

CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

FACULTY OF ENVIRONMENTAL SCIENCES

DEPARTMENT OF ENVIRONMENTAL GEOSCIENCES



Czech
University
of Life Sciences
Prague

PERSPECTIVES OF BIOCHAR-BASED
COMPOSITES IN METAL REMOVAL

DIPLOMA THESIS

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2023

DIPLOMA THESIS ASSIGNMENT

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Environmental Geosciences

Thesis title

Perspectives of biochar-based composites in metal removal

Objectives of thesis

The main aim of the diploma thesis will be to study the sorption abilities of biochar-based composites in metal-contaminated aqueous solutions. Firstly, general information about metals in the environment (including remediation techniques) will be mentioned. A significant part of the research will be devoted to metal capture mechanisms and suitable materials. In the experimental part, kinetic and equilibrium adsorption experiments of Zn and Cd at different pH values will be performed. Additionally, the solid-phase analyses using XRD and SEM/EDX will be included to show structural/morphological changes after individual experiments for selected materials. Finally, experiments in soil solutions will be described and evaluated. The results will be processed in detail and then discussed with the literature. The main benefit of the work will be the evaluation of the effectiveness of the studied materials against metals under different conditions and the demonstration of their potential as possible remedial agents.

Methodology

The first part of the diploma thesis will be focused on the general information about contaminants in the environment (with emphasis on metals) and methods of their remediation. Afterwards, specific mechanisms associated with metal capture (e.g., adsorption, precipitation, ion exchange) will be discussed in detail. Afterwards, comprehensive literature research on the suitable materials for metal capture will be provided. The structure of materials and mechanisms of the capture of contaminants on these materials will be described as well. The experimental part will include kinetic and equilibrium adsorption experiments, solid-state analyses and experiments in soil solutions. The obtained results will be discussed in detail with the relevant literature. The thesis will strictly follow the Methodological Guidelines for writing Diploma Thesis at the Faculty of Environmental Sciences.

The proposed extent of the thesis

40

Keywords

nano zerovalent iron, biochar, amorphous manganese oxides, soil, metals, remediation

Recommended information sources

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Expected date of thesis defence

2022/23 SS – FES

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Electronic approval: 24. 3. 2023

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Electronic approval: 27. 3. 2023

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Prague on 28. 03. 2023

Author's statement

I hereby declare that I have independently elaborated the diploma thesis with the topic of: Perspectives of biochar-based composites in metal removal and that I have cited all the information sources that I used in the thesis and that are also listed at the end of the thesis in the list of used information sources. I am aware that my diploma thesis is subject to Act No. 121/2000 Coll., on copyright, on rights related to copyright and on amendment of some acts, as amended by later regulations, particularly the provisions of Section 35(3) of the act on the use of the thesis. I am aware that by submitting the diploma thesis I agree with its publication under Act No. 111/1998 Coll., on universities and on the change and amendments of some acts, as amended, regardless of the result of its defence. With my own signature, I also declare that the electronic version is identical to the printed version and the data stated in the thesis has been processed in relation to the GDPR.

In Prague, 29 March 2023

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Kamran Nazarov

Acknowledgement

I would like to express my gratitude to the Department of Environmental Geosciences and my supervisor Ing. Barbora Böserle Hudcová, Ph.D. to let me participate and involve me in the project. In addition, I'd like to specially thank my supervisor for her insightful comments and suggestions on this thesis. I am also grateful to everyone who has helped me with the editing of this work.

Abstrakt

Diplomová práce se zabývá hodnocením účinnosti kompozitů na bázi biouhlu při odstraňování Cd a Zn z kontaminované vody se specifickým zaměřením na roli aktivní fáze na povrchu biouhlu (BC), konkrétně nulamocné nanoželezo (nZVI) a amorfní oxid manganu (AMO). K dosažení tohoto cíle byly provedeny tři typy experimentů, včetně adsorpční kinetiky, adsorpčních izoterm a kinetiky v půdních roztocích. Na vybraných vzorcích byly rovněž provedeny analýzy na pevné fázi. Studie zjistila, že AMO/BC byl nejúčinnějším materiálem při odstraňování Cd a Zn z kontaminované vody s účinností odstraňování 99,62% a 98,90%. Naopak nZVI/BC byl méně efektivním materiálem s účinností odstraňování 16,89% a 24,5%. Studie také zkoumala vliv pH na účinnost adsorpčního procesu. Bylo zjištěno, že adsorpční účinnost AMO/BC vzrostla z 65% na 82% při pH 6 pro Zn během dvou hodin, zatímco účinnost klesla z 38% na 22% při pH 4. Adsorpční účinnost AMO/BC se zvýšila při kontrolované pH 5 (81% až 94%) a pH 6 (69% až 81%) pro Cd, zatímco účinnost při pH 4 se v průběhu času mírně snižovala ze 47% na 37% a pomalu se vyrovnávala až do konce experimentu. Nejvyšší účinnost byla pozorována při pH 6. Výsledky také ukázaly, že koadsorpce Cd a Zn s AMO/BC byla mnohem účinnější pro Cd než Zn při různých hodnotách pH. Pokud jde o analýzy na pevné fázi, studie zjistila, že aktivní fáze na povrchu biouhlu hrála důležitou roli v procesu adsorpce, kdy přítomnost nZVI a AMO zvýšila počet aktivních míst, což zvýšilo adsorpční kapacitu BC. Studie přispívá k oblasti odstraňování rizikových kovů z kontaminované vody tím, že poskytuje vhled do účinnosti kompozitů na bázi BC při odstraňování Cd a Zn a na roli aktivní fáze na povrchu BC. Výsledky studie mohou sloužit jako podklady pro vývoj nízkonákladových a efektivních technologií odstraňování rizikových kovů z kontaminované vody. Zjištění také zdůrazňují důležitost pH v adsorpčním procesu a mohou být použity jako vodítko pro návrh a optimalizaci adsorpčních systémů pro odstraňování rizikových kovů.

Klíčová slova: Nano nulamocné železo, biouhel, amorfní oxidy manganu, půda, kovy, sanace

Abstract

The diploma thesis deals with the evaluation of the effectiveness of biochar-based composites in removing Cd and Zn from contaminated water, with a specific focus on the role of the active phase on the biochar (BC) surface, namely nano zero-valent iron (nZVI) and amorphous manganese oxides (AMO). Three types of experiments were conducted to achieve this goal, including adsorption kinetics, adsorption isotherms, and kinetics in soil solutions. Solid phase analyses were also carried out on selected samples. The study found that AMO/BC was the most effective material in removing both Cd and Zn from contaminated water, with removal efficiency of 99.62% and 98.90%, respectively. Contrarily, nZVI/BC was less effective material, with removal efficiency of 16.89% and 24.53%, respectively. The study also investigated the effect of pH on the efficiency of the adsorption process. It was found that the adsorption efficiency of AMO/BC increased from 65% to 82% at pH 6 for Zn within two hours, while the efficiency decreased from 38% to 22% at pH 4. The adsorption efficiency of AMO/BC increased at the controlled pH 5 (81% to 94%) and pH 6 (69% to 81%) for Cd, while the efficiency at pH 4 decreased from 47% to 37% slightly over time and slowly equilibrated until the end of the experiment. The highest efficiency was observed at pH 6. The results also showed that co-adsorption of Cd and Zn with AMO/BC was much more efficient for Cd than Zn at different pH values. In terms of solid phase analyses, the study found that the active phase on the BC surface played an important role in the adsorption process, i.e., increased the number of active sites, which enhanced the adsorption capacity of the BC. The study contributes to the area of risk metal removal from contaminated water by providing insight into the effectiveness of BC-based composites in removing Cd and Zn, and the role of the active phase on the BC surface. The results of the study can be used as a basis to the development of low-cost and effective technologies for removing risk metals from contaminated water. The findings also highlight the importance of pH in the adsorption process and can be used to guide the design and optimization of adsorption systems for risk metal removal.

Keywords: Nano zero-valent iron, biochar, amorphous manganese oxide, soil, metals, remediation

Table of Contents

1. Introduction.....	1
2. Objective of Thesis	3
3. Literature Review.....	4
3.1. Contaminants in the Environment.....	4
3.2. Remediation Methods	5
3.2.1. Physical Removal	5
3.2.2. Chemical stabilization	5
3.2.3. Phytoremediation.....	5
3.3. Metals in the Environment	6
3.3.1. General Introduction to Metal Contamination.....	6
3.3.2. Mobility of Metals in the Environment	6
3.3.3. Zinc	8
3.3.4. Cadmium.....	9
3.4. Principle of Selected Metal Capture Mechanisms	10
3.4.1. Adsorption	10
3.4.1.1. Type of Adsorption.....	10
3.4.2. Ion Exchange	12
3.5. Study of metal capture processes	13
3.5.1. Principle of Kinetic Experiments.....	13
3.5.1.1. Adsorption Kinetics Model.....	14
3.5.2. Principle of equilibrium experiments	15
3.5.2.1. Langmuir Isotherm Model.....	16
3.5.2.2. Freundlich Isotherm Model.....	17
3.5.2.3. Sips Isotherm Model.....	17
3.6. Materials usable for metal capture.	17
3.6.1. Biochar (BC).....	17
3.6.2. Nano Zero-Valent Iron (nZVI)	19
3.6.3. Amorphous Manganese Oxide (AMO)	20

3.7. Study of the Structure and Morphology of Solid Materials	21
3.7.1. X-Ray Diffraction	21
3.7.2. Electron Microscopy	23
3.7.2.1. Scanning Electron Microscopy (SEM).....	23
3.7.2.2. Transmission Electron Microscope (TEM).....	25
4. Experimental Part.....	26
4.1. Methodology	26
4.1.1. Used Chemicals and Materials	26
4.1.2. Kinetic Experiments	26
4.1.3. Equilibrium Experiments.....	27
4.1.4. Removal Efficiency in Soil Solutions	27
4.1.5. Solid-State Analyses.....	28
4.2. Results	28
4.2.2. Equilibrium Experiments.....	36
4.2.3. Solid-State Analyses.....	39
4.2.4. Removal Efficiency in Soil Solutions	44
4.3. Discussion	50
4.3.1. Adsorption Kinetics	50
4.3.2. Adsorption Isotherms	51
4.3.3. Solid-State Analyses.....	52
4.3.4. Soil Solutions.....	53
5. Conclusion	55
6. Bibliography and Sources	56

1. Introduction

The presence of hazardous metals in the environment has been a major concern in recent years, and several risk metals and metalloids can have adverse effects on air, water, and soil environments. While soil pollution is the primary focus of this study, it is important to note that soil plays a crucial role in the ecosystem and human survival (Kabata-Pendias, 2011).

Remediation of contaminated soil is a critical aspect of environmental protection and restoration. There are three primary strategies for removing risk elements from contaminated soil, which are physical removal, chemical stabilization, and biological methods. Physical removal involves complete extraction of contaminated soil from the site, while chemical stabilization relies on the application of reagents or solid materials that react with the metal to reduce its mobility and availability (Lambert, 2000; Yao et al., 2012). Phytoremediation is a biological method that utilizes plants to absorb, transform, and demolish contaminants in the soil. It involves phytodegradation and phytostabilization, which immobilize contaminants directly or prepare the contaminated area before further decontamination (Soudek et al., 2008).

The study discusses two transition metals, Zn and Cd. Zn, an important micronutrient for organisms, is commonly used for galvanization, alloys, motor equipment, building materials, pharmaceuticals, medical devices, cosmetics, manufacture of paint pigments, and various electronic applications (Arcasoy, 2002). Cadmium, on the other hand, is commonly found in zinc ores and has various applications in electroplating, production of easily melted alloys, paints, inks, plastics, ceramics, and batteries, among others. However, it is also considered a hazardous waste product in the metal plating industry (Zheng et al., 2007).

Biochar (BC), nano-iron (nZVI), and amorphous manganese oxide (AMO) are three types of sorbent materials that have been extensively studied for soil remediation. Biochar is a porous substance prepared by pyrolysis of various types of biomass or waste materials, which has the potential to be used as a source of energy, a soil amendment additive, and in waste management (Yaashikaa et al., 2020). On the other hand, nZVI is a highly reactive material that is effective in removing both organic and inorganic contaminants. It

is commonly used for the remediation of multi-contaminated locations due to its high reactivity and small particle size. When combined with biochar, nZVI can provide a greater number of active adsorption sites for both organic pollutants and risk metals (Chen et al., 2022). In addition, AMO have shown high sorption efficiencies for metals such as Cu, Cd, Zn, or Pb, but their usage can have drawbacks such as Mn leaching, production of secondary products during preparation, and high expenses (Ouředníček et al., 2019). One solution to these disadvantages is the combination of AMO with BC to prepare a composite material or optimizing synthesis conditions. The use of Mn oxides in biochar functionalization has become an area of interest due to its abundance, ease of processing, and environmental friendliness. Co-modifying biochar with Mn has shown improvements in metal elimination, particularly in the case of Cd (Shaheen et al., 2022).

An adequate analysis of the solid-state also plays an essential role in studies of potential adsorbents. X-ray diffraction (XRD) has found increasing use in a wide range of applications over the past few decades. In addition to its established use in areas such as corrosion studies, forensic research, and geological applications, XRD has also been utilized in the study of BC, nanoscale zero-valent iron/biochar (nZVI/BC), and amorphous manganese oxide/biochar (AMO/BC) composites (Bunaciu et al., 2015). XRD can identify changes in crystal structure and phase composition, which can provide valuable information on the effectiveness of these materials in removing risk metals from water and soil. It can also help investigate the influence of BC properties on metal ion removal efficiency (Bunaciu et al., 2015). Furthermore, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are powerful imaging techniques used in a wide range of industries and scientific fields. In environmental remediation applications, these techniques have been also used to investigate the adsorption mechanisms of risk metals by solid materials such as BC-based composites (Ford et al., 2022). By visualizing the surface morphology and structure of these materials before and after metal adsorption, as well as the distribution of metal ions on the surface, SEM and TEM can provide insights into the efficacy of adsorbent materials and help optimize their design for efficient metal removal (Sun et al., 2020).

2. Objective of Thesis

The main objective of the diploma thesis is to investigate the metal sorption capacities of biochar-based composites in aqueous solutions polluted with metals. To begin, generic information regarding toxins in the environment is provided (types of contaminants, remediation strategies). A major part of the study is devoted to metals, their capture methods, and, lastly, suitable metal capture materials. The experimental section includes kinetic and equilibrium adsorption studies using Zn and Cd. Furthermore, solid-state investigations using XRD and SEM/EDX are given to demonstrate structural/morphological changes following the experiments. Finally, soil solution experiments are described and evaluated in detail. The findings are thoroughly examined and analyzed in relation to the literature.

3. Literature Review

3.1. Contaminants in the Environment

Concentrations of hazardous metals in the environment have aroused considerable attention in recent decades (Takáč et al, 2009). Risk metals and metalloids such as As, Cd, Cr, Cu, Ni, Pb, and Zn can have an impact on the air (in PM10 and PM2.5 particles), water, and land/soil environment (Luo et al, 2022). However, this study will focus more on the soil pollution. Therefore, deeper attention will not be paid to other spheres. Soil is not only part of the ecosystem, but also plays a crucial role for human survival. Soil has very important and complex functions such as nutrient cycling, C storage and turnover, water maintenance, buffering, and the transformation of potentially dangerous elements and compounds. However, any imbalance has a negative effect on the basic properties and functions of the soil (Kabata-Pendias, 2011).

Metals and metalloids are one of the riskiest types of contaminants due to their extensive distribution, toxicity and their possible bioaccumulation in the food chain (Takáč et al., 2009). As a result, such risk elements are accumulated in the soils, where they are able to persist for a long time. Compared to organic contaminants, hazardous metals and metalloids are not subject to degradation and therefore their removal from the soil is very difficult (Bolan et al., 2014; Gil-Díaz et al., 2014).

It is also important to realize that some metals and metalloids are in fact necessary nutrients for organisms (e.g., B, Cu, Se, Zn). In some soils, nutrients may be deficient and selected elements are therefore added in a targeted manner. However, a problem may arise if the concentration of the element exceeds certain limit and this element becomes toxic. Negative effects are usually manifested when the balance is disturbed and the inability of the soil to retain these substances together with the ability of organisms in the ecosystem to cope with an excess of the element (Oliveira et al., 2017; Lombi et al., 2005).

As has been mentioned metals and metalloids, are not biodegradable, i.e., can accumulate in the environment and are subsequently involved in the food chain. Some of these elements are carcinogenic, mutagenic, teratogenic, endocrine disruptors or can cause neurological behavioral changes. There are many physical and chemical methods to remove these risk elements from the soil environment, however, some of them are accompanied by problems such as high financial costs, changes in soil properties,

disturbance of the natural microflora or excessive demands and therefore such methods are essentially unusable in practical application (Ali et al., 2013).

3.2. Remediation Methods

In general, there are 3 basic remediation strategies to remove risk metals from the soil. These are the physical removal of contaminated material from the site of contamination (ex situ methods), chemical stabilization of metals in the soil on site (in situ methods), and biological method, especially the use of plants to stop the spread of contamination or to extract metals from soils (Lambert et al., 2000; Yao et al., 2012; Bolan et al., 2014).

3.2.1. Physical Removal

The advantage of this method is the complete removal of pollution from the environment, however, the contaminants are only moved to another place where they must be secured, monitored or further processed. The disadvantage of this approach is the risk of spreading pollution during handling with land and especially the high financial costs associated with soil extraction, transport, and subsequent processing (Lambert et al., 2000; Yao et al., 2012).

3.2.2. Chemical stabilization

The method of chemical stabilization is based on the application of reagents/solid materials that act as effective sorbents or precipitating agents reducing the mobility and subsequent availability of risk metals in the soil. It is basically a reaction of a reagent/material surface with a metal reducing the toxic effects of the metal. This is due to immobilizing processes such as: adsorption, precipitation, ion exchange or formation of stable complexes with organic ligands (Lambert et al., 2000; Bolan et al., 2014).

3.2.3. Phytoremediation

During this process, the plant absorbs the contaminants itself, transforms them and demolishes them. A process in which a contaminant is reduced due to the release of enzymatic substances by the plant into the soil is also called phytodegradation. It is used mainly for the breakdown of organic pollutants. However, it needs to be considered that the enzymatic conversion of organic substances into metabolites can be much more dangerous in terms of toxicity than pollutant itself (Soudek et al., 2008).

Another method is phytostabilization, which can be used to directly immobilize contaminants and/or at least secure/prepare the contaminated area before further decontamination. Phytostabilization can be achieved, for example, by planting some fast-

growing woody plants whose roots system draws a considerable amount of water (Kučerová et al., 1999). The main advantage of phytostabilization is the reduction of the mobility of risk elements without the need to remove the soil. Compared to other methods, phytostabilization is the least expensive, but it can have a side effect which may prevent plants from growing if the contaminant concentrations increase to a high level (Pierzynski et al., 2002).

3.3. Metals in the Environment

3.3.1. General Introduction to Metal Contamination

Risk metals may accumulate in soils as a result of emissions from rapidly growing industrial areas, mine residues, high metal waste, the disposal of lead gasoline and paints, the application of fertilizers, coal burning residues, petrochemical and atmospheric runoff deposits (Raymond et al., 2011). Most risk metals, such as Cu and Zn, are micronutrients that are important for the optimal development and function of living organisms. Other metals, such as Cd, Hg and Pb, are detrimental to human health and environmental balance, especially in the aquatic environment (Kouali et al, 2020).

The ecotoxicity of metals in the soil environment is determined by their bioavailability. The most available part of metals in the soil is defined as the easily leachable and cation exchangeable fraction. Chemical extraction can be used to assess the percentage of soil available metal fraction that can be subsequently absorbed by plants or soil organisms. The bioavailability of metals is not necessarily the same for all metals and is also often unpredictable. It is largely controlled by a variety of physicochemical and biological factors, such as soil reactions, content of organic and clay minerals, oxygen status or biological activity (Kapusta et al., 2015).

3.3.2. Mobility of Metals in the Environment

Metal mobility is controlled by many chemical processes, including adsorption, desorption, oxidation-reduction, and precipitation-dissolution (Ma et al., 2020). Adsorption occurs when a molecule or ion, termed as adsorbate, in a gaseous or liquid bulk state adheres to the surface of a solid, or in rare cases, a liquid, called an adsorbent. It is a surface process, which means that just the surface of the adsorbent is involved, and the adsorbate does not permeate into the structure of the adsorbent. Desorption is the reverse process of the adsorption by which a molecule drops from a solid surface (Artioli, 2008). Redox reactions are chemical processes in which electrons are transferred between

two molecular species. The two species involved might be organic or inorganic, and they can exist in any phase of the ecosystem (gas, liquid, or solid). Precipitation is the removal of a substance from the solution. It is the total opposite of solvation or dissolution. The solute particles separate from each other and are surrounded by solvent molecules during dissolution. Contrarily, precipitation occurs when solute particles collide and form a solid compound (Brusseau et al., 2019). Many physico-chemical parameters, such as pH, Eh (redox potential) and/or coexisting chemical components, have an impact on the behavior of the elements in contaminated soils (Park et al., 2018). Changes in pH, Eh and ionic strength control the interactions between metal atoms, mineral dissolution, or precipitation reactions. The solubility, mobility, and bioavailability of metals in soil is influenced by four main factors: 1) change in pH, 2) change in redox conditions, 3) structure of organic complexes, and 4) change in salinity (Förstner et al., 1986). The change in pH and the change of redox potential affects the ion-exchangeable, carbonate and Fe-Mn (oxo)-hydroxide fractions of the sediment. In addition to the above, the presence of chemical species also plays a role in metal mobility, for example, in anoxic conditions, metals form complexes with organic material and especially chalcophile elements (Pb, Cu, Zn, Hg, Cd, Bi and Ag) tend to precipitate as their sulfidic forms (Luoma, 1990).

The main factors affecting the leaching of risk metals are the type of bond with the soil particles and its strength (individual soil particles can provide different binding sites with different strength) the size of soil particles, the pH values, the temperature, and the redox potential. The pH value of the environment is considered as an important parameter that affects the leachability of risk metals. Changes in pH value can result both an increase or decrease in the concentration of leached compounds depending on the type of metal. The pH value also affects the solubility of risk metal complexes, notably those in the form of oxides, hydroxides, carbonates, or mineral forms (Król et al., 2020). Risk metals linked with solid residue, such as Zn, As, Cd, and Pb, can infiltrate the surrounding soils and water bodies by leaching. As a result of the oxidation of metal sulfides and the breakdown of minerals, leachates from abandoned mine sites are frequently acidic and loaded with mine-related metallic elements (Kim et al., 2018).

3.3.3. Zinc

Zinc is an element in group II B of the transition elements in the periodic table. Zinc has an atomic number of 30 and an atomic weight of 65.39. Zinc was first isolated in 1746 by the chemist S. Margraaf by heating of coal and calamine. Due to the tendency of zinc to lose two electrons, it forms salts with varying solubility in aqueous solutions as a divalent cation. Zinc forms relatively stable coordinate bonds with electronegative ligands such as nitrogen, sulfur, and oxygen. Zinc forms zincates such as $[\text{Zn}(\text{OH})_4]^{-2}$ in aqueous alkaline medium. The solubility of individual zinc compounds differs from each other. For example, the solubility of zinc chloride (ZnCl_2) in water at 25°C is 432g/100mL, and contrarily, the solubility of zinc oxide (ZnO) at 29°C is 0.00016 g/100mL (Walsh et al., 1994). Zinc is never found in the free state in nature. It is found as ZnO in the mineral zincite, as zinc silicate (Zn_2SiO_4) in hemimorphite, as zinc carbonate (ZnCO_3) in the smithsonite mineral, as mixed ZnO and Fe_2O_3 (iron oxide) in the fraclinite mineral, and/or as zinc sulfide (ZnS) in the sphalerite mineral (Özçelik, 2012).

The most important application of zinc is galvanization. Zinc coating is mostly applied to steel materials and increases the resistance and life of the material galvanized with zinc against corrosion. Other uses of zinc include various alloys (especially brass), motor equipment, electrical appliances, building materials, pharmaceuticals, medical devices, cosmetics, manufacture of paint pigments, medicine as an antiseptic ointment, applications involving electroluminescence, photoconductivity, and other electronic applications (Arcasoy, 2002).

Zinc, which is included in the group of micro minerals, is present in all organs, tissues, and body fluids of organisms. Zinc plays a key role in enzyme catalysis by binding to the active sites of enzymes as well as entering the structure of proteins in living organisms. Zinc is also an intracellular regulator, providing structural support for proteins in molecular interactions. It maintains the stability and integrity of biological membranes and ion channels and acts as a structural element in nucleic acid or other gene regulatory protein. Due to the lack of redox activity, it makes the protein, to which it is attached, stable. It also has roles in carbohydrate, protein, lipid, nucleic acid, gene expression, reproduction, and embryogenesis (Arcasoy, 2002).

In general, zinc is an important element that also serves as a plant nutrient, although it is hazardous in high concentrations. Since it is absorbed so quickly by plants, it can be very

phytotoxic. Zinc toxicity causes growth suppression as a general phenomenon. It is affected by pH, which regulates the concentration of zinc in solution. Excessive zinc concentrations can be hazardous to plants. The most common signs are shoot stunting, curling and rolling of immature leaves, death of leaf tips, and chlorosis (Rout et al., 2003). Zn in cereal grain can be also hazardous to humans even at low amounts. Excessive Zn deposition in soil may boost crop absorption, resulting in an unexpectedly high Zn content in grain that exceeds the permissible intake limit (Arcasoy, 2002).

3.3.4. Cadmium

Cadmium is in Group II B in the periodic table, along with zinc and mercury. Cd is a silvery-white shiny metal, which can be easily cut with a sharp tool. It has a low melting point of 320.9 °C and a boiling point of 765 °C. Cd is stable in dry air, oxidizes slowly in moist air and reacts with water vapor forming cadmium oxide and hydrogen. It is insoluble in water, reacts rapidly with dilute HNO₃ and slowly with hot HCl. Some of the properties are similar to zinc, however, it is insoluble in bases which is a difference (Siegel, 2002).

Cadmium is commonly found in zinc ores, for example, sphalerite contains cadmium sulfide in solid solution. Although some zinc blend concentrates contain as much as 1% cadmium, the amount of cadmium generally varies from very little to 0.5%. However, richer cadmium deposits are also reported in some parts of the world. Cadmium is obtained in the form of steam during the refining of zinc sulfate, the superheating of sludge zinc ore. The most well-known cadmium mineral is Grinocite (CdS), which is a sulfide commonly found covered with a yellow layer of sphalerite (Adriano, 2001).

The most common use is in the field of electroplating. It is used as deoxidizer in nickel plating, in light solder and aluminum solders, in the production of easily melted alloys, in engraving processes, cadmium vapor lamps, paint, ink, and widely used in plastics, power transfer wires, basic colorants used in ceramics, photoelectric cells, ultraviolet solar radiation photometer and Ni-Cd batteries. Cadmium is also used in dentistry, it is used as a powdered amalgam (1Cd:4Hg). Among Cd applications, metal plating industry is the most important source of Cd-waste (Adriano, 2001).

Cd is one of the most toxic risk metals. Cadmium tends to accumulate in the tissues of plants and in some organs of animals such as kidneys and livers. Cadmium effects have been observed on adrenal glands, anemia, tissue destruction in the ovaries of females and

males, and reduced hemoglobin levels. Besides, cadmium disrupts the mechanism that repairs bones because it settles in the spaces inside the bones, making it difficult for the skeleton to support the body (Zheng et al., 2007).

3.4. Principle of Selected Metal Capture Mechanisms

3.4.1. Adsorption

Adsorption involves the process of forming a thin film on the surface of the adsorbent (i.e., solid material on which surface adsorption occurs) by the adsorbable ions, atoms or molecules (called adsorptive) reaching the surface of the adsorbent and being captured by physical or chemical forces. The adsorptive can be a gas, liquid, or dissolved phase (Dawood et al., 2014). Adsorption is a surface phenomenon that is widely used for the removal of organic and inorganic pollutants from aqueous (including soil) solutions. When a solution containing an adsorbable species comes into contact with a solid with a highly porous surface structure, a liquid-solid intermolecular attraction force occurs and some of the solute molecules from the solution accumulate on the solid surface (Rashed, 2013). Adsorption can provide effective results in removing metal contaminants, especially if they cannot be removed by conventional remediation methods. For this purpose, inorganic-based materials (e.g., Fe/Mn oxides and hydroxides, clays, zeolites, calcite, and/or apatite), commercial activated carbons, agricultural residues, microorganisms, pyrolyzed biomass (i.e., biochar), some industrial by-products and wastes (e.g., sludge), can be used as adsorbents (Tiwari et al., 2017).

3.4.1.1. Types of Adsorptions

The capture of the contaminant by adsorption depends on a number of factors. One of them is selectivity of the adsorbent to the contaminant, which should be adsorbed. Based on this selectivity and the corresponding type of bonds, adsorption can be divided into two main types, physical and chemical.

1) Physical Adsorption

Physical adsorption is characterized by low heat of adsorption and equilibrium is established very easily. In other words, physical adsorption is based on intermolecular van der Waals interactions involving continuous dipole, forced dipole and quadrupole interactions, rather than the formation of chemical bonds. For this reason, physical adsorption is also called "van der Waals adsorption". Physical adsorption is reversible and

can occur as both localized and non-localized. Moreover, in physical adsorption, the adsorptive must not overcome a potential energy barrier to be adsorbed on the adsorbent surface. Therefore, physical adsorption occurs spontaneously. However, this spontaneous process can be, on the other hand, influenced by desorption. Equilibrium time is defined as the state when adsorption and desorption are in equilibrium. For each adsorbed substance, it is therefore possible to talk about an adsorption equilibrium state, which is similar to the equilibrium between evaporation and condensation in the environment in the case of physical adsorption. Physical adsorption gains importance in the transfer of components in mixtures from one phase to another, in determining the surface area, pore size and their distribution, and in heterogeneous catalyzed reactions. In this type of adsorption, the adsorbed layer can be more than one molecule thick. Since the physical adsorption takes place very fast, the speed of the overall process is controlled by the transfer rate of the molecules to the surface, i.e., diffusion (Tchobanoglous et al., 2003).

2) Chemical adsorption.

Chemical adsorption is the adsorption that occurs with the transfer of electrons between the adsorbent and the adsorbed i.e., chemical bonds are formed between them. The activation energy released at this time is 10-50 kcal/mol. Chemical adsorption is specific and occurs by stronger forces than physical adsorption. Generally, new bonds are formed at normal temperatures. This type of adsorption also takes place at very high temperatures. For example, at temperatures above about 200°C, the activation energy is large enough to break chemical bonds or make new bonds. Chemical adsorption is also called “activated adsorption” (Karakaya, 2008).

Chemical adsorption is known as an exothermic process. However, when a molecule dissociates and the dissociation energy of the molecule is greater than the formation energy of the bonds on the surface, the process can be endothermic. In chemical adsorption, the activation energy is at the level of the heat of chemical reaction. The adsorbed layer is monomolecular thick. Chemical adsorption rate is lower than physical adsorption. Because chemical adsorption processes are characterized by a certain activation energy, so the reaction develops rapidly only at temperatures above a certain minimum temperature. Chemical adsorption also takes place at temperatures above the

boiling point of the substance or even its critical temperature (Tchobanoglous et al., 2003). Adsorption types are compared in Table 1.

Table 1. Comparison of adsorption types (Lin et al., 2009; Grassi et al., 2012).

Variable	Physical adsorption	Chemical adsorption
Specificity	↓	↑
Adsorption heat	↓	↑
Activation energy level	↓	Inactive: ↓ Active: ↑
Superficial Covering	Multi-layered	Single-layered
Reversibility	↑	↓
Advantages	Fast non-specific adsorption suitable for determining basic parameters (e.g., surface size, pore distribution, etc.) or reversible removal of contaminants.	Specific adsorption, in which strong bonds are formed with the surface, and is therefore suitable for more permanent capture of contaminants.

3.4.2. Ion Exchange

Ion exchange is a process based on the principle of replacing an ion in solution with another ion in the material. Ion exchangers are solid substances that take ions from the solution and give an equivalent number of other ions to the solution. The ability to exchange ions depends on the structural properties of the material. Ion exchangers consist of an extremely positively or negatively charged matrix. These overloads are located in specific regions or functional groups in the solid structure. The overload of the matrix is balanced by ions called counter ions. When the ion exchange liquid comes into contact with excess, the solvent passes into the ion exchanger and causes swelling. The ability to exchange ions is called ion exchange capacity (EC) and can be both cation (CEC) or anion (AES) (Jorgensen et al., 2003).

The most common application of the ion exchange method is water softening, in which calcium and magnesium in hard water are replaced by sodium. Ion exchange can be applied to water and wastewater for removal of ionized ammonia, risk metals and total dissolved solids. At the same time, deionized water can be produced by using anionic and cationic resins together. Synthetic resins with high ion exchange capacity are widely used

in water and wastewater treatment. Other known cation exchangers, also used for metal removal, are zeolites (Jorgensen et al., 2003).

In a principle, ion exchange and adsorption are similar processes, because the most intense mechanism in both processes is mass transfer from the liquid phase to the solid phase. Therefore, ion exchange also belongs to a group of sorption processes. Due to the process principle, ion exchange is categorized as a method of physical adsorption. An important feature of physical adsorption is that it is very fast, and as a result, the overall rate of reaction is controlled by the mass transfer coefficient rather than the surface sorption kinetics. Therefore, the physical sorption can be called “a diffusion-controlled process” (Jorgensen et al., 2003).

3.5. Study of metal capture processes

To understand the course of adsorption processes, it is necessary to further evaluate the obtained data using various approaches. One possibility is to perform and subsequently model kinetic or equilibrium adsorption experimental data. There is a whole range of models for the subsequent description of the data.

3.5.1. Principle of Kinetic Experiments

The consideration of kinetics gives an understanding of the adsorption process. The rate of adsorption and the residence time of the solute on the surface of the adsorbent is critical to assessing whether the removal process is complete or not. These time-dependent factors are very important to consider when developing a new treatment technology to remove various contaminants from the environment. In principle, the components being extracted from the solvent (i.e., those that should be adsorbed) must have access to the surface of the adsorbent. It has a sufficiently large surface area and/or well-developed porous structure (i.e., a large amount of internal volume in the structure of the adsorbent) as the adsorption processes is heavily influenced by surface area, particularly internal surface area, pore size distribution, and the form of the pores (Gupta et al., 2011).

Adsorption kinetics is the study of removal process rates in order to determine the factors that govern them. The research involves a close monitoring of the experimental settings that affect the rate of a surface reaction and, as a result, help to achieve the equilibrium in an acceptable time. These investigations provide a first insight into the adsorption process. The speed of these interactions can be described by the development of appropriate mathematical models. Once the reaction rates and dependent parameters are clearly

understood for the given material and contaminant, the material can be considered for use and production in a larger (commercial) scale, but further studies are needed to better understand the complicated dynamics of the adsorption process (Gupta et al., 2011)

3.5.1.1. Adsorption Kinetics Model

The most commonly used models to describe adsorption kinetics are pseudo-first-order (PFO), pseudo-second-order (PSO) and Weber and Morris intraparticle diffusion models (IPD) (Umeh et al., 2021). In general, the main goal of these models is to describe the course of adsorption, with respect to its rate. The main output is therefore the value of the rate constants of adsorption (PFO, PSO) or diffusion (IPD). However, in general, these types of models are not suitable for a detailed description of the adsorption mechanism. Normally, the dependence of the adsorbed amount on time is plotted and further modeled by appropriate models (Simonin, 2016).

Pseudo-first-order model

The Lagergren rate equation is used to describe PFO kinetics. The adsorption process rate determines the difference between the amount of adsorbed adsorbate molecules on adsorbents at equilibrium adsorption time and a predetermined time in this model.

$$q_t = q_e(1 - e^{-kt})$$

q_e and q_t (mg/g) - the amount of solute adsorbed per unit mass at equilibrium and at time t , respectively;

k (min^{-1}) - the pseudo-first-order adsorption rate constant.

Pseudo-second-order model

The pseudo-second-order model assumes that the limiting step rate, compared to pseudo-first-order model, is the surface adsorption, especially the chemisorption (i.e., formation of bonds with the surface).

$$q_t = \frac{kq_e^2t}{1 + kq_e t}$$

q_e and q_t (mg/g) - the amount of solute adsorbed per unit mass at equilibrium and at time t , respectively;

k (g/mg min) - the pseudo-second-order adsorption rate constant.

Intra-particle diffusion model

Compared to PFO and PSO, the intra-particle diffusion model, developed by Weber and Morris, is used to calculate the speed of molecule diffusion, which is provided by the equation below (Umeh et al., 2021):

$$q_t = K_{id}t^{\frac{1}{2}} + I$$

q_t (mg/g) - the amount of solute adsorbed per unit mass at time t ;

k_{id} (mg/g min^{1/2}) - the intra-particle diffusion constant.

I - intercept.

3.5.2. Principle of equilibrium experiments

An adsorption isotherm describes the retention of a substance from the aqueous media to a solid phase at a constant temperature and pH. Over time, three fundamental approaches have been used to create a wide range of equilibrium isotherm models. Firstly, the kinetic aspect needs to be considered. In this respect, achieving adsorption equilibrium, which is defined as a state of dynamic equilibrium in which the rates of adsorption and desorption are equal, plays role. The second approach, which is based on thermodynamics, can give a framework for deriving different adsorption isotherms models, but the third approach, which is based on potential theory, generally conveys the key notion in the development of characteristic curve. However, an intriguing tendency in isotherm modeling is the derivation of the model parameters using more than one approach, resulting in differences in the physical interpretation of the model parameters. Normally, the dependence of the adsorbed amount on the concentration in the solution is plotted and further modeled by appropriate models (Foo et al., 2010).

3.5.2.1. Langmuir Isotherm Model

The Langmuir adsorption isotherm, which was first created to explain gas-solid-phase adsorption onto activated carbon, has been used to compare and evaluate the performance of various (bio)sorbents. This empirical model assumes single-layer adsorption (the adsorbed layer is one molecule thick), while adsorption occurs only in a finite (constant) number of identical and equivalent localized centers, without lateral interactions and steric barriers between adsorbed molecules. It is graphically represented by a plateau, which is

an equilibrium saturation point where no additional adsorption can occur after a molecule has occupied a site (Foo et al., 2010).

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}$$

q_e – amount of adsorbate in the adsorbent at equilibrium (mg/g);

Q_0 - maximum monolayer coverage capacities (mg/g);

b - Langmuir isotherm constant (L/mg);

C_e - equilibrium concentration (mg/L).

Moreover, Webber and Chakkravorti established a dimensionless constant known as separation factor (R_L) that may be expressed as:

$$R_L = \frac{1}{1 + K_L C_o}$$

where the Langmuir constant is given by K_L (L/mg), and the adsorbate initial concentration is denoted by C_o (mg/L). A lower R_L value indicates that adsorption is more favorable. In further detail, the R_L value denotes whether the adsorption is unfavorable ($R_L > 1$), linear ($R_L=1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Foo et al., 2010).

3.5.2.2. Freundlich Isotherm Model

Freundlich isotherm is the first known relationship explaining non-ideal and reversible adsorption that is not limited to the formation of monolayer. This empirical model may be applied to multilayer adsorption with non-uniform adsorption heat and affinity distribution throughout the heterogeneous surface. The Freundlich isotherm is now frequently used to describe adsorption processes in heterogeneous systems, particularly in organic compounds and highly interacting species on activated carbon and molecular sieves (Foo et al., 2010).

$$q_e = K_F C_e^{\frac{1}{n}}$$

q_e – amount of adsorbate in the adsorbent at equilibrium (mg/g);

C_e - equilibrium concentration (mg/L);

n - adsorption intensity;

K_F - Freundlich isotherm constant related to adsorption capacity (mg/g) (dm³/g)ⁿ.

3.5.2.3. Sips Isotherm Model

Sips isotherm is a hybrid form of Langmuir and Freundlich expressions developed for predicting heterogeneous adsorption systems and overcoming the limitations of Freundlich isotherm model, i.e., the limitation connected to increasing adsorbate concentration. It reduces to the Freundlich isotherm at low adsorbate concentrations, whereas at high concentrations, it predicts a monolayer adsorption capacity similar to the Langmuir isotherm. The operating circumstances, such as changes in pH, temperature, and concentration, are, in general, the primary determinants of equation parameters (Foo et al., 2010).

$$q_e = \frac{K_S C_e^\beta S}{1 + a_S C_e^\beta S}$$

q_e – amount of adsorbate in the adsorbent at equilibrium (mg/g);

K_S - Sips isotherm model constant (L/g);

C_e - equilibrium concentration (mg/L);

β_s - Sips isotherm model exponent;

a_s - Sips isotherm model constant (L/mg).

3.6. Materials usable for metal capture.

3.6.1. Biochar (BC)

Biochar is a type of sorbent material prepared by pyrolysis of various types of biomass or waste materials. Crop residues from forestry, agriculture, and municipal solid trash, as well as food waste and animal manures, are examples of biomass waste products which are suitable for the manufacture of biochar. Biochar is inexpensive, affordable, and easy to make, compared to many other remediation agents (Yaashikaa et al., 2020).

In general, biochar has the potential to be used as a source of energy (biofuel), a soil amendment additive, and in waste management. Biochar is a carbon-neutral energy source, as are its combustible by-products. Currently, researchers are considering the use

of biochar as a soil supplement to improve soil quality and carbon sequestration. Biochar might be effective in storing carbon dioxide and preventing climate change if it were resistant against decomposition in soil conditions. However, it is still unknown how long biochar can remain in the soil before it decomposes and releases carbon dioxide into the atmosphere. The use of biochar in waste management is perhaps the most urgent and promising application (Liu et al., 2021).

Biochar has been shown in several studies to considerably reduce the availability of risk metals, such as Cd, Pb, Sb, Zn, and Ni, etc., in contaminated soil (Liu et al., 2021). Biochar is used to fix risk metals in soil by both physical and chemical adsorption, with the goal of changing the mobile chemical forms of risk metals in contaminated soil and inhibiting their activity and bioavailability. Because conventional biochars have certain limitations in terms of adsorption capacity, especially in adsorption of anionic species, more studies are focusing on modification of biochar in order to change its surface features to increase its adsorption capacity for risk metals (Tang et al., 2021). For example, a high affinity of BC for Cd in soils has been recently published. Biochar may efficiently immobilize Cd by electrostatic or binding adsorption, cation exchange, and surface complexation due to its numerous functional groups, large surface area, and porosity. Moreover, the high ash component, the amount of base cations, and carbonate concentrations resulted in an alkaline BC, which may accelerate Cd precipitation processes while decreasing its bioavailability and mobility. The affinity of biochar for Cd in soils can vary considerably due to variable environmental properties, such as soil characteristics and climatic conditions (Zuo et al., 2022).

As already mentioned, synthesis of composite materials with nZVI and Mn oxides is also possible to increase adsorption properties of BCs. For example, nZVI has recently emerged as a potential material for risk metal passivation due to its huge specific surface area and good reducing capacity. In addition to Fe-based material, Mn oxides have been also shown to have very high immobilization potential for metal(loid)s via adsorption processes onto amphoteric surface groups of the Mn oxide due to the oxidation/reduction process, subsequent sorption, surface complexation, and/or co-precipitation with hydrous manganese oxide (Trakal et al., 2018).

3.6.2. Nano Zero-Valent Iron (nZVI)

Iron-based synthetic materials have been the most studied materials in recent decades, not only because of their high efficiency and abundance, but also because of their relative non-toxicity, low cost, and environmentally friendliness. In general, iron can be used in different oxidation states, size of particles and species. Currently, zero-valent iron (ZVI) and nanoscale ZVI (nZVI) have recently be the subject for soil remediation studies, mainly due to its small size (less than 100 nm) and a high reactivity predisposing this material to promising results in this field. In general, ZVI and nZVI can be used for both organic and inorganic contaminants. For better performance in removing organic pollutants, nZVI has been supported by several source materials for increased stability, reactivity, and dispersion. For example, nZVI is used with granular activated carbon to remove trichloroethylene (TCE), thermally reduced graphene oxide is used to remove nitro compounds, and organobentonite is used to remove pentachlorophenol (PCP) (Ahmad et al., 2021).

To improve properties of nZVI (e.g., to prevent particle agglomeration), the combination of nZVI with biochar has become a promising option, because it may result in a significantly higher number of active adsorption sites for both for organic pollutants and risk metals. However, application of this composite material may possess a potential risk due to a strong reactivity of nZVI itself, which may facilitate mobility of some contaminants and thus raise environmental risk (Zhou et al., 2021). The synergetic impact of BC implanted with nZVI was reported to reduce more labile Zn in the soil. The possibility is that BC has electron-donating and electrical conductivity properties, which might accelerate nZVI corrosion. As a result, nZVI/BC is a promising material for multi-contaminated locations (Xiang, 2022). As compared to raw BC, nZVI/BC composites had a greater Cd removal effectiveness in wastewater. Moreover, nZVI/BC is less hazardous to the bacterial population in sediment, but it increases the variety and richness of the bacterial community after the treatment. As a result, the use of nZVI/BC for in situ sediment cleanup is also ecologically beneficial. Therefore, more research into the in-situ immobilization of Cd-polluted sediments using nZVI/BC is both promising and practicable (Liu, 2021).

3.6.3. Amorphous Manganese Oxide (AMO)

In the last few decades, Mn oxides have been used for water or soil treatment. In general, Mn oxides occur naturally as sediments and fine-grained aggregates in the soil and affect metal(loid) mobility even at low concentrations. Furthermore, Mn oxides are very often more powerful than Fe oxides in stabilizing some metal(loid)s, since the prevalent stabilization process is the development of inner-sphere complexes, which results in strong bonds between the metal(loid)s and the Mn oxide surface (Ouředníček et al., 2019). Poorly crystalline Mn oxides or amorphous Mn oxides (AMOs) are particularly effective as metal(loid)s stabilizing additives in water and soil. The synthesized AMOs showed significant sorption efficiencies for several metals from water and soil, including Cu, Cd, Zn or Pb, throughout a wide pH range. However, the usage of AMOs, on the other hand, can have several drawbacks (Ouředníček et al., 2019):

1. Mn leaching (particularly under reducing conditions and/or at lower pH values), which may cause a secondary pollution of water and soil.
2. Due to the inadequate KMnO_4 to sugar molar ratio, the reactions during preparation of the material might produce considerable quantities of secondary products (e.g., Mn oxalates) or unreacted molecules (e.g., glucose).
3. The final AMO product results in additional expenses, which can make it difficult to prepare AMO on a large-scale.

The above-mentioned disadvantages can be solved, for example, by combining AMO with BC to prepare a composite material and/or optimize synthesis conditions (Ouředníček et al., 2019). In general, the use of Mn oxides (MnO_x) in biochar functionalization has received a lot of interest, namely due to its natural abundance, easy processing, and environmental friendliness. In addition to metal stabilization, MnO_x is especially attractive due to its affinity for a variety of PTEs, high specific capacity, and structural adaptability. Additionally, MnO_x modified materials have a high oxidation potential and a great capacity to immobilize not only metal cations, but also metal(loid) anions (Shaheen et al., 2022

). It was observed that Mn co-modified BC had improved Cd adsorption and stability in soil. According to recent studies, co-modifying BC with Mn improves Cd elimination

(Tan, 2022). Among the several ways available, BC modification with potassium permanganate (KMnO_4) or manganese oxides (MnO_x) is a promising one due to its high sorption capacity, ease of processing, and environmental friendliness. The high oxidizing capacity of KMnO_4 allows for the formation of additional oxygen-containing functional groups on the BC surface and the immobilization of Cd through complexation. The direct pyrolysis of manganese (Mn)-hyperaccumulating plants yield a new MnO_x -loaded biochar. The creation of persistent double-edge sharing complexes and double corners between Cd and endogenous MnO_x contributes not only to a low Mn leaching rate but also to significantly decreased Cd desorption (Chen, 2022).

3.7. Study of the Structure and Morphology of Solid Materials

Solid-state analysis is crucial before and after the adsorption process to evaluate the stability of materials and any possible changes related to capture, such as precipitation. Before adsorption, solid-state analysis can help identify optimal material prerequisites for adsorption and ensure that the material is stable and suitable for the intended application. After adsorption, solid-state analysis can provide important information on the effectiveness of the adsorption process and any changes that may have occurred due to the capture of target molecules. This information can be crucial for evaluating the performance and lifespan of the material, as well as for developing and improving future adsorption processes. In addition, solid-state analysis can help researchers understand the fundamental mechanisms involved in the adsorption process and guide the design of more efficient and effective adsorbent materials (Sohrabi et al., 2013).

3.7.1. X-Ray Diffraction

One of the most powerful nondestructive techniques for characterizing crystalline materials is the X-ray diffraction (XRD). It can provide data about phases, structures, texture (preferred crystal orientations) and structural parameters for example crystal defects, average grain size, and crystallinity. Nowadays, X-ray diffraction is a widely used method for examining crystal structures and atomic distances. The concentration of X-rays is accomplished by using a cathode ray tube, a filter that produces monochromatic radiation, a collimator that concentrates it, and a direct beam that passes towards the sample. The three fundamental components of an X-ray diffractometer are an X-ray tube, a sample holder, and an X-ray detector (Figure 1.). According to Bragg's law, when

incident rays interact with the sample and create constructive interference (a diffracted ray), an interference pattern is formed (Bunaciu et al., 2015):

$$n\lambda = 2d\sin\theta$$

n - integer,

λ - wavelength of the X-rays,

d - the interplanar spacing generating the diffraction,

θ is the diffraction angle.

This law establishes a connection between the lattice spacing and diffraction angle in a crystalline sample and the wavelength of electromagnetic radiation (Bunaciu et al., 2015).

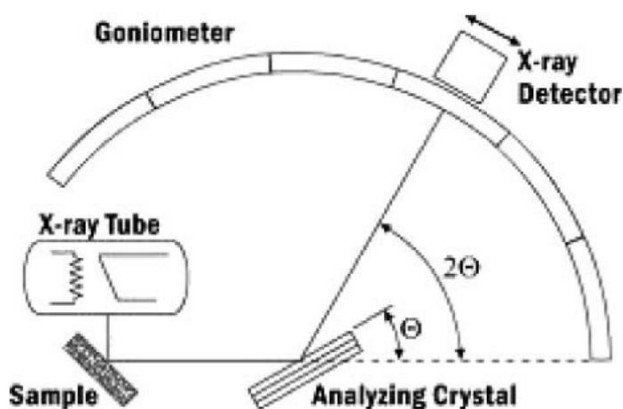


Figure 1. Figure 1. Schematic diagram of a diffractometer system (Bunaciu Andrei A et al., 2015).

Over the past five years, X-ray diffraction has been used in corrosion studies, forensic research, geological applications, medicines, microelectronics, and glass manufacture. XRD can also be used to identify the crystal structure and phase composition of BC, nZVI/BC and AMO/BC before and after exposure to metal ions. For example, changes in the XRD patterns of BC can indicate the formation of metal oxides or hydroxides as a result of adsorption (Xu et al., 2022, Abeysinghe et al., 2022, Hong et al., 2022). XRD patterns can reveal the formation of metal oxides on the surface of nZVI particles as a result of their corrosion (Xu et al., 2022). In the case of AMO/BC, the successful synthesis of novel materials was confirmed by XRD (Ouředníček et al., 2019)

3.7.2. Electron Microscopy

Electron microscopy (EM) is a method for acquiring excessive resolution images of organic and non-organic specimens. The utilization of electrons which have extremely short wavelengths as the source of illuminating light, contributes to the high resolution of EM images. Transmission electron microscopes (TEM) and scanning electron microscopes (SEM) are the two primary types of electron microscopes (Sun et al., 2020).

3.7.2.1. Scanning Electron Microscopy (SEM)

SEM is one of the most used techniques for capturing and visualizing the microstructure and morphology of the materials. SEM equipment consists of the following parts: electron gun, electron beam, anode, magnetic lens, backscattered electron detector, secondary electron detector, specimen, stage. SEM scans a sample with the use of electron beams. These beams are fired by an electron gun, and they rapidly go down the scanning electron microscope's column. The electron beams are focused as they move through a series of lenses and apertures during this process. As it takes place in a vacuum, no molecules or atoms that are already in the microscope column may interact with the electron beam. This guarantees excellent image quality. The sample is scanned by electron beams in a raster pattern, which involves moving over its surface in lines from side to side and top to bottom. Atoms on the sample's surface engage in interaction with the electrons. As a result of this contact, the sample-specific secondary electrons, backscattered electrons, and ray signals are produced. These signals are detected by the microscope's detectors, which produce the high-resolution pictures that are seen on the computer screen (Figure 2.) (Sun et al., 2020).

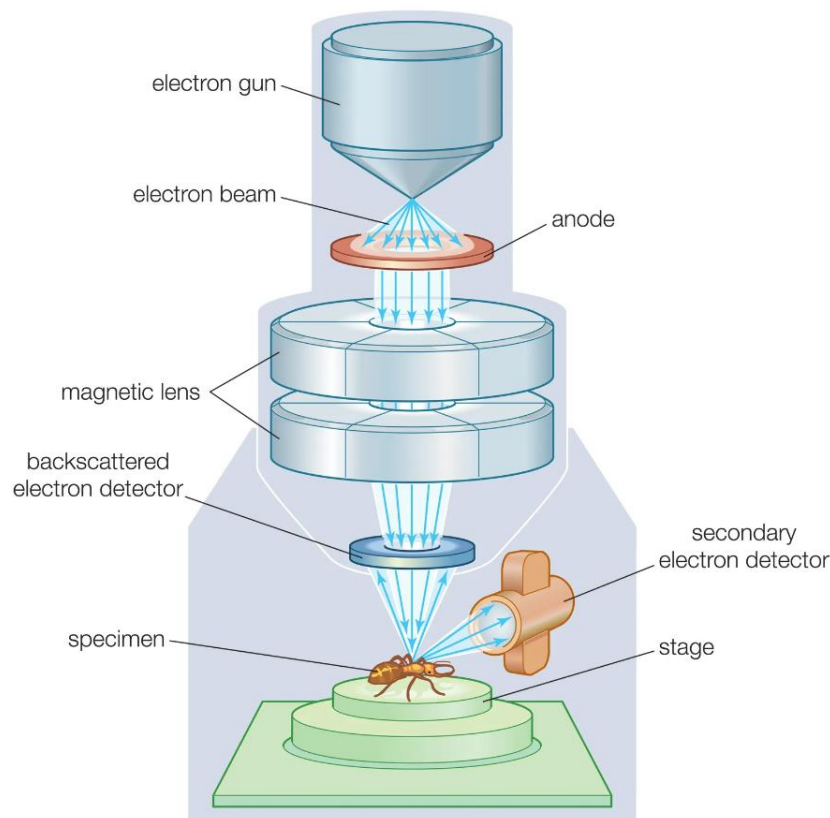


Figure 2. Scanning electron microscopes (SEM) (*Encyclopedia Britannica*, 2019).

SEM is used in several industries or sectors such as biological sciences, geological sampling, electronics, medical sciences etc. SEM can be used to visualize the surface morphology and structure of the adsorbent materials before and after metal adsorption, as well as the distribution of metal ions on the surface of the materials. SEM images can reveal changes in the surface morphology of biochar or the formation of metal oxides or hydroxides on the surface of nZVI/BC or AMO/BC composites after exposure to metal ions (Xu et al., 2022, Ouředníček et al., 2019). By using SEM to study the adsorption of risk metals such as Cd and Zn, insights can be gained into the mechanisms of metal removal and optimize the design of adsorbent materials for environmental remediation applications (Sun et al., 2020).

3.7.2.2. Transmission Electron Microscope (TEM)

TEM is one of the most frequently used structural analysis tools to date, playing a vital role in the study of materials, physics, chemistry, and biology. There are three fundamental systems comprise TEM – 1) an electron cannon that generates the electron beam and a condenser system that concentrates the beam on the target; 2) the system that

creates images, made up of the objective lens, moveable specimen stage, intermediate lens, and projector lens, focuses the electrons traveling through the specimen to create an accurate enlarged picture; 3) the image-recording device, which transforms the electron picture into a form that can be seen by the human eye. TEMs are used in sectors including cancer research, virology, materials science, pollution research, nanotechnology, semiconductor research, as well as in other disciplines like paleontology and palynology (Figure 3.) (Ford et al., 2022).

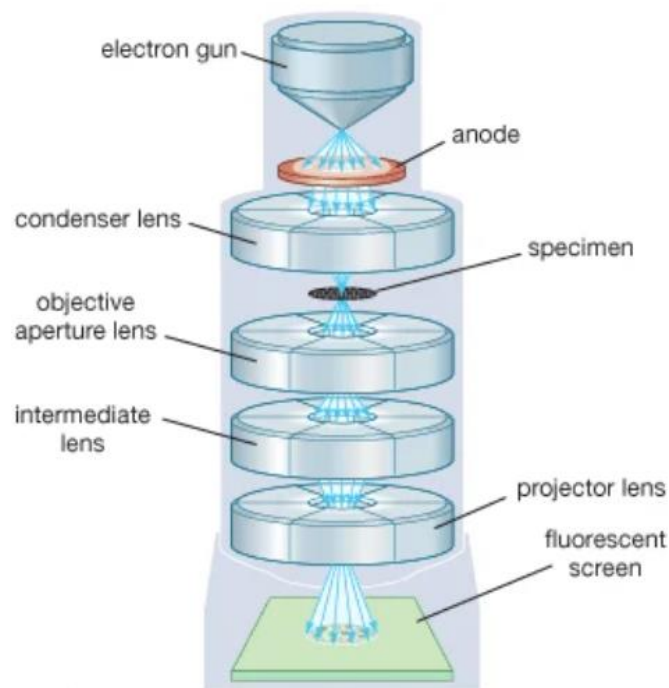


Figure 3. Transmission electron microscopes (SEM) (*Encyclopedia Britannica*, 2019).

The study by Bian et al. (2014) used TEM to investigate the adsorption of Cd by magnetic BC composites. The TEM images showed that the Cd ions were adsorbed onto the surface of magnetic biochar, and the presence of amino groups in the composite played a crucial role in the Cd adsorption process. Similarly, in a study conducted by Li et al. (2020), TEM was used to investigate the removal mechanism of Cd by nZVI/BC. The TEM images showed that Cd ions were captured by nZVI particles and precipitated as CdS. These studies demonstrate the usefulness of TEM in understanding the mechanisms of heavy metal removal by solid materials.

4. Experimental Part

4.1. Methodology

4.1.1. Used Chemicals and Materials

All of the chemical reagents utilized in this experiment were of analytical quality and were used without any purification or treatment. Deionized water (18.2 M Ω) was used in the preparation of all solutions. The pH for adsorption experiments was adjusted with analytical grade HNO₃ and NaOH (0.001, 0.01, 0.1 M). Three materials were used as adsorbents in the experimental part of this diploma thesis, namely wood biochar (BC) purchased from NANO IRON Ltd., nano zero-valent iron/biochar composite (nZVI/BC) purchased from NANO IRON Ltd. containing 40% nZVI and 60% BC, and amorphous manganese oxide/biochar composite (AMO/BC) synthesized according to Ouředníček et al. (2019) in the laboratories of KGEV (FŽP, ČZU) containing 40% nZVI and 60% BC. Preparation and/or synthesis of materials was not part of this thesis. All these materials were used to study the capture of Zn and Cd methods of adsorption kinetics, adsorption isotherms and kinetics in soils solutions.

To prepare the solution for adsorption experiments, zinc nitrate hexahydrate (Zn(NO₃)₂ x 6H₂O) and cadmium nitrate tetrahydrate (Cd(NO₃)₂ x 4H₂O) were weighed on analytical scales and then transferred to a volumetric flask using a funnel and a wash bottle with demineralized water. The volumetric flask was filled to the mark with demineralized water, the lid was wiped with pulp and mixed until everything has been dissolved. During all adsorption experiments, the pH values were monitored using an inoLab pH meter (pH 7310, WTW, Germany) equipped with a pH electrode (SenTix 41, WTW, Germany). Before every measurement, the pH meter was appropriately calibrated using three buffer solutions at pH values 4.00, 7.00 and 10.00.

4.1.2. Kinetic Experiments

The prepared Zn or Cd solution was transferred to a 0.5 L volumetric flask, 40 mL was removed back to the stock solution using pipette, resulting volume was 0.46 L. This solution was transferred to a 600 mL beaker, placed on a stirrer and inserted a magnetic stirring bar, calibrated pH probe was inserted, and the solution was started to mix on 750 rpm. Steady pH values have been recorded. To get the background value, 10 mL was collected in to the first tube. Another 10 mL was taken with the pipette and with this

collected solution the solid material (BC or nZVI/BC or AMO/BC; 0.45 g) was carefully transferred to the beaker. The resulting solid/liquid ratio was 1 g/L. To start the experiment, stopwatch was turned on. In the case of experiments with pH adjustment, it was necessary to reach a given value in the first minute of the experiment (using 0.01 – 1 M HNO₃). The sampling was provided at given time intervals (1 min, 3 min, 5 min, 10 min, 15 min, 20 min, 30 min, 60 min, 90 min, 120 min). At each interval, 10 mL of the solution was sampled using a pipette to transfer the solution to a syringe (with a 0.45 µm filter). The solution was filtered into the test tube and the tube was carefully closed. The pH value was monitored during the experiment at each time interval. At the end of the experiment, the whole solution was filtered using a hand-held vacuum pump (0.45 µm filter) and then the solid phase was placed in a petri dish. Lastly, the samples were prepared for the ICP/OES measurement and dilution was done if necessary. The selected data were modeled using the nonlinear form of PFO and PSO in Origin 9.0.

4.1.3. Equilibrium Experiments

In the case of equilibrium adsorption experiments, solutions of Zn and Cd were prepared in the 0.5-150 mg/L concentration range. Around 25 mL (the final amount exactly corresponded to the weight of the adsorbent to maintain a solid/liquid ratio of 1 g/L) of the given solution was added to the 100 mL beakers. All beakers were placed on an orbital shaker and the pH was adjusted at 6 (controlled throughout the experiment). At the end of the experiment (i.e., after 2 hours), 10 mL of the solution was sampled using a pipette to transfer the solution to a syringe (with a 0.45 µm filter). The solution was filtered into the test tube and the tube was closed. The selected solutions were also filtered using a hand-held vacuum pump (0.45 µm filter) and then the solid phase was placed in a petri dish. Lastly, the samples were prepared for the ICP/OES measurement (10-30 times of dilution was done if necessary). The selected data were modeled using the nonlinear form of Langmuir and Freundlich model in Origin 9.0.

4.1.4. Removal Efficiency in Soil Solutions

In order to obtain a soil solution, metal-contaminated soil from the alluvium of the Litavka River (soil L) and the forest plot near the smelter in Příbram (soil S) was extracted. The detailed characteristics of these soils were not determined within the diploma thesis, only the extractability of elements in water, as stated below, which signals the most soluble fraction, i.e., the riskiest. The soil was shaken for 72 hours on vertical shaker (200 rpm)

at solid/liquid ratio of 1:5 (soil L) and 1:10 (soil S). Samples were centrifuged for 20 min (6000 rpm). Once it has been done, hand-held vacuum pump (0.45 μm filter) was used to filter the solution, which would then be used for kinetic experiments. This experiment has been done without the pH control for up to 7 days. The sampling was provided after 1 day and 7 days. The pH value was recorded at each time interval. After the experiment, samples were prepared for the ICP-OES (cations) and IC (anions).

4.1.5. Solid-State Analyses

The structure and identification of the solid materials before and after adsorption was determined by the X-ray diffractometry (XRD; D2 PHASER XE-T, Bruker) in the range of 5-70° 2 θ . The step size was 0.04° 2 θ and the counting time was 2 s per step. The XRD measurements were carried out by a technical worker in KGEV laboratories (FŽP, ČZU). The morphology and chemical composition were studied by scanning electron microscopy (SEM; TESCAN VEGA 3 XMU) coupled with energy dispersive X-ray spectroscopy (EDX; QUANTAX 200). The SEM-EDX analysis was carried out at the Institute of Geology of the Academy of Sciences of the Czech Republic, v.v.i.

4.2. Results

The goal of the experimental part of the diploma thesis was to evaluate the effect of BC-based composites in the removal of Cd and Zn, especially the role of the active phase on the BC surface, i.e., nZVI or AMO. To this end, three types of experiments were performed as mentioned above, i.e., changes in adsorption efficiency over time with and without pH control (adsorption kinetics), equilibrium adsorption experiments in order to determine the maximum adsorption capacity (adsorption isotherms) and effectiveness in real metal-contaminated solutions (kinetics in soil solutions). Selected solid samples were further tested using solid phase analyses.

4.2.1. Kinetic Experiments

Removal efficiency without pH adjustment

According to the kinetic experiments without the pH control, it was found that AMO/BC (99.62%) was the most effective for Cd adsorption compared to BC (4.28%) and nZVI/BC (16.89%). Moreover, it was also evident that a very fast equilibrium was established in the case of AMO/BC, already in the first minutes of the experiment. Of the tested materials, BC itself was the least effective. With regard to the pH values, the final values (i.e., after 120 min) were 6.99 for BC, 7.37 for nZVI/BC, and 7.33 for AMO/BC. It is

therefore evident that the smallest increase in pH values occurred when pure BC was applied (Figure 4.).

In terms of the same experiment with Zn, almost identical results were obtained, i.e., AMO/BC (98.90%) was the most effective in Zn adsorption compared to BC (5%) and nZVI/BC (24.53%). The establishment of equilibrium was also similar to the kinetic experiments with Cd. The final pH values were only slightly different (lower or higher) compared to Cd, resulting in 7.18 for BC, 6.72 for nZVI/BC, , and 8.49 for AMO/BC (Figure 5.).

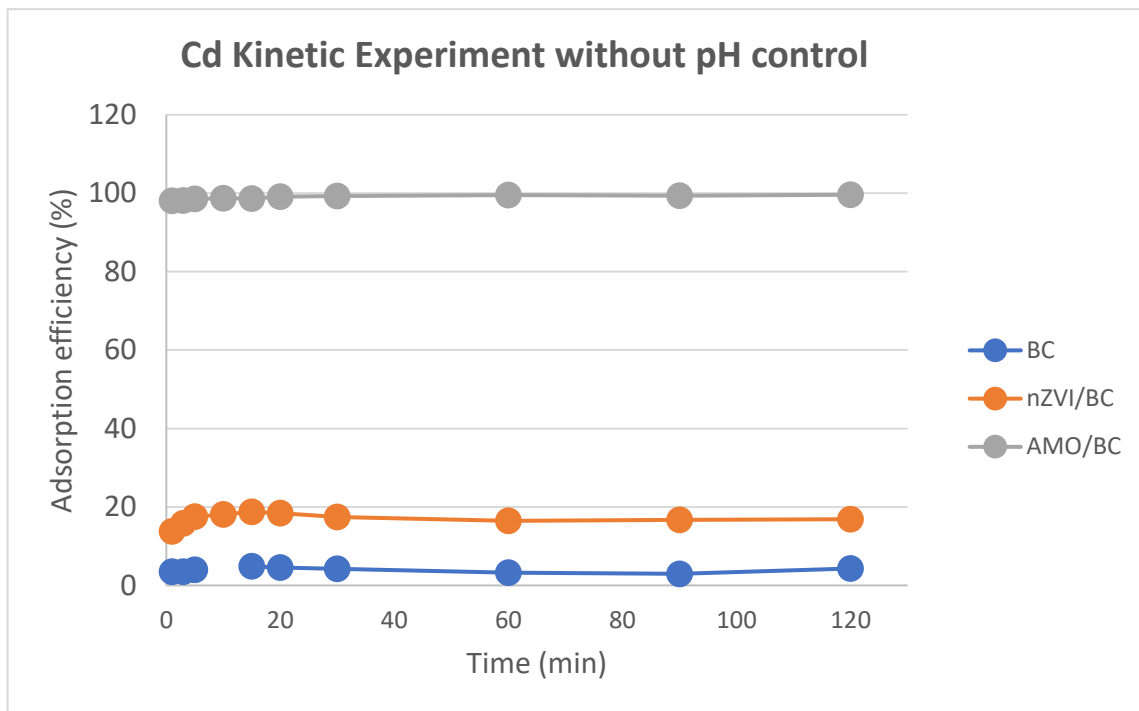


Figure 4. Kinetic experiment of Cd using BC, nZVI/BC, and AMO/BC without pH control.

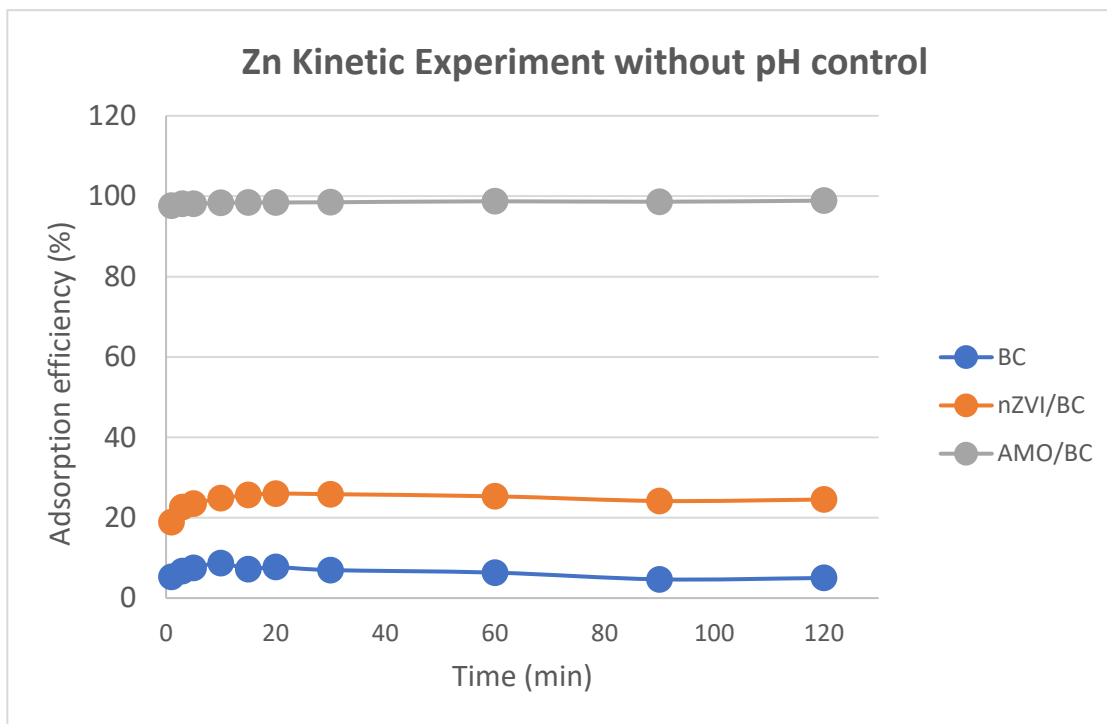


Figure 5. Kinetic experiment of Zn using BC, nZVI/BC, and AMO/BC without pH control.

Removal efficiency with pH adjustment

Furthermore, kinetic experiments at different pH values were performed. The pH values for individual materials were selected based on their effectiveness in solutions without pH adjustment, i.e., the most effective material AMO/BC was tested at controlled pH values 4, 5 and 6. Conversely, the less effective nZVI/BC was tested only at pH 5 and 6. The least effective BC was then tested only at pH 6. Figure 6. illustrates the kinetic experiment of Zn with AMO/BC under the pH control 4, 5, and 6. The adsorption efficiency of AMO/BC increased from 65% to 82% at pH 6 within 2 hours. At pH 4, the removal efficiency slowly decreased from 38% to 22% during the time of the experiment. In terms of pH 5, adsorption efficiency stayed almost stable (around 54%) compared to pH 4 and 6. In comparison to the experiment without pH adjustment, AMO/BC was less efficient. Similar to the experiment without pH adjustment, nZVI/BC showed lower efficiency than AMO/BC at pH 5 (14%) and pH 6 (18%) The adsorption efficiency of BC (3%) at pH 6 was almost the same in comparison to the experiment without pH adjustment. For the same experiment with Cd, slightly different results were obtained, i.e., higher efficiency at individual pH values. Figure 7. shows that the adsorption efficiency of AMO/BC increased at the controlled pH 5 (81% to 94%) and 6 (69% to 81%), while the efficiency at pH 4 slightly decreased from 47% to 37% over time and subsequently equilibrated until the end of the experiment. The highest efficiency was observed at pH 6. The adsorption efficiency of nZVI/BC in Cd removal was tested only at pH 5 and 6 as it was the less effective and the final result (i.e., after 120 min) was 8% and 15%, respectively. For Zn, the values were as 14% at pH 5 and 18% at pH 6. In terms of BC, it was again the least effective with the efficiency of 4% in Cd and 3% in Zn at pH 6. As has been said,

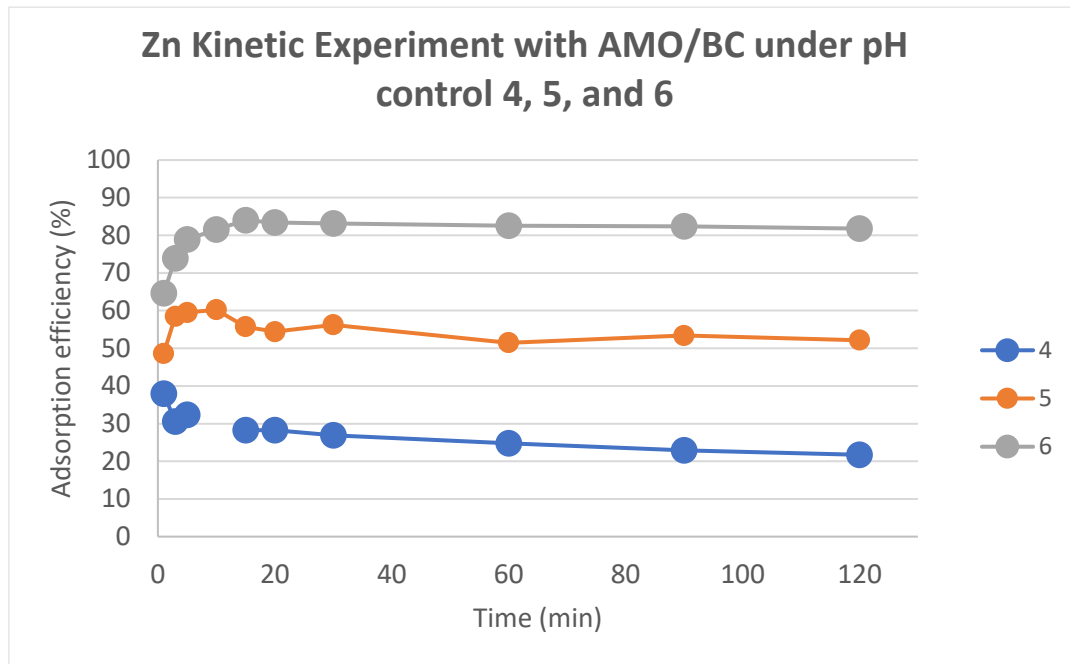


Figure 6. Kinetic experiment of Zn using AMO/BC at pH 4, 5, and 6.

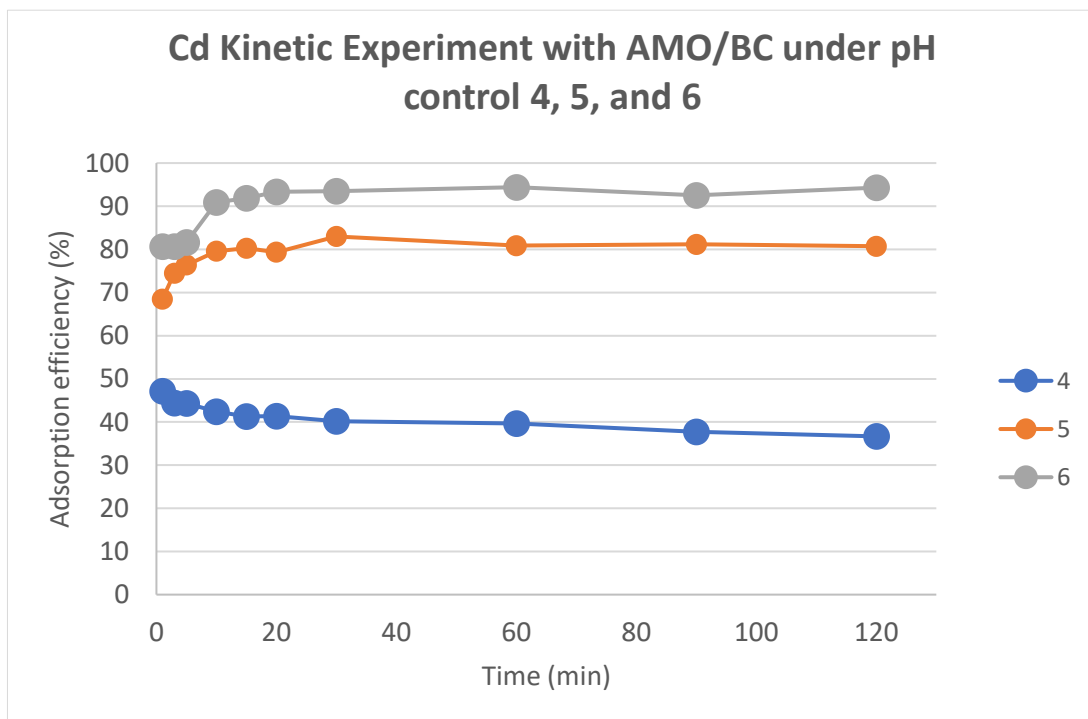


Figure 7. Kinetic experiment of Cd using AMO/BC at pH 4, 5, and 6.

AMO/BC, nZVI/BC and BC showed better results without pH adjustment, i.e., at natural pH, compared to the pH-controlled experiment.

In addition, co-adsorption kinetic experiment with both Cd and Zn (both metals in the same container) was performed using the most efficient material, i.e., AMO/BC. The results are illustrated below in the Figure 8. Adsorption efficiency of the metals fluctuated within the given time period. According to the values obtained, it can be noted that AMO/BC was much more efficient for Cd at different pH values (i.e., 49% at pH 4, 73% at pH 5, and 93% at pH 6) compared to Zn (i.e., 23% at pH 4, 42% at pH 5, and 73% at pH 6).

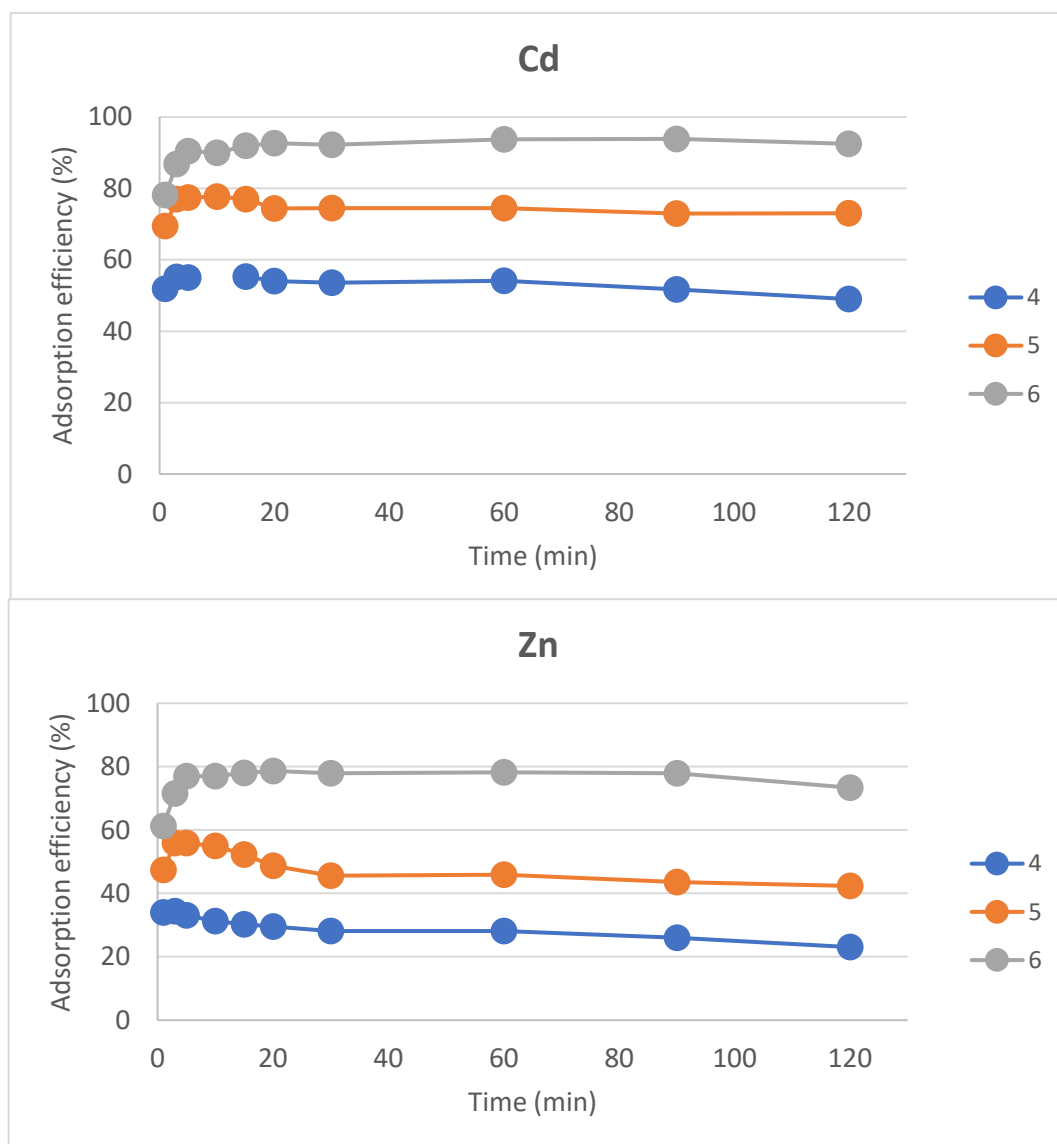


Figure 8. Co-adsorption kinetic experiment of Cd and Zn using AMO/BC at controlled pH 4, 5 and 6.

Kinetic modeling

Kinetic data obtained after application of AMO/BC to individual solutions of Zn and Cd and to solutions containing both metals (i.e., co-adsorption experiments) were further fitted using non-linear form of PFO and PSO (Figure 9. and 10.). Based on the results, PSO was the better model with the higher R^2 value of 0.998 for Cd and Zn at pH 6 in comparison to PFO ($R^2 = 0.988$ for Zn and $R^2 = 0.982$ for Cd at pH 6). The value of the kinetic constant from the better model, i.e., PSO, was 0.60 for Zn and 0.52 for Cd. This shows that Zn had faster adsorption. As for the co-adsorption (Figure 11), the adsorption of Zn was also faster with the kinetic constant of 0.72 compared to Cd with the kinetic constant of 0.48.

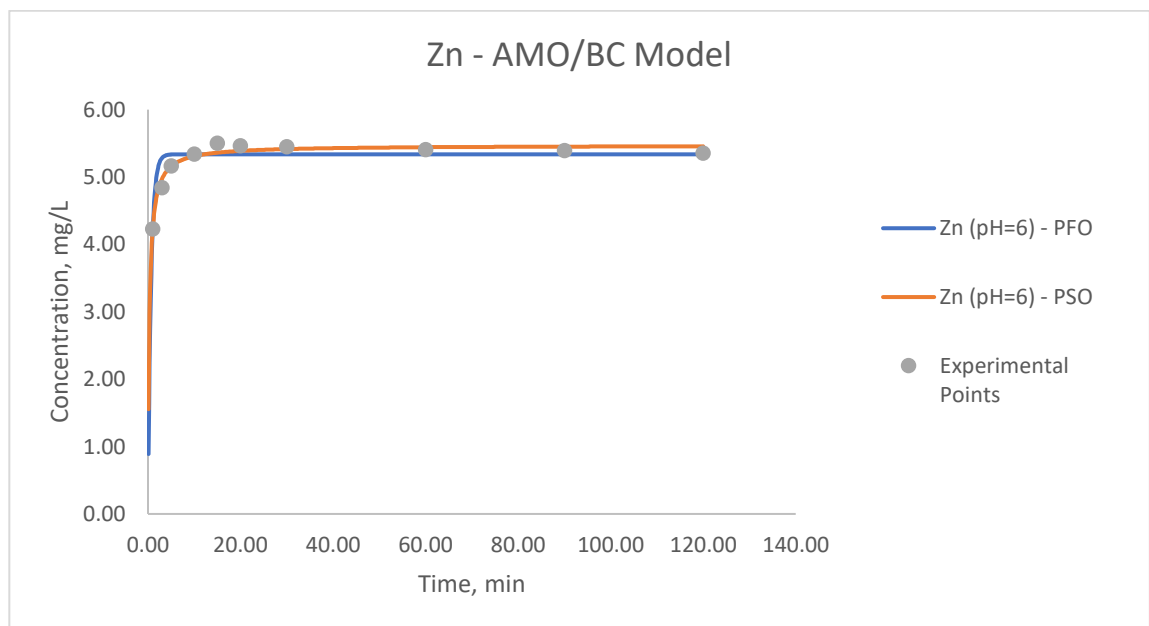


Figure 9. Kinetic models of Zn – AMO/BC.

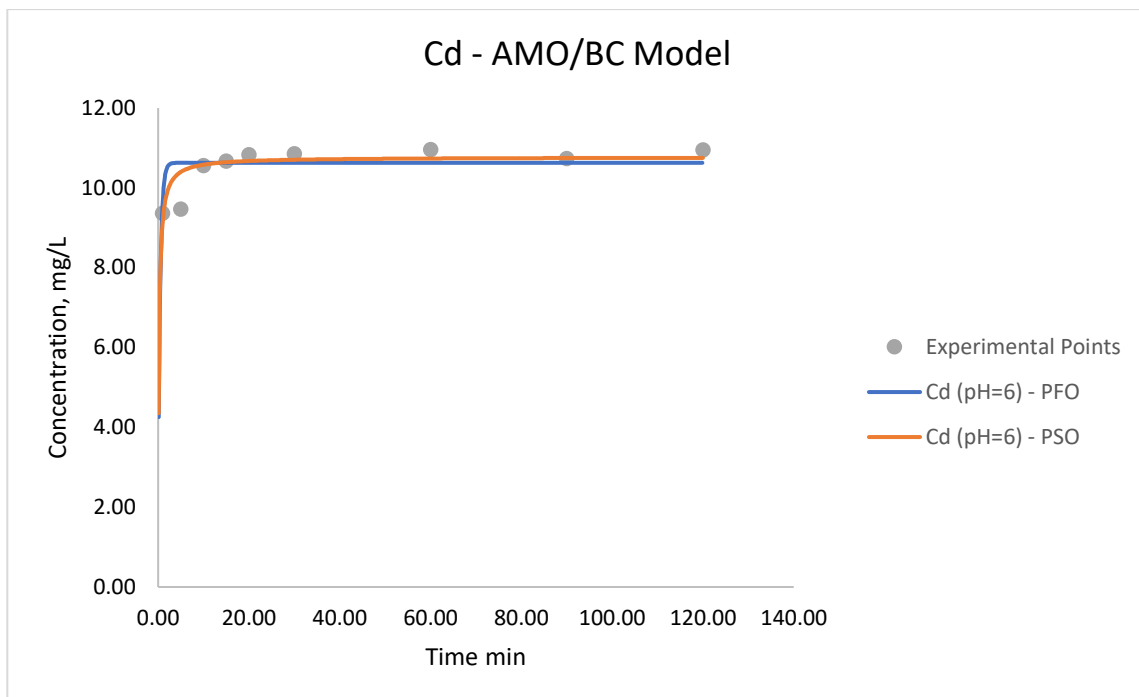


Figure 10. Kinetic models of Cd – AMO/BC.

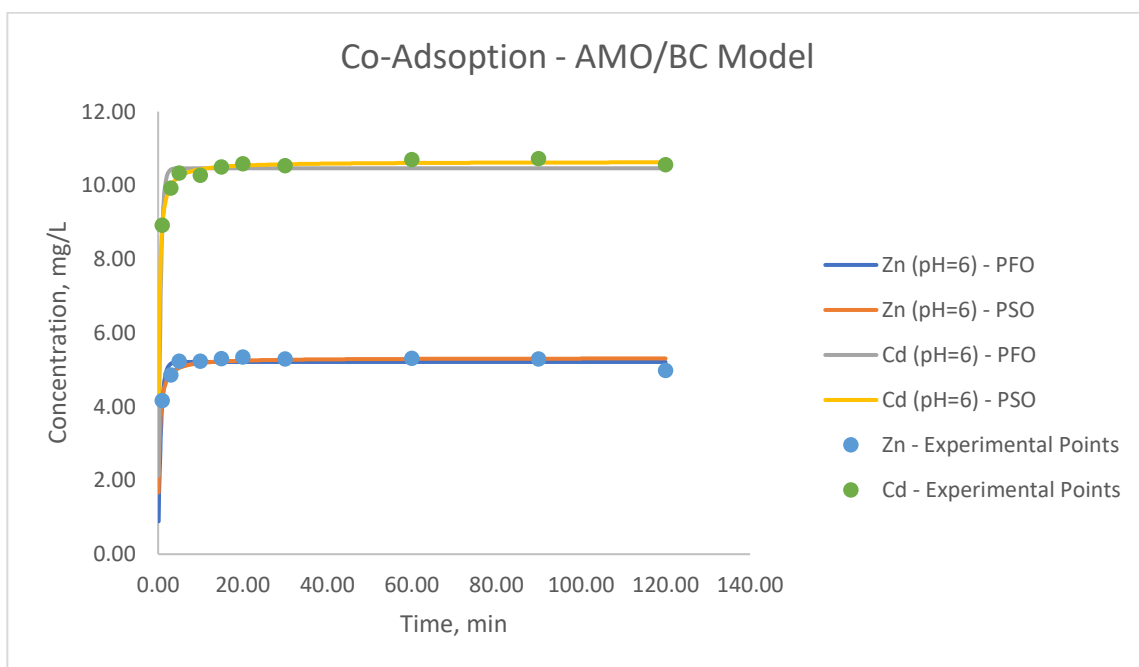


Figure 11. Kinetic models of Zn and Cd (Co-Adsorption) – AMO/BC.

4.2.2. Equilibrium Experiments

The equilibrium adsorption experiments (i.e., adsorption isotherms) were done for Zn and Cd using nZVI/BC and AMO/BC at pH 6. Based on the figure 12, the measured adsorbed amounts of Zn on nZVI/BC reached only 2.5 mg/g, while AMO/BC was able to adsorb 28.25 mg/g which is approximately 10 times more than nZVI/BC. Moreover, AMO/BC showed even better results in Cd adsorption, with 42.24 mg/g absorbed. In contrast, nZVI/BC adsorbed only a very small amount of 0.71 mg/g (Figure 13.). It is therefore evident that the efficiency of these two materials, despite the same proportion of the active phase, is very different.

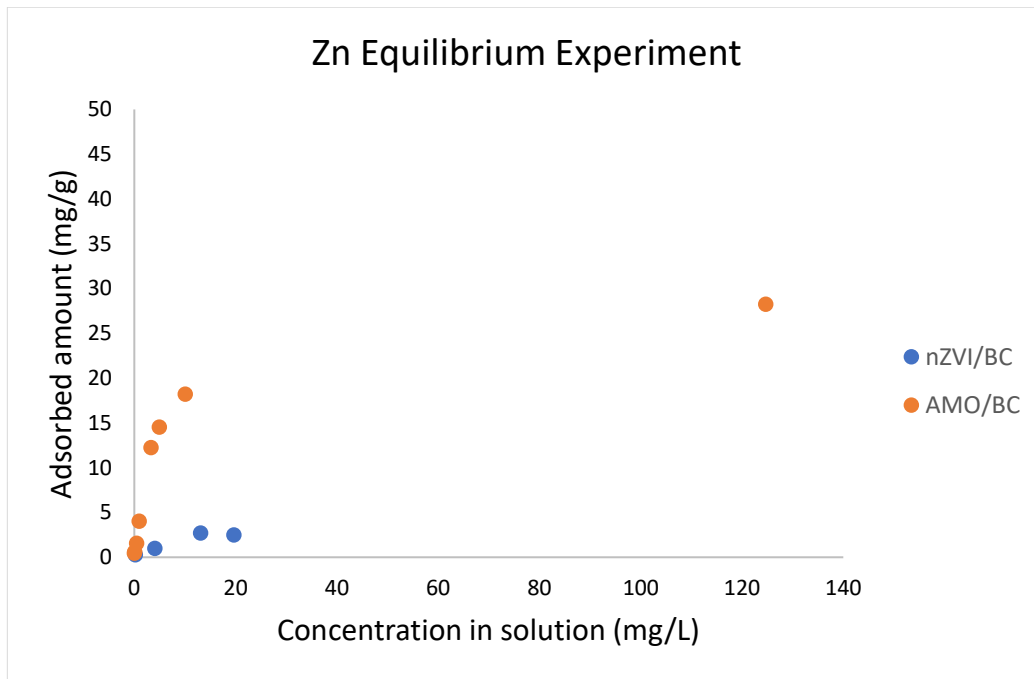


Figure 12. Zn adsorption isotherms of nZVI/BC and AMO/BC at pH 6.

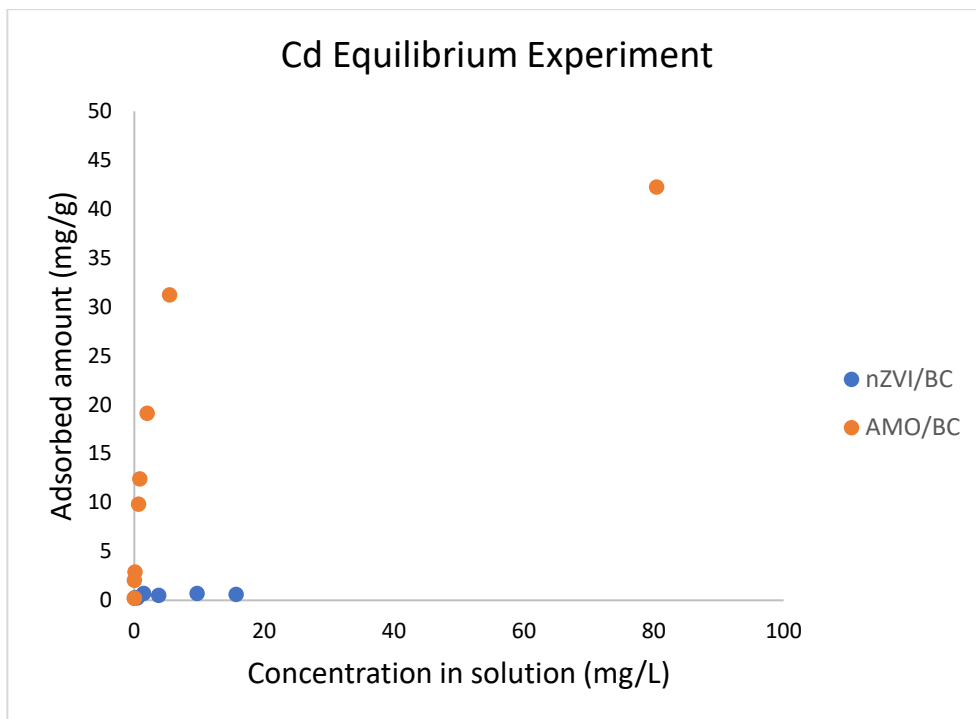


Figure 13. Cd adsorption isotherms of nZVI/BC and AMO/BC at pH 6.

Modeling of adsorption isotherms

Equilibrium data obtained at different Zn/Cd concentration after application of AMO/BC at pH value of 6 were further fitted using non-linear form of Langmuir and Freundlich model (Figure 14. and 15.). According to the data, Langmuir was the better model with the higher R^2 value of 0.99 for Zn and Cd at pH 6 in comparison to Freundlich model ($R^2 = 0.93$ for Zn and $R^2 = 0.91$ for Cd at pH 6). The maximal adsorbed amount of Cd was higher (43.52 mg/g) than Zn (29.14 mg/g). It is also shown from the Langmuir constant that Cd (0.44) had higher affinity than Zn (0.19).

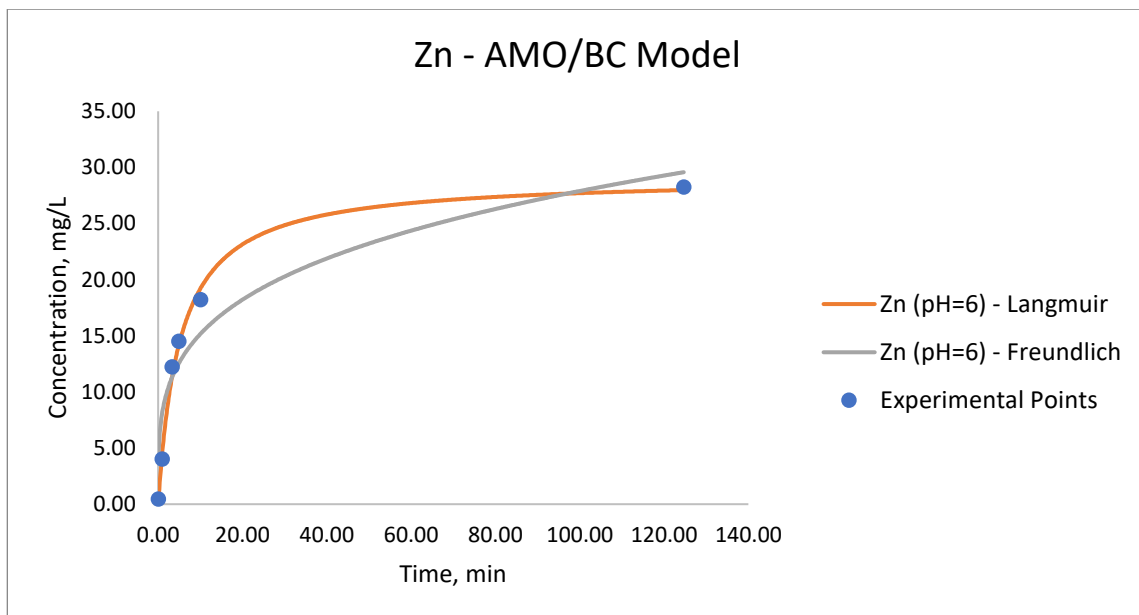


Figure 14. Equilibrium models of Zn – AMO/BC.

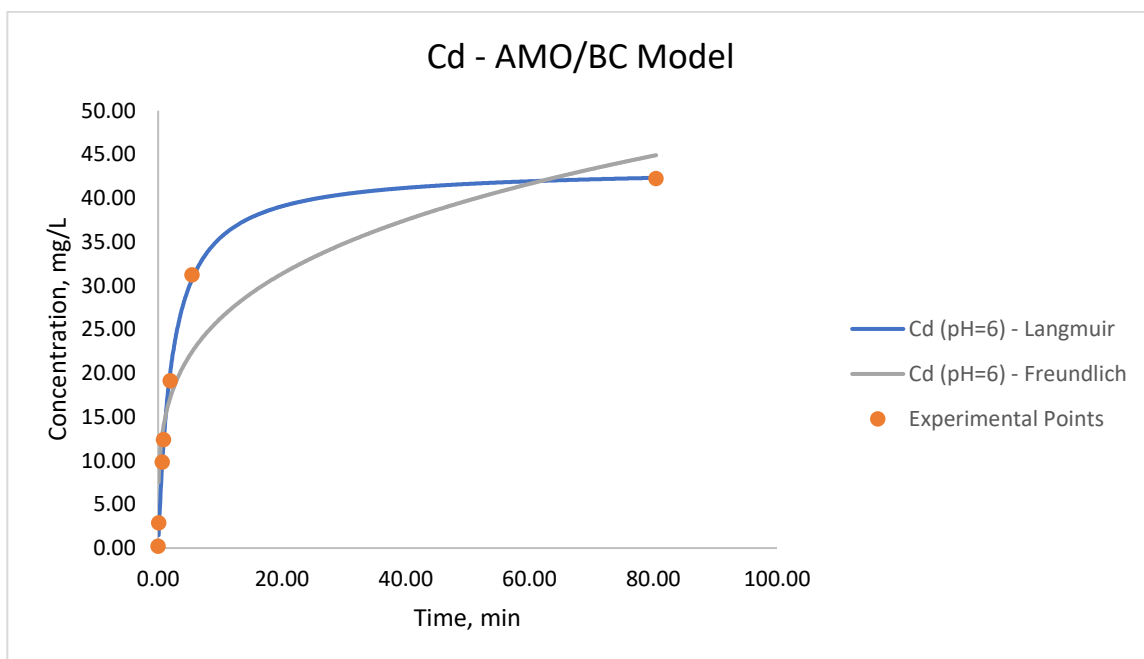


Figure 15. Equilibrium models of Zn – AMO/BC.

4.2.3. Solid-State Analyses

The individual particles of BC, nZVI/BC and AMO/BC were visualized by SEM/EDX (Figure 16, Table 2.). Energy dispersive X-ray spectroscopy (EDX) is often coupled with SEM and provides information about the chemical composition of a sample, including the type of elements, its distribution and concentration. In general, concentrations below 0.5% wt% are close to the detection limit of the machine. The spots which were found on BC can be grouped to: 1) higher Fe content – spot 2 (24.7±4.19%) and spot 5 (13.15%); 2) higher Ca content – spot 3 (29.8%); 3) higher Si content – spot 4 (54.5±6.28%), spot 5 (30.4%), spot 6 (24.4%), spot 7 (32.6%); 4) higher Si, Fe and Al content – spot 2 and 5) higher Si, and K content – spot 7. The observed elements on the surface of pure BC are related to the biomass from which the given BC was prepared by the pyrolysis process. In the case of composite materials, two types of spots can be found: 1) with higher content of nZVI (Fe – spot 1) and AMO (Mn – spot 1), and 2) with lower or none nZVI (Fe – spot 2) and AMO (Mn – spot 2), i.e., BC phase predominated. In the case of nZVI/BC and AMO/BC some redundant Si and K, respectively, can be found originating probably from the synthesis procedure. The spot without any elements means pure biochar structure since carbon is not measured by SEM/EDX.

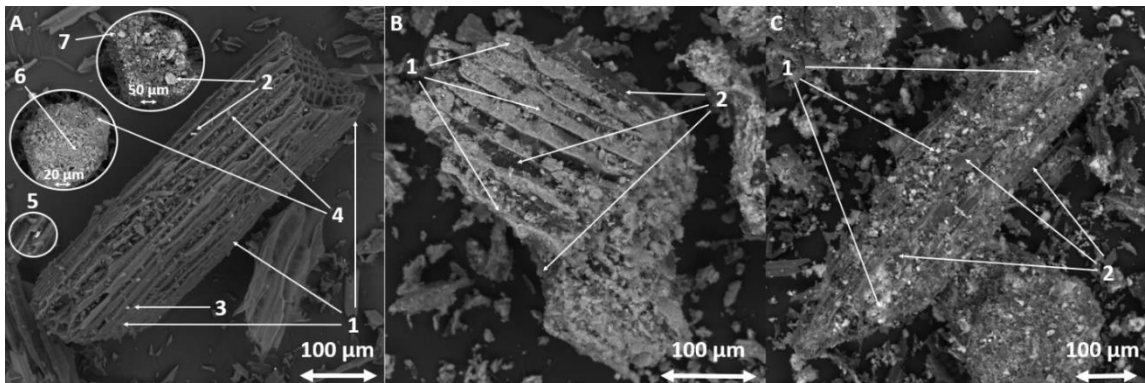


Figure 16. SEM image of pristine before adsorption: A: BC; B: nZVI/BC; C: AMO/BC.

Table 2. Chemical composition (wt%) of materials before adsorption based on EDX measurement.

Material	Spot	O	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
BC	1	-	-	-	-	-	-	-	-	-	-
	2	50.9±6.86	-	6.92±1.04	13.7±0.65	17.5±0.18	1.12±0.24	0.28±0.14	-	0.55	24.7±4.19
	3	46.5	-	-	0.35	0.49	-	29.8	-	1.52	-
	4	82.6±3.77	-	-	0.72±0.45	54.5±6.28	0.92	-	-	-	0.47
	5	28.0	-	3.35	5.95	30.4	-	-	-	-	13.1
	6	25.7	-	0.91	10.9	24.4	4.68	-	0.54	-	4.45
	7	44.6	0.46	-	10.34	32.6	14.9	-	-	-	-
nZVI/BC	1	2.70±0.22	-	-	-	1.44±0.55	-	-	-	-	48.4±7.00
	2	0.68±0.27	-	-	-	0.52±0.12	-	0.44	-	-	8.57±2.79
AMO/BC	1	38.6±5.01	-	-	-	-	7.50±2.31	0.31	-	50.9±9.56	-
	2	6.76±2.47	-	-	-	-	1.15±0.25	-	-	6.54±2.39	-

* individual spots on the surface of the given material (see Figure. 16)

The individual particles of AMO/BC were further studied after kinetic experiments (Figure 17.) and equilibrium experiments (Figure 18.). The chemical composition is given in Table 3. For detailed analyses after adsorption, only the most efficient material, i.e., AMO/BC, was selected. Based on the results, more adsorption was observed on spots with higher AMO content, i.e., higher adsorption because of more AMO (spot 1). On spots with insignificant AMO content, adsorption was not observed or was very low, i.e., lower adsorption (or below detection limit) because of less AMO (spot 2). Cadmium was better detectable even in spots with less AMO compared to zinc (probably also caused by better detection of heavy elements by EDX – Cd is heavier than Zn). Lastly, there was no adsorption found in spot 3 where pure BC was present.

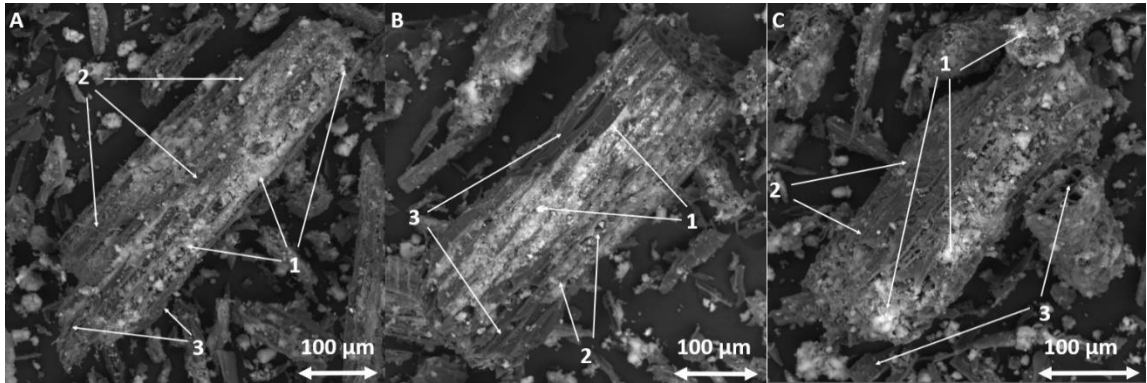


Figure 17. SEM images of AMO/BC after Zn a Cd kinetic adsorption experiments. A: AMO/BC after adsorption of Zn at pH = 6 – kinetics; B: AMO/BC after adsorption of Cd at pH = 6 – kinetics; C: AMO/BC after coadsorption of Zn and Cd at pH = 6 – kinetics.

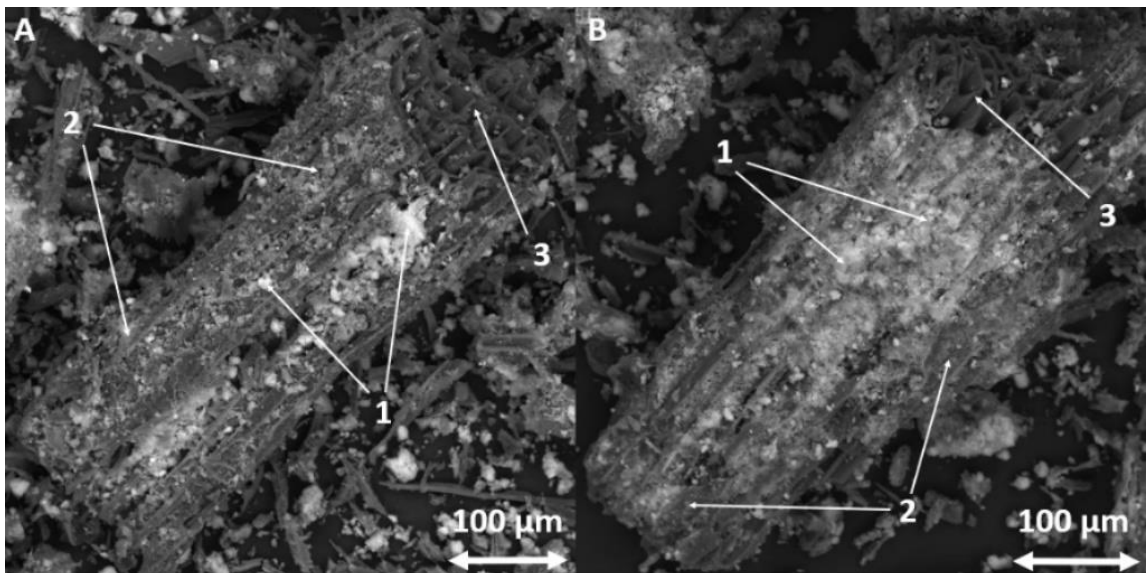


Figure 18. SEM images of AMO/BC after Zn a Cd equilibrium adsorption experiments. A: AMO/BC after adsorption of Zn at pH = 6 – maximum amount adsorbed; B: AMO/BC after adsorption of Cd at pH = 6 – maximum amount adsorbed.

Table 3. Chemical composition (wt%) of materials before adsorption based on EDX measurement.

Type of experiment	Metal	Spot*	O	K	Mn	Zn	Cd
Kinetics	Zn	1	25.9±4.72	1.04±0.20	44.4±5.35	1.95±0.21	-
		2	4.06±1.09	-	6.67±1.97	-	-
		3	2.96	-	2.81	-	-
	Cd	1	26.9±2.72	0.98±0.14	41.8±4.28	-	3.8±0.42
		2	4.33±2.80	-	8.73±2.23	-	0.81±0.34
		3	2.24	-	2.04	-	-
	Zn + Cd	1	27.9±3.63	0.92±0.12	39.8±4.49	1.36±0.17	2.80±0.30
		2	4.46±0.42	-	7.88±1.89	-	0.79±0.16
		3	3.88	-	1.23	-	-
Isotherms	Zn	1	21.1±5.33	0.62±0.12	38.9±9.29	8.77±0.89	-
		2	3.14±1.19	-	4.97±1.33	1.27±0.38	-
		3	1.63	-	1.52	-	-
	Cd	1	22.6±6.48	-	36.8±3.81	-	11.5±1.17
		2	3.17±0.09	-	2.27±0.72	-	0.91±0.23
		3	1.63	-	0.8	-	-

* individual spots on the surface of the given material (see Figure 17 and Figure 18)

The structure of all materials before adsorption was monitored using XRD analysis (Figure 19.). The broad XRD patterns of AMO/BC (3) provided evidence of its amorphous nature and indicated the presence of Mn-oxide hydrate. In the case of BC (1), characteristic amorphous structure with some sharp peaks associated with the crystal structure of quartz were presented on/in the BC structure, probably originating from the initial biomass. When biomass was pyrolyzed to produce biochar, the inorganic components of the biomass, including minerals like quartz, were retained in the char. More crystalline phases were observed in the XRD pattern of nZVI/BC (2), especially zero-valent iron phases, such as ferrite and austenite. Moreover, further crystalline phases corresponded to the BC structure (graphite) or originating from the initial biomass (quartz) were detected. It also included cementite which has an orthorhombic crystal structure and is a compound of iron and carbon.

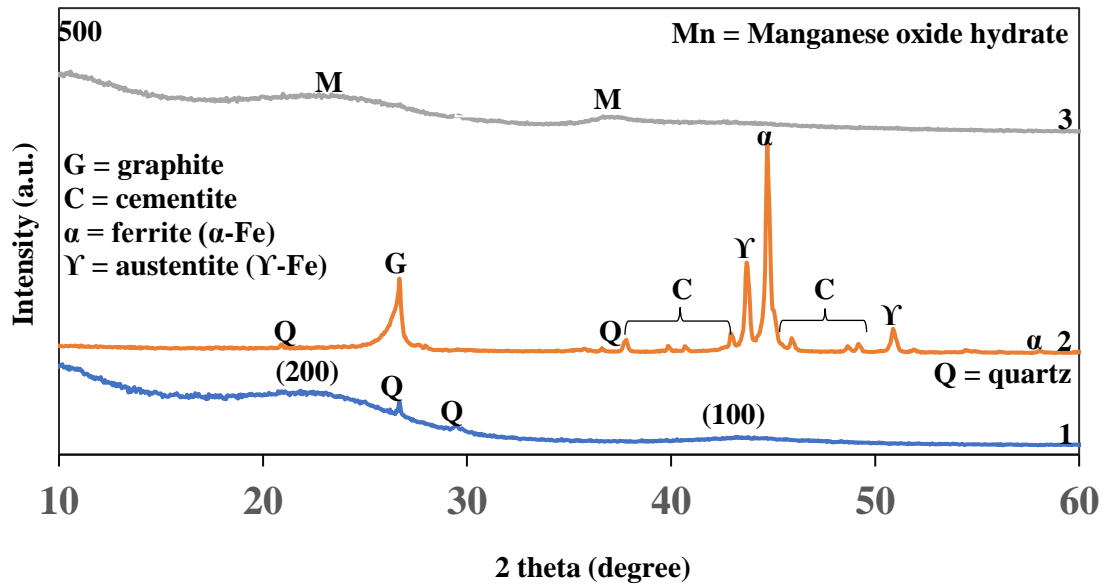


Figure 19. XRD diffractograms of BC (1), nZVI/BC (2) and AMO/BC (3) before adsorption.

Additionally, AMO/BC, as the most effective material, was subjected to XRD analysis after adsorption which may help to identify individual phases (Figure 20.). The material before and after adsorption showed the same record confirming the amorphous nature of the sample (amorphous manganese oxide and biochar are both amorphous materials), so it is evident that after adsorption there were no changes, for example due to the precipitation of crystalline Zn/Cd new phases at given conditions.

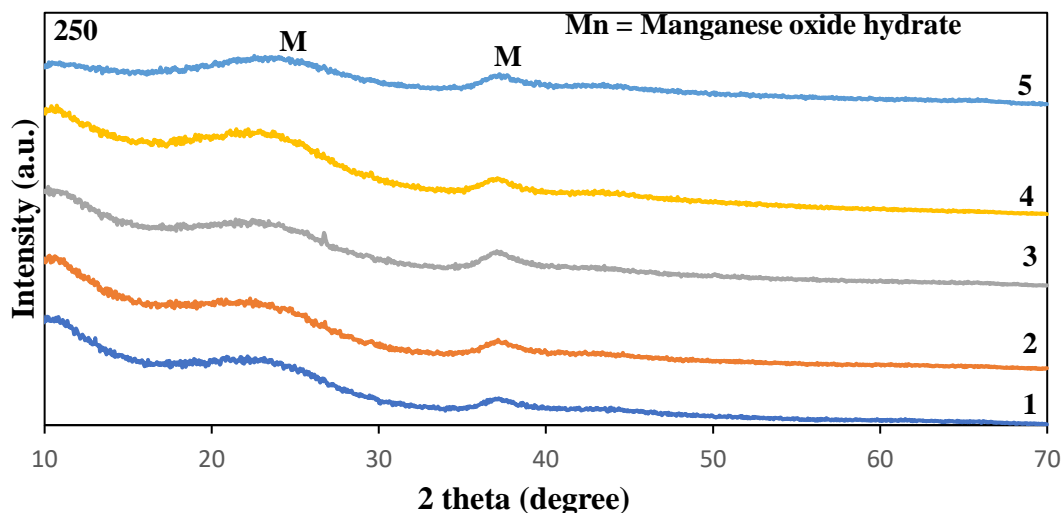


Figure 20. XRD diffractograms of AMO/BC after Zn and Cd kinetic and equilibrium adsorption experiments. 1: after adsorption of Zn at pH = 6 – kinetics; 2: after adsorption of Cd at pH = 6 – kinetics; 3: after coadsorption of Zn and Cd at pH = 6 – kinetics; 4: after adsorption of Zn at pH = 6 – maximum amount adsorbed; 5: after adsorption of Cd at pH = 6 – maximum amount adsorbed.

4.2.4. Removal Efficiency in Soil Solutions

The main goal of the last experiment in this diploma thesis was to study the effectiveness of BC, nZVI/BC, and AMO/BC in more complex solutions containing hazardous metals, such as Zn and Cd. Moreover, the concentrations of other elements after application of these solid materials were also monitored in order to evaluate the stability of materials and/or their effect on the remobilization of other elements.

Zn and Cd.

Zn removal efficiency after one day and seven days is given in Figure 21. The initial concentration of Zn in soil L was around 7 mg/L while it was 3.5 mg/L in soil S. As for Cd, the initial concentration was higher compared to Zn. It was about 10.3 mg/L in soil L and 14.6 mg/L in soil S. The results for alluvial soil solution shows that BC was not effective in the removal of Zn at given conditions, which further confirmed the low efficiency of this material, as was also observed in Zn laboratory solutions. Removal efficiency reached even negative values after one day of the experiment and also at the

end of the experiment, i.e., seven days. In terms of forest soil solution, similar results were observed.

For nZVI/BC, the removal efficiency of Zn also reached negative values after one day of the experiment which increased to 6.31% after seven days. Even better results were obtained in the forest soil solution where the removal efficiency increased from 10.34% to 30.89% after one day and seven days, respectively.

The data for Zn showed that AMO/BC was the best agent to remove Zn from both alluvial and forest soil solutions. The removal efficiency of Zn in alluvial soil solution increased from 37.89% to 57.26% within 7 days. Even higher increase of the removal efficiency was observed in the forest soil solution which was from 9.38% to 67.33%.

With regards to Cd, it was also impossible to remove it from both alluvial and forest soil solutions using BC. The measurements showed that the removal efficiency also reached negative values.

However, the numbers demonstrated that the use of nZVI/BC and AMO/BC were better options for Cd removal. According to the nZVI/BC results, the removal efficiency increased from 7.17% to 17.55% in the alluvial soil solutions, while AMO/BC was much more effective with efficiencies ranging from 76.38% to 81.73%. In the forest soil solution, the removal efficiency of Cd using nZVI/BC increased from 17.42% to 31.95%. Using AMO/BC, even better results were obtained, i.e., the removal efficiency increased from 26.81% to 67.43%.

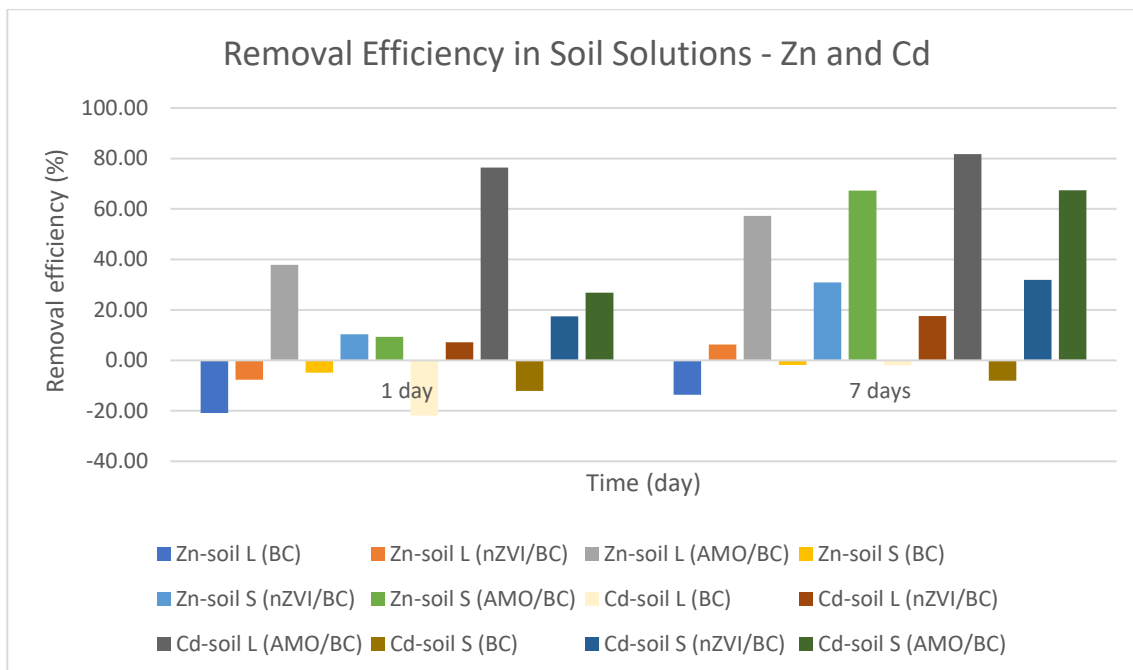


Figure 21. Removal Efficiency in soil L and soil S solutions using BC, nZVI/BC, and AMO/BC for Zn and Cd.

Mn and Fe.

As materials based on Mn- and Fe- were tested, possible release of these elements was also monitored (Figure 22.). From the soil solutions themselves before the experiment, it was observed that the concentration of Mn in the soil solution is higher for the soil S (10.58 mg/L for BC, 11.50 mg/L for nZVI/BC, 11.29 mg/L for AMO/BC), on the contrary, the Fe concentration was higher for the soil L (2.31 mg/L for BC, 2.16 for nZVI/BC, 1.97 for AMO/BC). According to the data, no release of these elements was observed from BC in both soil solutions. On the contrary, both composites showed lower stability in the forest soil solution, i.e. leaching of Mn from AMO/BC and leaching of Fe from nZVI/BC. Less stability in this solution may be due to lower pH of this soil solution which lead to the subsequent release of these elements from the materials.

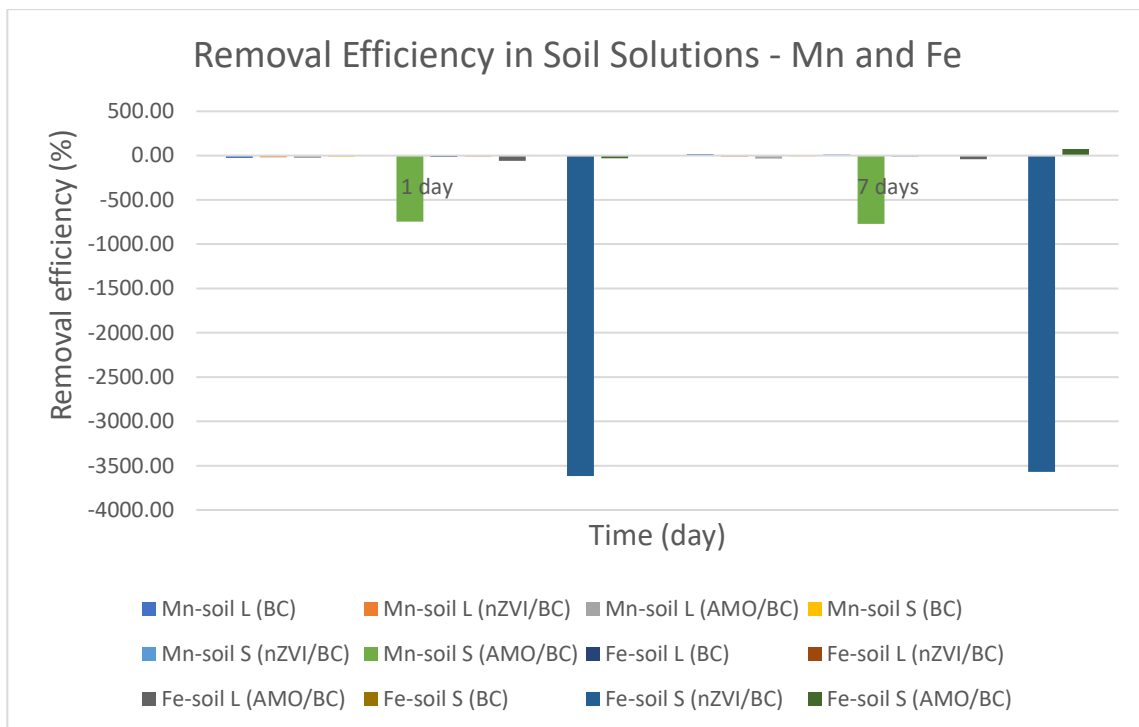


Figure 22. Removal Efficiency in soil L and soil S solutions using BC, nZVI/BC, and AMO/BC for Mn and Fe.

Other Elements.

Apart from the metals mentioned above, other elements such as Pb, As, P and Al were detected (Figure 23.). Finally, selected anions, such as sulphate and chloride, were also monitored. According to the outcomes from ICP/OES, the results showed that Pb was even leached from alluvial soil solution using BC and nZVI/BC. In the case of AMO/BC, which was the most effective material for previous metals, the removal efficiency increased from negative values to 24.99%. Similar, Pb was leached when using BC and nZVI/BC from the forest soil solutions. Compared to alluvial soil solution, AMO/BC was much more effective, i.e., around 27% and 95%, respectively. Although As was even slightly leached using all agents (except nZVI/BC after 7 days with removal efficiency of 6.03%), both composites were somehow effective in the forest soil solution. However, the initial As concentrations in both solutions were generally low. P was leached using AMO/BC in the alluvial soil solution, while no leaching was observed in the forest soil. BC was efficient in the alluvial soil which increased to 22.89%, although AMO/BC was

much more efficient in forest soil solution which increased to 88.55%. For Al, nZVI/BC was better option in comparison to BC and AMO/BC in the alluvial soil solution. In terms of the forest soil, BC showed leaching after 1 day, but removal efficiency increased to 2.41% after seven days, while nZVI/BC and AMO/BC demonstrated very good results, i.e., the removal efficiency increased to 39.02% using nZVI/BC and 67.24% using AMO/BC. Finally, data obtained from IC showed that chloride and sulphate were leached when using all the agents within 7 days.

In terms of the pH values of the alluvial soil solution, it ranged between 7.33 and 7.52 using BC. The pH values of the alluvial soil solution using nZVI/BC ranged between 7.52 and 7.57 while the values of 7.53 and 7.30 were observed using AMO/BC. Initial values were 6.55 (before adding BC), 6.70 (before adding nZVI/BC), and 6.76 (before adding AMO/BC) for the alluvial soil. As for the pH values of the forest soil solution, it ranged between 3.69 and 4.23 when BC was used (the initial value was 3.00). Adding of nZVI/BC resulted in the increase of the pH values of the forest soil to 5.57-6.52 (the initial value was 3.63). The pH value of the forest soil solution ranged from 4.28 to 7.25 after adding AMO/BC (the initial value was 3.63).

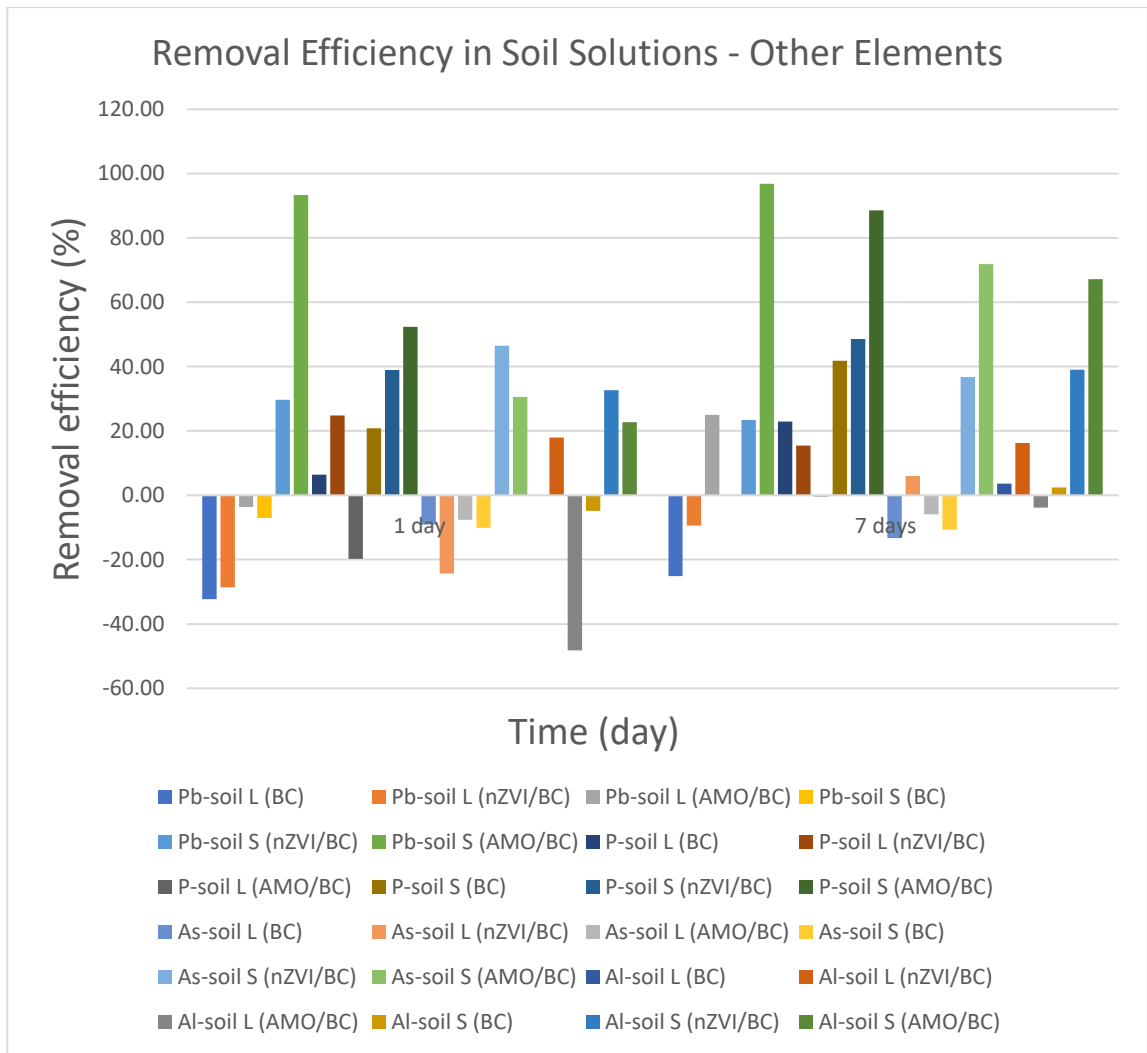


Figure 23. Removal Efficiency in soil L and soil S solutions using BC, nZVI/BC, and AMO/BC for other elements.

4.3. Discussion

4.3.1. Adsorption Kinetics

The results of the kinetic experiments showed that AMO/BC was the most effective material for both Cd and Zn adsorption compared to nZVI/BC and BC. The reaching of equilibrium was fast in the case of AMO/BC, already in the first minutes of the experiment. The pH values of the final solutions were higher in the case of AMO/BC than for nZVI/BC and BC. In the experiments with controlled pH, the adsorption efficiency of AMO/BC was higher at pH 6 for both Cd and Zn removal compared to lower pH values. However, the overall efficiency was lower when the pH was controlled compared to uncontrolled experiments. The co-adsorption experiment showed that AMO/BC was more efficient for Cd removal than for Zn removal. The study also employed kinetic modeling using PFO and PSO, and the results showed that PSO was the better model, with Zn exhibiting faster adsorption kinetics than Cd. These findings highlight the potential of AMO/BC as an effective adsorbent for risky metal removal. . The results of the study are also consistent with previous scientific articles that have evaluated the use of biochar and metal oxide/biochar composites for risk metal removal from aqueous solutions. For instance, Ouředníček et al. (2019) reported that AMO/BC was more effective than BC itself in the removal of risk metals. Moreover, some previous studies also investigated the chosen kinetic models for biochar-based materials. For example, Hudcová et al. (2022) pointed the importance of modeling approaches in understanding the adsorption behavior of sorbent materials, specifically in the removal of Zn and As from aqueous solutions. In accordance with our study, the use of pseudo first and second order models was used for the kinetics data which demonstrated the validity of these models in predicting the adsorption behavior of sorbents. Mitzia et al. (2020) discussed the importance of understanding the behavior of products such as BC and nZVI under changing soil conditions (including different time intervals), particularly in predicting the behavior of metals in amended soils. In comparison to our study, they found that BC containing treatments were the most efficient in terms of metal stabilization and pH conservation, with a more pronounced immobilization efficiency over time compared to other amendments. In contrast, nZVI treatments were more rapid, showing short-term metal stabilization in the soil. Therefore, a combination of these two amendments may ensure the functionality and applicability for both short- or long-term soil remediation.

The pH values observed in the current experiment appear to fall within the typical range of pH values reported in other studies involving similar materials. For example, the study on the use of AMO for removing metal(loid)s from aqueous solutions reported final pH values ranging from 9.02 to 9.52 (Trakal et al., 2018). These values are a bit more than the pH values reported in the current study. The fact that the smallest increase in pH values occurred when pure BC was applied suggests that BC may have a buffering effect on the system, preventing significant changes in pH. This is consistent with previous research on the use of BC for environmental applications, which has shown that BC can act as a pH buffer due to its ability to exchange H^+ and OH^- ions with the surrounding environment (Lehmann et al., 2009). Finally, the differences in pH values observed between the different treatments (i.e., nZVI/BC, BC, and AMO/BC) suggest that the choice of material and/or the specific application can have a significant impact on pH. This is consistent with previous research on the use of different materials for environmental applications, which has shown that the choice of material can impact the pH of the system due to differences in surface chemistry, reactivity, and other factors (Chen et al, 2022). Apart from that, in soils with high pH levels, $Cd(OH)^+$ that is adsorbed on soil particles can easily undergo hydrolysis and release Cd ions. Thus, the impact of biochar on regulating pH levels should be taken into account in alkaline soils (Wei et al., 2023).

4.3.2. Adsorption Isotherms

The results of the equilibrium adsorption experiments showed that AMO/BC was significantly more efficient than nZVI/BC in adsorbing both Zn and Cd at pH 6. AMO/BC was able to adsorb approximately 10 times more Zn than nZVI/BC, and for Cd, AMO/BC was able to adsorb over 40 mg/g, while nZVI/BC only adsorbed a small amount of 0.71 mg/g. These results suggest that the efficiency of the materials was not solely determined by the proportion of the active phase, but other factors such as the specific surface area and the distribution of active sites on the surface of the materials may have also played a role. The Langmuir model was found to be a better fit for the equilibrium data obtained for Zn and Cd adsorption using AMO/BC at pH 6, indicating that the adsorption of these metals on AMO/BC followed a monolayer adsorption process. The maximal adsorbed amount of Cd was higher than Zn, and Cd also had a higher affinity than Zn, as evidenced by the Langmuir constant.

The results of this study showed that AMO/BC had a significantly higher adsorption capacity for both Zn and Cd compared to BC, which is in line with previous studies. For example, a study by Shaheen et al. (2022) reported that Mn oxides/BC had a much higher adsorption capacity for the risk metals such as Cd, Pb, Cu compared to raw biochar. The authors attributed the higher adsorption capacity of Mn oxides/BC to the presence of multiple active sites on the surface of the material, which provide more opportunities for metal ion binding.

In terms of the use of Langmuir and Freundlich models, Liu et al. (2021) used these models to describe the adsorption thermodynamic characteristics of Zn in various biochars. The maximum adsorption capacity of Zn was observed according to the Langmuir parameters which showed it was the better model. Apart from that, another study was done by Hudcová et al. (2021) to describe the monolayer and multilayered adsorption of zeolite using Langmuir and Freundlich models. The Langmuir model was found to be a better fit for adsorption data, specifically for metal cation adsorption, as it assumes that the materials have a limited number of accessible sites available. In our study, we observed that the Langmuir model was a better fit for the experimental data, which suggests that the adsorption of Zn and Cd onto AMO/BC occurs through a monolayer adsorption mechanism. Hien et al. (2020) analyzed the adsorption of Zn onto biochar to identify which model best describes the removal of adsorptive from the solution onto the biochar surface. In comparison to our study, the authors found that the Freundlich model provides a better fit to the data than the Langmuir model, as indicated by the higher R^2 values. They also found that the q_{\max} values of the Langmuir model were lower than the values found in the experimental part of this work..

4.3.3. Solid-State Analyses

The SEM/EDX analysis provided valuable information about the chemical composition of the materials and their distribution. The results showed that spots with higher content of AMO were more efficient in adsorbing Cd and Zn, while spots with insignificant AMO content did not show any significant adsorption. XRD analysis confirmed that the AMO/BC composite material was amorphous before and after adsorption, indicating that there were no changes in the material structure due to the adsorption process. These findings suggest that AMO/BC could be a promising material for the removal of risk

metals from contaminated soil. However, further research using advanced analytical techniques is needed to investigate the efficiency of the material under different conditions and to optimize its performance.

In accordance with the current study, Trakal et al. (2018) used SEM/EDX to analyze the composite of AMO and biochar which consists of separate particles of each material, with clusters of AMO containing Mn-oxalates and/or secondary precipitated rhodochrosite partially occupying the surface of the biochar. The presence of rhodochrosite, which was verified by the XRD pattern was detected through the use of high-resolution SEM. Puppa et al. (2013) discussed SEM images of the AMO particles and their size distribution, as well as XRD spectra of both the AMO and birnessite. The SEM images show that the particles of AMO are agglomerates several micrometers in size and display conchoidal fractures. The presence of a film covering the surface is characteristic of a solid originating from a sol-gel procedure, which does not reflect any defined morphology that would indicate the amorphous nature of the solid. The organic compound used during the synthesis procedure was found to play a significant role in determining the morphology of the AMO particles. The XRD spectra of both the AMO and birnessite were obtained, and it was found that the synthesized AMO is amorphous, as evidenced by the absence of any sharp peaks in the XRD pattern. In contrast, the prepared birnessite is a single-phase mineral, as indicated by three peaks in its XRD pattern, which prove to be characteristic for this mineral phase. In this thesis, only amorphous manganese oxides were used as the active phase, but their high efficiency was also confirmed.

4.3.4. Soil Solutions

The experiment aimed to evaluate the effectiveness of BC, nZVI/BC, and AMO/BC in the removal of hazardous metals like Zn and Cd in complex soil solutions. The results showed that BC was not effective in removing Zn and Cd, and even led to negative removal efficiencies. However, nZVI/BC and AMO/BC showed better results, with AMO/BC being the most effective agent for Zn and Cd removal. The stability of the materials was also evaluated, and it was observed that the release of Mn and Fe occurred in the forest soil solution due to lower pH. Other elements like Pb, As, P, and Al were also detected, and their leaching varied depending on the agent and soil solution used. Chloride and sulfate were leached when using all the agents within seven days.

In terms of monitoring the concentrations of other elements, previous studies have also investigated the effect of BC, nZVI/BC, and Mn oxide/BC on the remobilization of elements. Aydın et al. (2004) reported the leaching of Fe and Mn from BC-based materials in soil solutions showing the same trend as for the materials in this thesis. In accordance with our study, Song et al. (2022) analyzed that nZVI/BC composite shows promising potential as an effective material for the remediation of multiple risk metals such as Zn, As, Cd from the contaminated soil than biochar alone. Moreover, the study showed that the nZVI/BC composite treatment increased the soil pH, available iron, cation exchange capacity, total organic carbon, and dissolved organic carbon.

With regards to the stability of Mn and Fe, Rotter et al. (2017) studied that the leaching of these elements can be influenced by factors such as pH and the presence of organic matter. The observation that the forest soil solution had lower stability for both composites may be attributed to the lower pH of this solution compared to the alluvial soil solution. In relation to thesis study, it is noteworthy that the forest soil solution exhibited less stability for Mn and Fe which also could be due to its comparatively lower pH when compared to the alluvial soil solution.

5. Conclusion

In conclusion, the experimental part of the diploma thesis evaluated the effectiveness of biochar-based composites in the removal of Cd and Zn, specifically looking at the role of the active phase on the biochar surface. Three types of experiments were conducted: adsorption kinetics, adsorption isotherms, and kinetics in soil solutions. The results showed that AMO/BC was the most effective material for the removal of both Cd and Zn. Kinetic experiments showed that the establishment of equilibrium was very fast for AMO/BC. Additionally, it was found that pH adjustment affected the efficiency of the materials, with better results obtained without pH adjustment. The co-adsorption experiment using AMO/BC showed that it was more efficient for Cd removal than Zn removal. Kinetic modeling was also applied to the data obtained from the experiments. These findings provide insights into the effectiveness of biochar-based composites in metal removal and can serve as a basis for further research in this area. Overall, the results suggest that biochar-based composites, particularly those with AMO as the active phase, have potential for use in the removal of heavy metals from contaminated solutions. Future research can focus on the optimization of the synthesis process of biochar-based composites and the evaluation of their long-term performance in the removal of metals from contaminated soil.

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