Engineered adsorptive materials for water remediation

Development, characterization, and application

Maryam Roza Yazdani
Engineered adsorptive materials for water remediation

Development, characterization, and application

Maryam Roza Yazdani

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Engineering, at a public examination held at the lecture hall A2 of the school on 13 April 2018 at 12:00.

Aalto University
School of Engineering
Department of Built Environment
Water and Environmental Engineering
Supervising professor
Professor Riku Vahala, Aalto University, Finland

Thesis advisor
Associate Professor Amit Bhatnagar, University of Eastern Finland, Finland

Preliminary examiners
Associate Professor Julie Beth Zimmerman, Yale University, The United States
Professor Éder Cláudio Lima, Federal University of Rio Grande do Sul, Brazil

Opponent
Professor Ulla Lassi, University of Oulu, Finland

Aalto University publication series
DOCTORAL DISSERTATIONS 58/2018

© 2018 Maryam Roza Yazdani

ISBN 978-952-60-7919-6 (printed)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

Unigrafia Oy
Helsinki 2018

Finland
# Abstract

**Author**
Maryam Roza Yazdani

**Name of the doctoral dissertation**
Engineered adsorptive materials for water remediation: Development, characterization, and application

**Publisher**
School of Engineering

**Unit**
Department of Built Environment

**Series**
Aalto University publication series DOCTORAL DISSERTATIONS 58/2018

**Field of research**
Water and Environmental Engineering

**Manuscript submitted**
13 November 2017

**Date of the defence**
13 April 2018

**Permission to publish granted (date)**
19 March 2018

**Language**
English

- [ ] Monograph
- [x] Article dissertation
- [ ] Essay dissertation

**Abstract**
Engineering alternative eco-friendly techniques for water remediation is a global aim due to the serious contaminations of water sources and strict standards of water quality. Engineered polymer-based adsorptive materials have emerged as new alternatives to activated carbon. Engineered adsorptive materials with embedded inorganic constituent(s) in polymeric matrix provide an opportunity to remove a diverse range of contaminants. Combining the advantages of inorganic and polymeric materials, these engineered materials exhibit enhanced properties e.g., porous structure and easy separation. Particularly, engineered adsorptive materials containing nano-sized titanium dioxide (n.TiO₂) exert simultaneous adsorption and photocatalysis. These newly raised materials are new alternatives with a bright prospect in environmental remediation.

This dissertation introduces new-engineered adsorptive materials for water remediation. It highlights the fundamental challenges of engineering adsorptive materials from well-known initial materials, chitosan, n.TiO₂, and feldspar, for the remediation of water polluted with arsenic, Acid Black 1 dye, and phosphate in laboratory-scale. It focuses on preparing the engineered adsorptive materials, charactering them via common methods e.g., Fourier Transform Infrared Spectroscopy and X-ray Diffraction, and applying them for adsorptive (photoactive) removal of the target pollutants. The adsorption process is explored via kinetic, isotherm, and thermodynamic studies.

The adsorptive materials are engineered considering the strengths and drawbacks of initial materials; e.g., n.TiO₂ provides high surface area and photo-oxidation, chitosan supplies support matrix and gravity separation, and feldspar lowers the cost and improves the surface texture. The engineered materials showed improved structures and removal performances. The study of material properties revealed their functional groups, compositions, and porosity. The engineered materials embedding n.TiO₂ showed enhanced UV-assisted adsorption of the dye and arsenic. UV irradiation enhanced the removal from 33% to 73% for arsenate (5 mg/L), from 23% to 84% for arsenite (5 mg/L), and from 86% to 97% for the dye (50 mg/L). Zinc-functionalized chitosan showed an improved phosphate uptake from 1.45 to 6.55 mg/g compared with plain chitosan. Adsorption kinetics indicated fast removal rates. Modeling of adsorption isotherm and kinetics via theoretical models provided fundamental information about the adsorptive surface properties and adsorption reactions. The adsorption reactions were thermodynamically spontaneous and favorable. The correspondence between the theory behind the models and properties of the engineered materials along with removal mechanisms are discussed. This dissertation provides fundamental knowledge e.g., in designing water treatment units. In summation, the experimental data and theoretical considerations support the applicability of the engineered adsorptive materials for water remediation.

**Keywords**
Engineered adsorptive materials, UV-photoactive, Chitosan, TiO₂, Feldspar, Adsorption, Water treatment, Arsenic, Dye, Phosphate

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ISSN-L</td>
<td>1799-4934</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISSN (printed)</td>
<td>1799-4934</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISSN (pdf)</td>
<td>1799-4942</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location of publisher</td>
<td>Helsinki</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location of printing</td>
<td>Helsinki</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Year</td>
<td>2018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pages</td>
<td>125</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
When I was a little girl, I used to sit under a tree in my father’s fruit garden and study joyfully. Once I remember my father came to my tiny study desk which I made it by myself from fruit boxes with the most beautiful and proud smile on his face; a friend of his had told him your little daughter would make a great doctor one day. Of course, they meant a “doctor of medicine” but I would say a doctor of science and technology suits my spirit better. Thank you Pedar for being the most amazing father and for your everyday support and inspiration!

I am deeply thankful to Professor Riku Vahala for accepting me in his research group. Working with him has been a privilege and has taught me that it is not always enough to make science but to make a difference though application. Thank you Riku, for providing me with the opportunity and resources required for preparing this dissertation, and for giving me the freedom to shape my career perspective. I am also very fortunate and grateful of having the chance to work with Associate Professor Amit Bhatnagar acting as advisor of this dissertation and co-authoring in appended articles.

I would like to thank Associate Professor Julie Beth Zimmerman and Professor Eder Claudio Lima for pre-examining this dissertation and providing valuable comments. Professor Zimmerman’s research in the field of green chemistry has been of vital help while conducting my doctoral research and I feel honoured that she has acted as the evaluator of this dissertation. Professor Ulla Lassi, I am grateful that you has accepted to act as my opponent in the public defence of the dissertation. Kindly be gentle.

The research articles included in this dissertation would not have been possible without all the other co-authors, Professor Mokhtar Arami, Professor Hajir Bahrami, Dr. Tanja Tuutijärvi, Dr. Kevin Conley, and M. Sc. Elina Virolainen, to whom goes my sincere acknowledgment. I would particularly like to express my gratitude to Professor Arami who also supervised my master’s thesis where I initially got the idea of this dissertation. I am honoured to have the experience of working with him and to have his advice and encouragement in choosing my career direction while doing my master’s thesis with him. I would also like to thank Kevin for his precise help with the last article appended to this dissertation and for his helpful feedbacks on the compilation part.

While conducting my doctoral research, I have been fortunate to instruct master’s theses, which not only has helped me to develop my instructing skills but to broaden my perspective on the topics of my current and future research. It
has been a great pleasure to work and to share knowledge with M. Sc. Elina Virolainen and M. Sc. Nicola Duimovich while accomplishing their master’s theses under my instruction. I would like to thank Ari Järvinen, Aino Peltola, and Marina Sushko for their tremendous assistance for both the master’s theses and my doctoral research. Particularly thank you Ari and Aino, for being very kind and helpful to me and for taking care of many practicalities that have eased my work. I would also like to acknowledge the kind help from Taneli Tiittanen, Department of Chemistry, in conducting XRD analysis on feldspar samples.

It has been a great pleasure to work in the good-natured atmosphere of Water and Environmental Engineering group with all the past and present colleagues. Plenty of doctoral candidates, post-doctoral researchers, professors, master’s thesis workers and other employees have worked in the group during conducting my doctoral research and I am thankful for all the great moments that I have shared with many of them. I would like to thank all of my co-workers and doctoral students under water and wastewater engineering discipline for all the lively discussions about the doctoral research during past couple of years.

This dissertation would not be near possible without funding supports that I have received during all these years. I am truly grateful to Maa– ja vesitekniikan tuki ry, Aalto ENG Doctoral Programme, Foundation for Aalto University Science and Technology, Doctoral Programme in the Built Environment (RYM-TO), and Water and Environmental Engineering group for believing in this work and for helping me to concentrate on my research instead of filling endless funding applications.

I do not think I could make it happen until the end without my passion, floorball. Dr. Marko Keskinen, thank you very much for Aalto staff floorball! Time to play floorball has been the highlight of my weeks after long hours of working on my dissertation - it was perfectly counterbalanced. I want to thank my floorball buddies: Paavo Niskala, Dr. Ulla Vainio, and Kersti Haahti. Particularly, thank you Paavo, for being a great teamie with all the passes when I was a new bee in floorball and for listening when I needed a friend to hear me complain.

I am grateful to all my past and current friends who lifted me up and reminded me that there is also a life outside of doctoral research. I would like to thank my mentor Pia Nurmi for all the relieving talks we had during Aalto mentoring programme. I am thankful to Kilian Kottemeier for all of our discussions on my research and for being the first reader of this dissertation. Dankeschön, Kilian! Thanks also to Elena Hautala and Fang Hu for being my caring friends. Thank you Elena, for all of those dance nights, and Fang, for all of our funny talks until the small hours of the morning! I particularly want to thank my best friend, Kersti Haahti; I am beyond happy for getting to know you while we were finalizing our dissertations in the same time and for our friendship. Thank you Kersti, for being a supportive ystäväni! In addition to this dissertation, I have made some true friends for which I am the most thankful.

I would like to express my gratitude to all of my teachers during all those study years at school. Teachers who believed in me and told me that they were amazed with my talents. My particular thanks to my first grade teacher, Mr. Akhlaghi!
The courage that I got from you lightened my way and gave me the strength to become who I am today.

I am certain that I would not be here if it were not for my beloved family, my parents and my siblings. My heroes, Madar and Pedar, thank you for supporting me in choosing the direction of my life - while making sure it is the right one. I would not make a doctor of science and technology if it were not for your everyday reminder telling me “Rozmary, my daughter, focus on your studies”. I truly thank all my siblings, who have always been there for me and helped me to pursue my dreams. My dearest brother, Mehrdad, in no word I can express how much I am thankful to you. The earliest childhood memory I remember is you smiling while giving me New Year present, or you smiling while buying me pistachio to eat in the plane on my way back to Finland. A paragon of kindness, mercy for all of your support and life lessons, which you never hesitate to provide your little sister with in reaching her dreams!

Espoo, 5 February 2018
Roza Yazdani
CONTENTS

LIST OF PUBLICATIONS ........................................................................................................ 1

AUTHOR’S CONTRIBUTION IN THE PUBLICATIONS .................................................... 2

1. INTRODUCTION AND OBJECTIVES ......................................................................... 3

2. RESEARCH BACKGROUND ......................................................................................... 7

  2.1 Target pollutants ....................................................................................................... 7
    2.1.1 Arsenic ................................................................................................................ 7
    2.1.2 Dyes ...................................................................................................................... 9
    2.1.3 Phosphate ........................................................................................................... 12

  2.2 Adsorption ................................................................................................................ 14
    2.2.1 Influencing factors ............................................................................................. 14
    2.2.2 Kinetics ................................................................................................................ 14
    2.2.3 Isotherm ............................................................................................................. 16
    2.2.4 Thermodynamic ................................................................................................. 16
    2.2.5 Mechanism ......................................................................................................... 17

  2.3 Low-cost adsorptive materials ................................................................................. 18

  2.4 Engineered adsorptive materials .......................................................................... 20
    2.4.1 Chitosan-based engineered adsorptive materials ............................................ 23
    2.4.2 TiO₂-based engineered photoactive-adsorptive materials ................................. 24

  2.5 Regeneration of adsorptive materials (Desorption) ......................................... 26

  2.6 Stabilization and disposal of exhausted adsorptive materials ............................ 26

3. EXPERIMENTAL SETUP .......................................................................................... 27

  3.1 Preparation of engineered adsorptive materials ................................................. 27

  3.2 Characterization of engineered adsorptive materials .......................................... 28

  3.3 Concentration measurement of solutions ............................................................. 28

  3.4 Batch experiments ................................................................................................. 29
    3.4.1 Adsorption Studies ............................................................................................. 29
    3.4.2 Photocatalytic studies ......................................................................................... 29

4. RESULTS AND DISCUSSION .................................................................................... 31
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Characterization of engineered adsorptive materials</td>
<td>31</td>
</tr>
<tr>
<td>4.2</td>
<td>Adsorption</td>
<td>34</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Effect of adsorbent dose</td>
<td>34</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Effect of solution pH</td>
<td>35</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Effect of co-existing ions</td>
<td>36</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Kinetics</td>
<td>36</td>
</tr>
<tr>
<td>4.2.5</td>
<td>Equilibrium</td>
<td>38</td>
</tr>
<tr>
<td>4.2.6</td>
<td>Thermodynamics</td>
<td>40</td>
</tr>
<tr>
<td>4.3</td>
<td>UV-assisted adsorption system</td>
<td>41</td>
</tr>
<tr>
<td>4.4</td>
<td>Removal mechanism</td>
<td>43</td>
</tr>
<tr>
<td>4.5</td>
<td>Evaluation of engineered adsorptive materials</td>
<td>44</td>
</tr>
<tr>
<td>5.</td>
<td>CONCLUSIONS</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>51</td>
</tr>
</tbody>
</table>
This dissertation consists of a synthesis and the following publications:


The publications I-IV are reprinted with permission and copyrighted as follows:

Publication I © 2017 Elsevier B.V.

Publication II © 2015 Elsevier B.V.

Publication III © 2013 Wiley Periodicals, Inc.

Publication IV © 2018 Authors. Distributed under the terms of the Creative Commons Attribution 4.0 license.
AUTHOR’S CONTRIBUTION IN THE PUBLICATIONS

Publication I The author conceived and designed the research. The author designed and carried out the experimental parts for material preparation and adsorption. The author collected the data from the experiments and characterization analyses e.g., SEM, XRD, and FT-IR. The author analyzed the data and designed the article. The author wrote the article, with assistance from Assistant Professor Amit Bhatnagar. Professor Riku Vahala commented on the article.

Publication II The author conceived and designed the research. The author designed and carried out the experimental parts related to material preparation and adsorption, with assistance from Dr. Tanja Tuutijärvi. The author collected the data from the experiments and characterization analyses e.g., SEM, XRD and FT-IR. The author analyzed the data and designed the article. The author wrote the article, with assistance from Assistant Professor Amit Bhatnagar. Professor Riku Vahala commented on the article.

Publication III The author conceived and designed the research. The author designed and carried out the experimental parts related to material preparation and adsorption. The author collected the data from the experiments and characterization analyses e.g., SEM, XRD, and FT-IR. The author analyzed the data and designed the article. The author wrote the article, with assistance from Professor Mokhtar Arami.

Publication IV The author conceived and designed the research. The author designed and supervised the experimental parts related to material preparation and adsorption conducted by M. Sc. Elina Virolainen. The author supervised collecting the data from the experiments and characterization analyses e.g., SEM, XRD, and FT-IR. The author analyzed the data and wrote the article together with M. Sc. Elina Virolainen and Dr. Kevin Conley. Professor Riku Vahala commented on the article.
1. INTRODUCTION AND OBJECTIVES

Saving water to save the planet for the future generation is an urgent need. Although water is one of the most plentiful resources on the earth, only less than 1% of the global water supply accounts for safe human consumption. In 2015, the World Health Organization [1] reported over 663 million people around the world still without adequate potable water sources. Even when it is available, the cost of producing suitable drinking water continuously increases due to the rising energy cost, growing population, changing global climate, and many other environmental issues [2]. Moreover, many of drinking water sources worldwide indicate signs of serious contamination, especially by pollutants like arsenic, phosphate, and dyes. For instance, it is reported that only in the district Murshidabad of West Bengal, India; about 1.25 million of the people are exposed to groundwater arsenic pollution [3]. Likewise in southern part of the Pirkanmaa regions, Finland, elevated arsenic concentrations with the average above 100 $\mu$g/L in groundwater sources e.g., drilled wells which are used by private households, have been reported since the early 1990's [4]. In addition, phosphate and dyes have been commonly found in drinking water sources worldwide due to the polluted inflows of industrial and urban wastewaters and agricultural run-offs. Pollutants in surface waters pose a risk to water supplies since contamination may leak into aquifers.

Many conventional water and wastewater treatment processes are not effective in treating different pollutants, and in different cases, may be incapable of sufficient remediation to meet the exacting standards of water quality [2]. These issues, among others, usher in a new era for alternative water treatment and remediation techniques to assist or replace current technologies. Recent research on engineered materials for water and wastewater treatment has focused on exploring their potential as efficient adsorbents [5], filter media [6] and disinfectants [7], promising practical implementation for full scale water and environmental remediation.

To provide an up-to-date reference in the state of engineering novel adsorptive materials for scientific and industrial applications in water and environmental engineering field, this dissertation explores different aspects of preparation, characterization, and application for engineering adsorptive materials composed of low-cost, locally available, bio-based, and eco-friendly materials (namely nano-sized TiO$_2$, chitosan, and feldspar) for water pollution remediation. As the individual features of the initial materials are not always optimal and identical, material engineering creates effective engineered materials that
INTRODUCTION AND OBJECTIVES

minimize the inherited problems related to the individual constituent and optimize the performance. For instance, from the initial materials employed in this dissertation, nano-sized titanium dioxide (n.TiO$_2$) is well documented for water treatment for many attractive features e.g., large surface area for enhanced adsorption and oxidation, yet, the nano-size creates a need for energy intensive post-filtration to separate the nano-particles from the processed water. Likewise, chitosan has attracted great attention for being biocompatible and available with a minimal environmental cost; yet, pure chitosan has low chemical and physical stability and agglomerates easily. Feldspars, one of the most abundant minerals, also suffers from low adsorption capacities for anionic species. Therefore, the idea of engineering effective adsorptive materials that overcome the drawbacks of the individual constituents and provide better quality for the removal of the target pollutants are conceptualized herein. The dissertation aims to increase the understanding about the trends and suitability of the newly raised engineered adsorptive materials for water remediation via compiling fundamental information on the processes of creating and analyzing them in laboratory-scale. The pollutants, viz. arsenic, dye, phosphate, are selected from different categories of inorganic and organic species to depict a detailed picture of wide applicability of our engineered adsorptive materials for water remediation. The objectives of this dissertation are approached through detailed research questions (RQ) examining various aspects of preparation, characterization, and application of engineered (photoactive-) adsorptive materials based on well-known initial materials, nano-sized TiO$_2$, chitosan, and feldspar, for water remediation focusing on the removal of three target pollutants viz. arsenic, Acid black 1 dye, and phosphate (Figure 1).

RQ 1. What are the characteristics and UV-assisted adsorption performance of the engineered photoactive-adsorptive materials from nano-sized TiO$_2$, chitosan, and feldspar in removing inorganic arsenic from water?
RQ 2. How do feldspars perform as low-cost and locally available adsorptive materials for the adsorptive remediation of arsenic-polluted water?
RQ 3. What are the characteristics and UV-assisted adsorption performance of the engineered photoactive-adsorptive materials from nano-sized TiO$_2$, chitosan, and feldspar in removing organic dyes from water?
RQ 4. What are the characteristics and adsorption performance of the engineered chitosan-based adsorptive materials in removing phosphate from water?

The RQs 1-4 are examined via the optimization of the effect of parameters e.g., pH, dose, and temperature, along with the investigation of the isotherm, kinetics, thermodynamics, and mechanism of adsorption.
INTRODUCTION AND OBJECTIVES

Figure 1. Primary research questions (RQ. 1-4) of the dissertation and the publications (P. I-IV) covering each question. The research includes the steps (rectangles) of developing, characterizing and using engineered (photoactive-) adsorptive materials from initial materials viz. chitosan, nano-sized TiO$_2$ and feldspar, for the remediation of three water pollutants, arsenic, dye, and phosphate (circles). For instance, P. III answers the RQ. 3 in order to explore three different aspects of development, characterization and application of TiO$_2$-based engineered photoactive-adsorptive materials for dye removal.

The research questions are addressed in four appended publications, which are complemented by this compilation that brings the main findings together. Publication I covers the research question 1 focusing on three aspects of preparation, characterization, and application of an engineered photoactive-adsorptive material based on nano-sized TiO$_2$, chitosan, and feldspar minerals for aqueous arsenic remediation. Publication II analyses feldspar minerals as low-cost and locally available adsorptive media, responding to the research question 2. Publication III, corresponding to the research question 3, examines the engineered photoactive-adsorptive material based on nano-sized TiO$_2$, chitosan, and feldspar for the removal of organic dyes from water. Finally regarding to answering the research question 4, publication IV compiles the data on different aspects of preparation, characterization, and application of chitosan-based adsorptive materials for aqueous phosphate remediation.
2. RESEARCH BACKGROUND

2.1 Target pollutants

2.1.1 Arsenic

Arsenic is ubiquitous in the environment. It stands as the 20th most abundant element in the Earth’s crust and 12th in the human body. In small quantities, it is a necessary nutrient to humans. However, when ingested in small quantities over a long period, it is a carcinogen and if ingested in large doses, it is a poison [8, 9]. It appears in –III, 0, +III and +V oxidation states in the environment. In natural water bodies, it mostly exists as either inorganic oxyanions e.g., arsenite (As(III), H3AsO3) or arsenate (As(V), H3AsO4), which are soluble over a wide range of pH and redox conditions [9, 10]. Figure 2 displays the diagram of arsenic chemical speciation calculated according to the stability constants [11]. For instance, the monovalent anionic arsenate is the dominant species under pH range 2–6, whereas the monovalent anionic arsenite dominates more in the alkaline region around pH 9–12.

![Figure 2. Distribution of arsenate (H\textsubscript{3}AsO\textsubscript{4}) and arsenite (H\textsubscript{3}AsO\textsubscript{3}) with the pH variation [11].]
The excessive release of arsenic into the environment originates mainly from natural sources e.g., the weathering of arsenic containing rocks. However, it can also come from anthropogenic sources such as mining and agricultural activities [8, 12]. Elevated concentrations of arsenic have been reported for groundwater supplies from arsenic-rich areas, where arsenic level has reached even up to 50 mg/L due to the geothermal activities [3]. Long-term exposure to drinking water polluted with arsenic causes detrimental effects to many organs such as nervous and respiratory systems resulting in both cancer (skin and liver) and non-cancerous diseases [9, 12]. Considering the toxicology and harmful health effects of arsenic, World Health Organization (WHO) [13] has set a maximum level of 0.01 mg/L for arsenic in drinking water. While groundwater arsenic contamination has been reported in different countries worldwide e.g., China, Chile, Canada, Hungary, and New Zealand, the major population at risk lives in Bangladesh and Bengal region of India [12].

Several methods such as precipitation, adsorption, ion-exchange, and membrane have been applied for arsenic removal from water and have been reviewed previously [8, 12]. Some of the remediation technologies are compiled in Table 1. The success of a particular method relies on several factors including the water source, arsenic concentration, co-existing ions, waste disposal, etc. The limitations on the application of practiced technologies are large volume of arsenic-containing sludge, competing effect of co-existing ions e.g., phosphate and sulfate, and high costs of operation and installation. In the case of arsenic contamination, it is possible to use these technologies as point-of-use (POU) in smaller-scale, which is technologically and economically a more viable option for the areas lacking access to water distribution networks or for the areas where private wells are the source of drinking water for the single households [5, 12]. Among the mentioned removal techniques, adsorption has evolved to the most promising method for its low cost, high efficiency, and environmental and user friendliness. Conventional adsorptive materials used for arsenic removal include activated alumina and carbons, which can also be modified with different materials like iron or alumina [14].
Table 1. Arsenic removal technologies; a brief overview on strengths and drawbacks [8, 12, 14-16].

<table>
<thead>
<tr>
<th>Technology</th>
<th>Strengths</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>oxidation of different impurities disinfection of microbes, relatively simple/rapid process, and minimum residual mass</td>
<td>pH control, and oxidation step control</td>
</tr>
<tr>
<td>Alum-coagulation</td>
<td>available durable powdered chemicals, relatively low capital cost, simple operation, and effective over a wider pH range</td>
<td>toxic sludge, low removal performance, and required pre-oxidation</td>
</tr>
<tr>
<td>Iron-coagulation</td>
<td>available common chemicals, and more efficient than alum coagulation on weigh basis</td>
<td>medium removal of arsenite, and necessary sedimentation and filtration</td>
</tr>
<tr>
<td>Adsorption and ion-exchange</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated alumina</td>
<td>relatively well known, and commercially available</td>
<td>necessary replacement after four to five regeneration cycles</td>
</tr>
<tr>
<td>Iron coated sand</td>
<td>low price, no required regeneration, and remove arsenite and arsenate</td>
<td>not standardized, and toxic solid waste</td>
</tr>
<tr>
<td>Ion-exchange resin</td>
<td>well-defined capacity, pH independency, and exclusive ion specific resin for arsenic removal</td>
<td>high cost, high-tech operation/maintenance, sludge disposal problem related to regeneration, difficulty in removing arsenite, and resin life time</td>
</tr>
<tr>
<td>Membrane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>high-removal performance</td>
<td>high-capital and running cost, required pre-conditioning, and high water rejection</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>no toxic solid waste</td>
<td>high-tech operation/maintenance</td>
</tr>
</tbody>
</table>

2.1.2 Dyes

Dyes are typically complex organic compounds and are resistant to different processes e.g., the action of detergents or the exposure of light. Up to the nineteenth century, the majority of dyes were derived from natural origins like plants and insects, and were generally produced in small scales. The discovery of the first synthetic dye, mauveine, in 1856, was the beginning of the era for manufacturing dyes synthetically and in large scales [17]. Synthetic dyes are extensively employed in different industries such as textile, pulp and paper, leather tanning, food processing, plastics, cosmetics, rubber, and printing [18]. The discharge of these dyes into the environment is a major source of environmental pollution due to their recalcitrant nature, causing an undesirable color, reduced light penetration, and increased chemical oxygen demand (COD) level in the aquatic ecosystems [19]. Many of these synthetic compounds are toxic or carcinogenic posing serious hazards to aquatic living organisms. Excessive exposure to these pollutants can lead to skin irritation and respiratory problems and, in some cases, increases the risk of cancer in humans [20].

There are several ways to classify dyes e.g., based on chemical structure, ionic charge, and applications. The classification based on chemical structure is given in Figure 3 (in green). Figure 3 also classifies dyes based on ionic charge along with providing their properties, some of the reported toxicity impacts, and chemical types (in blue). As seen most of dyes are carcinogenic, indicating the
necessity of effective removal of dyes from the wastewater of related industries [18, 20]. Dyes can cause severe damage to human including dysfunction of kidney, reproductive system, liver, brain and central nervous system. Thus, due to the toxicity of dyes, it is required to treat the wastewaters containing these coloring substances effectively before their release into the environment. However, the complex molecular structure and synthetic nature of dyes make them stable to the action of oxidizing agents, photo-degradation and biodegradation [19]. Different methods are employed for the treatment of waters containing dyes e.g., coagulation, chemical oxidation, membrane, electrochemical, and aerobic and anaerobic biological processes [17, 18]. Each of these techniques has inherent limitations. Table 2 compiles the strengths and drawbacks of different dyes removal methods, which are divided into three categories of physical, chemical and biological treatments [18]. Adsorption is a widely employed method due to the lower cost, flexibility and simplicity in design and operation, insensitivity to toxic pollutants, and the high quality treated effluents especially for well-designed processes. It can remove certain types of chemical contaminants, which cannot be treated by conventional biological treatments. Activated carbon is a common adsorbent for industrial dyes cleanup before discharging into the environment e.g., the removal of reactive textile dyes from aqueous solutions was studied using powdered activated carbons [21]. However, activated carbon has some disadvantages such as the high cost of activated carbon, the need of regeneration and the loss of carbon and efficiency after regeneration [17]. These limitations have led the research interest into finding new alternatives to replace conventional adsorbents. To date, there has been a growing interest on the application of mineral adsorbents [22] e.g., bentonite, zeolites and feldspars, for their ability to remove both inorganic and organic pollutants. Yazdani et al. [23-25] used feldspar mineral and derivatives for removing different cationic and anionic dyes from water. While a successful removal of cationic dyes by feldspars was reported, higher removal of anionic dyes was achieved by the derivatives viz. surfactant-modified feldspar [24] and chitosan-supported feldspar [25].
Figure 3. Classification of dyes based on ionic charge with corresponding properties, chemical types and some of the reported toxicity impacts (in blue), and based on chemical structure with corresponding chromospheres (in green) [18, 20].
Table 2. Dye removal technologies; a brief overview on strengths and drawbacks [17, 18, 26].

<table>
<thead>
<tr>
<th>Technology</th>
<th>Strengths</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical treatment</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorine oxidation</td>
<td>simplicity of application, and low cost</td>
<td>unavoidable side reactions, toxic by-products</td>
</tr>
<tr>
<td>Hydrogen peroxide (H₂O₂) oxidation</td>
<td>simplicity of application</td>
<td>pH dependency, and sludge production</td>
</tr>
<tr>
<td>Ozonation</td>
<td>gaseous state of ozone reagent, no increase in water volume, and no sludge production</td>
<td>short half-life (20 min)</td>
</tr>
<tr>
<td>Fenton’s reagent</td>
<td>efficient decolorization of soluble/in-soluble dyes, effective reduction of COD (chemical oxygen demand), total organic carbon and toxicity, and applicable even with high-suspended solid concentration</td>
<td>sludge production, effectiveness within narrow pH range, and longer reaction time</td>
</tr>
<tr>
<td>Coagulation/flocculation</td>
<td>economically feasible, and satisfactory removal of disperse, sulfur, and vat dyes</td>
<td>large quantities of concentrated sludge, pH dependency, and unsatisfactory removal for highly soluble dyes; azo, reactive, acid and basic dyes [17]</td>
</tr>
<tr>
<td><strong>Physical treatment</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption with activated carbon</td>
<td>high quality treated water, effective for variety of dyes</td>
<td>expensive, need of regeneration otherwise disposal of the concentrates has to be considered, and reduced performance after regeneration/re-use</td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>effective for all dye types, resistance to: temperature, adverse chemical environment and microbial attack, and high-quality treated effluent</td>
<td>high working pressure, significant energy consumption, high cost, relatively short membrane life, and frequent clogging</td>
</tr>
<tr>
<td>Ion-exchange resin</td>
<td>no weight loss in regeneration reclamation of solvent after use, and effective for soluble dyes</td>
<td>not effective for all dyes: not effective for disperse dyes, high cost, and expensive organic solvents</td>
</tr>
<tr>
<td><strong>Biological treatment</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerobic</td>
<td>low running costs, and non-toxic end products of complete mineralization</td>
<td>synthetic dyes are not uniformly decolorized [17], many dyes are recalcitrant to biological breakdown and nontransferable under aerobic conditions</td>
</tr>
<tr>
<td>Anaerobic</td>
<td>inexpensive, well-established degradation of variety of synthetic dyes, no foaming problems with surfactants, and cheap removal of biochemical oxygen demand (BOD)</td>
<td>insufficient BOD removal, dyes and other refractory organics are not mineralized, nutrients (N, P) are not removed, and transformation of sulfates to sulfide</td>
</tr>
</tbody>
</table>

### 2.1.3 Phosphate

Phosphate is listed among essential and limiting nutrients in aquatic ecosystems. However, excessive load of phosphate entering into the water bodies, due to the inflows of municipal and industrial wastewaters and agricultural run-offs, leads to the acceleration of eutrophication [27, 28]. Even a small amount of phosphate (e.g. > 0.02 mg/L) in freshwater sources like lakes may majorly cause eutrophication [29], which is associated with wider issues including the reduced recreational value of water pathways, the depletion of dissolved oxygen, the overgrowth of microorganisms, the massive formation of algal blooms, and the
elevated costs of water treatment. In addition, algal blooms including cyanobacteria may pose serious hazards to animals and humans due to the production of cyanotoxins [30]. Thus, developing reliable remediation technologies for aquatic phosphate is of growing environmental interest. Worth noting, even though phosphate at higher concentrations contaminates the environment, there is a growing demand for phosphate in industries like fertilizer and detergent manufacturers while it is considered among non-renewable resources with no known alternatives. Therefore, it necessitates future studies to focus not only on reliable technologies for phosphate removal but also on phosphate recovery. There are several physical, chemical and biological remediation techniques in practice for phosphate. Table 3 represents the strengths and drawbacks of common phosphate removal technologies in brief. Among all these methods, there has been a growing interest on adsorption as a promising alternative capable of both removing and recovering aqueous phosphate, which can achieve much lower level of phosphate in the discharged water compared with conventional methods. Various adsorptive materials including fly ash [31], mesoporous materials [32], and metal-based hydroxide [29] have been studied for phosphate removal. Yet for further improving the removal and recovery aspects, it is of practical importance to develop new phosphate-specific adsorbents with superior adsorption and regeneration capacities, hence minimizing sludge disposal and making adsorption cost-effective. The removal of phosphate from aqueous solutions was studied using a chemically activated carbon residue as a low cost phosphate adsorbent. The phosphate-loaded carbon residue was suggested to be used as a phosphorus rich forest fertilizer [33].

Table 3. Phosphate removal technologies; a brief overview on strengths and drawbacks [32, 34-36].

<table>
<thead>
<tr>
<th>Technology</th>
<th>Strengths</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation with alum, lime or iron salts</td>
<td>well-established and most commonly used, effective for removal of high phosphate concentrations, and easy installation/operation</td>
<td>costly process, transportation and storage of chemical precipitants, sludge productions, dependency to influent parameters and coagulant dosage, effluent neutralization, and variable phosphate recovery</td>
</tr>
<tr>
<td>Physical methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>simple operation, less residue production, fast adsorption rate especially at low phosphate concentrations, high-quality treated effluent from well-designed process, and removal/recovery of phosphate</td>
<td>dependency on the selection of suitable adsorbents, and unsure technology</td>
</tr>
<tr>
<td>Ion-exchange</td>
<td>well-defined capacity, and high recycling potential as phosphate-based agricultural fertilizer</td>
<td>high regeneration costs, ineffective at low phosphate concentrations, and complex technology</td>
</tr>
<tr>
<td>Biological methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional activated sludge</td>
<td>high-removal performance</td>
<td>less effective at trace level, sensitive to operation conditions, specific care/strict control during implementation, and difficult phosphate recovery from generated sludge</td>
</tr>
</tbody>
</table>
2.2 Adsorption

Adsorption is a mass transfer phenomenon by which substances (ions or molecules) are transferred from a solution phase to the surface of a solid phase so that are removed from the solution. In a general term, adsorption can be described as an enrichment of chemical species from a solution phase on the surface of a solid. The substance that is transferred to the surface is referred to as the adsorbate, and the solid at which the adsorbate is accumulated is referred to as the adsorbent (adsorptive material) [37, 38]. Adsorption is widely practiced to remove substances from fluid phases (gases or liquids). It also occurs as a natural process in the environment. In drinking water production, this process is employed for the removal of e.g., taste- and odor-causing compounds, color-forming organics, and disinfection by-product (DBP) precursors [37].

Adsorptive surfaces are characterized by active sites capable of interacting with solute species in the adjacent solution for their specific electronic and physicochemical properties. Typically, the surface is energetically heterogeneous meaning the active sites have different energies. Adsorbed species on the surface can be released back to the solution phase (referred as desorption) via changing the characteristics of the solution including concentration, pH, and temperature. As adsorption is a surface process, the surface properties e.g., surface area, are key quality parameters of adsorptive materials. Engineered adsorptive materials are usually highly porous, providing large surfaces as internal surfaces constituted by the pore walls [38].

2.2.1 Influencing factors

There are different factors affecting adsorption including the properties of the adsorbate and the adsorptive material and the process parameters. Influential criteria related to the adsorbate include polarity, molecular structure and stability, and concentration. The equilibrium capacity and kinetics are the major determinants of adsorption, and are influenced by the surface affinity for different species, physicochemical and morphological characteristics, surface charge, surface area, and porosity of the adsorptive materials. Operational parameters e.g., solution pH, temperature, and co-existing species in the solution also influence the adsorptive performance of the system [37, 38]. It is necessary to study and optimize the affecting factors on the adsorption system before applying the system in full scale.

2.2.2 Kinetics

Adsorption is not reached instantly, but the transfer of adsorbate from the solution to the adsorptive sites within the pores of adsorbent is usually restricted with mass transfer resistances, which determine the time needed to reach the equilibrium phase, i.e. the adsorption kinetics. The adsorption rate is usually controlled by diffusion mechanisms of adsorbate from bulk solution towards the external surface and within the pores of the adsorptive materials. Studying the adsorption kinetics explains the rate-controlling mechanisms of mass transfer
and determines the mass transfer parameters, which along with the equilibrium data, are necessary for estimating the required contact time for the design of batch reactors and fixed-bed adsorber systems [38].

Adsorption kinetics progress in four consecutive stages: (i) adsorbate transport from the bulk solution to the hydrodynamic boundary layer surrounding the adsorptive particles; (ii) adsorbate transport through the boundary layer to the external surface of the adsorptive particles, so-called film or external diffusion; (iii) adsorbate transport into the interior of adsorbent pores via surface and pore diffusions, intraparticle or internal diffusion; (iv) interaction between the adsorbate and the adsorptive sites. Generally, it is assumed that while the first and the fourth stages occur fast, the total adsorption rate is determined by film and/or intraparticle diffusions [38]. Film and intraparticle diffusions differ in their dependency on the hydrodynamic conditions, particularly stirring velocity in batch reactors and flow velocity in fixed-bed system. While the intraparticle diffusion is independent of the stirring or flow velocity, film diffusion rate increases with increasing stirring or flow velocity because of the reduction of the boundary layer thickness. The radius of adsorptive particles affects both the film diffusion and the intraparticle diffusion for the change of surface area and diffusion paths [38, 39]. To study the adsorption kinetics, the change of adsorbate concentration is measured over time and the resulting data are fit to kinetic models (Table 4) applied for determining the adsorption parameters.

Table 4. Kinetics and isotherm models employed in this dissertation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Nonlinear form</th>
<th>Linear form</th>
<th>Linear plot</th>
<th>Factors</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kinetics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>( q_t = q_e (1 - e^{-k_1 t}) )</td>
<td>( \ln \left( q_e - q_t \right) = \ln q_e - k_1 t )</td>
<td>( \ln(q_e - q_t) ) vs. ( t ) ( k_1 ) and ( q_e ) [40]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>( q_t = \frac{k_2 q_e t}{1 + k_2 q_e t} )</td>
<td>( \frac{t}{q_t} = \frac{1}{k_2 q_e t} + \frac{t}{q_e} )</td>
<td>( t/q_t ) vs. ( t ) ( k_2 ) and ( q_e ) [41]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
<td>( q_t = k_{id} t^{1/2} + C )</td>
<td>( q_t ) vs. ( t^{1/2} ) ( k_{id} ) [42]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| **Isotherm**      |                                                                                |                                                                            |                                |         |      |
| Freundlich        | \( q_e = K_F C_e^{1/n} \)                                                    | \( \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \)                              | \( q_e \) vs. \( \ln C_e \) \( K_F \) and \( n \) [43]               |         |      |
| Langmuir          | \( q_e = \frac{q_s K_L C_e}{1 + K_L C_e} \)                                 | \( \frac{C_e}{q_e} = \frac{1}{1 + K_L C_e} \)                              | \( 1/q_e \) vs. \( 1/C_e \) \( K_L \) and \( q_s \) [44]            |         |      |
| Sips              | \( q_e = \frac{q_s C_e^{n_S}}{1 + K_S C_e^{n_S}} \)                        | –                                                                          | –                             | \( K_S \) and \( n_S \) [45]                                         |         |      |

Note: \( q_t \): adsorbate uptake (mg/g) at time \( t \) (min); \( q_e \): the uptake of adsorbate at equilibrium; \( k_1 \): rate constant of pseudo-first-order; \( k_2 \): rate constant of pseudo-second-order; \( k_{id} \): intra-particle diffusion rate constant (mg/min^{1/2} g); \( C \): intercept; \( n \): adsorption intensity \( K_F \): empirical constant of Freundlich (\( \mu g/g/\mu g/L)^{1/n} \)); \( q_s \): maximum monolayer adsorption capacity; \( K_L \): equilibrium constant related to adsorption rate (L/\( \mu g \)); \( q_s \): Sips maximum adsorption capacity (\( \mu g/g \)); \( K_S \): Sips equilibrium constant (L/\( \mu g \)^{n_S}); and \( n_S \): Sips model exponent.
2.2.3 Isotherm

Adsorption isotherms quantify the affinity of adsorbate for the adsorptive material via estimating the amount of the adsorbate that can be adsorbed at equilibrium and at a constant temperature. For water treatment applications, the amount of adsorbate adsorbed at equilibrium is a function of the aqueous-phase concentration. Isotherm studies are carried out by exposing a known amount of adsorptive materials in a fixed volume of solution with various concentration of adsorbate [37, 38]. At the end of the equilibration phase, the aqueous concentration of the adsorbate is measured and the adsorption equilibrium capacity \(q_e\) is calculated for each sample using the following mass balance equation:

\[
q_e = \frac{(C_0 - C_t)V}{m} \tag{1}
\]

where \(C_0\) represents the initial concentration of adsorbate (mg/L); \(C_t\) is the final concentration (at time t or at equilibrium) (mg/L); \(V\) is the volume of the solution (L); and \(m\) is the mass of the adsorbent used (g). Adsorption isotherm can be modeled via isotherm models some of which compiled in Table 4. In this research, the focus was mainly on Langmuir and Freundlich isotherms. The Langmuir isotherm describes the equilibrium between the solid surface and the solution as a reversible chemical equilibrium [44]. Based on this model, the surface is composed of fixed individual adsorptive sites where the adsorbate may be chemically bound. The surface is homogeneous meaning the adsorption has a constant free-energy change for all sites. Each site is able to bind at most with one molecule of adsorbate, hence assuming a monolayer adsorption on the surface. The Freundlich isotherm [43], an empirical model, explains the equilibrium data for heterogeneous surfaces e.g., activated carbon. This model usually provides a better fit for the isotherm data for granular activated carbon (GAC) than the Langmuir model as multiple layers of adsorbates can adsorb onto the GAC providing a distribution of sites with different adsorption energies. The Freundlich model describes a multilayer adsorption onto the surface of heterogeneous sites with different bond energy. This isotherm is commonly employed to characterize the adsorption from aqueous solutions and has become as a standard equation in describing adsorption process in water treatment [38].

2.2.4 Thermodynamic

In surface processes, the Gibbs free energy depends on different parameters e.g., temperature, pressure, and system composition. The Gibbs free energy change \(\Delta G_{ads}\) reflects the spontaneity of adsorption; the higher the negative value of \(\Delta G\), the more energetically favorable the adsorption is. The \(\Delta G_{ads}\) is calculated as follows:

\[
\Delta G_{ads} = -RT\ln K_a \tag{2}
\]

where \(T\) is the absolute temperature in kelvins, \(R\) the gas constant (8.314 J/mol·K), and \(K_a\) the thermodynamic equilibrium constant without units that is expressed as follows:
where $a_s$, $a_{ad}$, and $a_{s, ad}$ are the respective activities of species: solute molecules, adsorption sites, and solute molecules adsorbed on the surface at equilibrium, and $C_s$ and $C_{s, ad}$ are the respective concentration of solute molecules in the solution and adsorbed on the surface at equilibrium. Note that the usage of $K_c$ for $K_a$ calculation is valid only for a dilute solution, as discussed in detail previously [46, 47]. The distribution constant ($K_c$) can be determined by plotting $\ln(C_{s, ad}/C_s)$ versus $C_{s, ad}$ and extrapolating $C_{s, ad}$ to zero. The relationship between $\Delta G$, enthalpy change ($\Delta H_{ads}$), and entropy change ($\Delta S_{ads}$) of adsorption is stated as:

$$\ln K_a = -\frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R}$$

The thermodynamic parameters provide insights into the type and mechanisms of the adsorption process. Physical adsorption, the most common type of adsorption in water treatment, occurs rapidly via nonspecific binding mechanisms such as van der Waals forces and is similar to vapor condensation or liquid precipitation. It is a reversible reaction so that the adsorbate is able to desorb in response to the decrease in solution concentration caused by adsorption. Physical adsorption is usually exothermic with a heat of adsorption typically ranging from 4 to 40 kJ/mol (about two times greater than the heat of vaporization) [37]. On the contrary, in chemisorption, a chemical reaction occurs involving the transfer of electrons between adsorptive sites and adsorbate, hence, chemical binding with the surface. The heat evolved during chemisorption is typically above 200 kJ/mol [37]. Chemical adsorption is usually not reversible, even though desorption can occur while accompanied by a chemical change in the adsorbate. Typically, these two categories can easily be distinguished. In some cases, the reaction falls between the two since an exceedingly unequal sharing of electrons may not be easily differentiated from the high degree of distortion of an electron cloud involved in physical adsorption [37]. Positive $\Delta H_{ads}$ indicates an endothermic process, whereas, a negative $\Delta H_{ads}$ indicates an exothermic process. The $\Delta S_{ads}$ explains the change in the degree of disorder in the considered system. The immobilization of adsorbate results in a decrease of disorder in the adsorbate-adsorbent interface indicating a negative sign for the entropy change. However, exceptions could be resulted from dissociation during adsorption by displacement processes where more species are desorbed than adsorbed. If $\Delta S_{ads}$ is negative, then adsorption usually is exothermic if spontaneous [38].

2.2.5 Mechanism

The interaction between adsorbate molecules/ions and the adsorptive sites of adsorptive materials is studied via adsorption mechanism, or surface complexation. Adsorption mechanism is classified based on surface complexes formed during adsorption as outer- and inner-sphere surface complexes, or as physical
and chemical adsorption. The surface charge is a key factor in outer-sphere complexation due to electrostatic interactions and van der Waals forces involved. Inner-sphere complexation occurs independent of the surface charge via formation of covalent or ionic bonds. In addition, adsorption can involve both complexations simultaneously, yet, the inner-sphere complexation occurs with a slower rate than outer-sphere complexation [48].

2.3 Low-cost adsorptive materials

Low-cost adsorptive materials include natural materials and wastes/by-products of different industries, and are used as adsorbents as such or after some minor treatment [17]. They are classified in two categories based on (i) their availability (Table 5) and (ii) their nature [17]. Low-cost adsorptive materials might be interesting financially, but studies on these materials are limited to specific applications providing insufficient general information. Besides, the adsorption properties of low-cost adsorptive materials vary [38]. Adsorbents must be certified and fulfill high quality standards to guarantee the safety of drinking water. Therefore, low-cost adsorbents are more suitable for treating wastewater than drinking water.

Table 5. Low-cost adsorptive materials studied for the removal of the target pollutants selected from literature.

<table>
<thead>
<tr>
<th>Low-cost adsorbents</th>
<th>arsenic removal</th>
<th>dye removal</th>
<th>phosphate removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>iron oxide minerals [49]</td>
<td>feldspars [23]</td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>sorghum biomass [51]</td>
<td>agricultural peels [52]</td>
<td>rice husk ash [53]</td>
</tr>
<tr>
<td>wastes/by-products</td>
<td></td>
<td></td>
<td>woodchip [54]</td>
</tr>
<tr>
<td>Industrial</td>
<td>fly ash [55]</td>
<td>bagasse fly ash [57]</td>
<td>fly ash [31]</td>
</tr>
<tr>
<td>wastes/by-products</td>
<td>solid waste from leather industry [56]</td>
<td></td>
<td>alkaline residue [58]</td>
</tr>
</tbody>
</table>

Aredes et al. [49] introduced the natural iron oxide minerals, e.g. hematite, magnetite, goethite and iron rich laterite soil, as a simple arsenic remediation technology capable of meeting drinking water standards. Iron rich laterite was the most effective adsorbent for arsenic, followed by goethite, magnetite and hematite. Arsenic adsorption occurred over the entire pH range of 4-11 and the observed shift in the isoelectric point of the minerals after arsenic adsorption suggested specific ion adsorption [49]. Luukkonen et al. [59] used blast-furnace-slag and metakaolin geopolymers, an emerging group of sorbents, and their raw materials for the removal of arsenic (As(III)). Blast-furnace-slag geopolymer proved to be the most efficient of the studied materials. While the experimental maximum As sorption capacity was 0.52 mg/g, up to 100% removal was achieved when adsorbent dosage was increased appropriately. Removal kinetics fitted well with the pseudo-second-order model. Geopolymer technology was introduced as a simple and effective way to turn blast-furnace slag to an effective sorbent with a specific utilization prospect in the mining industry.
Yazdani et al. [23] studied feldspars as low-cost and locally available alternatives for the treatment of aqueous solutions containing cationic dyes. The adsorption of the dyes onto feldspar was fast, and more than 80% of the dye concentration was removed within minutes. The optimal feldspar dosage was determined to be 2.5 g/L. The removal efficiency was higher in alkaline conditions and it was explained due to the electrostatic attraction between the dye cations and the negatively charged feldspar surface. The electrostatic charge of the feldspar surface is influenced by pH as follows:

\[
\begin{align*}
\text{Si} - \text{OH} + \text{H}^+ & \rightarrow \text{Si} - \text{OH}_2^+ & (5) \\
\text{Si} - \text{OH} + \text{OH}^- & \rightarrow \text{Si} - \text{O}^- + \text{H}_2\text{O} & (6) \\
\text{Si} - \text{O}^- + \text{Dye}^+ & \rightarrow \text{Si} - \text{O}^- ... \text{Dye}^+ & (7)
\end{align*}
\]

As the pH of the solution increases, the positive charge at the surface-solution interface decreases and the adsorptive surface becomes negatively charged due to the deprotonation of active surface sites. The negatively charged sites favor the adsorption of dye cations due to electrostatic attraction. The adsorption is spontaneous, endothermic, and physical. As feldspars possess permanent negative charges in their crystal structure, they have a naturally high adsorption capacity for cationic species. However, their capacity for removing anionic species is quite low. Thus, to improve the affinity of feldspars for anionic dyes, the surface can be modified via different modification methods e.g., treatment with organic compounds and polymers. A common surface modification of minerals includes the surface treatment with cationic surfactants. This process involves both cation exchange and hydrophobic bonding mechanisms. Through the ion-exchange mechanism, the inorganic cation in the mineral framework is replaced with the organic surfactant cation so the surfactant cations shifts the surface from hydrophilic to hydrophobic. Consequently, the surfactant-modified minerals are able to adsorb hydrophobic and anionic organic compounds from water. Yazdani et al. [24] modified the surface of feldspars using hexadecyltrimethyl ammonium bromide (HDTMA) to improve the capacity for the removal of an anionic dye. The monolayer coverage capacity of surfactant-modified feldspar for the dye was 6.37 mg/g. The adsorption kinetics follows the pseudo-second-order model. The adsorption is exothermic.

Fly ash, a by-product of coal-burning power plants, was studied as a phosphate adsorbent [31]. It removed phosphate up to 68–96% rapidly. The removal mechanisms involved a fast and large phase of precipitation followed by a slower and smaller phase of adsorption. Adsorption contributed around 30–34% of the total removal, depending on the CaO content of fly ash [31]. Phosphate removal from aqueous solutions was also investigated using calcite as a cheap and abundant natural adsorbent [60]. Higher removal efficiency was observed at higher solution pH. The phosphate adsorbed-calcite was introduced as an environmentally friendly product for the fertilization of acid soils.
2.4 Engineered adsorptive materials

Engineered adsorptive materials are typically produced under strict quality control conditions to provide constant properties and high adsorption capacities. These materials are categorized into different categories e.g., carbonaceous, polymeric, and oxide adsorbents. The number of common adsorbents in drinking water treatment is limited to commercial activated carbons and oxide adsorbents as they fulfil the high quality standards of safe drinking water production. Activated carbons are developed from carbonaceous materials by chemical or gas activations [38]. However, commercial activated carbon is fairly expensive and it has energy consuming preparation steps. After extensive usage, exhausted activated carbon requires regeneration via chemical or thermal treatments, which increase the cost and carbon loss. It has a non-polar surface incapable of sufficient removal of inorganic pollutants. Moreover in multicomponent systems, decreased adsorption of a considered compound in comparison with its single solute adsorption is observed due to a competitive adsorption onto activated carbon [38]. Therefore, development of inexpensive products for water treatment has been of growing interest with a global aim for the utilization of wastes and by-products as initial materials [33].

Recent research has highly focused on new possibilities that alternative engineered adsorptive materials provide for real world water treatment application. Engineering new adsorptive materials is an emerging science, where researchers and experts from different fields, such as environmental, chemical, biotechnological, and material sciences, have come together to develop novel materials with a wide range of applications in the remediation of environmental problems. Biochar-based nanocomposites [61], chitosan-based composites [62], spinel ferrite magnetic materials [63], clay-polymer nanocomposites [64], and nanoparticles as adsorbents [3] are some examples of recently engineered adsorptive materials for water remediation. However, many of newly engineered adsorptive materials are in nano-size, which makes them difficult to separate from processed water, and involve toxicity concerns. Separation and recovery of adsorptive particles from treated water are essential to avoid secondary pollution and to lower the cost. New generation of engineered adsorptive materials such as hybrid adsorptive materials featured with magnetism and embedded nanoparticles in an easily separable matrix e.g., polymers, are introduced as solutions for these obstacles [3, 63].

Hybrid adsorptive materials are usually engineered by coupling two or more phases (inorganic, organic, or carbon based) to achieve features that are not usually the actual sum of the properties of the individual constituents, but the results of synergistic interaction between the phases. A hybrid material can provide properties related to the close interaction between the involved phases and to the peculiar characteristics of the interface properties. Hybrid adsorptive materials are engineered for the sole aim of improving their selectivity, surface area and chemistry, mechanical strength, and regeneration or a combination of these features. For instance, hybrid adsorptive materials with embedded semiconductors e.g., TiO₂, in the matrix of organic/inorganic phases e.g., chitosan and
montmorillonite, have been investigated not only for enhancing the overall removal efficiency of the process by combining the adsorption/photo-oxidation features, but also for visible-sensitizing the photo-catalysis process and for easing the recovery and separation process [5, 16, 65]. The integration of conventional adsorbents with emerging novel materials can be achieved via several methods e.g., grafting, impregnation, chelation and crosslinking, and provide better properties than the individual components.

Figure 4 illustrates the steps involved in creating engineered adsorptive materials. Engineered adsorptive materials can be tailor-made with specific set of features making them suitable for target applications. They can be developed via strategic selection of the design parameters to tailor make adsorptive products that fully suit the targeted applications (Figure 4). After targeting the application and setting the goals, the desired characteristics of engineered products including physical and chemical properties can be achieved by monitoring the initial materials (e.g., composition of various precursors), selecting the preparation methods (e.g., grafting and impregnating), and optimizing the process parameters (e.g., temperature, rate and residence time) [66]. To date, a wide range of novel engineered hybrid adsorptive materials have been tailor-made for the remediation of metals, pharmaceuticals, dyes and pesticides [6, 61, 62, 66]. Table 6 compiles some of the novel engineered hybrid materials engineered for water remediation purposes.

Figure 4. Schematic diagram of development steps for creating engineered adsorptive materials.

Engineering biochar-based adsorptive materials, for instance, is nowadays an important practice for the environmental application of carbon- and nano-technologies. Tan et al. [61] reviewed recent advances on biochar-based nano-composites combining the advantages of biochars and nano-materials. These emerging composites exhibit significant improvement in functional groups, pore properties, surface active sites, catalytic degradation capacities, and ease of separation. These materials provide high capacities of removing diverse range
of contaminants from water. In particular, the hybrid of semiconductor photocatalysts, e.g. TiO$_2$, and biochars [67] can offer simultaneous adsorption and enhanced photo-catalysis functions for treating a variety of contaminants.

**Table 6.** Recent researches on preparation, characteristic, and application of engineered (photo-active-) adsorptive materials.

<table>
<thead>
<tr>
<th>Engineered material</th>
<th>Characteristic/advantages</th>
<th>Contaminants</th>
<th>Removal capacity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-impregnated chitosan bead</td>
<td>enhanced arsenic removal under UV irradiation, obviation of post-filtration, superior implementation perspective for decentralized water treatment</td>
<td>arsenic</td>
<td>2198 $\mu$g/g for As(III) and 2050 $\mu$g/g for As(V) without UV 6400 $\mu$g/g for As(III) and 4925 $\mu$g/g for As(V) under UV</td>
<td>[5]</td>
</tr>
<tr>
<td>TiO$_2$ pillared montmorillonite</td>
<td>microporous structures, economical value, high cation exchange capacity, environmentally friendly, high adsorption and efficient photocatalytic ability</td>
<td>arsenic</td>
<td>4.58 mg/g for As(III) and 4.86 mg/g for As(V) without UV 5.19 mg/g for As(III) and 5.16 mg/g for As(V) with UV</td>
<td>[16]</td>
</tr>
<tr>
<td>Nano-magnetic activated microfibrillated cellulose</td>
<td>magnetic properties, high surface area, good adsorption capacity</td>
<td>arsenate</td>
<td>2.46 mmol/g</td>
<td>[14]</td>
</tr>
<tr>
<td>TiO$_2$–Chitosan/Glass photocatalyst</td>
<td>synergetic photodegradation–adsorption processes</td>
<td>monoazo dye</td>
<td>87% dye removal from 20 mg/L dye solution</td>
<td>[68]</td>
</tr>
<tr>
<td>Carbon nanotubes (CNTs)</td>
<td>well defined cylindrical hollow structure, large surface area, high aspect ratios, hydrophobic wall and easily modified surfaces</td>
<td>dyes</td>
<td>-</td>
<td>[19]</td>
</tr>
<tr>
<td>Chitosan-clay composite</td>
<td>high adsorption, regeneration, and reuse capacities</td>
<td>methylene blue dye</td>
<td>142 mg/g</td>
<td>[6]</td>
</tr>
<tr>
<td>Zirconium-modified chitosan beads</td>
<td>easily hydrolyzed zirconium ions resulting in a large number of hydroxyl ions which can take part in the ligand exchange reaction with the target pollutant</td>
<td>phosphate</td>
<td>60.60 mg/g</td>
<td>[69]</td>
</tr>
<tr>
<td>Mg–Fe–Cl based layered double hydroxide (LDH)</td>
<td>achieving more demanding effluent discharge regulation high regeneration and recovery capacities</td>
<td>phosphate</td>
<td>95% of total phosphate dosed into the system</td>
<td>[29]</td>
</tr>
<tr>
<td>Magnetic calcium and magnesium-modified iron oxide adsorbents</td>
<td>improved phosphate adsorption capacity, easy to separate from solution via magnetism</td>
<td>phosphate</td>
<td>from 12.39 to 16.74 mg/g</td>
<td>[28]</td>
</tr>
<tr>
<td>Biochar/AlOOH nanocomposite</td>
<td>effective removal of the contaminants, environmentally friendly materials</td>
<td>arsenic, methylene blue dye, and phosphate</td>
<td>17.41 mg/kg As(V), 85.04 mg/kg for dye, and 135 mg/kg for phosphate</td>
<td>[70]</td>
</tr>
</tbody>
</table>
2.4.1 Chitosan-based engineered adsorptive materials

Engineered adsorptive materials based on biopolymers e.g., chitosan, cellulose, and lignin, are listed among important adsorbents due to their unique features e.g., biocompatibility, high adsorption capacity, and recyclability. Recently for engineering hybrid adsorptive materials, chitosan has played a key role as a supporting bio-matrix and a provider of large number of hydroxyl and amino groups for adsorption. Chitosan [62, 71] is a polyaminosaccharide, derived from deacetylation of chitin that is the second most plentiful biopolymer after cellulose. However, the application of chitosan suffers from a major limitation, solubility in acidic medium (pH < 4). Significant effort has been directed towards modifying chitosan physically or chemically to improve its adsorption-related properties. The chemical crosslinking of surface with crosslinking reagents e.g., glutaraldehyde, is practiced in order to improve the acidic resistance of chitosan. However, as the crosslinking reagents mainly engage with the amino groups, the main adsorptive functional sites, chemical crosslinking usually reduces the adsorption capacity of chitosan. To prevent the amino groups from crosslinking and preserving the adsorption efficiency, new crosslinking regents are employed to shield the amino groups and subsequently release them for adsorption [71].

Chitosan is traditionally employed in the form of flake or powder, which practically limits its column applications due to several drawbacks e.g., swelling, crumbling and poor mechanical strength. Progress has been made to overcome these limitations through developing chitosan beads, which not only improves the adsorption performance by reducing the crystallinity through the gel formation, but also provides the potential of easy separation and reuse of the beads after adsorption [5, 72]. The chitosan capacity for anionic species relies on the protonation of its amino groups under acidic condition; yet, acidic condition also leads to its solubility. Metal oxide impregnation has been used to enhance the uptake of oxyanions e.g., arsenic, and the selectivity over other co-existing ions. Metal oxides e.g., Fe₃O₄ and TiO₂, are capable of forming complexes with oxyanions like arsenic [73]. Chitosan beads are developed by dissolving chitosan into acetic acid and pumping the obtained viscous solution into a precipitation bath. The impregnation of the metal oxide is done either (i) by adding the metal oxide to the viscous solution before pumping to precipitation bath, (ii) by immersing the beads into a solution containing the metal oxide, and (iii) by changing the precipitation bath to a metal solution [73]. Chitosan-immobilized sodium silicate, for instance, is prepared by setting the sodium silicate solution as precipitation bath. Yazdani et al. [25] developed a feldspar/chitosan bio-bead for acid dyes removal by adding feldspar mineral to the viscous solution of chitosan before pumping to the NaOH precipitation bath. Figure 5 categorizes chitosan-based hybrid adsorptive materials [74].

RESEARCH BACKGROUND
2.4.2 TiO₂-based engineered photoactive-adsorptive materials

Engineered hybrid adsorptive materials embedding a semiconductor e.g., TiO₂, benefit from enhanced photocatalytic-adsorption properties as: (i) most of these hybrid photocatalysts provide high adsorption properties due to their high surface area. (ii) The potential gradient at the interface can help the separation of the photogenerated charges in the proximity of the interface. (iii) One of the involved phases is usually able to absorb visible light. (iv) The coupling of a second phase with a traditional semiconductor can enhance the selectivity of the process [75]. Figure 6 classifies the types of engineered hybrid photoactive-adsorptive materials [75]. The class of hybrid adsorptive materials embedding TiO₂ semiconductor within a polymeric matrix e.g., chitosan, (inorganic/organic hybrids) usually provide larger efficiency than other inorganic semiconductor-based materials. TiO₂ is considered as the most efficient, stable, nontoxic and inexpensive catalyst in heterogeneous photocatalytic systems for pollution remediation. However, there are major obstacles for its application in photocatalytic reactors e.g., a relatively slow degradation rate, low adsorption capacity and limited reusability. Embedding TiO₂ in the matrix of supportive materials like polymers provides the advantages of supporting TiO₂ particles, facilitating a more effective removal due to the concentration of pollutants and intermediates around the surface of TiO₂ for oxidation and degradation, and easing the separation process [76]. Recent studies [5, 65, 76] have reported the multi-functional performance of TiO₂ with chitosan in heterogeneous photocatalysis systems by enhancing the adsorption–photocatalytic processes. For instance, Miller et al. [5, 65] fabricated TiO₂-impregnated chitosan beads as a photoactive arsenic adsorbent. The role of TiO₂ was reported as crucial for arsenite uptake, since UV light promotes the oxidation of arsenite to arsenate on the surface of TiO₂-impregnated beads. Of the two components coupled in the hybrid
bead, TiO₂ was mentioned as responsible for more than 85% of arsenate uptake and for almost 100% of arsenite removal. The role of chitosan was to support TiO₂ nanoparticles and to facilitate the separation process.

**Figure 6.** Engineered adsorptive materials studied for photocatalytic-adsorptive removal of pollutants.

TiO₂ is a well-known photo-catalyst for many organic substrates, which have shown oxidative (in some cases reductive) degradation and complete mineralization under TiO₂/UV system. The semiconductor is an excellent photo-oxidant for arsenic with demonstrated capability of oxidizing arsenite to arsenate under UV exposure [5, 77]. The mechanisms involved in TiO₂/UV photocatalytic process are well discussed and understood in the literature, yet some features are still subject to debate. For instance, in the case of photo-oxidation of specific species like arsenite, the main oxidant initiating the process is still unclear [78].

**Figure 7** shows a general schematic diagram of the photocatalytic pathway involving TiO₂. After activation by UV light (\( \lambda < 387 \) nm), promoted electrons to the conduction band (CB) are scavenged by the molecular oxygen yielding superoxide radical ions, \( O_2^{•−} \), which then get involved in generating HOO• radicals from protons. HO₂• radicals contribute for the formation of \( •OH \) radicals. Moreover, the positively charged holes formed at the valence band (VB) directly lead to the generation of \( •OH \) radicals with the oxidation of either surface OH⁻ groups and/or H₂O molecules. The active radicals, \( O_2^{•−}, HO_2^{•}, \) and \( •OH \), are able to oxidize and/or degrade inorganic and organic pollutants. The photocatalytic system has attracted many interests for treating polluted waters [65, 77, 79, 80].

**Figure 7.** General schematic diagram of photocatalytic pathway of TiO₂ under UV irradiation [8].
2.5 Regeneration of adsorptive materials (Desorption)

Adsorptive materials are no longer effective after saturation and require regeneration/desorption. The regeneration of exhausted adsorptive media provides benefits of reusing the media, recovering the adsorbate, finding the adsorption mechanism, and reducing the cost [37, 81]. An effective regeneration process restores the re-adsorption capacity close to the initial properties for several cycles of regeneration. Regeneration can be thermal or physicochemical. For instance, activated carbon is regenerated thermally under hot air or steam and chemically with acid and base solutions [37]. Yazdani et al. [23] recovered the low-cost feldspar adsorbent thermally at 400°C (30 min). Re-adsorption of dyes onto recovered feldspar indicated a satisfactory dye removal. Acids e.g., HCl, H₂SO₄, H₃PO₄, alkali, NaOH, and electrolytes, NaNO₃ and NaCl, are widely used as regenerating agents for the desorption of different adsorbates from exhausted adsorptive materials [81, 82]. NaOH is an effective elute for desorption of dyes. Lima et al. [82] used desorption process for regenerating the adsorbent and also confirming the electrostatic attraction of positively charged surface of the adsorptive material with the dyes. They studied NaOH, KCl and NaCl solutions for the regeneration of loaded adsorbent. Higher concentrations of NaOH desorbed the uptaken dye immediately, while, the recovery of adsorbent using KCl and NaCl took longer time. The desorption of arsenic oxyanions from the exhausted adsorptive materials was studied using HNO₃, NaOH and NaNO₃ solutions [81]. Low desorption was achieved by HNO₃ and NaNO₃, whereas, high desorption efficiency was provided by NaOH. Mesoporous materials with superior adsorption and regeneration capacities were studied for both enhanced removal and recovery of phosphate [32]. The spent mesoporous materials can be regenerated using chemical reagents e.g., NaOH, KOH, NaCl, or Na₂SO₄ solutions without sacrificing adsorption capacity. The process of regeneration/desorption is crucial for cost determination and adsorbate recovery in a concentrated form. The regeneration of exhausted adsorptive materials are often supplied by suppliers and off-site of water treatment facilities. However, treatment plants may also employ non-regenerable adsorptive materials in the first place.

2.6 Stabilization and disposal of exhausted adsorptive materials

The disposal of spent adsorptive materials after total exhaustion is a major concern due to the possibility of toxic pollutants leaching into the environment and consequent environmental problems. Therefore, the exhausted adsorptive materials must be disposed safely after stabilization. For instance, the stabilization of the arsenic loaded sludge-based adsorbents was carried out using cement and lime mixture [81]. A reduction in leach-ability of arsenic from solid media after stabilization was found due to the precipitation of arsenic as calcium arsenates. Lime addition closes the pores of the cement media due to calcite formation, which prevents arsenic leaching. Bhatnagar et al. [83] immobilized the spent adsorptive materials after heavy metal adsorption via binding in the cement based system. The calcium silicate hydrates existing in the cement bind the metal ions and prevent the leaching.
3. EXPERIMENTAL SETUP

This dissertation focuses on the development of new engineered (photoactive-) adsorptive materials and the study of their applicability in removing different pollutants, viz. arsenic, dyes and phosphate, from water in laboratory scale. It includes the steps of preparing, characterizing, and applying the engineered materials (EMs) from well-known initial materials, viz. nano-sized TiO₂ (n.TiO₂), chitosan and feldspar, as adsorbents for the remediation of target pollutants from aqueous solutions. Adsorption batch experiments are conducted to scrutinize the kinetics, isotherm, thermodynamics and mechanism of removal process by the developed materials along with the effect of operational parameters including pH, adsorptive material dosage, and co-existing ions.

The research is conducted on engineering several adsorptive materials, with a focus on an engineered photoactive-adsorptive material composed of n.TiO₂, chitosan, and feldspar to provide a general picture of the developed EMs as an adsorbent of inorganic arsenic and organic Acid Black 1 dye in publications I and III. Feldspars as a group of aluminosilicate minerals are also explored for arsenic removal in publication II as aluminum-based materials are among the common adsorbents of arsenic. In publication IV, chitosan-based EMs (zinc-functionalized chitosan beads) are developed as a biosorbent for phosphate. In this way, this research has been directed towards providing fundamental perspectives on new EMs as a solution for a wide range of water pollution.

3.1 Preparation of engineered adsorptive materials

The engineered materials are developed in the form of beads via a simple fabrication method as follows:

For preparing the EMs based on n.TiO₂, chitosan and feldspar, chitosan is dissolved in 0.1 M CH₃COOH and stirred continuously to be fully dissolved, creating a viscous solution into which n.TiO₂ is added and agitated overnight. Feldspar immersed in 0.2 M NaCl is added to the n.TiO₂/chitosan solution followed by continuous stirring for 24 h [1 g chitosan/0.5 g n.TiO₂/0.5 g feldspar] (more in detail in publication I and III).

EMs based on chitosan and feldspar is developed by dissolving chitosan in CH₃COOH. Then feldspar suspension in NaCl is added to the chitosan solution.
followed by continuously stirring for 24 h [1 g chitosan/0.5 g feldspar] (see publication I).

Similarly, to prepare EMs based on n.TiO\textsubscript{2} and chitosan, chitosan is dissolved in CH\textsubscript{3}COOH and n.TiO\textsubscript{2} is added into the chitosan solution [1 g chitosan/0.5 g n.TiO\textsubscript{2}] (publication I).

To prepare the zinc-functionalized chitosan (chitosan-Zn) bio-sorbent, chitosan is dissolved in CH\textsubscript{3}COOH. After fully dissolving chitosan, ZnCl\textsubscript{2} aqueous solution is added to the chitosan solution. For the fixation of Zn-chitosan complexation, the final solution is heated to 80°C and then cooled to room temperature for the next step [1 g chitosan/0.35 g ZnCl\textsubscript{2}] (publication IV).

Bio-beads are formulated by dispensing the final solutions via a syringe pump into 0.1 M NaOH, where the inorganic constituents are embedded in the chitosan matrix. The solidified beads are filtered, rinsed, dried, and stored in a dark place for future usage.

### 3.2 Characterization of engineered adsorptive materials

The morphology and composition of the engineered materials are characterized via powder X-ray diffraction (XRD) (PANalytical X’Pert Pro MPD α1). Scanning electron microscopy (SEM) is conducted with a JEOL JSM-7500FA analytical Field Emission SEM using 1.5–2 kV acceleration voltage and 10 lA probe current, detecting secondary electrons. Fourier transform infrared spectroscopy (FT-IR) is carried out on a Thermo Scientific Nicolet iS50 FT-IR spectrometer for molecular level investigations.

The point of zero charge pH (pH\textsubscript{PZC}) of the engineered (photoactive-) adsorptive materials and feldspars is determined via drift method [84]; 0.05 g of adsorptive materials is added to 20 mL of 0.1 M NaCl applied as an inert electrolyte. The initial pH values are adjusted within the range of 3–11 using 0.1 M HCl or 0.1 M NaOH. The mixtures are equilibrated for 24 h, and the final pH values of the solutions are measured.

### 3.3 Concentration measurement of solutions

Arsenic concentration is measured with an inductively coupled plasma-optical emission spectrometer (iCAP 7600 ICP-OES Radial) according to the SFS-EN ISO 11885:2009 and SFS-EN ISO 17294-2:2005. The dye concentration is determined via a UV–VIS spectrophotometer at wavelength 618 nm. Phosphate concentration is analyzed according to the SFS-EN ISO 15681-1 (dated 2005) by flow analysis (FIA) and spectrometric detection using tin chloride method. The equipment used for the measurement is FOSAS Tecator, FIAstar 5000 Analyzer & Sampler 5027.
3.4 Batch experiments

3.4.1 Adsorption Studies

Batch experiments are performed to study and optimize the operational parameters e.g., dose, concentration, pH, and co-existing ions, along with the kinetics, isotherm and thermodynamics of adsorption. A known amount of the adsorptive material is added to 50 or 100 mL of properly diluted solutions of the target pollutants using 250 mL Erlenmeyer flask. The samples are prepared in duplicate or triplicate allowing to report an average together with corresponding standard deviations. The pH effect is studied in the range of 3 to 12, adjusted with HCl or NaOH. Solutions with initial concentrations of the target pollutants varying in the ranges of 200-10,000 $\mu$g/L for arsenic, 10-150 mg/L for the dye, and 1-15 mg/L for phosphate are used to study the adsorption isotherm at 15, 25, and 35$^\circ$C. Kinetic studies are conducted with three concentrations of target pollutant at different time intervals. The effect of different co-existing ions e.g., sulfate, chloride, and nitrate, is investigated via adding each co-existing ion to the specific concentration of the target pollutant solutions.

After the desired time of adsorption, the samples are filtered by means of 0.45 $\mu$m filters (Sartorius Minisart) and the pollutant concentration is measured. In the case of arsenic, the samples are diluted and acidified with 2% HNO$_3$ before the concentration measurement. The removal percentage (R%) are calculated using the following equation:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100$$

where $C_0$ and $C_t$ (mg/L or $\mu$g/L) are the initial concentration and the concentration at time $t$ of the pollutant, respectively.

3.4.2 Photocatalytic studies

The UV-assisted batch experiments are carried out using 9-W Phillips and 11W AquaEL Sterilizer UV lamps with a wavelength in the range of 200–280 nm. The experimental set-up includes a 1 L reactor equipped with the light source at the center of the reservoir and a magnetic stirring, while it is protected from any other external light. Under similar experimental conditions to the adsorption experiments, the adsorption kinetics of arsenic and the dye are studied under and without UV exposure. Duplicate samples are collected and are analyzed at several contact time intervals. Sampling is done using a 10-mL syringe intermittently during the experiments. The samples are filtered through 0.45 $\mu$m filters before concentration measurement. A schematic of UV-assisted experimental set-up is provided as supplementary information in the publication I.
4. RESULTS AND DISCUSSION

4.1 Characterization of engineered adsorptive materials

Energy Dispersive Spectroscopy (EDS) is used to explore the composition of the EMs. The presence of metal oxides e.g., TiO$_2$, Al$_2$O$_3$, and SiO$_2$ is detected in the n.TiO$_2$/feldspar/chitosan EMs (see publication I). The results also confirm the presence of Si, O, Al, Na and K in the feldspar samples (see publication II). In the case of two feldspar samples employed for arsenic removal in the publication II, the sample B collected from Italy showed a lower Si/Al ratio compared to the sample A collected from Finland. The XRD measurement also confirms the major constituents of feldspars as SiO$_2$ and Al$_2$O$_3$, the difference in the patterns of feldspars collected from different areas is explained by the fact that feldspars exist as solid solutions between their principal end member compositions e.g., sodium, potassium, or calcium. Figure 8 shows that the XRD pattern of the n.TiO$_2$/feldspar/chitosan EMs indicates combined characteristics of n.TiO$_2$ and feldspar (see publications III and I). The peaks around 27° correspond to the feldspar. The identified mineral phases in feldspar composition include oligoclase (27°), quartz (21°), and calcite (23°). The corresponding peaks to n.TiO$_2$ appear around 25.3°, 37.8°, 48°, 55° and 62.7°. The major phase of TiO$_2$ was anatase. The XRD pattern of n.TiO$_2$/feldspar/chitosan showed changes between 18° and 40° 2θ when compared to that of feldspar, suggesting the intercalation of feldspar. The lower intensities and broadened peaks for the developed EMs confirms some degrees of delamination and disorientation of feldspar.

Figure 8. XRD patterns of the developed EMs and initial materials adopted from publication I.
The FT-IR spectra of the developed EMs are presented in Figure 9. Chitosan is well known for providing a large number of functional groups acting as adsorptive sites for a wide range of pollutants. The FT-IR spectra reveal a broad band around the region 3020–3400 cm\(^{-1}\) attributed to the N–H and O–H stretching vibrations of chitosan. The peak at 1591 cm\(^{-1}\) corresponds to \(–\text{NH}_2\) bending vibrations of chitosan. These functional groups on chitosan structure can serve as coordination and reactive sites for the adsorption of transition metals and organic species [68]. In the case of n.TiO\(_2\)/feldspar/chitosan EMs, the peak at 2882 cm\(^{-1}\) and the band in the region 405–770 cm\(^{-1}\) indicate, respectively, the surface TiO\(_2\)–OH group and the existence of Ti-O and/or the bending vibrations of Si/Al–O bonds. On the spectrum of chitosan-Zn EMs, the peak related to the \(–\text{NH}_2\) bending vibration is shifted to higher frequencies (1660 cm\(^{-1}\)) suggesting the involvement of the \(–\text{NH}_2\) groups of chitosan in forming the chitosan-zinc complexation. The peaks around 450 and 570 cm\(^{-1}\) are related to the stretching vibrations of Zn–O and Zn–N (see publication IV).

![FT-IR spectra](image)

**Figure 9.** FT-IR spectra of the n.TiO\(_2\)/feldspar/chitosan and chitosan-Zn EMs.

Among the main characteristics of adsorptive materials, the surface morphology plays a key role in the determination of surface availability and adsorptive area. Herein, the morphological characteristics of the developed EMs and feldspar are investigated via SEM analysis (see publications I-IV). Figure 10 indicates the differences between the surface morphology of developed EMs and feldspar particles. The EMs developed in publications III and I show highly heterogeneous surface and porous structure with aggregated particles of n.TiO\(_2\) and feldspar. Figure 10 (a and b) confirms the bead-like shape of the developed EMs. The feldspar particles (Figure 10c) show a crystalline and irregular layered structure. Figure 10d displays the surface of chitosan flakes used for preparing the EMs.
RESULTS AND DISCUSSION

Figure 10. SEM images of a) n.TiO2/chitosan/feldspar b) chitosan-Zn, c) feldspar and chitosan.

Figure 11 depicts the results of drift method for pH\textsubscript{PZC} determination. The pH at which a solid immersed in an electrolyte exhibits zero electrical surface charge is called pH\textsubscript{PZC}. For n.TiO2/feldspar/chitosan EMs, the initial pH equals to the final pH around pH 8.1, considered as pH\textsubscript{PZC}, which is reasonable considering the pH\textsubscript{PZC} of feldspar (7) and TiO2 (7.3) and the p\textsubscript{Ka} of chitosan, varying from 6.3 to 7.2 [5]. For the chitosan-Zn EMs, the pH\textsubscript{PZC} is at pH 7.1, which gave the smallest shift of initial to final pH. The pH\textsubscript{PZC} is important in environmental interfaces as it determines how easily an adsorbent can adsorb different ions. At pH values below the pH\textsubscript{PZC}, the system is called to be “below the PZC” (point of zero charge), where the acidic condition donates more protons than hydroxides so the surface is positively charged. At pH values above the pH\textsubscript{PZC}, the system is called to be “above the PZC” and the surface is negatively charged.

Figure 11. Drift-method for pH\textsubscript{PZC} determination adopted from publications II-IV.
4.2 Adsorption

4.2.1 Effect of adsorbent dose

The adsorption results for the optimization of the EMs dosage for the removal of target pollutants is given in Figure 12. An increasing dose increased the removal percentage for all three pollutants, while more than 70% removal is achieved with 1 g/L of dose. The increasing removal with an increasing dose is due to more available surface area for adsorption. For optimizing the dose, the balance between the adsorption equilibrium capacity ($q_e$) and removal percentage is taken into consideration. It was noticed that for all three adsorptive materials, increasing dose decreased the equilibrium capacity (see publications I, III and IV). An increasing dose for a constant concentration of the adsorbate (target pollutant) causes the unsaturation of adsorptive sites with exceeding dose. Furthermore, the gap in the flux or the gradient between the concentration of the pollutant in the liquid and on the solid phases can lead to decreasing amount of molecules adsorbed onto the unit weight of the adsorptive materials. Thus, the dosage is optimized as 1.0 and 0.4 g/L of n.TiO$_2$/feldspar/chitosan EMs for the removal of arsenate and the dye, respectively, and 0.5 g/L chitosan-Zn for the removal of phosphate. The 1.0 g/L of n.TiO$_2$/feldspar/chitosan EMs was also used to study the adsorption of arsenate under lower and more likely occurring concentrations of arsenic in the environment; around 99% removal from 200 μg/L and 97% removal from 400 μg/L arsenate solutions were observed that meet the WHO standard of 10 μg/L.

Figure 12. Effect of adsorbent dosage on the removal of the target pollutants using the developed EMs (Experimental conditions: concentration: 1000 μg/L As, 50 mg/L dye, 5 mg/L phosphate; natural pH).

For arsenate removal by feldspars, different results were noticed: the removal raised with the increasing feldspar dose to a maximum point, after which it dropped. The maximum removal percentages amount to 60 and 55% with 8 and 15 g/L for the feldspar samples B and A, respectively (see publication II). The
decreasing stage in removal is caused by the agglomeration of feldspar particles due to the high dosage, which decreases the available surface area [85].

4.2.2 Effect of solution pH

The solution pH significantly influences the adsorptive removal of different ions as the acidity of the solution affects the ionization of the target ions and the concentration of the counter hydrogen ions covering the surface functional groups. Thus, it is important to optimize the pH towards maximizing the removal of target pollutants by the developed EMs. The adsorption efficiency of the pollutants was strongly dependent on the solution pH. For all the developed EMs, adsorption efficiency decreased with the increasing pH (figures are provided in the publications I-IV). While a major pH effect was observed on the dye removal in publication III, a slighter pH-dependency was noticed for the arsenate uptake by the n.TiO₂/feldspar/chitosan EMs in publication I. Acidic condition favors the protonation of the surface as it is “below the PZC”, so it benefits the removal of the dye and arsenate anions due to the electrostatic attraction. Whereas, under basic conditions, mainly “above the PZC”, the negatively charged surface expands and decreases the adsorption of anions onto the EMs by the electrostatic repelling. The difference in intensity of the pH influence on the removal of these pollutants can be explained by the fact that the adsorption of arsenate onto metal oxide-based materials occurs via inner-sphere surface complexation (publications I), which is not significantly affected by the pH, whereas, the dye removal is mainly based on electrostatic attraction. However, as the electrostatic repulsion increases between arsenate ions and negatively charged surface, the inner-sphere surface complexation and consequently the uptake may drop. For arsenate adsorption onto feldspars (publication II), the highest capacity was observed in pH 3 which agrees with the findings of the EMs and previously reported studies [86]. As showed in publication II (see Fig. 3), feldspar has a buffering effect on the solution e.g., for solutions with initial pH ≥ 4, the final pH shifted to ≥ 8 where mainly HAsO₄²⁻ is the predominant arsenate species which is more resistant to be absorbed on negatively charged surface of feldspar in the basic pH (≥ 8). While, for the solution with initial pH 3, there is only a small pH shift to around 4 where H₂AsO₄⁻ is the predominant arsenate species which is easier to be adsorbed on positively charged surface of feldspar in acidic pH. Further studies can be conducted on using buffering agent to control the rising pH induced by feldspar in the solution. A decreasing phosphate uptake by the chitosan-Zn EMs was noticed by varying the pH from acidic to basic (publication IV). The observed results are related to the change in the distribution of phosphate species (H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻) and the change in surface charge of the EMs. Higher pH values cause a change in the aqueous phosphate species from H₂PO₄⁻ to PO₄³⁻. PO₄³⁻ strongly resists against adsorption by the surface hydroxyl groups [87]. Lower pH protonates the surface of the EMs, leading to higher phosphate removal via electrostatic attraction.
4.2.3 Effect of co-existing ions

Co-existing ions in water can interfere with the adsorption of the target pollutants. For instance, different inorganic ions e.g., sulfate, phosphate, and nitrate, co-exist with arsenic in natural waters that can adversely affect arsenic uptake by metal oxides. These anions can directly compete with arsenic for adsorptive sites or indirectly impact the adsorption by shifting the electrostatic charge on the adsorptive surface [88]. The effect of some common co-existing anions on the removal efficiency of the target pollutants are studied in publications IV, II and I. The presence of chloride, nitrate, and sulfate show negligible impact on the removal of arsenate by feldspar and n.TiO₂/feldspar/chitosan EMs (publications II and I). However, the co-existence of phosphate decreases the removal of arsenate by both adsorptive materials; yet, the lower the phosphate concentration, the lower was the interfering effect on arsenate adsorption. The similar structures and deprotonation constants of aqueous phosphate and arsenate increase the possibility of phosphate interfering effect on arsenic removal. Furthermore, both of these oxyanions are capable of forming inner-sphere complexation. Chloride and nitrate ions form only outer-sphere complexes, thus, not potentially competing for the same adsorptive sites with arsenate. Fluoride showed negligible effect on arsenate removal by the EMs while it decreased the adsorption onto feldspar. These results can be due to the different affinity of fluoride for the adsorption onto the TiO₂-based EMs compared with aluminum silicate (feldspar). With the latter material, it is able to compete with arsenate. Sulfate, which is classified as both outer- and inner-sphere complexation formers, did not show adverse effect on the arsenate removal in both cases. This can be due to the weaker binding affinity of sulfate for the adsorptive sites and the different adsorption mechanism of two species onto the adsorptive materials. The effect of co-existing anions, NO₃⁻, SO₄²⁻ and Cl⁻, on phosphate removal by the developed chitosan-Zn EMs is studied in publication IV. Phosphate uptake by the developed EMs was 7.63 mg/g while this amount decreased to 4.26, 4.79 and 7.15 mg/g in the presence of NO₃⁻, SO₄²⁻ and Cl⁻ ions, respectively. These results are consistent with previous studies on phosphate [69]. The sensitivity of phosphate removal to the presence of background ions e.g., SO₄²⁻ and NO₃⁻, suggests the formation of outer-sphere complexation between phosphate and surface functional groups of the chitosan-based EMs.

4.2.4 Kinetics

The effect of contact time on the adsorption of target pollutants is given in Figure 13. All of the kinetic graphs in Figure 13 show an initial rapid stage followed by a slower stage, which may be indicative of different kinds of complexes forming. In the rapid stage, the surface provides a large number of vacant adsorptive sites for the pollutant so a fast adsorption occurs. The adsorption rate gradually drops as time goes by due to decreasing number of available sites until the equilibrium is reached. The equilibrium is obtained after 120, 180, and 180 min for arsenate, dye, and phosphate removal by the EMs respectively (publications I, III and IV) and after 72 hours for arsenate removal by feldspar (publication II).
RESULTS AND DISCUSSION

Figure 13. Adsorption kinetics of target pollutants onto the EMs and feldspar (Experimental conditions: n.TiO₂/feldspar/chitosan 1 g/L_arsenate and 0.4 g/L_dye, pH 4; feldspar 15 g/L_arsenate, pH 3).

Pseudo-first-order [40], pseudo-second-order [41] and intra-particle diffusion models are used to study the kinetics of adsorption (see publication I-IV). Calculated kinetic parameters are compiled in Table 7. According to the obtained correlation coefficients, the pseudo-second-order model gives the best fit for the experimental kinetic data ($r^2 \geq 0.98$). The model-calculated capacities are also found to be very close to experimental capacity data (figures provided in publication I-IV). Weber and Morris intra-particle diffusion model [42] is used to determine the potential rate-limiting steps involved in the adsorption of target pollutants. Diffusion mechanisms usually involve the boundary layer and intra-particle diffusion rate-controlling stages. The intra-particle diffusion model as seen in Figure 14 attains multi-linear graphs. The sharper initial stage known as boundary layer is related to the diffusion of adsorbate molecules from the solution to the adsorptive surface. In the following slower stage, a gradual pore diffusion takes place until the equilibrium is reached. The values of intercept (higher than zero) suggest the intra-particle diffusion is not the only rate-controlling mechanism and the adsorption may include other mechanisms e.g., film and pore diffusions [89].
Table 7. Kinetics parameters for the adsorption of target pollutants onto the developed EMs.

<table>
<thead>
<tr>
<th>C_{int} (μg/L)</th>
<th>q_{exp} (μg/g)</th>
<th>C_{cal} (μg/g)</th>
<th>k_1 (1/min)</th>
<th>r^2</th>
<th>q_{cal} (μg/g)</th>
<th>k_2 (g min/μg)</th>
<th>r^2</th>
<th>k_{id} (μg/g.min^{1/2})</th>
<th>C (μg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenate_n.TiO2/feldspar/chitosan (publication I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>954</td>
<td>275.89</td>
<td>5.30×10^{-3}</td>
<td>0.61</td>
<td>1000</td>
<td>3.75×10^{-5}</td>
<td>0.99</td>
<td>427.29</td>
<td>13.54</td>
</tr>
<tr>
<td>2800</td>
<td>1640</td>
<td>659.18</td>
<td>10.80×10^{-3}</td>
<td>0.92</td>
<td>1666.67</td>
<td>2.93×10^{-5}</td>
<td>0.99</td>
<td>726.78</td>
<td>31.17</td>
</tr>
<tr>
<td>4800</td>
<td>1600</td>
<td>140.75</td>
<td>10.40×10^{-3}</td>
<td>0.40</td>
<td>1666.67</td>
<td>1.82×10^{-5}</td>
<td>0.99</td>
<td>554.39</td>
<td>37.00</td>
</tr>
<tr>
<td>Arsenate_feldspar (publication II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>7.3</td>
<td>7.90</td>
<td>7×10^{-3}</td>
<td>0.97</td>
<td>8.60</td>
<td>7×10^{-5}</td>
<td>0.98</td>
<td>0.11</td>
<td>0.62</td>
</tr>
<tr>
<td>1000</td>
<td>36</td>
<td>32</td>
<td>0.7×10^{-3}</td>
<td>0.97</td>
<td>42.40</td>
<td>3×10^{-5}</td>
<td>0.98</td>
<td>0.53</td>
<td>3</td>
</tr>
<tr>
<td>5000</td>
<td>107</td>
<td>115</td>
<td>1.2×10^{-3}</td>
<td>0.91</td>
<td>118</td>
<td>2×10^{-5}</td>
<td>0.99</td>
<td>1.30</td>
<td>24</td>
</tr>
<tr>
<td>Dye_n.TiO2/feldspar/chitosan (publication III)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mg/L)</td>
<td>(mg/g)</td>
<td>(mg/g)</td>
<td>(mg/g)</td>
<td>(g min/mg)</td>
<td>(mg/g.min^{1/2})</td>
<td>(mg/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>22.30</td>
<td>29.50</td>
<td>0.04</td>
<td>0.86</td>
<td>27</td>
<td>0.003</td>
<td>0.99</td>
<td>1.80</td>
<td>4.10</td>
</tr>
<tr>
<td>50</td>
<td>44.60</td>
<td>58.90</td>
<td>0.05</td>
<td>0.80</td>
<td>46.30</td>
<td>0.002</td>
<td>0.99</td>
<td>2.70</td>
<td>10.70</td>
</tr>
<tr>
<td>70</td>
<td>62.20</td>
<td>57.50</td>
<td>0.04</td>
<td>0.85</td>
<td>63.30</td>
<td>0.016</td>
<td>0.99</td>
<td>3.00</td>
<td>25.10</td>
</tr>
<tr>
<td>90</td>
<td>68.90</td>
<td>97.70</td>
<td>0.05</td>
<td>0.81</td>
<td>71.40</td>
<td>0.001</td>
<td>0.99</td>
<td>4.60</td>
<td>12.50</td>
</tr>
<tr>
<td>Phosphate_chitosan-Zn (publication IV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.99</td>
<td>0.61</td>
<td>0.003</td>
<td>0.66</td>
<td>2.01</td>
<td>0.03</td>
<td>1.00</td>
<td>0.03</td>
<td>0.88</td>
</tr>
<tr>
<td>5</td>
<td>6.34</td>
<td>2.03</td>
<td>0.033</td>
<td>0.50</td>
<td>5.85</td>
<td>1.48</td>
<td>0.99</td>
<td>0.07</td>
<td>3.54</td>
</tr>
<tr>
<td>10</td>
<td>10.44</td>
<td>4.64</td>
<td>0.002</td>
<td>0.76</td>
<td>10.46</td>
<td>0.004</td>
<td>1.00</td>
<td>0.15</td>
<td>4.31</td>
</tr>
</tbody>
</table>

Figure 14. Intra-particle diffusion plots for the adsorption of target pollutants onto the EMs.

4.2.5 Equilibrium

To explore the adsorption capacity of the developed EMs for the target pollutants, the equilibrium studies are conducted as a function of initial pollutant concentration at several temperatures (publications I-IV). Freundlich isotherm model fitted well to the equilibrium data, which was also confirmed via non-linear regression provided in the related publications if needed (see publication IV and I). This is indicative of the heterogeneous distribution of active sites.
on the surface of the developed EMs. For the adsorption of arsenate and phosphate by the developed TiO$_2$-based and chitosan-based EMs, Sips model [45] was also studied which gave a close fit to the experimental data in both cases (confirmed by non-linear regression provided in publication I and IV). This model combines the basics of Langmuir and Freundlich isotherms and represents systems where an adsorbed molecule can be involved with more than one adsorptive site. Table 8 shows that the constants $K_F$ and $1/n$ are affected by varying temperature. The adsorption of two different pollutants e.g., inorganic arsenate and organic dye, onto the n.TiO$_2$/feldspar/chitosan EMs responds differently to the varying temperature, which can indicate the different thermodynamic nature of their adsorption. The Freundlich adsorption coefficient, $K_F$, characterizes the strength of adsorption: the higher the value of $K_F$, the higher is the achievable adsorption capacity. With an increase in temperature, the increasing $K_F$ values from 147.4 to 187.2 for the adsorption of arsenate suggests an endothermic process, whereas, the decreasing $K_F$ values from 8.93 to 2.92 for the dye adsorption shows an exothermic process. Similarly, the higher $K_F$ value at lower temperature for the adsorption of phosphate on chitosan-Zn EMs indicates an exothermic adsorption. The $1/n$ value indicates the energetic heterogeneity of the adsorptive surface [38]. For all of the adsorption reactions, the values of $1/n$ fall between 0 to 1 indicating a favorable adsorption. These results show that the developed EMs are highly effective in removing organic dyes and inorganic arsenic and phosphate from water; the removal performance reached up to 80%, 98%, and 91%, respectively, for the studied concentrations of the pollutants.

Table 8. Isotherm parameters for the adsorption of the target pollutants onto the developed EMs.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_L$ (μg/g)</td>
<td>$K_L \times 10^{-3}$ (L/μg)</td>
</tr>
<tr>
<td>Arsenate_n.TiO$_2$/feldspar/chitosan (publication I)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2000</td>
<td>6.10</td>
</tr>
<tr>
<td>25</td>
<td>2000</td>
<td>7.90</td>
</tr>
<tr>
<td>35</td>
<td>1666.70</td>
<td>10.00</td>
</tr>
<tr>
<td>Arsenate_feldspar (publication II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>89.21</td>
<td>2.37</td>
</tr>
<tr>
<td>Dye_n.TiO$_2$/feldspar/chitosan (publication III)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mg/g)</td>
<td>(L/mg)</td>
<td>$((mg/g)/(mg/L)^{1/n})$</td>
</tr>
<tr>
<td>25</td>
<td>76.90</td>
<td>0.11</td>
</tr>
<tr>
<td>35</td>
<td>50</td>
<td>0.06</td>
</tr>
<tr>
<td>45</td>
<td>34.50</td>
<td>0.06</td>
</tr>
<tr>
<td>Phosphate_chitosan-Zn (publication IV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>7.37</td>
<td>1.32</td>
</tr>
<tr>
<td>25</td>
<td>5.33</td>
<td>1.85</td>
</tr>
<tr>
<td>30</td>
<td>5.40</td>
<td>1.56</td>
</tr>
</tbody>
</table>
4.2.6 Thermodynamics

Table 9 compiles the thermodynamic parameters calculated for the adsorption of target pollutants. The $K_C$ values show the temperature dependency of the adsorption [90]; these values increase as the temperature increases in the case of arsenic adsorption while the trend reverses for the adsorption of dye and phosphate. An increasing $K_C$ with increasing temperature indicates an endothermic reaction while its decreasing trend signifies an exothermic reaction. These findings are consistent with calculated $\Delta H$ values for all of the adsorption studies. The positive values of $\Delta H$ show an endothermic adsorption of arsenate onto the feldspar and n.TiO$_2$/feldspar/chitosan EMs. The negative $\Delta H$ for the adsorption of dye and phosphate indicates an endothermic adsorption. The change in Gibbs free energy reveals the spontaneous nature of the adsorption reaction; a negatively signed $\Delta G$ indicates a favorable adsorption. The negative values of $\Delta G$ in Table 9 suggest that the adsorption of arsenate occurs spontaneously and more favorable at higher temperatures. In the case of the dye and phosphate, the negative values of $\Delta G$ at lower temperatures indicate that spontaneity of adsorption is favored at lower temperatures. Furthermore, for arsenate adsorption by both feldspar and the EMs, the positive values of $\Delta S$ indicate an increased randomness at the solid-liquid interface during the process. The negative entropy change for the phosphate and dye adsorption can be caused by the immobilization of the adsorbate in the system [38]. A negative value of $\Delta S$ also suggest a fast adsorption process occurring on the adsorptive sites.

Table 9. Thermodynamic parameters for adsorption of target pollutants onto the developed EMs.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$K_C$</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>44.70</td>
<td>-3.30</td>
<td>26.22</td>
<td>123.88</td>
</tr>
<tr>
<td>298</td>
<td>75.19</td>
<td>-3.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>99.48</td>
<td>-3.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>0.64</td>
<td>1.07</td>
<td>50</td>
<td>170</td>
</tr>
<tr>
<td>298</td>
<td>1.60</td>
<td>-0.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>2.47</td>
<td>-2.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>1.15</td>
<td>-0.36</td>
<td>-54.58</td>
<td>-181.80</td>
</tr>
<tr>
<td>308</td>
<td>0.60</td>
<td>1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>0.29</td>
<td>3.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>2.16</td>
<td>-5.30</td>
<td>-37.90</td>
<td>-111.30</td>
</tr>
<tr>
<td>298</td>
<td>1.86</td>
<td>-4.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>1.63</td>
<td>4.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3 UV-assisted adsorption system

Due to the photocatalytic properties of TiO₂, a photocatalysis-adsorption hybrid system is conducted to study the synergistic photoactive-adsorptive performance of n.TiO₂/feldspar/chitosan EMs for arsenic and the dye removal under UV exposure. The performance of n.TiO₂/feldspar/chitosan EMs is tested in several time intervals under and without UV exposure in order to investigate the relationship between each functional performance and the operating time (Figure 15). For both pollutants, UV exposure enhances the removal, which is consistent with previously reported studies [5, 68, 91]. For instance, the maximum removal increased from 59% to 81% and from 53% to 89% for the 2800 µg/L arsenate and 50 mg/L dye, respectively. Engineered materials based on TiO₂ and chitosan have previously been reported with enhanced arsenate and dye removal under UV irradiation [65, 76]. Miller et al. [5, 65] reported the TiO₂ constituent of TiO₂-chitosan photo-catalyst as the main contributor for the photoactive-adsorptive removal of arsenic. Zainal et al. [68] reported around 87% of methyl orange dye removal using TiO₂-chitosan/glass photo-catalyst. The functional groups on chitosan backbone e.g., –NH₂, –OH, and the metal oxide content of the prepared photo-catalyst were suggested as the main functional sites for the synergetic photodegradation-adsorption of the dye.

Figure 16 compares the dye and arsenate removal in the presence and absence of UV exposure by n.TiO₂/feldspar/chitosan EMs. The n.TiO₂/feldspar/chitosan EMs removed higher percentages of the organic dye compared with inorganic arsenic. Figure 16 also displays the difference of arsenate removal by three EMs of n.TiO₂/feldspar/chitosan, n.TiO₂/chitosan, and feldspar/chitosan. In the absence of UV light, n.TiO₂/chitosan (39%) showed a slightly higher arsenate removal compared with n.TiO₂/feldspar/chitosan EMs (32%). While under UV exposure, the removal by n.TiO₂/feldspar/chitosan EMs reached that of n.TiO₂/chitosan (73%). The EMs without TiO₂ showed the lowest removal confirming the key role of TiO₂ for enhanced UV-assisted adsorptive removal (see publication III and I). By adding a third constituent, feldspar, to the combination of n.TiO₂ and chitosan, it is aimed to improve its mechanical properties while reducing the required amount of TiO₂ without affecting its overall removal capacity of the EMs. The benefits of feldspar can be sought in economical aspect as it is cheap and it reduces the amount of n.TiO₂ used in the material. As seen in Figure 16 and reported in publication I, the n.TiO₂/feldspar/chitosan EMs performs as high as TiO₂/chitosan EMs in removing arsenic under both UV and dark conditions while it contains lower amount of TiO₂.
RESULTS AND DISCUSSION

Figure 15. Removal percentage by n.TiO₂/feldspar/chitosan under dark and UV irradiation (dosage: 1 g/L (2800 μg/L arsenate) and 0.4 g/L (50 mg/L dye)); adopted from publications III and I.

Figure 16. Dye and arsenate removal by n.TiO₂/feldspar/chitosan, n.TiO₂/chitosan, feldspar/chitosan under dark and UV systems (Dose: 1 g/L (5 mg/L arsenate) and 0.4 g/L (50 mg/L dye)).
4.4 Removal mechanism

Earlier research [10, 92] introduces TiO₂ as an effective adsorbent and photocatalyst for the removal of arsenic and dyes. TiO₂ provides both a large adsorption capacity for arsenic species, and the oxidation capacity of arsenite to arsenate under UV exposure [5]. It is also reported to successfully remove dyes as it can degrade many aromatic compounds effectively to safer end products e.g., CO₂, H₂O, and mineral acids [68].

TiO₂ can remove arsenic via forming binuclear complexes. UV/TiO₂ system leads to an enhanced removal of both arsenate and arsenite species. One causation of the enhanced performance lies in the lowered pH of the solution under UV-exposed system. UV light can also cause, to some degree, the scission of polymeric chain on the chitosan backbone so that new structural carboxyl groups are formed. As additional functional groups, the new carboxyl groups take part in arsenic oxidation and adsorption and similarly form complexes with the coordinating sites of TiO₂ [65]. Like other TiO₂-based materials, the developed n.TiO₂/feldspar/chitosan EMs is able to oxidize arsenite to arsenate under UV and oxygen exposures. Previous research [80, 92] reports the possible involvement of hydroxyl (OH) and superoxide (O₂⁻) radicals and trapped holes (h⁺) in the photo-oxidation of arsenic under UV/TiO₂-based systems, given in the following reaction equations. The photo-oxidation of As(III) proceeds to As(V) via the intermediate As(IV) state, which is rapidly converted to As(V) by dissolved oxygen once it is produced. UV light (λ < 387 nm) is absorbed by TiO₂ particles resulting in promotion of electrons (e⁻) to the conduction bands and the creation of positively charged holes (h⁺) in the valence band. The free e⁻ and h⁺ are capable of reducing and oxidizing different species (see publication I).

\[
\begin{align*}
TiO_2 & \rightarrow ^h v h^+ + e^- \quad (9) \\
h^+ + OH^- & \rightarrow \cdot OH \quad (10) \\
e^- + O_2 & \rightarrow O_2^• \quad (11) \\
As(III) & \rightarrow As(IV) \rightarrow As(V) \quad (12)
\end{align*}
\]

Likewise, light (wavelength ≤ 390 nm) initiates the photoactive degradation of organic dyes by TiO₂ with promoted e⁻ from the valence band to the conduction band and remained h⁺ in the valence band. The e⁻·h⁺ pairs on the photo-activated TiO₂ interacts with organic species in a similar manner mentioned for arsenic. The h⁺ is strong enough to generate •OH radicals and the e⁻ is able to reduce molecular oxygen. As powerful oxidizing agent •OH radical catalyzes the degradation and eventually causes the total mineralization of the organic substrate [68, 79, 93]. Our proposed photo-oxidation process of the organic dye by the developed EMs is depicted in Figure 17. Similar illustrations of the removal mechanisms for arsenic and phosphate are provided in the publication I and IV.

\[
dye \rightarrow ^{\cdot OH} degradation \ of \ dye \quad (13)
\]
\[ \text{dye} \xrightarrow{h^+} \text{dye}^{+} \xrightarrow{\text{OH} / \text{O}_2} \text{oxidation of dye} \rightarrow \text{degraded and mineralized products} \quad (14) \]

Chitosan provides a low affinity for oxyanions including phosphate mainly because of the pKₐ value of its electron-donor functional sites, viz. –NH₂. To overcome this obstacle, the introduction of metal ions, e.g. zinc(II) and copper(II), to chitosan is recently practiced. Metal ions are capable of forming complexes with the functional groups on the chitosan chain, and consequently the complexed metal ions on the chitosan structure can chelate with other ligands including oxyanions. The mechanism of complexation for chitosan-zinc-phosphate system is thoroughly explained in publication IV.

![Figure 17. Schematic diagram of mechanisms involved in the adsorptive/photoactive removal of the dye by the developed EMs (FS: feldspar and CS: chitosan).](image)

**4.5 Evaluation of engineered adsorptive materials**

The adsorption capacities of target pollutants achieved by (photoactive-) adsorptive materials engineered in our research are compared with those of reported earlier including activated carbons, chitosan derivatives, and titanium dioxide [5, 94, 95], given in Table 10. As seen, the adsorption capacities of our engineered (photoactive-) adsorptive materials are superior or comparable to those of reported for other engineered adsorbents in the literature.
### Table 10. Adsorption of target pollutants on different engineered (photoactive-) adsorptive materials.

<table>
<thead>
<tr>
<th>Engineered adsorbent</th>
<th>Pollutant</th>
<th>C&lt;sub&gt;0&lt;/sub&gt; (mg/L)</th>
<th>q&lt;sub&gt;max&lt;/sub&gt; (mg/g)</th>
<th>Removal (%)</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n.TiO&lt;sub&gt;2&lt;/sub&gt;/chitosan/feldspar Arsenic(V)</td>
<td>1</td>
<td>0.95</td>
<td>94</td>
<td>4</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>n.TiO&lt;sub&gt;2&lt;/sub&gt;/chitosan/feldspar Arsenic(V)</td>
<td>4.8</td>
<td>1.60</td>
<td>33</td>
<td>natural</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>n.TiO&lt;sub&gt;2&lt;/sub&gt;/chitosan/feldspar Arsenic(V)</td>
<td>4.8</td>
<td>3.60</td>
<td>73 (under UV)</td>
<td>natural</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Feldspar Arsenic(V)</td>
<td>1</td>
<td>0.68</td>
<td>54</td>
<td>3</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Arsenic(V)</td>
<td>10</td>
<td>2.05</td>
<td>-</td>
<td>7.7</td>
<td>[5]</td>
<td></td>
</tr>
<tr>
<td>Biochar-AlOOH Arsenic(V)</td>
<td>10</td>
<td>2.99 (under UV)</td>
<td>-</td>
<td>7</td>
<td>[5]</td>
<td></td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/montmorillonite Arsenic(V)</td>
<td>5</td>
<td>4.86</td>
<td>-</td>
<td>-</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/montmorillonite Arsenic(V)</td>
<td>5</td>
<td>5.16 (under UV)</td>
<td>-</td>
<td>-</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td>Granular ferric hydroxide Arsenic(V)</td>
<td>0.1</td>
<td>1.1</td>
<td>-</td>
<td>6.5</td>
<td>[90]</td>
<td></td>
</tr>
<tr>
<td>Modified activated carbon Arsenic(V)</td>
<td>1</td>
<td>-</td>
<td>&gt;80</td>
<td>6</td>
<td>[95]</td>
<td></td>
</tr>
<tr>
<td>n.TiO&lt;sub&gt;2&lt;/sub&gt;/chitosan/feldspar Acid dye</td>
<td>50</td>
<td>72.30</td>
<td>87</td>
<td>natural</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>n.TiO&lt;sub&gt;2&lt;/sub&gt;/chitosan/feldspar Acid dye</td>
<td>50</td>
<td>-</td>
<td>98 (under UV)</td>
<td>natural</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Chitosan Acid dye</td>
<td>50</td>
<td>80.70</td>
<td>97</td>
<td>natural</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Feldspar Acid dye</td>
<td>50</td>
<td>1.21</td>
<td>1.50</td>
<td>natural</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Chitosan/glass Reactive dye</td>
<td>50</td>
<td>71.04</td>
<td>-</td>
<td>6</td>
<td>[76]</td>
<td></td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/chitosan/glass Reactive dye</td>
<td>30</td>
<td>-</td>
<td>67.60</td>
<td>6.8</td>
<td>[76]</td>
<td></td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/chitosan/glass Reactive dye</td>
<td>30</td>
<td>-</td>
<td>99 (under UV)</td>
<td>6.8</td>
<td>[76]</td>
<td></td>
</tr>
<tr>
<td>Chitosan/clay Cationic dye</td>
<td>30</td>
<td>29</td>
<td>-</td>
<td>-</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; Anionic dye</td>
<td>50</td>
<td>-</td>
<td>100 (under UV)</td>
<td>7</td>
<td>[91]</td>
<td></td>
</tr>
<tr>
<td>Biochar-AlOOH Cationic dye</td>
<td>50</td>
<td>8.70</td>
<td>-</td>
<td>-</td>
<td>[70]</td>
<td></td>
</tr>
<tr>
<td>Activated carbon Remazol dye</td>
<td>100</td>
<td>40</td>
<td>-</td>
<td>6</td>
<td>[96]</td>
<td></td>
</tr>
<tr>
<td>Chitosan-Zn Phosphate</td>
<td>5</td>
<td>7.37</td>
<td>-</td>
<td>4</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Chitosan-Zn Phosphate</td>
<td>5</td>
<td>6.30</td>
<td>-</td>
<td>natural</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Chitosan Phosphate</td>
<td>5</td>
<td>1.45</td>
<td>-</td>
<td>natural</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Chitosan Phosphate</td>
<td>5</td>
<td>4.75</td>
<td>-</td>
<td>4</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Modified carbon residue Phosphate</td>
<td>25</td>
<td>3.48</td>
<td>-</td>
<td>6</td>
<td>[33]</td>
<td></td>
</tr>
<tr>
<td>Iron oxide coated sand Phosphate</td>
<td>5-30</td>
<td>1.50</td>
<td>-</td>
<td>5</td>
<td>[97]</td>
<td></td>
</tr>
<tr>
<td>Magnetic illite clay Phosphate</td>
<td>10-100</td>
<td>5.48</td>
<td>-</td>
<td>-</td>
<td>[98]</td>
<td></td>
</tr>
<tr>
<td>Zirconium-chitosan Phosphate</td>
<td>5–50</td>
<td>60.6</td>
<td>4</td>
<td>6</td>
<td>[69]</td>
<td></td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; Phosphate</td>
<td>-</td>
<td>2.63</td>
<td>-</td>
<td>5</td>
<td>[94]</td>
<td></td>
</tr>
<tr>
<td>Biochar-AlOOH Phosphate</td>
<td>50</td>
<td>44</td>
<td>-</td>
<td>-</td>
<td>[70]</td>
<td></td>
</tr>
<tr>
<td>Physically activated carbon residue Phosphate</td>
<td>20</td>
<td>-</td>
<td>~90</td>
<td>6</td>
<td>[99]</td>
<td></td>
</tr>
</tbody>
</table>
5. CONCLUSIONS

The objective of this dissertation was to engineer and characterize new adsorptive materials featuring higher quality characteristics compared with those of the initial materials, viz. feldspars, chitosan, and nano-sized TiO$_2$, and to provide fundamental information on their application for water remediation. Arsenic, an acid dye, and phosphate were the target pollutants to picture the wide applicability of the engineered materials in treating water polluted with different organic and inorganic species. After monitoring the selected initial materials, the adsorptive materials were engineered via a simple fabrication method and characterized using several characterization techniques e.g., SEM, XRD, and FTIR. Adsorption experiments were conducted in a batch mode to study the effect of parameters e.g., pH, dose, and temperature, along with the kinetics, isotherm, thermodynamics, and mechanisms of adsorption. UV-assisted adsorption experiments were carried out to investigate the synergetic photocatalytic-adsorptive removal of arsenic and the dye by the TiO$_2$-based engineered photoactive-adsorptive materials. The research was done based on four research questions exploring several aspects of developing, characterizing and using the engineered materials for the remediation of polluted water, as follows:

RQ 1. What are the characteristics and UV-assisted adsorption performance of the engineered photoactive-adsorptive materials from nano-sized TiO$_2$, chitosan, and feldspar in removing inorganic arsenic from water?

Main findings achieved via researching the first question:

Unlike other TiO$_2$-based remediation techniques, the engineered photoactive-adsorptive materials effectively removed arsenic in a wide range of pH. A selective removal for arsenate in the presence of co-existing ions e.g., fluoride, sulfate, and nitrate, was observed. However, the co-existence of phosphate decreases the removal of arsenate; yet, the lower the phosphate concentration, the lower was the interfering effect on arsenate adsorption. Freundlich and Sips isotherm and pseudo-second-order kinetic models best fitted to the experimental data. Langmuir’s maximum adsorption capacity was determined to be 2000 μg/L. The adsorption system equipped with UV exposure resulted in higher removal of both arsenate and arsenite. Enhanced removal efficiencies from 33% to 73% for arsenate and from 23% to 84% for arsenite were achieved under the exposure of UV light. The adsorption is thermodynamically spontaneous and favorable. The functional groups on chitosan structure including –NH$_2$ and –OH along with the
metal oxide contents of the bio-photocatalyst are identified as the adsorptive-photoactive sites.

RQ 2. How do feldspars perform as low-cost and locally available adsorptive materials for the adsorptive remediation of arsenic-polluted water?

Main findings achieved via researching the second question:

Arsenate adsorption onto feldspars was influenced by the physicochemical properties of the mineral, where Si/Al ratio of the mineral played a major role. The sample with the lower Si/Al ratio showed the highest removal capacity. Electrostatic forces between the terminal aluminol groups of the feldspar samples and predominant form of arsenate in acidic medium were found to be the driving force of the adsorption reaction. Solution pH and temperature significantly influenced the adsorption performance. Higher adsorption capacities were achieved in lower pH and at higher temperature. The adsorption followed pseudo-second-order kinetic and Freundlich isotherm models. The adsorption is endothermic and favorable at higher temperature.

RQ 3. What are the characteristics and UV-assisted adsorption performance of the engineered photoactive-adsorptive materials from nano-sized TiO₂, chitosan, and feldspar in removing organic dyes from water?

Main findings achieved via researching the third question:

The adsorption of the dye by the TiO₂-based engineered material was significantly higher than that of feldspar and slightly lower than that of chitosan. When exposed to UV light, a synergistic adsorption–photocatalysis removal of the dye was observed and the removal efficiency reached that of chitosan. The dye removal percentage was 86% (72 mg/g) without UV exposure, while it reached 97% under UV exposure. The point of zero charge for the engineered adsorptive material was determined to be pH 8.3, and higher removal of the dye was achieved below this pH. The pseudo-second-order kinetic and Freundlich isotherm models best depicted the kinetic and isotherm experimental data. The adsorption is exothermic and spontaneous at lower temperature.

RQ 4. What are the characteristics and adsorption performance of the engineered chitosan-based adsorptive materials in removing phosphate from water?

Main findings achieved via researching the fourth question:

The developed bio-sorbent showed a fast phosphate uptake within the three hours of contact time. The phosphate removal is favored when the surface charge was positive to neutral e.g., within the pH range inferior or around its pH_PZC, 7. Decreasing temperature enhanced the phosphate abatement. As co-existing ions,
CONCLUSIONS

chloride showed minor effect, whereas nitrate and sulfate compete with phosphate for the adsorptive sites. The introduction of zinc ions into chitosan improved the phosphate uptake from 1.45 to 6.55 mg/g. Chitosan provides a low affinity for oxyanions e.g., phosphate mainly due to the pKₐ value of its electron-donor functional sites, e.g. –NH₂. The zinc ions are capable of forming complexes with the functional groups on the chitosan chain, and consequently the complexed zinc ions on the chitosan structure can chelate with other ligands like phosphates oxyanions. The adsorption kinetics is best described with the pseudo-second-order model. The Freundlich isotherm better suits the experimental data. The phosphate–Zn–chitosan reaction is exothermic, favorable and spontaneous.

This dissertation highlights the need of engineered adsorptive materials for water remediation. Our laboratory-scale research indicated the applicability of the engineered (photoactive-) adsorptive materials developed from initial materials, viz. nano-sized TiO₂, chitosan and feldspar, for three target pollutants, arsenic, acid dye, and phosphate. The reasons are several e.g., the benefits of a simple fabrication method, low-cost inorganic and bio-polymeric initial materials, satisfactory removal of a diverse range of pollutants, easy handling and separation from processed water via gravity, and minor sensitivity to interfering effect of co-existing ions. The results of this dissertation can be employed as ground information for subsequent continuous pilot-scale studies as well as similar research in the area of engineering new adsorptive materials featuring specific and higher quality characteristics for targeted applications.

The increasing water shortages and the stringent water quality standards arise the need for alternative remediation techniques. Efforts have been directed towards engineering new adsorptive materials via coupling a wide range of materials e.g., nanoparticles and polymers, to overcome the limitations related to conventional adsorbents like activated carbons. Tailor-made adsorptive materials with desired characteristics e.g., size, composition, and structure, are currently used for treating polluted waters. These engineered adsorptive materials have opened a door of possibilities to enhanced removal of trace inorganic/organic pollutants. Despite the great progress in contaminant remediation by alternative engineered materials, there are still knowledge gaps that need to be filled. Future studies should focus on further improving the adsorption capacity and selectivity of engineered adsorptive materials and estimating the production cost and reuse. As a new type of highly effective adsorbents, their adsorption mechanism of the targeted species should be further elucidated via more experimental evidences and mathematical modeling. Research should continue in order to produce efficient and eco-friendly adsorptive materials and to establish the stability of their adsorption-desorption and mechanical strength along with overall performance characteristics. Furthermore, adsorption modelling, performance predicting, and system/operation optimizing are highly required to set the basis for the system scaling up and to identify the appropriate adsorptive materials for treating various waters of known characteristics and volumes. Almost all these newly engineered adsorbents are still fabricated in the laboratory scale; hence, the production of these high-performance adsorbents in large scale requires further exploration.
REFERENCES

REFERENCES

[40] S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens Handlingar 24 (4) (1898) 1–39.