<td>76</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>57</td>
<td>55</td>
<td>0.0126</td>
<td>55</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>73</td>
<td>56</td>
<td>0.0124</td>
<td>56</td>
<td>0.958</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>64</td>
<td>48</td>
<td>0.0144</td>
<td>48</td>
<td>0.988</td>
</tr>
<tr>
<td>Diuron</td>
<td>4</td>
<td>44</td>
<td>108</td>
<td>0.0064</td>
<td>108</td>
<td>0.981</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>96</td>
<td>17</td>
<td>0.0408</td>
<td>17</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>85</td>
<td>26</td>
<td>0.0262</td>
<td>26</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>81</td>
<td>38</td>
<td>0.0183</td>
<td>38</td>
<td>0.988</td>
</tr>
</tbody>
</table>

The experiments in the diluted industrial wastewater matrix and the corresponding experiments in distilled water were done in a Teflon reactor with the initial organic compound concentrations of 15 mg/l. The wastewater, even diluted, had an alkaline pH of approximately 10, therefore also the initial pH of the synthetic solutions with organic compounds was adjusted to 10. First, the adsorption properties of the photocatalyst Aeroxide P25 were studied for the four organic compounds at pH 10. Adsorption of these compounds was not observed in three hours, except with diuron, which was removed by 5%. Thus the effect of adsorption was negligible in all the cases. Secondly, the removal of the model pollutants by photolysis under UV-A irradiation in the absence of the photocatalyst was tested with the initial concentration of 15 mg/l (Fig. 22).
From Fig. 22 it is seen that BPA was more efficiently removed from the diluted wastewater matrix (~30% removal) than from distilled water (0% removal) by photolysis. PCOU had the highest removal levels (over 40%) in both the studied matrices by photolysis compared to the other compounds. However, in distilled water the removal reached its maximum already during the first 10 minutes, and in the wastewater matrix the removal increased gradually as a function of the UV-A irradiation time. PHA was not removed at all by photolysis in either of the matrices. The removal of diuron was slightly higher in the wastewater matrix (~22%) than in distilled water (~16%), but the removal rates were quite similar in both cases.

The photocatalytic removal experiments were done with the initial pollutant concentrations of 15 mg/l and the catalyst dose of 200 mg/l both in the diluted industrial wastewater matrix and in distilled water. The measured removal of the compounds in the wastewater matrix was compared to the results gained in distilled water (Fig. 23).
Fig. 23. Comparison of the photocatalytic removal of the model pollutants in a) distilled water and in b) the wastewater matrix. An initial pollutant concentration of 15 mg/l and catalyst dose of 200 mg/l in alkaline conditions (Paper V).

Fig. 23 shows that the industrial wastewater matrix, even though diluted, remarkably affects the purification efficiency of the model pollutants. However, all the studied compounds reached over 70% removal percentages in the wastewater matrix whereas in distilled water the final removal levels were over 90% in all the cases. There are several other organic compounds present in the wastewater, and they are most likely competing for the active sites on the catalyst surface, and thus decrease the removal of the studied compounds. In addition, the interference of other compounds, i.e. degradation products, should be studied in the future by analysing the waters by different methods including e.g. LC-MS to identify the intermediate products.

The degradation of the organic compounds was studied by analysing the total organic compounds (TOC) from the water samples. The TOC removal values in 3 hours in the photocatalytic experiments both in distilled water and in industrial wastewater solutions are shown in Fig. 24. The diluted wastewater without the added model pollutants was also studied for the TOC removal for comparison. The TOC removals in distilled water solutions are evidently higher than in wastewater, most probably due to the lower initial TOC values, i.e. the diluted wastewater solution had approximately a 10 times higher TOC content in the beginning. The maximum TOC removal was observed in the case of BPA degradation (~70%).
Fig. 24. Total organic carbon removal after 3 hours of UV-A irradiation with the initial pollutant concentrations of 15 mg/l and a catalyst dose of 200 mg/l both in distilled water solutions and in diluted wastewater. The last column represents the TOC removal from the diluted wastewater solution without added model pollutants (Paper V).

The photocatalytic degradation results were fitted to the apparent first order rate equation, Eq.(19), with reasonably good correlations. The kinetic parameters together with the removal percentages are shown in Table 20.

Table 20. The removal percentages after 3 hours of photocatalysis, the apparent first order rate constants, the reaction half-lives and the correlation coefficient for the degradation of BPA, PCOU, PHA and diuron with the initial concentration of 15 mg/l and the catalyst dose of 200 mg/l in distilled water and diluted wastewater matrix (Paper V).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Water matrix</th>
<th>Removal (%)</th>
<th>$k_{app}$ (1/min)</th>
<th>$t_{1/2}$ (min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
<td>Distilled water</td>
<td>92</td>
<td>0.0359</td>
<td>19</td>
<td>0.963</td>
</tr>
<tr>
<td></td>
<td>Wastewater</td>
<td>72</td>
<td>0.0082</td>
<td>85</td>
<td>0.996</td>
</tr>
<tr>
<td>PCOU</td>
<td>Distilled water</td>
<td>98</td>
<td>0.0469</td>
<td>15</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>Wastewater</td>
<td>89</td>
<td>0.0138</td>
<td>50</td>
<td>0.974</td>
</tr>
<tr>
<td>PHA</td>
<td>Distilled water</td>
<td>96</td>
<td>0.0771</td>
<td>9</td>
<td>0.9437</td>
</tr>
<tr>
<td></td>
<td>Wastewater</td>
<td>73</td>
<td>0.0083</td>
<td>84</td>
<td>0.9762</td>
</tr>
<tr>
<td>Diuron</td>
<td>Distilled water</td>
<td>99</td>
<td>0.0967</td>
<td>7</td>
<td>0.9603</td>
</tr>
<tr>
<td></td>
<td>Wastewater</td>
<td>85</td>
<td>0.0188</td>
<td>37</td>
<td>0.9832</td>
</tr>
</tbody>
</table>
The reaction half-lives shown in Table 20 increase from 7 to 19 minutes and from 37 to 85 minutes, in distilled water and diluted wastewater, respectively. This confirms the decelerating effect of the wastewater matrix on the degradation of the studied pollutants, i.e. the half-lives are multiplied even 9-fold when changing from distilled to the diluted wastewater solutions.

The apparent first order rate constant was used to calculate the specific applied energy values, i.e. the energy needed to degrade one mol of the pollutant. The applied energy (E_{AE}) is the electric power needed for the irradiation of a photocatalytic system, and it can be calculated by Eq.(26)

$$E_{AE} = Pt$$

(26)

where P is the electric power [kW] of the irradiation source and t is the irradiation time [h]. Here six UV-A lamps were used [15W x 6 lamps = 0.09 kW] in the quartz reactor and one UV-A lamp [0.036 kW] in the Teflon reactor, the lamp powers were given by the manufacturer. Combining the apparent first order rate equation, Eq.(19) with the Eq.(26) gives Eq.(27):

$$\ln \frac{c_0}{c} = \frac{k_{app}}{P} E_{AE} = K'E_{AE}$$

(27)

where K' = k_{app}/P [1/kWh].

Bolton et al. (2001) have recommended certain types of figures of merit for the photochemical processes. These figures of merit should be independent of the used system and hence, enable a better comparison of different AOPs. In addition, by using these figures of merit data for scaling-up and also for economic analyses can be gained. With low concentrations, a value named the electric energy per order (E_{EO}) for batch operations can be calculated by a simplified equation for an idealized batch reactor by assuming the first-order kinetics, Eq.(28):

$$E_{EO} = \frac{38.4P}{vk_{app}}$$

(28)

where E_{EO} is expressed as [kW min/l] and k_{app} is the apparent first order rate constant. Eq.(28) can be further modified to represent the specific applied energy E_{S,E} giving the energy required for breaking one mole of the pollutant [kWh/mol]:

$$E_{S,E} = \frac{0.64P}{vc{k}_{app}}$$

(29)

where c is the concentration of the pollutant [mol/l].
The specific applied energy values for the experiments in distilled water and in diluted wastewater solutions, calculated by Eq.(29), are summarized in Table 21. The specific applied energy values seem to vary a lot depending on the pollutant molecule. Phthalic anhydride had the lowest value in distilled water, 98 kWh/mol, but in wastewater it is over 900 kWh/mol. In distilled water the values are of course a lot lower than in the wastewater matrix. The $E_{SAE}$ values are quite high and small differences in the rate constant (a factor of 2) are significant in terms of the applied energy. The application of this amount of energy leads to a partial degradation of pollutants from 79 to 99% after 3h. In addition, the specific applied energy enables estimation of the system costs and gives indications of the total power and/or capital investments required for a specific application.

Table 21. The specific applied energy ($E_{SAE}$) values for the photocatalytic degradation of the studied pollutants with an initial concentration of 15 mg/l and a catalyst dose of 200 mg/l under UV-A irradiation (Paper V).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>$E_{SAE}$ (kWh/mol)</th>
<th>Distilled water</th>
<th>Diluted wastewater matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
<td>326</td>
<td>1425</td>
<td></td>
</tr>
<tr>
<td>PCOU</td>
<td>179</td>
<td>609</td>
<td></td>
</tr>
<tr>
<td>PHA</td>
<td>98</td>
<td>914</td>
<td></td>
</tr>
<tr>
<td>Diuron</td>
<td>123</td>
<td>635</td>
<td></td>
</tr>
</tbody>
</table>

For the treatment costs of the model pollutants, a rough estimation can be made using the EU-28 average electricity price for industrial consumers, 0.119 € per kWh (2/2013) (Eurostat 2014). Assuming one hour treatment time for the pollutants in the wastewater matrix, the estimated prices are 170, 72, 109 and 76 €/mol for BPA, PCOU, PHA and diuron, respectively. Even if the prices look rather high, the concentrations in the real wastewaters and natural waters are in ppm or ppb levels, giving molar concentrations significantly below 1 mol. For example, BPA has been found from the wastewater in a wastewater treatment plant in concentrations varying from 0.07 µg/l to 1.68 µg/l ($3\times10^{-10}$ mol/l – $7.4\times10^{-9}$ mol/l) (Mohapatra et al. 2011). With the higher concentration of 1.68 µg/l, the price would be only $1.3\times10^{-3}$ €/m³ for BPA, and assuming e.g. 1000 m³ flow per day, the price would be roughly 1.3 €/day. Of course this estimation takes into account only the energy needed to degrade 1 mol of BPA, no other variables have been considered here, so in principle this would be the share of degrading bisphenol A from the total costs.
The experimental results from both the reactors (quartz and Teflon) are compared in Table 22. The aim of this comparison was to find out the effect of the reactor configuration on the degradation of the studied compounds. This is especially important for the calculation of the values. According to Bolton et al. (2001), the advanced oxidation process should not affect the calculation of the proposed figures of merit.

Table 22. Comparison of the reactor configuration with an initial pollutant concentration of 15 mg/l and catalyst dose of 200 mg/l in alkaline conditions in distilled water solutions (Paper V).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Quartz reactor</th>
<th>Teflon reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial pH</td>
<td>Removal (%)</td>
</tr>
<tr>
<td>BPA</td>
<td>9</td>
<td>62</td>
</tr>
<tr>
<td>PCOU</td>
<td>8</td>
<td>36</td>
</tr>
<tr>
<td>PHA</td>
<td>8</td>
<td>43</td>
</tr>
<tr>
<td>Diuron</td>
<td>9.6</td>
<td>68</td>
</tr>
</tbody>
</table>

Table 22 shows the initial pH, the pollutant removal after 45 minutes of photocatalysis, the calculated reaction half-lives and the estimated specific applied energies obtained from the experiments done in distilled water solutions in both the reactor types. Based on the results it is obvious that the Teflon reactor is more efficient in the removal of the pollutants, when all the parameters in Table 22 are considered. This might be due to the fact that the Teflon reactor is annular meaning that the lamp is closer to the irradiated solution giving higher irradiance power than in the quartz reactor. In addition, in the Teflon reactor the suspension with the pollutant and the catalyst is irradiated continuously, as with the quartz reactor the suspension is circulated outside the reactor, thus reducing the effective irradiance time. Also the smaller total volume of the suspended solutions might have an effect, since in the Teflon reactor the total volume is only half of that of the quartz reactor. The initial pH values were not exactly the same in both the reactors which also might have affected the different purification results. The E_{SAE} values are from 4- to 10-fold higher in the quartz reactor than in the Teflon reactor. The quartz reactor has six lamps, i.e. 6x15 W, compared to the Teflon reactor which has only one lamp of 36 W, which means that the Teflon reactor has lower energy consumption due to the lamp power needed.
7.3.2 Photocatalytic performance of tailor-made titanium dioxide nanofibers

The experimental nanofiber catalyst powders in Paper VI had an anatase phase and a fibre length and diameter of a few micrometres and approximately 50 nm, respectively (Wu et al. 2011a and 2011b). The materials were characterized by nitrogen adsorption and desorption analysis to obtain the BET surface area (SBET), pore volume (VP) and average pore width, and by Scanning Electron Microscope imaging to visualize their morphologies. The SBET values of the nanofibers varied between 13 and 24 m²/g, and the pore volumes were between 0.034 and 0.061 cm³/g (Table 23). For Degussa P25, these values were considerably higher; 56 m²/g and 0.128 cm³/g, respectively. The average pore widths for all the studied materials vary between 8 and 11 nm. The materials are individual nanofibers in powder form and hence, do not form any well-defined inter-particulate pore structure, which gives an explanation for the remarkably low pore volumes.

Table 23. Surface characteristics of TiO₂ nanofibers and Degussa P25 determined from N₂ physisorption at -195.8 °C (Paper VI, ©Springer).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SBET (m²/g)</th>
<th>Average pore width (nm)</th>
<th>VP (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-TiO₂(A) NF</td>
<td>24.2</td>
<td>9.6</td>
<td>0.057</td>
</tr>
<tr>
<td>N-TiO₂(A)-Pd NF</td>
<td>20.7</td>
<td>11.3</td>
<td>0.056</td>
</tr>
<tr>
<td>N-TiO₂(A)-Pt NF</td>
<td>21.5</td>
<td>11.5</td>
<td>0.061</td>
</tr>
<tr>
<td>N-TiO₂(B) NF</td>
<td>22.1</td>
<td>8.1</td>
<td>0.043</td>
</tr>
<tr>
<td>N-TiO₂(B)-Pd NF</td>
<td>13.2</td>
<td>10.3</td>
<td>0.034</td>
</tr>
<tr>
<td>N-TiO₂(B)-Pt NF</td>
<td>19.4</td>
<td>10.8</td>
<td>0.050</td>
</tr>
<tr>
<td>TiO₂ P25</td>
<td>56.4</td>
<td>9.1</td>
<td>0.128</td>
</tr>
</tbody>
</table>

FESEM micrographs (Fig. 25) confirm the weak interaction between the nanofibers since any significant aggregation cannot be seen. All the nanofiber powder samples have typical nanofibrous structures consisting of thin individual cords, indicating that the nanofibers are well dispersed in aqueous solutions allowing easy access to the surface by the reactants. The pore volume of the dry TiO₂ P25 powder is 2-4 times higher than those of the NFs suggesting an evolution of the porous structure within the agglomerated spheres of different sizes found by the FESEM analysis.
The photocatalytic activity of the materials was studied by the degradation of butanol with an initial concentration of 0.25 vol% (i.e. 27.3 mmol/l) (Fig. 26). The Pd decorated NF catalysts reached almost two times higher conversions for butanol (>60%) than the other studied catalysts within six hours of UV-A irradiation. Here, the platinum co-catalyst was not improving the butanol conversion, which is in line with the results by Herrmann (2010) and Courbon et al. (1985). The reason palladium enhances the oxidation activity over titanium dioxide while platinum has only a small effect, is not clear. The charge separation after photogeneration in TiO₂ is enhanced by both Pd and Pt, producing positively charged centres for oxidation on the surface of the semiconducting material (TiO₂). The main difference between the TiO₂-Pd and TiO₂-Pt catalysts might be due to the easier oxidation of palladium ($E^{\circ}_{\text{Pt}} \sim 1.2$ V, $E^{\circ}_{\text{Pd}} \sim 0.8$ V (Weast 1978)) that in turn can act as an active site for adsorption or even for oxidation.
Fig. 26. Photodegradation of butanol with a catalyst loading of a) 50 mg/l, and b) 100 mg/l. Conversion of butanol as a function of the UV-A irradiation time (Paper VI, ©Springer).

The parent nitrogen-doped nanofiber photocatalyst without any metal decoration (N-TiO₂(A)), had significantly lower efficiency than the Pd decorated one or the commercial TiO₂ P25 catalyst. However, the other parent nanofiber (N-TiO₂(B)), was almost as effective as TiO₂ P25, however, the experimental conditions differed from the other experiments, since no cooling was used, which increased the solution temperature by about 20 °C. Nevertheless, no differences were detected between the results obtained with or without cooling during the experiments. The increase in the catalyst amount from 50 to 100 mg/l caused only a slight improvement in the final conversion values indicating that the catalyst concentration of 50 mg/l in the experimental solution used was close to optimum.

The pH values of the butanol degradation decreased as a function of UV-A irradiation times indicating H⁺ generation. With the most active catalyst, N-TiO₂(A)-Pd, the pH decrease was the most significant, possibly due to a better radical formation ability (Vamathevan et al. 2002).

The apparent first-order rate equation, Eq.(20), was used for modelling the photocatalytic degradation of butanol with fairly good correlations (R² values between 0.97-0.999). This indicates that the photocatalytic degradation of butanol can be described by the first order kinetics The apparent first order rate constants (k_{app}) for the reactions were obtained from the slopes of the linear plots, shown together with the correlation coefficients (R²) in Table 24. The apparent rate constants confirm that the Pd decorated TiO₂ nanofiber (N-TiO₂(A)-Pd) was the
most effective catalyst in butanol degradation, and it gave the best linear fitting to the rate data of the reaction.


<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dose (mg/l)</th>
<th>k_{app} (1/h)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-TiO₂(A)</td>
<td>100</td>
<td>0.0374</td>
<td>0.972</td>
</tr>
<tr>
<td>N-TiO₂(A)-Pd</td>
<td>100</td>
<td>0.1744</td>
<td>0.999</td>
</tr>
<tr>
<td>N-TiO₂(B)</td>
<td>100</td>
<td>0.0903</td>
<td>0.979</td>
</tr>
<tr>
<td>N-TiO₂(B)-Pd</td>
<td>50</td>
<td>0.1433</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.1569</td>
<td>0.998</td>
</tr>
<tr>
<td>N-TiO₂(B)-Pt</td>
<td>50</td>
<td>0.0601</td>
<td>0.996</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>50</td>
<td>0.0701</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.0963</td>
<td>0.987</td>
</tr>
<tr>
<td>Photolysis</td>
<td>-</td>
<td>0.0155</td>
<td>0.903</td>
</tr>
</tbody>
</table>

The total organic carbon (TOC) analyses were carried out in order to follow the mineralization of butanol during the photocatalytic degradation experiments (Fig. 27). It was found that the TOC removal level increased as a function of UV-A irradiation time. However, TOC reduction is only approximately one third of the butanol conversion, indicating the partial mineralization of butanol. The difference between the butanol conversion and the TOC reduction can be attributed to the formation of degradation products such as aldehydes (butanal, propanal, crotonaldehyde) (Kirchnerova et al. 2005).

Fig. 27. Removal of total organic compounds (TOC) as a function of time with a catalyst loading of a) 50 mg/l and b) 100 mg/l (Paper VI, ©Springer).
8 Summary and concluding remarks

Water has a major role in the wellbeing of all humans, however, over 760 million people do not have access to safe, and clean drinking water. Arsenic in particular is a global problem since over 130 million people are exposed to levels of arsenic in drinking water above the World Health Organization’s drinking water standard. On the other hand, companies are increasingly being forced both by regulatory and cost pressures to reduce the amount of waste they produce and the hazard it places on the environment. The purification of wastewater minimizes wastewater volumes and reduces the harm towards human beings and the environment by eliminating the discharges of harmful compounds, improving the resource efficiency of valuable compounds and promoting water re-use and thus reducing the freshwater consumption.

Industrial water treatment is important, since industrial effluents are often discharged straight into the environment and the contaminants may end up in fresh water sources such as rivers, lakes and ground water. In rural areas, people are consuming these waters without any purification. For example, uncontrolled mining activities and illegal mining in developing countries have created substantial environmental hazards and numerous different types of pollutants. Under this framework, this study has been focused on examining novel adsorbents and photocatalytic materials in order to achieve more efficient and affordable water treatment.

The first main objective of this thesis was to study the use of waste materials, local agricultural waste and industrial side products, as adsorption materials by making efficient and viable adsorbents out of the waste. The second main objective was to study the utilization of those materials in water treatment to enhance sustainability in water purification, e.g. overcoming the need for extra chemicals as is the case with traditional methods (e.g. coagulation/precipitation). The third objective was to study the use of photocatalysis in water treatment with the aim of degrading and even mineralizing organic pollutants. Finally, these methods are evaluated and discussed for their future application possibilities.

The first experimental part of this thesis consisted of studying local and abundant Peruvian agro-waste raw materials in activated carbon (AC) production (Papers I, II, and III). Three different raw materials were selected for this study; cocoa (*Theobroma cacao*) pod husk (CPH), red mombin (*Spondias purpurea* L.) seeds (RMS) and ice-cream bean (*Inga edulis*) seeds (GS). The materials were activated with chemical activation agents and characterized for physico-chemical
properties as well as for the removal of organic (methylene blue) and inorganic (As, Pb, Cd) contaminants from both synthetic water and real polluted river water (Puyango-Tumbes River, Peru).

It was shown that the studied raw materials proved to be really promising for the AC production with ZnCl₂ as the activation agent, showing high adsorption efficiencies for both inorganic and organic pollutants from aqueous solutions. The CPH ACs were able to remove As(V), Cd(II) and Pb(II) in different levels from multicomponent aqueous solutions with the highest adsorption capacity towards Pb(II). It was noted, that the adsorption of these three pollutants from the real polluted river water was influenced by the adsorption of Al and Fe present in the water sample. Furthermore, it was found that the pHₚZC played a very important role during the adsorption of As(V), Cd(II) and Pb(II) in multicomponent solutions. However, when used in the purification of the real polluted river water, the competitive adsorption of other elements present in the water was substantial. In addition, during the adsorption experiments ions were dissolved from the activated carbons as impurities, Zn in the case of CPH AC and Cr in the case of the commercial activated product Chemviron. All these aspects need to be taken into account in the materials development.

The results of this thesis showed that RMS and GS ACs had over 90% removal efficiency of the organic pollutant methylene blue (MB) within 1 h, while in the case of the As(V) removal, RMS-AC showed a significantly better adsorption performance (close to 100 % in 2 h) than GS-AC (60 % in 2 h). It was concluded that in the case of MB adsorption, the specific surface area and the pore size distribution play an important role in the adsorption efficiency, while for the As(V) uptake, the ash content plays the determining role in adsorption.

In the second part of the adsorption studies, an industrial intermediate product, a mixture of titanium hydroxide and titanium dioxide, was studied for its applicability as an adsorption material in the removal of arsenic from aqueous solutions (Paper IV). The results proved that the intermediate product had a high adsorption capacity towards both As(III) and As(V) achieving over 96% removal levels within 4 hours, possibly due to the high surface area and the presence of high affinity surface hydroxyl groups. One important finding was that the typically more challenging As(III) was also removed effectively without pre-oxidation, which is necessary in the case of traditional methods. To conclude, the studied material has the potential to be developed into a material that can remove arsenic both from natural waters and wastewaters due to its adsorption properties, availability, low
cost, non-toxicity, and competitive arsenic removal capacity compared to other titanium based materials.

The third experimental part of this thesis was to study photocatalysis, which is one of the advanced oxidation processes (AOPs). AOPs involving the generation of highly reactive oxidants, e.g. hydroxyl radicals, have emerged as important processes for the oxidation and removal of a wide range of organic pollutants existing in waters and air. In this work, different forms of titanium dioxide photocatalysts were studied for the removal and degradation of several different organic pollutants.

First, the photocatalytic degradation of four organic pollutants originating from different types of industry was studied both in synthetic solutions and in a diluted industrial wastewater matrix with a commercial photoactive TiO\textsubscript{2} Aeroxide (Degussa) P25 (Paper V). The findings of this thesis conclude that all the studied pollutants including diuron (pesticide), \textit{p}-coumaric acid (agro-industrial wastewaters), bisphenol A and phthalic anhydride (plasticizers) were effectively removed from both synthetic solutions and from a diluted industrial wastewater matrix with removal percentages of approximately 95%. Diuron was removed most efficiently reaching 99% removal within one hour, and its removal consumed the least amount of energy in terms of the specific applied energy (123 kWh/mol). Bisphenol A was found to be the most difficult to remove by photocatalysis among the studied pollutants obtaining the removal efficiency of 70% in one hour. Further, the results have shown that the TOC removal was in the range of 40-80%, showing that the complete mineralization of the pollutants is still a challenge to be faced.

In the second phase of the photocatalytic studies, the photocatalytic performance of novel, tailor-made TiO\textsubscript{2} based nitrogen doped nanofibers with Pt/Pd decorations was studied in water purification by photocatalytic degradation of butanol (Paper VI). Butanol was selected as a model compound, since it is a common effluent in wastewaters, and only a few studies are reported for aqueous phase reactions. The nitrogen doped Pd-decorated nanofibers were proven to have the highest activity clearly outperforming the other materials tested for butanol degradation in aqueous solutions. It was also concluded that the presence of active metals played a more important role in improving the activity compared to the specific surface areas. According to the results obtained, the nanofiber materials are promising for the efficient photocatalytic degradation of organic effluents in aqueous streams such as wastewaters originating from e.g. the biofuel production plants or the fine chemicals and pharmaceutical industry.
To conclude, this thesis has shown that it is possible to consider local abundant waste as a resource for novel materials for water treatment. In addition, this thesis also aimed at utilizing the prepared novel materials as more sustainable water treatment materials. The sustainability concept consists of three aspects: environmental, social and economic. By utilising e.g. local agricultural waste as the raw material, using local labor in the activation process and operating the water treatment facilities, covers all the three aspects of sustainability. Further, utilizing waste materials or industrial side products in water treatment minimizes the need for virgin or non-renewable raw materials, and thus the sustainability of the process is increased. Both adsorption and photocatalysis can be performed in ambient conditions and thus energy needed for heating and pressurizing water treatment systems is minimized, which as well enhances the sustainability. In addition, the use of photocatalysis in water treatment also contributes positively to the sustainability of a water treatment process, e.g. by decreasing the environmental load of the purified water due to mineralization. Additionally, solar light can possibly be used to activate the photocatalysts, so there is no need for energy consuming artificial UV-irradiation. In addition, the organic load of the water can by photocatalysis be used in gaseous fuel or energy vector production, e.g. by using the organic load as a source for hydrogen.

However, this thesis has also shown that there are limitations and challenges to be overcome concerning the applications of both the studied techniques. For example, the AC production, needs the activation process for the raw materials, which is often obtained with the activation chemicals. Activation through the use of chemical agents enables a well-developed micro/mesoporous structure to be obtained that enhances the adsorption capacity towards the aqueous pollutants. The use of chemicals has a negative impact on sustainability. However, this can be overcome by studying more environmentally friendly activation agents and the degradation ability of the compounds already present in the waste materials. In addition, if the high removal capacity compared to other adsorbents is considered, the production costs do not turn out to be very high. The search for the appropriate mechanism for the activation process is an important factor for dealing with the production costs. Furthermore, the final waste disposal or reuse of the adsorbents and the captured metals and valuable compounds has to be studied, i.e. there needs to be a methodology applied regarding what to do with the used adsorbent and the captured compounds attached to it. Naturally, the regeneration of the adsorption materials needs to be studied. However, if the material is easy to produce at relatively low cost, regeneration might not be reasonable, but instead, if the
pollutants are held strongly by the material, it could be used for other purposes such as in construction materials e.g. when building roads.

The final challenge, after gaining knowledge of the adsorption and photocatalysis separately, is the consideration of the possible combination of adsorption and photocatalysis into a hybrid technique. Some of the drawbacks of the individual techniques can be overcome by some characteristics of other techniques, and the benefits of each process can be consolidated, and thus the sustainability and process efficiency can be improved by hybrid methods. The benefits of the hybrid process will be e.g. that it will simultaneously disinfect the water from bacteria and microbes, it will degrade organic pollutants and remove inorganic ions. Furthermore, the organic load in the water can be utilized in energy production. Photocatalysis can also be used to oxidize metals/metalloids into a form that is easier to remove from waters, e.g. As(III) to As(V). Therefore, future work should be focused on the development of hybrid systems.

In the future studies it would be important to study the levels of organic matter, silica and other compounds in waters that can affect the adsorption of the target ions such as As, Cd and Pb. In addition, the agro-waste based ACs need further development that enables their utilization in water purification for natural waters with a wide variety of different interfering ions, microbes and organic compounds. One challenge in photocatalysis is to achieve the complete mineralization of the pollutants, however it might be enough to convert the pollutants into less harmful or lower molecular weight compounds which can then be treated e.g. biologically. Further analyses will be done in the future to obtain more information about the by-products formed and to be able to understand the mineralization of the pollutants.

Overall, this thesis provides valuable information and new knowledge for (1) the utilization of local, low-cost and abundant waste materials as adsorbents for the removal of both inorganic and organic pollutants from aqueous solutions in a more sustainable way, and (2) the use of photocatalysis for the degradation of organic pollutants originating from different types of industries.


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## Appendix 1

Table 25. Concentration of different elements during the adsorption experiments with the Puyango-Tumbes River water by the tree tested ACs (particle size < 0.25 mm) (Paper II).

<table>
<thead>
<tr>
<th>Element</th>
<th>Initial river water</th>
<th>CPH-21</th>
<th>CPH-22</th>
<th>Chemviron</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0min</td>
<td>3 h</td>
<td>22 h</td>
<td>3 h</td>
</tr>
<tr>
<td>Al (µg/l)</td>
<td>22.7</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
</tr>
<tr>
<td>As (µg/l)</td>
<td>43.2</td>
<td>41.7</td>
<td>39.3</td>
<td>41</td>
</tr>
<tr>
<td>B (µg/l)</td>
<td>13.3</td>
<td>19.7</td>
<td>20.6</td>
<td>16.7</td>
</tr>
<tr>
<td>Ba (µg/l)</td>
<td>59.7</td>
<td>56.7</td>
<td>56.5</td>
<td>57.5</td>
</tr>
<tr>
<td>Cd (µg/l)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Co (µg/l)</td>
<td>2.2</td>
<td>2.2</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Cr (µg/l)</td>
<td>&lt; 0.2</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>1.3</td>
</tr>
<tr>
<td>Sb (µg/l)</td>
<td>2.4</td>
<td>1.32</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Pb (µg/l)</td>
<td>2.6</td>
<td>1.6</td>
<td>3</td>
<td>0.96</td>
</tr>
<tr>
<td>Ni (µg/l)</td>
<td>2.4</td>
<td>2.6</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Zn (mg/l)</td>
<td>0.151</td>
<td>10.5</td>
<td>10.9</td>
<td>4.36</td>
</tr>
<tr>
<td>Sr (µg/l)</td>
<td>40.2</td>
<td>41.8</td>
<td>41.7</td>
<td>40.4</td>
</tr>
<tr>
<td>Ca (mg/l)</td>
<td>14.8</td>
<td>16.1</td>
<td>16.6</td>
<td>15.8</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>1.02</td>
<td>2.4</td>
<td>1.64</td>
<td>1.09</td>
</tr>
<tr>
<td>Mg (mg/l)</td>
<td>2.11</td>
<td>2.55</td>
<td>3.06</td>
<td>2.3</td>
</tr>
<tr>
<td>Na (mg/l)</td>
<td>234</td>
<td>242</td>
<td>241</td>
<td>237</td>
</tr>
<tr>
<td>Fe (µg/l)</td>
<td>28</td>
<td>&lt; 15</td>
<td>&lt; 15</td>
<td>&lt; 15</td>
</tr>
<tr>
<td>Mn (mg/l)</td>
<td>0.44</td>
<td>0.46</td>
<td>0.46</td>
<td>0.45</td>
</tr>
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</table>
Original publications


II Pirilä M, Cruz GJF, Ainassaari K, Gomez MM, Matějová L & Keiski RL. Removal of As(V), Cd(II) and Pb(II) from multicomponent aqueous systems using activated carbons. Manuscript.


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Original publications are not included in the electronic version of the dissertation.
507. Jurmu, Marko (2014) Towards engaging multipurpose public displays: design space and case studies
509. Huang, Xiaohua (2014) Methods for facial expression recognition with applications in challenging situations
510. Ala-aho, Pertti (2014) Groundwater-surface water interactions in esker aquifers: from field measurements to fully integrated numerical modelling
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Title: Adsorption and Photocatalysis in Water Treatment

Author: Minna Pirilä

Abstract: This thesis focuses on the use of active, abundant, and inexpensive materials for adsorption and photocatalysis in water treatment. The research explores new methods and materials to enhance the efficiency and sustainability of water purification processes. The study contributes to the development of cost-effective solutions for the treatment of contaminated water sources.