

DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**DEVELOPMENT OF LOW COST MODIFIED
ADSORBENT BY METAL COATING PROCESS
FOR ARSENIC AND/OR ANTIMONY REMOVAL**

by

Berna KAVACIK

June, 2022

İZMİR

**DEVELOPMENT OF LOW COST MODIFIED
ADSORBENT BY METAL COATING PROCESS
FOR ARSENIC AND/OR ANTIMONY REMOVAL**

A Thesis Submitted to the

Graduate School of Natural and Applied Sciences of DokuzEylül University

In Partial Fulfillment of the Requirements for the Degree of Doctor of

Philosophy in Environmental Engineering, Environmental Engineering

Program

by

Berna KAVACIK

June, 2022

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Ph. D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**DEVELOPMENT OF LOW COST MODIFIED ADSORBENT BY METAL COATING PROCESS FOR ARSENIC AND/OR ANTIMONY REMOVAL**” completed by **BERNA KAVACIK** under supervision of **PROF. DR. DENİZ DÖLGEN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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ACKNOWLEDGEMENTS

I desire to state my gratitude and blessing for my supervisor Prof. Dr. Deniz DÖLGEN whose consistent support and guidance has been invaluable during the running of my PhD study. She continuously provided encouragement and was always willing and enthusiastic to assist in any way she could along the study.

I also want to thank to my thesis committee members, Assoc. Prof. Dr. Ebru ÇOKAY and Prof. Dr. Ali Aydın GÖKTAŞ, and Prof. Dr. Mehmet Necdet ALPASLAN for their guidance, precious offers and commentaries.

I would like to thank Dokuz Eylül University Environmental Engineering Department and IZSU General Directorate, Department of Water Treatment in order to give the opportunity for laboratory use. And I also would like to special thank IZSU Department of Water Treatment in order to provide materials and groundwater samples I used in experimental studies.

This thesis study was funded by Dokuz Eylül University, Scientific Research Project Program (Project No: BAP 2018.KB.FEN.036). I would like to acknowledge DokuzEylül University for this financial backing.

I also want to say special thankto Leader of Rural Drinking Water Treatment Plant of IZSU, without his help and wise guidance this study would have not been the same.

I would like to give special thanks to my husband and my children for their motivation along my life.

Berna KAVACIK

DEVELOPMENT OF LOW COST MODIFIED ADSORBENT BY METAL COATING PROCESS FOR ARSENIC AND/OR ANTIMONY REMOVAL

ABSTRACT

In this study, the adsorption of arsenic and antimony by using a drinking water treatment sludge (DWTS) were investigated. Iron hydroxide containing DWTS was modified mainly by heating at 200°C and coating with zirconium oxide. Then, modified materials, i.e. DWTS-200 and ZOC-DWTS were used in the experiments. Elemental analyses and surface morphologies were carried out by scanning electron microscope (SEM) and energy disperse X-ray spectroscopy (EDS) for DWTS-200 and ZOC-DWTS to assess effect of modification. Phase compositions of adsorbents were determined by X-ray diffraction (XRD) and surface area and pore volume were analyzed by Brauner-Emmer-Teller method (BET). Batch experiments were done to determine adsorption parameters and optimum conditions (pH, adsorbent dose, initial concentration, contact time, and competing ions). Adsorption kinetics fitted in pseudo second order reaction kinetics and adsorption mechanisms were defined by Freundlich isotherm for DWTS-200 and ZOC-DWTS. Column studies were performed in a fixed bed, and dynamics of the adsorption process were modeled by well-known mathematical models, e.g. Thomas, Clark, Adams & Bohart, and Yoon–Nelson Model. The adsorption capacities were determined as 6.53 and 9.13 mgAsg⁻¹ for DWTS-200 and ZOC-DWTS, respectively. Regeneration studies were shown that ZOC-DWTS were no longer effective after regeneration for arsenic and antimony removal, whereas, DWTS-200 could be reused after regeneration. The results stated that each adsorbent were effective and producing the Fe-hydroxides (DWTS-200) and Fe-Zr binary oxide (ZOC-DWTS) from a waste material (i.e., sludge) by using a simple and low-cost process offered an advantage in terms of sustainability and economy.

Keywords: Arsenic, antimony, adsorption, drinking water treatment sludges

ARSENİK ve/veya ANTİMON GİDERİMİ İÇİN METAL KAPLAMA PROSESİ İLE MODİFİYE EDİLMİŞ DÜŞÜK MALİYETLİ ADSORBAN GELİŞTİRİLMESİ

ÖZ

Bu çalışmada, içme suyu arıtma çamuru (DWTS) kullanılarak arsenik ve antimon adsorpsiyonu incelenmiştir. Demir hidroksit içeren DWTS, temelde 200°C'de ısıtılarak ve zirkonyum oksit ile kaplanarak modifiye edilmiştir. Böylelikle, modifiye edilmiş malzemeler DWTS-200 ve ZOC-DWTS deneylerde kullanılmıştır. Modifikasyonun etkisini değerlendirmek için DWTS-200 ve ZOC-DWTS için taramalı elektron mikroskobu (SEM) ve enerji dağılımlı X-ışını spektroskopisi (EDS) ile element analizleri ve yüzey morfolojileri yapılmıştır. Adsorbanların faz bileşimleri X-ışını kırınımı (XRD) ile belirlenmiş ve yüzey alanı ve gözenek hacmi Brauner-Emmer-Teller yöntemi (BET) ile analiz edilmiştir. Adsorpsiyon parametrelerini ve optimum koşulları (pH, adsorban dozu, başlangıç konsantrasyonu, temas süresi ve yarışan iyonlar) belirlemek için toplu deneyler yapılmıştır. Adsorpsiyon kinetiği, yalancı ikinci derecede reaksiyon kinetiğine uygun bulunmuş ve DWTS-200 ve ZOC-DWTS için adsorpsiyon mekanizmaları Freundlich izotermi ile açıklanmıştır. Kolon çalışmaları sabit yatakta gerçekleştirilmiş ve adsorpsiyon sürecinin dinamikleri Thomas, Clark, Adams & Bohart ve Yoon-Nelson Modeli gibi iyi bilinen matematiksel modeller ile modellenmiştir. Adsorpsiyon kapasiteleri DWTS-200 ve ZOC-DWTS için sırasıyla 6,53 ve 9,13 mgAsg⁻¹ olarak belirlenmiştir. Rejenerasyon çalışmaları, ZOC-DWTS'nin rejenerasyondan sonra arsenik ve antimon giderimi için etkili olmadığını, buna karşın DWTS-200'ün rejenerasyondan sonra yeniden kullanılabileceğini göstermiştir. Sonuçlar, her bir adsorbanın etkili olduğunu göstermiştir; ayrıca atık malzemeden (çamur) basit ve düşük maliyetli işlem ile elde edilen Fe-hidroksit (DWTS-200) ve Fe-Zr ikili oksit (ZOC-DWTS) sürdürülebilirlik ve ekonomi açısından avantaj sağlamıştır.

Anahtar kelimeler: Arsenik, antimon, adsorpsiyon, içme suyu arıtma tesisi çamuru

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CHAPTER 1

INTRODUCTION

1.1 The Problem Definition

Arsenic is a common element in nature and can be detected in soil, aquatic environment, atmosphere and bios. Arsenic can be found in water sources, especially as a result of groundwater dissolving certain compounds and minerals, such as arsenic, as it passes through soil and rock. Due to the carcinogenic effects of some of the arsenic compounds; according to the Annex 1 list of the European Union's directive 67/548/EEC, it is included in the class of toxic and dangerous substances for the environment. In addition, the US Environmental Protection Agency (US EPA) classified arsenic as a class A carcinogen, and the International Agency for Research on Cancer (IARC) included arsenic in the first group of carcinogenic compounds. For this reason, regulations have been made on the standards for permissible arsenic amounts in drinking water sources. In 1993, World Health Organization (WHO) reduced the limit value of arsenic in drinking water from 50 μ /L to 10 μ /L. Within the scope of the “Regulation on Water Intended for Human Consumption” dated 17 February 2005 and numbered 25730, which is valid for drinking and utility water in our country; the maximum arsenic limit has been reduced from 50 μ g/L to 10 μ g/L. The tightening of the limit values restricted the use of drinking water resources in many settlements in our country; especially in the Aegean, Central Anatolia and Eastern Anatolia Regions. The water sources, which have arsenic measured above the standard value, have become unusable without treatment.

In this framework, wellhead treatment systems (packaged drinking water treatment plants) are recommended as a solution, especially for settlements in rural areas. In these systems, adsorption, ion exchange and filtration processes are used as purification methods. Adsorption is preferred especially in small-scale facilities due

to its features such as high treatment efficiency, low initial investment and operator requirement. Adsorption technology is more advantageous if the materials used as adsorbent are easily available and cheap. In applications in our country, adsorbent materials imported from abroad are generally used, which causes high operating costs. For this reason, studies on the use of efficient and low-cost adsorbents have recently gained importance.

Adsorbents obtained from waste materials (e.g. nut shell, peanut, olive waste, almond, apricot kernel, cherry, rice, corn, wheat husk, sugarcane pulp, tea and coffee waste, coconut waste, red mud from aluminum production, iron and steel mills, sludges from chrome plating, fly ash from thermal power plants, etc.) is an alternative in order to meet the need. In this study, it was predicted that the chemical sludge obtained as a result of the processes applied in drinking water treatment plants and containing iron can be used for arsenic and/or antimony removal. If waste chemical sludge is used as an adsorbent, it is possible to provide advantages such as arsenic and antimony removal in water, as well as reducing the amount of waste generated, saving in waste disposal costs, minimizing negative environmental effects, and it is considered that it can be used in small-scale package facilities, especially in rural areas.

1.2 Objective and Scope of The Study

In arsenic-containing water resources, antimony compounds are frequently detected together with arsenic, and while existing adsorbents show high performance in arsenic removal, they are insufficient in antimony removal. On the other hand, it is stated that high levels of antimony cause health problems and in this context, it causes lung and heart damage. With this understanding, the main objective of the presented study is to develop low-cost adsorbent materials that can remove arsenic and antimony from waters, and thus to utilize water resources that cannot be used due to arsenic or antimony for small-scale settlements such as villages and towns.

Iron compounds, especially iron (hydr)oxides are very effective for arsenic removal. Because ferrous iron [Fe(II)], which is in reduced form in groundwater, is oxidized to iron hydroxides as a result of aeration in drinking water treatment plants (DWTP). Similarly, when Fe(II) and/or Fe(III) salts are added as coagulant, iron (hydr)oxides are formed. These iron (hydr) oxides ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ with varying degrees of hydration) are removed from the water by precipitation or filtration units, and sludge containing iron (hydr)oxide is produced as a residue. There are some studies in the literature using drinking water treatment plant sludge (Razali et al., 2007; Nagar et al., 2010; Caporale et al., 2013; Sun et al., 2015; Ocinski et al., 2016; Wang et al., 2018). In these studies, by using the treatment sludge obtained from drinking water and wastewater treatment plants; arsenic, phosphate and sulfate removal were investigated. In the literature, there is no study in which waste sludge and antimony and arsenic are removed together. As stated before, many water sources contain antimony together with arsenic, and existing adsorbents are insufficient especially for antimony removal. Based on this need, arsenic and antimony removal was investigated by using iron-containing drinking water treatment plant sludge (DWTS).

Within the scope of the study, sludge samples taken from the drinking water treatment plant were modified with heat treatments and zirconium coating. In this way, 2 different adsorbent materials (DWTS-200 and ZOC-DWTS) were developed and their characterization was determined. The surface area and pore volume of the materials were analyzed by the BET method and the phase composition was determined by X-ray diffraction (XRD). Surface morphologies and elemental analysis were performed by scanning electron microscopy (SEM) and X-ray spectrometry (EDS). Arsenic and antimony removal by DWTS-200 and ZOC-DWTS were investigated by batch and column experiments. While determining the optimum working parameters through batch adsorption experiments; with column experiments, important parameters such as column turning point curves, which are used to determine the lifetime of adsorbents were obtained. In addition, kinetic and isotherm studies were carried out to evaluate the adsorption of arsenic and antimony on the developed adsorbents, and fixed bed column modeling was performed on four different models. After the column studies, due to the high cost of changing the

adsorbent material, the regeneration of the used adsorbents was carried out, and their reusability was investigated.



CHAPTER 2

ARSENIC AND ANTIMONY CHEMISTRY, POLLUTION AND TREATMENT TECHNOLOGIES

2.1 Chemistry and Sources of Arsenic and Antimony

In recent years, researchers and authorities have shown interest to arsenic (As) and antimony (Sb), and have described as critical matters in many research papers (Ungureanu et al., 2015). Arsenic and antimony may naturally available in the environment and/or originated by human activities. They show metals and nonmetals properties and pertain to the same group of the periodic table (third and fourth elements of the Group VA, respectively). Thus, they have similar chemistry and mostly exist together (An & Kim, 2009; Lehr et al., 2007).

Arsenic and antimony compounds in natural water originate from the geochemical characteristics of the aquifers. Redox conditions affect the mobility and retaining of different contaminant species. They are found in soil, some rock types and minerals and ores containing lead and copper. They can pass into water as a result of runoff and underground infiltration. Natural sources of arsenic include hot springs, volcanic rocks, metamorphic rocks, seawater and mineral deposits. In addition, volcanic movements rock erosion and forest fires are also among the natural sources of arsenic (EPA, 2003). Also, arsenic and antimony can release to the environment from uncontrolled anthropogenic activities, use of wood preservatives and arsenical pesticides (Bhattacharya et al., 2010; Kolbe et al., 2011). Also, catalysts, electronics and batteries production industries widely use arsenic and antimony. Antimony is found in the environment to a lesser extent than arsenic, but it has equally devastating effect for the environment and for human health. Antimony contamination arises from power plants, copper smelting or mining labours. Antimony global consumption was forecasted as 188,000 tones, about five times

more than arsenic in 2016 (Wu et al., 2018). According to literature data, the amount of arsenic in groundwater is in the range of 0.5-5000 µg/L (Vieira et al., 2017).

In many countries around the world, about 100 million people have faced with arsenic poisoning due to arsenic pollution in groundwater resources. Bengal Delta (West Bengal, India and Bengaldesh), China, America and New Zealand are among the places with high arsenic content.

Arsenic is found in organic and inorganic forms in nature, but the inorganic forms are more toxic and more common in water. Inorganic arsenic stays on particulate and soluble form. Soluble form of inorganic As(III) and As(V) forms being subject to oxidation-reduction conditions. While arsenic mostly exists in As(III) form in groundwater which has anoxic conditions, it is found in As(V) form in surface water principally has aerobic conditions. Both arsenite and arsenate are found in four various species (H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} , AsO_3^{3-}). The speciation of these molecules is pH dependent and changes by dissociation. The dissociation kinetics for each is almost momentary (EPA, 2003).

Chemical species are very important for arsenic treatability. Negative surface charges enable to removal of arsenic by co-precipitative processes, anion exchange and adsorption. As(III) is not readily eliminated because the net charge of arsenite is neutral at 6-9 pH levels. Nevertheless, at natural pH levels, the net charge of arsenate is negative (-1 or -2) and it can be removed with better performance productivity. As(III) is converted to As(V) by adding an oxidizing agent at arsenic treatment plants. Optimum oxidation technology should be selected by taking into considerations compatibility with available treatment, cost, disinfection necessities, and secondary impacts (EPA, 2003).

There is not enough knowledge about speciation and global cycling of antimony (Fiella et al., 2002; Fiella et al., 2009). However, it has four valences: Sb(V), Sb(III), Sb(0), and Sb(-III) but generally presents as Sb(III) and Sb(V) in nature (Filella et al., 2002). Sb(V) and Sb(III) are found in oxic and in anoxic media, respectively according to thermodynamic predictions. Nevertheless, this is not always valid because Sb(III) was found in oxygenated natural waters and Sb(V) in anoxic conditions, conversely. Probable explanations of these incoordination were indicated as biological activity and kinetic effects. In excessive acidic conditions, antimony is charged positively. Sb(OH)_6^- and Sb(OH)_3 found in natural waters are the two extensive inorganic forms of antimony (Ungureanu et al., 2015).

In addition to the inorganic species, there are also organic compounds of arsenic and antimony. Organic species can be found in polluted and natural waters (Kolbe et al., 2011).

2.2 Health Effects of Arsenic and Antimony and Applied Standards

Although arsenic and antimony cause many types of cancer, they also have many negative effects on health. Arsenic causes skin damage, hair loss, easy breakage of nails, heart rhythm disorder, eye diseases, different organ and system cancers (respiratory, tract, lung, liver, prostate, skin). Antimony causes a breakdown in the immune system and negative effects in the nervous system, digestive system and other systems of the human body. Regardless of how antimony enters the body, it collects especially in the the lungs, stomach and intestines and causes gastric contractions, stomach pains, vomiting, skin redness and wounds. However, the most striking effect of antimony compounds is abnormal heart rhythm and irreparable damage in the nervous system. Continuous exposure to antimony leads to low blood sugar, weight loss and acceleration of metabolism (Asan, 2011). In many countries of the world such as India, Bangladesh, China, Chile, Taiwan and Argentina, groundwater contamination with arsenic and the existence of its long-term effects are

documented problems (Vieira et al., 2017). It is estimated that around 40-60% of people in Bangladesh are adversely affected by drinking water contaminated with arsenic. Therefore, arsenic pollution is still a problem and the lowering the limit values of the standards makes it more important to find different treatment methods (Yadav et al., 2014).

Standards for arsenic and antimony are aimed to protect the human health. Although both compounds have different toxicity, there is only one limit value for total concentrations. In 1993, the The World Health Organization (WHO) reduced arsenic concentration in drinking water from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ in order to mitigate negative impacts of arsenic on human health. Because this element is found abundantly in the environment, to achieve this limit value may be crucial in various areas of the world (Smedley & Kinniburgh, 2002). Also, some authorities set the arsenic limit value even lower, for instance, National Health and Medical Research Committee (NHMRC), Australia, in 1996 commended this value as 7 $\mu\text{g/L}$. European Union (EU) and most countries like Japan, Syria, Namibia, the USA and Turkey accepted the arsenic limit value as 10 $\mu\text{g/L}$, while Canada adopted the value of 25 $\mu\text{g/L}$. The maximum arsenic limit value is still 50 $\mu\text{g/L}$ in countries like China, Taiwan, Bangladesh, Vietnam, India (Yadav et al., 2014). Besides, the maximum antimony limit varies from 5 $\mu\text{g/L}$ (WHO, 2003; EC, 1998) to 6 $\mu\text{g/L}$ (US EPA, 2009) and these limit values (5 or 6 $\mu\text{g/L}$) adopted by the countries varies in each country (Kolbe et al., 2011).

2.3 Arsenic and Antimony Treatment Strategies

Because antimony and arsenic resemble each other chemically, treatment processes for the removal of these elements are approximate.

Treatment Strategies may be classified as;

- Wellhead Treatment – Treatment is positioned at the head of the well without mixing with other water resources.
- Centralized Treatment –Water from different water resources transfers to a central area for treatment before entering the water distribution system.
- POU Treatment – Treatment is positioned at the Point-Of-Use inside the building or house and only purifies water, usually consumed directly from a single tap.

If a treatment process is operated to reduce the trouble of As or Sb from multiple sources, the institution will have to decide whether to use a wellhead or central treatment. Wellhead treatment purifies water near the wellhead or from each well. Multiple treatment facilities can be considered if there are more than one well. It may be more economical to pipe water from multiple sources in to one treatment plant. Some factors to consider include:

- the closeness of wells to be treated,
- feasibility of piping water from sources to a central treatment plant,
- existence of power and land at the treatment site(s), and
- work force necessity for multiple places instead of a single place.

2.4 Arsenic and Antimony Treatment Methods

Current treatment processes are grouped into three main categories.

- Sorption Treatment Processes

- Activated Alumina (AA)
 - Ion Exchange (IE)
 - Iron Based Sorbents (IBS)
- Membrane Treatment Processes
 - Electrodialysis
 - Reverse Osmosis (RO)
- Precipitative Processes
 - Enhanced Conventional Gravity Coagulation/Filtration (CF)
 - Coagulation Assisted Microfiltration (CMF)
 - Coagulation-Assisted Direct Filtration (CADF)
 - Oxidation/Filtration (OxFilter)
 - Enhanced Lime Softening (LS)

Costs, feasibility and system constraints should be taken into consideration when choosing the most appropriate treatment strategy (EPA, 2003).

Some criteria must be taken into account to determine the appropriate treatment method. These can be listed as efficiency, oxidation stage, amount of produced-treated water (water loss), operator requirement, amount of waste and cost. Detailed information about the oxidation stage is explained in Section 2.5.

Some treatment processes, such as reverse osmosis, might have substantial water losses. All incoming water does not come out of the system as treated water and

water loss occurs. The amount of treated water obtained is low depending on the membrane performance. The comparison of the treatment processes operated under normal conditions are demonstrated in Table 2.1.

Table 2.1 Comparison of typical treatment processes (EPA, 2003)

CRITERIA	CF	CMF	CADF	OXFILT	LS	IE	AA	IBS	RO
Efficiency (%)	90-95	90	90	50-90	90	95	95	98	>95
Pre-oxidation	√	√	√	√	√	√	√	√	√
Water Loss(%)	0	5	1-2	1-2	0	1-2	1-2	1-2	15-75
Operator requirement	High	High	High	Medium	High	High	Low	Low	Medium
Waste	BW*, Sludge	BW*, Sludge	BW*, Sludge	BW*, Sludge	Sludge	Resin, Salt, BW*	AdsorbentBW*	AdsorbentBW*	Reject Water
Cost	Low	High	Medium	Medium	Low	Medium	Medium	Medium	High
Cost (POU)	N/A	N/A	N/A	N/A	N/A	-	Medium	Medium	Medium

* Backwash water

2.4.1 Coagulation/Flocculation

Coagulation/flocculation is a simple and relatively cost-effective operation for removing As and Sb. While not specific for removing arsenic or antimony, this technique has been shown in multiple researches to decrease both metalloids. It can be performed at a comprehensive pH range and on large volumes of water (Mondal

et al., 2013). Although, it still yields moderate removal for As(III), requires significant chemical doses, and forms toxic sludge.

Studies have reported that aluminum and ferric salts are effective for removing arsenic from mg/l levels (Yan et al., 2010; Zouboulis and Katsoyiannis, 2002) and $\mu\text{g/l}$ levels (Gregor, 2001; Pallier et al., 2010). Coagulation is often efficient for removing antimony, with ferric coagulants showing better effect compared to aluminium sulphate (Guo et al., 2009; Kang et al., 2003; Wu et al., 2010). Guo et al. (2009) reported considerable Sb(V) removal (i.e. 98%) efficiency with ferric coagulants at suitable pH conditions. They also successfully removed Sb(III) using less ferric coagulants at a pH range of 4-10. According to research, effectiveness of removal by coagulation is the highest for As(V), followed by Sb(III), As(III), and Sb(V). The flow chart of the coagulation/flocculation system is shown in Figure 2.1.

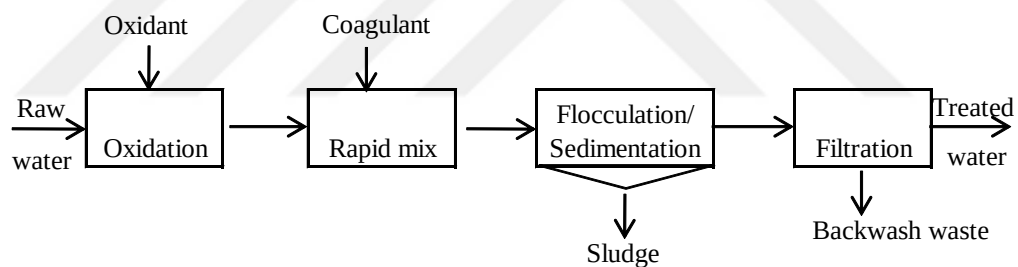


Figure 2.1 Flow diagram of conventional coagulation/flocculation system

2.4.2 Ion-Exchange

This method depends on exchanging Cl^- anions or arsenic species in water using strong-base chloride resins. As(V) is in an anionic form in neutral pH or a close pH range and it holds electrostatically on the resin areas. As(III)-uncharged species cannot be removed. This requires another step prior to oxidation when treating arsenite solutions. Ion-exchange resins are rather insensitive to pH and can help obtain an outlet arsenic concentration $\leq 2 \mu\text{g/L}$. Yet, their performance may be

limited by competing ions (Ungureanu et al., 2015). The current diagram of a typical ion-exchange process is shown in Figure 2.2.

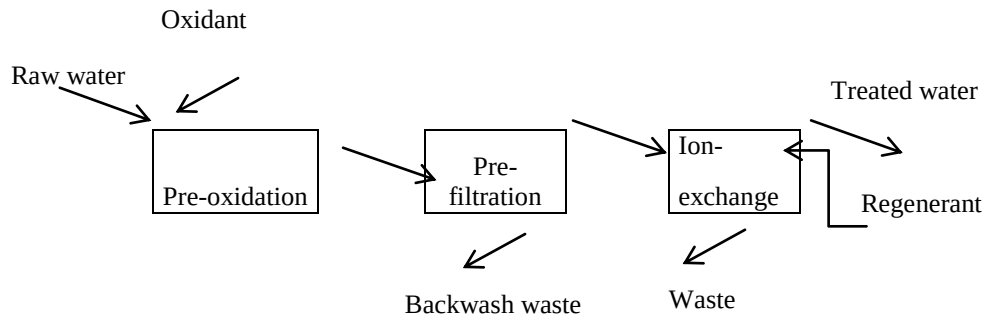


Figure 2.2 Flow diagram of ion-exchange process

2.4.3 Membrane Separation

Membrane processes separate components into molecules on the basis of their molecular weights and sizes. They can be classified as microfiltration, ultrafiltration, nanofiltration and reverse osmosis filtration based on pore sizes and pressure driving force. Microfiltration membranes specifically retain particles, while reverse osmosis membranes retain macromolecules such as dissolved salts. Ultrafiltration or microfiltration membranes allow the passage of water and most soluble substances, while retaining salt, microorganisms, and other large components of similar size.

Shih (2005) reports membrane separation to be efficient in removing arsenic in maximum acceptable concentrations, particularly in high-pressure processes. These include nanofiltration (NF) and reverse osmosis (RO), where a greater effect can be obtained. According to research, rejection rates in NF and RO range between 85-99% for As(V) and 61-87% for As(III) (Jekel and Amy, 2006). Despite the higher rate of success, As(III) can not be transformed to As(V) beforehand due to potential

membrane damage. High-pressure membrane processes tend to be expensive due to installation and energy costs, with a high rejection of water (Shih, 2005).

There is a lack of recent research on removing antimony using membrane separation operations. RO can show better treatment success in Sb(V) compared to Sb(III) with no major pH dependence (Kang et al., 2000). Also, some authors have reported using chelating porous hollow-fiber membranes (Nishiyama et al., 2003; Saito et al., 2004). Figure 2.3 shows the flow diagram of a typical membrane system.

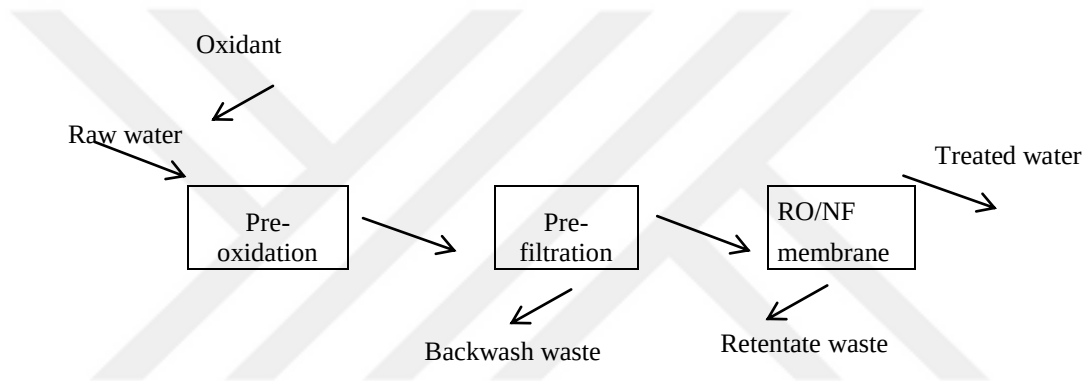


Figure 2.3 Flow diagram of membrane systems

2.4.4 Coagulation Assisted Microfiltration (CMF)

Arsenic compounds which are converted to a precipitable form after the coagulation process are separated from the water by processes such as sedimentation or filtration. While the physical separation process is performed with conventional filters in conventional treatment plants, in the CMF method, it is performed using membranes (Alpaslan et al., 2010).

Coagulation-assisted microfiltration has been reported to be more effective than conventional filtration methods for removing arsenic. One study even highlights a

rate of 97% for 100 $\mu\text{g/L}$ of arsenic under optimum conditions (Molgora et al., 2013). A schematic diagram of CMF is shown in Figure 2.4.

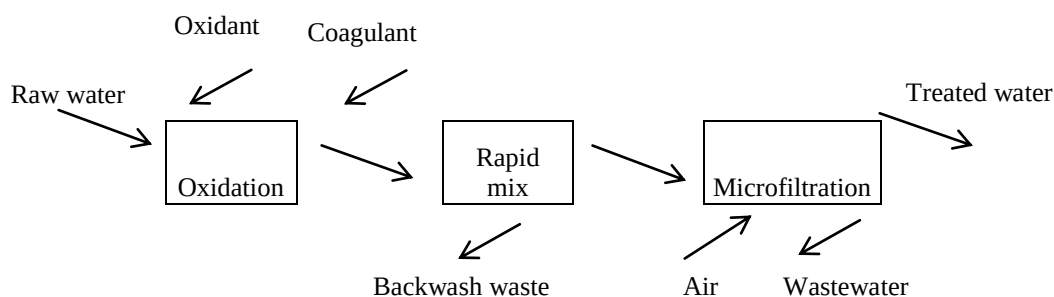


Figure 2.4 Flow diagram of coagulation assisted microfiltration

2.4.5 Adsorption

Adsorption is an effective method mostly used for arsenic and antimony removal due to low/no sludge production and easy operation. Contaminants are separated from the liquid phase and pass into the solid phase.

Adsorption has been used for more than a century to purify water for being simple and cost-effective, allowing regeneration, and forming minimal sludge (Gu et al., 2005; Rahaman et al., 2008). Adsorption of antimony and arsenic has been studied comprehensively using a vast variety of materials (Ungureanu et al., 2015).

The adsorptive behaviors of adsorbents depend heavily on the chemical form of the adsorbate, requiring a deep understanding regarding the chemistry and speciation of arsenic and antimony for optimum performance. Beside the numerous studies on the adsorption of arsenic and antimony using traditional adsorbents, research suggests other materials to be potential adsorbents for aqueous phase, including

biomaterials and wastes (Ungureanu et al., 2015). Figure 2.5 shows the flow diagram of adsorption process.

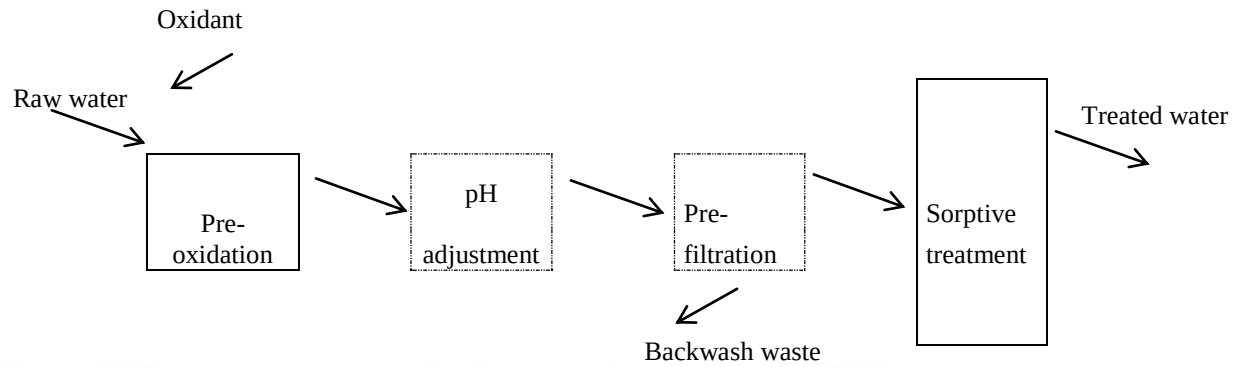


Figure 2.5 Flow diagram of adsorption process

2.4.6 Oxidation/Filtration

This process is normally used for iron/manganese removal from water. The principle of the process is the oxidation of iron and manganese in groundwater, which forms precipitable compounds and is retained in filters. When arsenic is present in the water, dissolved iron and arsenic (As^{3+}) are oxidized, then arsenic (As^{5+}) is adsorbed onto iron hydroxide compounds and retained in filters (Alpaslan et al., 2010). The most common techniques often involve medium filtration after air or chemical oxidation. Arsenic can also be removed by this process simultaneously by adsorption and coprecipitation mechanism. Suitable Fe:As ratio in water is important in order to remove arsenic efficiently (Arıkan, 2016). The flow chart of the oxidation/filtration is presented in Figure 2.6.

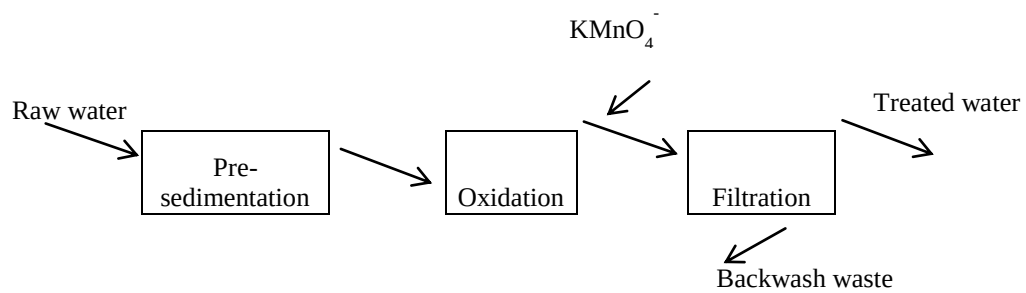


Figure 2.6 Flow diagram of oxidation/filtration process

2.5 Pre-Oxidation Processes

Converting reduced inorganic arsenite to arsenate, is crucial for optimum yield during removal and can be done using an oxidizing agent prior to any arsenic removal operation. Agents that are efficient in this step include chlorine, permanganate, and ozone, while chlorine dioxide, monochloramine, and ultraviolet (UV) light inefficient in oxidizing As(III). Although, UV photo-oxidation could perform well if the water is spiked with sulfite (Ghurye & Clifford, 2001).

Table 2.2 includes a summary of the advantages and disadvantages of some oxidation technologies.

Table 2.2 Comparison of oxidizing agents (EPA, 2003)

Oxidant	Benefits	Drawbacks
Chlorine	-Not costly (\$0.50/lb.) -Able to do primary disinfection -Secondary disinfectant residual -MnO₂ media regenerant -Oxidizes arsenic in less than 1 minute	-Forms disinfection by-products -Membrane fouling -Special handling and storage requirements
Permanganate	-Unreactive with membranes -Does not form disinfection by-products -MnO₂ media regenerant? -Oxidizes arsenic in less than 1 minute	-Costly (\$1.35/lb.) -Cannot do primary disinfection -Forms MnO₂ particulates -Pink Water -Difficult to handle -May require an additional oxidant for secondary disinfection
Ozone	-Does not require chemical storage or handling -Able to do primary disinfection -Does not leave chemical by-product in the water -Oxidizes arsenic in less than 1 minute in the absence of interfering reductants	-Sulfide and TOC interfere with conversion and increase the required contact time and ozone dose for oxidation -May require an additional oxidant for secondary disinfection

The most suitable oxidation technique depends largely on which arsenic treatment technology will be used, along with the advantages and disadvantages

involved. Small water systems tend to use chlorine disinfection with or without other methods, most often optimizing the chlorination process to also achieve As(III) oxidation.



CHAPTER 3

ADSORPTION OF ARSENIC/ANTIMONY COMPOUNDS

3.1 Theory of Adsorption

Adsorption refers to the separation of soluble substances that accumulate in a solution. The interface used for this purpose could be between the liquid and a gas, solid, or other liquid. Sufficient contact between the adsorbent and adsorbate results in equilibrium between adsorbed adsorbate and adsorbate in the solution. Adsorption capacity stands for how much material is adsorbed, and is a function of the concentration at a stable temperature. The outcome function is referred to as an adsorption isotherm (Tchobanoglous and Burton, 1991). A number of isotherms are used to define adsorbent capacity, including Brunauer-Emmett-Teller (BET), Freundlich, Tempkin, Langmuir, and Dubinin–Radushkevich. Here, we aimed to assess the Freundlich, Langmuir, and Temkin adsorption isotherms. Because Freundlich and Langmuir models mathematically describe adsorption from dilute solutions, when studied at average concentration ranges, adsorption data is known to conform to these isotherms. Therefore, these isotherms were used in this study.

3.2 Adsorption Isotherms

Equilibrium studies provide the capacity of the adsorbent (as mass of contaminant adsorbed per unit mass of adsorbent) for specific contaminants and graphically represented by isotherms.

The amount of arsenic uptake by adsorbents is calculated using the equation below:

$$q = \frac{(C_0 - C_e)V}{m} \quad (3.1)$$

Where q stands for the adsorption capacity (mg/g), C_0 for the initial arsenic concentration (mg/l), C_e for the equilibrium concentration of arsenic in the solution (mg/l), V for the volume of the solution (l), and m for the adsorbent mass (g).

3.2.1 Freundlich Isotherm

Freundlich isotherm can be used when there are more adsorption sites than contaminant molecules/ions, therefore defining multilayer and physical adsorption on a heterogeneous surface (Dada et al., 2012). Based on the unique bond energy for each adsorbing site, this isotherm assumes that sites with higher energy will be occupied first and adsorption energy will show an exponential decrease after the operation ends (Chaudhry et al., 2017).

Freundlich isotherm can be defined by the equation below:

$$q_e = k_f (C_e)^{\frac{1}{n}} \quad (3.2)$$

Where k_f stands for the capacity of adsorption (mg/g), q_e for adsorbed adsorbate amount per unit mass of adsorbent at equilibrium (mg/g), C_e for the equilibrium concentration (mg/L), and $1/n$ for the affinity coefficient.

Linearized form of equation (3.2) is:

$$\ln q_e = \ln k_f + \frac{1}{n}(\ln C_e) \quad (3.3)$$

If a plot of $\ln C_e$ vs. $\ln q_e$ gives a straight line which approves that the adsorption process complies with Freundlich Equation. The equilibrium constants can be determined from the slope and the intercept. The two model parameters, K_f and n , represent the sorption capacity and sorption intensity, respectively (Weber et al., 1991). A large value of n signifies that any large change in concentration at equilibrium would not affect the adsorption on the media. When n is equal to 1, the partitioning between the solid and liquid phase is linear and Freundlich coefficient (K_f) becomes same as distribution coefficient K_d . The Freundlich model does not account for finite adsorption capacity at high concentrations of solute, but when considering trace constituent adsorption, ignoring such physical constraints is usually not critical.

3.2.2 Langmuir Isotherm

This isotherm identifies the correlation between the concentration of adsorbate species in the solution and the number of active sites on adsorbent surface at equilibrium (Uslu et al., 2016). The adsorbate ion binds to a well-defined site on adsorbent surface, resulting in equivalent energy among all sites. After adsorption, the ion does not interact with the other ions. Hence, only a homogeneous monolayer is created on the surface (Dada et al., 2012).

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3.4)$$

Where q_e stands for the amount of adsorbed arsenic at equilibrium (mg/g), q_m for the capacity of adsorption (mg/g), C_e for the equilibrium concentration (mg/L), and b for the adsorption energy (L/mg).

The linearized form of equation (3.4) is:

$$\frac{1}{q_e} = \frac{1}{qm} + \frac{1}{qmb} \left(\frac{1}{C_e} \right) \quad (3.5)$$

If a plot of $1/C_e$ vs. $1/q_e$ gives a straight line which approves that the adsorption process complies with Langmuir Equation. The adsorption energy is obtained from the slope of the best-fit line and the maximum adsorption capacity of the adsorbent is determined from the intercept.

3.2.3 Temkin Isotherm

According to this isotherm, the decline in adsorption heat is linear, unlike suggested by the Freundlich isotherm. The Temkin isotherm involves a factor that primarily considers the interaction between adsorbate and adsorbent, which is the reason for the linear decline. Also, it considers that sites with higher energy will be occupied first (Chaudhry et al., 2017).

$$q_e = \frac{RT}{bt} \ln(AtCe) \quad (3.6)$$

Where q_e stands for the amount of arsenic adsorbed at equilibrium (mg/g), At for the equilibrium binding constant in the Temkin isotherm (L/g), bt for the constant in the Temkin isotherm (J/mol), R for the universal gas constant (8,314 J/mol.K), T for temperature (K), and C_e for the equilibrium concentration (mg/L).

The linearized form of equation (3.6) is:

$$qe = \frac{RT}{bt} \ln At + \frac{RT}{bt} \ln Ce \quad (3.7)$$

If a plot of qe vs. $\ln C_e$ gives a straight line which approves that the adsorption process complies with Tempkin Equation. The constants are determined from the slope and intercept.

Table 3.1 presents different adsorbents and their isotherm models.

Table 3.1 Adsorbents and suitable isotherm models

Adsorbents	Oxidation state	Isotherm model	R ²	Q _{max} (mg/g)	Reference
Iron-oxide coated natural rock(IOCNR)	As(T)	Langmuir	0.97	0.36	(Maji et al., 2011)
Bagasse fly ash-iron coated (BFA-IC)	As(III)	Temkin	0.99	0.0395	(Yadav et al., 2014)
	As(V)	Freundlich	0.99	0.0258	
Sponge iron char (SIC)	As(III)	Freundlich	0.98	0.0278	
	As(V)	Freundlich	0.99	0.0285	
Evaporation UltraCarb	As(III)	Langmuir	0.94	38.8	(Chen et al., 2007)
	As(V)	Langmuir	0.96	51.3	
Potassium ferrate	As(V)	Freundlich	0.98	162.02	(Lan et al., 2016)
	Sb(V)	Freundlich	0.98	129.93	
Synthesized akaganeite (SynA)	As(III)	Langmuir	0.96	35.0	(Kolbe et al., 2011)
	As(V)	Langmuir	0.96	30.7	
	Sb(V)	Langmuir	0.87	61.2	
GEH	As(III)	Langmuir	0.97	32.6	
	As(V)	Langmuir	0.94	29.1	
	Sb(V)	Langmuir	0.92	60.8	
WTRs	As(III)	Freundlich	0.98	132	(Ocinski et al., 2016)
	As(V)	Freundlich	0.99	76.73	
Iron-coated seaweeds	As(III)	Freundlich	0.98	4.2	(Vieira et al., 2017)
	As(V)	Freundlich	0.98	7.3	
DWTS-200	As(T)	Freundlich	0.98	6.527	This study
ZOC-DWTS	As(T)	Freundlich	0.97	7.38	

3.3 Adsorption Kinetics

Kinetic studies explain how fast the reaction proceeds towards equilibrium and define the reaction constant or adsorption coefficient.. Adsorption kinetics is based on the physical and chemical properties of the adsorbate and the adsorbent (Chaudhry et al., 2017). It is operated to designate the rate of adsorption by using concentration of adsorbate at a specific time and to define the rate constant or adsorption coefficient. In this study, kinetic coefficients were estimated using first order reaction, pseudo-first order reaction, second order reaction, and pseudo-second order reaction models.

3.3.1 First-Order Reaction Model

The equation for the first order rate depends on the concentration of the solution.

$$\frac{dC_t}{dt} = kC_t \quad (3.8)$$

Where C_t stands for the concentration at a contact time (mg/L), k for the first order adsorption rate constant, and C_0 for the initial concentration (mg/L).

The linearized form of equation (3.8) for boundary conditions $t=0$ to $t=t$ and $C_t=C_0$ to $C_t=C_t$ is:

$$\ln C_t = \ln C_0 - kt \quad (3.9)$$

Kinetic parameters can be obtained from the plot of $\ln C_t$ against time at initial concentration.

3.3.2 Pseudo-First Order Reaction Model

The pseudo-first order model is established upon the solid capacity.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3.10)$$

Where q_e stands for the capacity of adsorption at equilibrium (mg/g), q_t for the capacity of adsorption (mg/g), and k_1 for the pseudo-first order adsorption rate constant.

The linearized form of equation (3.10) for boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3.11)$$

k_1 can be obtained from the plot of $\ln(q_e - q_t)$ against time.

3.3.3 Second Order Reaction Model

Commonly used for adsorption, the equation for the second order rate is as follows:

$$\frac{dC_t}{dt} = k_2 C_t^2 \quad (3.12)$$

Where C_t stands for concentration at a contact time (mg/L), k_2 for the second order adsorption rate constant, and C_0 for the initial concentration (mg/L).

The linearized form of equation (3.12) for boundary conditions $t=0$ to $t=t$ and $C_t=C_0$ to $C_t=C_t$ is:

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \quad (3.13)$$

k_2 can be obtained from the plot of $(1/C_t)$ against time.

3.3.4 Pseudo-Second Order Reaction Model

This model predicated the adsorption capacity upon and can be formed as:

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \quad (3.14)$$

Where q_e stands for the adsorption capacity at equilibrium (mg/g), q_t for the capacity of adsorption (mg/g), and k_{p2} for the pseudo-second order adsorption rate constant.

The linearized form of equation (3.14) for boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ is:

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{1}{q_e} t \quad (3.15)$$

From the plotting the t/q_t versus t , k_{p2} is found from slope of line.

3.4 Adsorbents Used For Arsenic and Antimony Treatment

A variety of materials have been used as adsorbents for arsenic and antimony removal, such as granular ferric hydroxide, Fe–Mn binary oxide, activated carbon, alumina, granular titanium dioxide, potassium ferrate, ferrous sulfate, chitosan-coated biosorbent, and so on. The adsorbents are either of natural origin (e.g. clay minerals, natural zeolites, etc.) or the result of an industrial production and/or activation process (activated carbon, activated carbon, media with MnO_2 a TiO_2 layer, activated alumina, sand covered by iron hydroxides, etc.). Research so far has focused on using certain materials in their natural form or by chemical modifications for better durability, filterability, and adsorption performance (Ungureanu, 2015).

The maximum adsorption capacities (Q_m) for numerous adsorbents are given in Table 3.2 and Table 3.3. These values were often achieved using the Langmuir model. Because Q_m changes based on temperature, pH, etc., the experimental conditions for the given findings were also considered, although some studies fail to clearly lay out these conditions. Also, when comparing the Q_m values, the concentration range needs to be taken into account, as it tends to differ in a wide range between articles (from ≥ 100 mg/l to several $\mu\text{g/l}$).

Table 3.2 Maximum adsorption capacities (Q_m) reported in literature, for arsenic removal from aqueous solutions

Adsorbent	Initial concentration range (mg/L)	As oxidation state	pH	Q_m (mg/g)	T (K)	Ref.
Chars and activated carbons						
AC (from apricot stone)	4.5	As(V)	3	0.034	298	(Tuna et al., 2013)
AC-Fe(II)	4.5	As(V)	3	2023	298	
AC-Fe(III)	4.5	As(V)	3	3009	298	
AC(from oat hulls)	0.025-0.200	As(V)	5	3.08	-	(Chuang et al., 2005)
Biochar(derived from rice husk)	3-300	As(III)	8	19.3	298	(Samsuri et al., 2013)
Activated alumina, oxides and minerals						
AA	$\sim 0.1^1$	As(III)	7.6	0.18	-	(Singh & Pant, 2004)
AA grains	0.79-4.9	As(III)	7	3.48	-	(Lin & Wu, 2001)
Fe-Cu binary oxide	5-60	As(III)	7	122	298	(Zhang et al., 2013)
	5-60	As(V)	7	82.7	298	
Fe-Ti bimetal oxide	5-250	As(III)	7	85	303	(Gubta & Ghosh, 2009)
Fe-zeolite	0.05-2	As(III)	6.5	0.025	291	(Jimenez-Cedillo et al., 2011)
Sorbents based on residues and waste materials						
Concrete sludge heat treated	10-700	As(V)	~ 12	175	-	(Sasaki et al., 2014)
Fe-impregnated volcanic ash	5-100	As(V)	6.9	5.3	293	(Chen et al., 2011)
Magnetic Fe ₃ O ₄ nanoparticles(from tea waste)	2	As(III)	7	189	303	(Lunge et al., 2014)

Table 3.2 Continues

Adsorbent	Initial concentration range (mg/L)	As oxidation state	pH	Q _m (mg/g)	T (K)	Ref.
Sorbents based on residues and waste materials						
Water treatment residuals (Fe/Mn-WTRs)	20	As(III)	7.5-7.7	132.0	-	(Ocinski et al., 2016)
	20	As(V)	7.5-7.7	77.0	-	
Baggase fly ash-iron coated (BFA-IC)	0.050-0.150	As(III)	7.0	0.040	-	(Yadav et al., 2014)
	0.050-0.150	As(V)	12.0	0.026	-	
	0.050-0.150	As(III)	12.0	0.028	-	
	0.050-0.150	As(V)	12.0	0.029	-	
Drinking water treatment residuals (Al-WTR)	0.125-6.25 mmol/L	As(III)	6.0	0.537 mmol/g	-	(Caporale et al., 2013)
	0.125-6.25 mmol/L	As(V)	6.0	0.667 mmol/g	-	
Drinking water treatment residuals (Fe-WTR)	7.5x10 ⁻² -2.5 mmol/L	As(III)	6.0	0.149 mmol/g	-	
	7.5x10 ⁻² -2.5 mmol/L	As(V)	6.0	0.122 mmol/g	-	

Table 3.2 Continues

Adsorbent	Initial concentration range (mg/L)	As oxidation state	pH	Q_m (mg/g)	T (K)	Ref.
Oxides and minerals						
Iron (hydr) oxide modified zeolite (IHOMZ)	10	As(V)	3.5	1.69	326	(Nekhunguni et al., 2017)
Sorbents based on residues and waste materials						
Water treatment residual solids (lime WTRS)	0.043±0.0042	As(T)	8.11	0.16	295	(Gibbons&Gagnon, 2010)
Water treatment residual solids (alum WTRS)	0.043±0.0042	As(T)	7.96	0.003	295	
DWTS-200	0.040	As(T)	3.0	6.53	298	This study
ZOC-DWTS	0.040	As(T)	3.0	9.13	298	

Table 3.3 Maximum adsorption capacities (Q_m) reported in literature, for antimony removal from aqueous solutions

Adsorbent	Initial concentration range (mg/L)	Sb oxidation state	pH	Q_m (mg/g)	T (K)	Ref.
Metal oxides, hydroxides and minerals						
Ferric hydroxide	24-244	Sb(III)	3	101	293	(Xu et al., 2011)
Ferric hydroxide	0-25	Sb(V)	7	18.5	298	(Li et al., 2012)
Bentonite	0.05-4	Sb(III)	6	0.5	298	
	0.05-4	Sb(V)	6	0.556	298	(Xi et al., 2011)
Goethite	0.05-15	Sb(V)	7	18.3	298	(Xi et al., 2013)
Fe-Mn binary oxide	24-244	Sb(III)	3	214	293	(Xu et al., 2011)
Fe-Zr binary oxide	0-25	Sb(V)	7	60.4	298	(Li et al., 2012)
Sorbents based on residues and waste materials						
Zr(IV)-loaded saponified orange waste	$\sim 0-30^1$	Sb(III)	10.5	114	303	(Biswas et al., 2009)
	$\sim 0-36^1$	Sb(V)	2.5	145	303	
Fe(III)-loaded saponified orange waste	$\sim 0-30^1$	Sb(III)	10.5	136	303	(Biswas et al., 2009)
	$\sim 0-36^1$	Sb(V)	2.5	145	303	

¹Estimated range of equilibrium concentration

Table 3.3 Continues

Adsorbent	Initial concentration range (μmol/L)	Sb oxidation state	pH	Q _m (mmol/g)	T (K)	Ref.
Metal oxides, hydroxides and minerals						
Synthetic manganite	3.99-808	Sb(V)	3.0	0.784	298	(Wang et al., 2012)
			7.0	0.711		
			9.0	0.635		
Calcined Mg/Al LDH (CLDH)	50 mg/L	Sb(V)	7.0	303.3 mg/g	298	(Lee et al., 2018)
9.41 mg/g						
Uncalcined Mg/Al LDH (ULDH)	50-100	Sb(III)	4.0	0.353	293	(Guo et al., 2014)
			7.0	0.365		
			9.0	0.439		
Sb(V)		4.0	0.201			
		7.0	0.062			
		9.0	0.067			
Sb(V)		4.0	0.192			
		7.0	0.091			
		9.0	0.064			

Table 3.3 Continues

Adsorbent	Initial concentration range (μmol/L)	Sb oxidation state	pH	Q _m (mmol/g)	T (K)	Ref.	
Metal oxides, hydroxides and minerals							
β-FeOOH	50-100	Sb(III)	4.0	0.194	293	(Guo et al., 2014)	
			7.0	0.228			
			9.0	0.280			
		Sb(V)	4.0	0.240			
			7.0	0.165			
			9.0	0.091			
		Sb(III)	4.0	-			
			7.0	-			
			9.0	-			
γ-FeOOH		50-100	Sb(V)	4.0			0.280
				7.0			0.087
				9.0			0.053
			Sb(III)	4.0			0.208
				7.0			0.249
				9.0			0.258

3.4.1 Activated Carbons

ACs are the most common commercial materials when treating water and wastewater, though their potential to adsorb As species and the conditions for optimal performance are yet to be clarified (Dambies, 2004). They demonstrate no particular affinity for removing heavy metals or arsenic in their virgin form (Deng et al., 2005; Gu et al., 2005; Tuna et al., 2013). Besides, research reports ACs to not remove As(III) (Dambies, 2004). Still, there are studies highlighting significant amounts of adsorption for As(V) and As(III) (34,5 mg As(V)/g and 89,2 mg As(III)/g) (Pattanayak et al., 2000).

3.4.2 Activated Alumina

The United Nations Environmental Program (UNEP) agency has suggested activated alumina (AA) as one of the best materials for removing As from water. AA is used in fixed bed reactors for the removal of certain water contaminants, including fluoride, silica, selenium, arsenic, and organics. Saturated AA beds are regenerated using a strong base, flushed with water, and neutralized using a strong acid. However, AAs are costly to prepare and generate solid and liquid wastes (Choong et al., 2007).

AA has low selectivity against As(III) because of the neutral molecular charge at <9.2 pH, necessitating the pre-oxidation of As(III) to As(V) (EPA, 2003).

3.4.3 Other Metal Oxides

There are other natural or synthesized metal oxides that are considered alternatives to AA for the adsorption of arsenic. Giles et al. (2011) reviewed studies on removing arsenic for drinking water treatment using some iron and aluminum-based adsorbents. These include ferrihydrite, iron oxides/oxyhydroxides, granular ferric hydroxide, synthetic and iron-aluminum hydroxides, bauxite, alumina, calcined bauxite, and layered double hydroxides.

Titanium, manganese, and zirconium are other metal oxides used to remove As. Moreover, recent research has focused on bimetal oxides for their synergistic effect and significant adsorption capacity (Table 3.1 and Table 3.2).

Other adsorbents and oxidants for antimony include minerals. Research reports that iron and aluminum oxides can uptake Sb(III) by the inner-sphere complexation (Xi et al., 2011, 2013). Bentonite was found to have an adsorption capacity of 0.37-0.56 mg/g for Sb(III) and 0.27-0.50 mg/g for Sb(V) and at 278-323 K temperature and a pH of 6 (Xi et al., 2011). Goethite was shown to have an adsorption capacity of 18-19 mg/g for Sb(III) at a pH of 7 using initial concentrations up to 15 mg/l (Xi et al., 2013). Both minerals were found to demonstrate equilibrium after a contact time of 24 hours (Xi et al., 2011, 2013).

Binary iron oxides have been studied for their performance in removing Sb(V) thanks to their significantly better adsorption capacity than single metal oxides (Li et al., 2012; Xu et al., 2011). Research reported iron-zirconium bimetal oxide to have an adsorption capacity of 51 mg/g at a pH of 7 using the Langmuir model (Li et al., 2012). The adsorption of Sb (V) on iron-zirconium bimetal oxide has been called endothermic, with well modeled kinetics using the pseudo second-order model. Co-existing anions like sulfate, nitrate, and chloride have provided no significant yield in

removing Sb(V) at normal concentrations. Besides, phosphate, carbonate, and silicate have demonstrated inhibitory effect at high concentrations.

3.4.4 Waste Materials

One group of potential adsorbents for arsenic and antimony are waste materials used in agriculture, fishery, livestock, industry, and construction, as they already have almost no economic value and constitute problems in disposal. They still need to be disposed when no more regeneration is possible. Also, landfill disposal and incineration processes require considering the amount of arsenic and antimony in the adsorbents to prevent hazards. Eco-friendlier alternatives like their use in construction materials appeals to researchers, although this needs to be investigated accurately.

For this purpose, several waste materials like concrete sludge, fly ash, volcanic ash, green bean husk waste, tea waste, blue pine wood shavings, walnut shell, chick peatesta, and drinking water treatment sludges were used in the literature (Caporale et al., 2013; Chen et al., 2011; Iqbal et al., 2013; Lunge et al., 2014; Saqib et al., 2013; Sasaki et al., 2014; Wang and Tsang, 2013).

Caporale et al. (2013) analysed the adsorption of As(III) and As(V) using iron and aluminum-based water treatment residuals (WTRs) at different pH values with competing ligands (phosphate, citrate, and oxalate). Both residuals were found to have a high affinity for As oxyanions, with better adsorption capacity for As(III) and As(V) in the aluminum-based WTR, which was associated with its bigger surface area. The authors reported a higher influence of particle size on adsorption in iron-based WTR. Also, smaller fractions were found to adsorb more As(III) and As(V) than larger fractions. For both WTRs, As(III) adsorption was found to increase with pH up to near neutral values and decrease at higher values. As(V) adsorption, on the

other hand, showed a steady decline with increasing pH. Competing ligands showed a higher ability to inhibit adsorption in As(III) compared to As(V), especially in aluminum-based WTR.

Gregor (2001) investigated As(V) and As(III) using synthetic flocculent aid and aluminum-based WTRs, and found that As(III) could be adsorbed after being converted to As(V) during a chlorination step.

Jung et al. (2016) analyzed the recovery of coagulants from WTRs and reusing recovered coagulant residuals (CRs) using response surface methodology (RSM). The authors used this method for the optimization of independent variables like pH and reaction time on aluminum recovery. They reported a recovery rate of $97.5 \pm 0.4\%$, at 99.5% of their prediction. After comparing the recovered coagulant with commercial coagulants from textile wastewater treatment, they found performance values of $68.5 \pm 2.1\%$ COD, $97.2 \pm 1.9\%$ turbidity, and $64.3 \pm 1\%$ color removal at 50 mg Al/l, suggesting a fair potential of using recovered coagulants in treating wastewater. They also performed a feasibility test for using CR as an adsorbent for the adsorption of phosphate from aqueous solution. Considering the adsorption equilibrium at temperatures of 10-30°C and baseline pH values of 3-11, the main mechanism of phosphate adsorption onto CR was found to be endothermic, with energetically heterogeneous surfaces. The highest adsorption capacity (11.93 mg P/g) was achieved at a baseline pH of 5.0. Although, a pH of 7.0 appears to be more appropriate for maintaining adsorption capacity at 11.71 mg P/g and for the equilibrium pH of 6.4. The authors concluded that with its low cost, CR could potentially be an alternative for removing phosphate in wastewater treatment.

Ocinski et al. (2016) tested the adsorption of As(III) and As(V) using WTRs that are by-products of de-ironing and demanganization of infiltration water. They observed a high surface area of WTRs ($120 \text{ m}^2\text{g}^{-1}$), with mostly amorphous structure and small fractions of crystalline quartz and ferrihydrite. The maximum

adsorption capacities were found as 132 mg for As(III)g⁻¹ and 77 mg for As(V)g⁻¹. The removal of As(V) was found to decrease with increasing pH, with a clear decline above pH_{pzc}. The adsorption of As(III), on the other hand, stayed constant at acidic and neutral pH values. Moreover, the spent adsorbent was found to have a potential for regeneration. The adsorbed arsenic could be desorbed with high effectiveness using NaOH/NaCl solution, but the second step of regeneration was unlikely because the WTRs consisted of fine particles, smaller than 1 mm in size.

3.5 Pre-treatment and Modifications Reported in the Literature

According to the literature, materials are generally pre-processed by using physical or mechanical methods (i.e. drying, milling, sieving, washing, etc.). After these pre-operations, materials are modified by coating. In certain cases, coating may be accomplished with heating. The results of the literature survey on this subject are summarized in Table 3.4. In table, processes and their objectives are presented together with methods applied for each operation.

In generally, modification is performed by coating. For iron coating purposes FeCl₃+NaOH solutions or FeNO₃ solution have been extensively used. Zirconium, lanthanum and manganese coating processes have been achieved by ZrOCl₂.8H₂O, ZrOCl₂, MnCl₂, KMnO₄ and LaCl₃ (Arıkan, 2016; Chaudhry et al., 2017a; Chaudhry et al., 2017b; Chaudhry et al., 2017c; Gupta et al., 2005; Jeon et al., 2009; Li et al., 2011; Liu et al., 2018; Maji et al., 2011; Mostafa et al., 2011; Nouh et al., 2015; Tan et al., 2018; Wang et al., 2018b). Also, a Fe-Zr binary oxide adsorbent has been consisted of using zirconium and iron sulphate for antimony removal (Li et al., 2012). Ocinski et al., 2016 was performed arsenic removal using water treatment sludges containing iron and manganese oxides as synergetic effect of two metals.

Table 3.4 Pre-processing and modification methods for DWTRs

Process	Method (how?)	Goal	References
Drying	On air and oven (105-140°C)	to evaporate water and to prepare milling	Caporale et al., 2013; Hofman-Caris et al., 2017; Ocinski et al., 2016; Wang et al., 2016; Wang et al., 2018a
Milling	In a china mortar	to cut into small pieces and prepare to sieving	
Sieving	With standard sieve	to obtain various size of DWTRs (as powder and granule)	
Washing and drying again	Deionized water and oven	to remove impurities and get ready usage	
Heating	Oven (200-1600°C)	to increase surface area of materials	Afarani et al., 2013; Chaudhry et al., 2017b ; Wang et al., 2016; Wang et al., 2018a
Coating	With metal like iron, manganese, lanthanum and zirconium	to increase adsorption capacity of materials and create synergetic effect via more than one metal	Arikan, 2016; Chaudhry et al., 2017a; Chaudhry et al., 2017b; Chaudhry et al., 2017c; Gupta et al., 2005; Jeon et al., 2009; Li et al., 2011; Liu et al., 2018; Maji et al., 2011; Mostafa et al., 2011; Nouh et al., 2015; Tan et al., 2018; Wang et al., 2018b; Xu et al., 2011

References marked bold were treated arsenic/antimony.

On the other hand, data regarding to modification by heating process for iron based adsorbents is rare (Chaudhry et al., 2017b; Wang et al., 2016, 2018a).

The results of the literature survey on modification of the materials are shown in Table 3.5 and 3.6.

Table 3.5 Material coating methods in the literature

Modified material	Preparation for coating	Coating with	Contact time	After coating process	Explanation	Reference
Ironoxide coated sand and sepiolite (20 g)	Washed and dried 105°C	50 ml 0.5 M FeNO ₃ (pH 10)	2 h	200°C drying for 15 h, rinsing with distilled water, 200°C drying	As removal, over 90% efficiency	Arkan, 2016
Zirconium oxide coated sand (50 g) (106-125 µm)	Treated with H ₂ O ₂ and HNO ₃	2 ml, 1 M citric acid and 250 ml, 0.125 M ZrOCl ₂ .8H ₂ O	Agitated 323 °K for 30 min and room temperature for 10 h	378°K drying, treated thrice, rinsing with distilled water, 378°K drying for 5 h	As removal, 94.3% efficiency	Chaudhry et al., 2017a
Iron-Zirconium Binary Oxide-Coated Sand (IZBOCS) (50 g)	Washed, treated with HCl sol. and washed, soaked 2%H ₂ O ₂ for 24 h and washed, dried 105°C for 5 h	100 ml, 0.025 M ZrOCl ₂ and 100 ml, 0.1 M FeCl ₃	Agitated 40 °C for 1 h and pH 7.5 for 5 h	Aged for 24 h, filtered, 105°C drying for 24 h, rinsing several times with distilled water, 300°C drying for 5 h	As removal, 92.4% efficiency	Chaudhry et al., 2017b
Manganese oxide coated sand grain (20 g)	Sieved (106-125 µm), soaked 2%H ₂ O ₂ for 24 h and washed	250 ml, 0.025 M MnCl ₂ and 200 ml, 0.05 M KMnO ₄	Agitated 70-80 °C for 24 h	Aged for 10 h, filtered, drying at room temperature, 160°C drying for 5 h, rinsing with distilled water and 105°C drying	Chrome removal, 97.5% efficiency	Chaudhry et al., 2017c

Table 3.5 Continues

Modified material	Preparation for coating	Coating with	Contact time	After coating process	Explanation	Reference
Ironoxide coated sand (200 g)	Washed and dried in oven	80 ml 2 M FeNO_3 (pH 11)	2 min	110°C drying for 14 h, rinsing with distilled water, 105°C drying	As removal, 99% efficiency	Gupta et al., 2005
Iron coated zeolite (2000 g)	-	1 L 10% FeCl_3 (pH 10)	Agitated 50 °C for 1 h	drying	As removal, max. ads. capacity: 0.68 mg/g	Jeon et al., 2009
Fe exchanged natural zeolite (120 g) (2 mm)	-	360 ml 20 mmol/L Fe(III) solution (pH 9)	20 h 150 rpm	Rinsing, allow to dry naturally	As removal, max. ads. capacity: 100 mg/kg	Li et al., 2011
Hydrated zirconium oxide coated carbon nanotubes (CTNs) (200 mg)	-	7 ml zirconium n-propoxide in 100 ml absolute ethanol	30 min	75°C drying for 90 min, rinsing with mixture of water and ethanol, 105°C drying	As removal, max. ads. capacity: 78.2 mg/g As(III) , 124.6 mg/g As(V)	Liu et al., 2018
Ironoxide coated rock (100 g) (0.148 mm)	Washed and dried 140oC	50 g FeNO_3 in 150 ml water	30 min	140°C drying, rinsing and 140°C drying	As removal, 75% efficiency	Maji et al., 2011

Table 3.5 Continues

Modified material	Preparation for coating	Coating with	Contact time	After coating process	Explanation	Reference
Ironoxide coated perlite (100 g)	Soaked in H ₂ SO ₄ sol. (pH 1) for 24 h then rinse 3 times with distilled water dried 105oC for 24 h	FeCl ₃ (pH 9.5)	60°C 200 rpm for 24 h	105°C drying for 24 h, rinsing 6 times with distilled water, 60°C drying	As removal, 100% efficiency, max. ads. capacity: 0.39 mg/g	Mostafa et al., 2011
Manganese oxide coated zeolite	Soaked in tap water for 24 h then rinse with distilled water dried 373°K	0.5 M KMnO ₄ and 37.5% HCl	Agitated for 1 h	Filtered, rinsing to pH 7 with distilled water, drying at room temperature	Fe(III) 93.3%, Cu(II) 83.3%, Ni(II) 71.2%, Zn(II) 81%, Cr(III) 80% efficiencies	Nouh et al., 2015
Manganese oxide coated rice straw biochar (2 g)	Washed, dried 80°C for overnight and sieved (0.154 mm)	100 ml, 0.632 g KMnO ₄	Agitated 30 oC for 8 h	Aged for overnight, rinsing with distilled water, 80°C drying for 24 h	Lead removal, max. ads. capacity: 305.25 mg/g	Tan et al., 2018
Lanthanum-modified DWTR	heat treated at 500°C for 4 h	LaCl ₃ solution (pH 9)	Agitated 60°C for 5 h	Aged for 24 h, filtered, rinsing three times with distilled water, drying in oven.	Phosphorus removal, max. ads. capacity: 2.87-18.1 mg/g.d	Wang et al., 2018b
Fe-Mn Binary Oxide(Fe/Mn:3/1)	-	200 ml KMnO ₄ and 200 ml FeSO ₄ (pH 7-8)	Agitated for 5 h	Aged for 5 h at room temperature, washed distilled water 3 times, filtered and dried 60oC, sieved <50µm)	Antimony removal, 81.3% efficiency, max ads. capacity:1.76 mmol/g	Xu et al., 2011

Table 3.6 Heating experiences reported in the literature

Heated material	Preparation for heating	Temperature	Contact time	After heating process	Explanation	Reference
Alumina granules (300 g)	Alumina and 5 wt% of silica powders granulated using a liquid binder, dried at room temperature	1400, 1500, 1600°C	2 h	sieved with mesh numbers 6-100	-	Afarani et al., 2013
Iron-Zirconium Binary Oxide-Coated Sand (IZBOCS) (50 g)	Washed, treated with HCl sol. and washed, soaked 2% H ₂ O ₂ for 24 h and washed, dried 105°C for 5 h, coated with ZrOCl ₂ and FeCl ₃ , dried and washed	300°C	5 h	cooling at room temperature	As removal, 92.4%	Chaudhry et al., 2017b
DWTRs (20 g)	Air-dried, sieved less than 0.25 mm	200, 300, 400, 500, 600°C (oxygen limited environment)	4 h	rinsing with distilled water, 50°C drying	Mercury removal, max. ads. capacity: 147 mg/g	Wang et al., 2016
DWTRs	Air-dried, ground, and sieved to a diameter of less than 0.147 mm.	500°C (oxygen limited environment)	4 h	washing with deionized water and oven-dried	Phosphorus removal	Wang et al., 2018a

Batch studies are carried out to specify operational parameters and adsorption capacity of the materials. The results of the literature survey on this subject are summarized in Table 3.6. In table, adsorbent dose, contact time, pH, temperature, initial arsenic concentration, arsenic removal efficiency and adsorption capacity are presented. Beside batch studies, column studies to remove arsenic and antimony in the literature are quite limited. Thirunavukkarasu et al., 2003 reported 100 $\mu\text{g/L}$ initial As containing water 96% arsenic removal for 6 hours equilibrium time with GFH at a pH of 7.6. For column studies, bed volumes achieved up to 5 ppb were 1140 for As(V) removal and 1260 for As(III) removal. Kundu & Gupta (2007), performed arsenic removal by iron oxide-coated cement (IOCC) from 0.5 mg/L to 2.7 mg/L initial arsenic concentrations with continuous fixed bed columns and found IOCC an effective adsorbent. In another study, water treatment ferric and lime residual solids was used in fixed bed and batch system for arsenic removal and carried out likewise to GFH in batch adsorption studies. Ferric residuals and GFH performed similarly to or better than GFH performed in column experiments (Gibbons & Gagnon, 2010).

Regeneration and reuse of adsorbent is very important issue for a more cost effective treatment. But, due to particle deformation of granular iron based media, it is not possible to regenerate media in most instances and there are limited studies about regeneration. Chen et al. (2015) searched regeneration of ferric adsorbent removed arsenic and showed up to 80% of the arsenic can be cleared from exhausted media. Regenerated media was able to obtain arsenic removal parallel to virgin media. But, the authors reported that media dissolution under the acidic condition could be problematic if the pH is below 2.

A summary for batch and column studies in the literature are shown in Table 3.7 and Table 3.8, respectively.

Table 3.7 Performances of various materials in the literature (Batch experiments)

Adsorbent and dose	pH- temperature	Initial As/Sb Concentration ($\mu\text{g/l}$)	As Removal (%)	Sb Removal (%)	Contact Time	Adsorption Capacity	Reference
Modified Sepiolite (5 g/L)(Synthetic water)	7.0	538	91.6 AsT	-	4 h	0.501 mg/g	Arıkan, 2016
Modified Sand (5 g/L)(Synthetic water)	7.0	100	91.2 AsT	-	4 h	0.142 mg/g	Arıkan, 2016
Ironoxide coated sand (20 g/L) (Synthetic water)	7.5	100	99 As(III)	-	2 h	0.02857 mg/g	Gupta et al., 2005
Iron Oxides (HFO, γ -FeOOH, β -FeOOH, α -FeOOH, α -Fe ₂ O ₃) (0,4 g/L)	4 Sb(V)- 9 Sb(III) 20.5oC	50-200 $\mu\text{mol/L}$	-	-	24 h	936 $\mu\text{mol/g}$ HFO-Sb(V) 440 $\mu\text{mol/g}$ α -FeOOH-Sb(III)	Guo et al., 2014
DWTRs (0.5 g/L)	15°C	100 As	-	-	72 h	0.4 mg/g As(V)	Hofman-Caris et al., 2017

Table 3.7 Continues

Adsorbent and dose	pH- temperature	Initial As/Sb Concentration ($\mu\text{g/l}$)	As Removal (%)	Sb Removal (%)	Contact Time	Adsorption Capacity	Reference
Iron coated zeolite (33 g/L) (Synthetic water)	3-10	20120	99.9 As(V)	-	30 min	0.68 mg/g As(V)	Jeon et al., 2009
GEH (2 g/L)(Synthetic water)	7.0	10000	-	-	24 h	0.25 mg/g Sb(V) 2.05 mg/g As(V) 0.07 mg/g As(III)	Kolbe et al., 2011
Potassium Ferrate(K_2FeO_4)(0.05 g/L)	6.5 As(III) 4 Sb(III)	2000	-	65	24 h	162.02 mg/g As(III) 129.93 mg/g Sb(III)	Lan et al., 2016
Mg/Al CLDH(400oC calcination) (0.2 g/L)	7.0-25°C	50000	-	-	6 h As(V) 3 h Sb(V)	102.9 mg/g As(V) 303.3 mg/g Sb(V)	Lee et al., 2018
Mg/Al ULDH (not calcination) (0.2 g/L)	7.0-25°C	50000	-	-	2 h As(V) 2 h Sb(V)	22.6 mg/g As(V) 19.2 mg/g Sb(V)	Lee et al., 2018
Fe-exchanged natural zeolite (20 g/L) (Synthetic water)	7.8	500	-	-	24 h	0.1 mg/g As(III) 0.05 mg/g As(V)	Li et al., 2011

Table 3.7 Continues

Adsorbent and dose	pH-temperature	Initial As/Sb Concentration (µg/l)	As Removal (%)	Sb Removal (%)	Contact Time	Adsorption Capacity	Reference
Fe-Zr bimetal oxide (0.2 g/L)	7-25°C	10000	-	-	3 h	51 mg/g Sb (V)	Li et al., 2012
ZIF-8 nanoparticles (0.2 g/L) (Syntetic water)	8.6-25°C	0.06-1.10 mmol/L	-	-	5 h As(III) and As(V) 7.5 h Sb(V)	2.02 mmol/g As(III) 1.42 mmol/g As(V) 0.86 mmol/g Sb(V)	Liu et al., 2018
Zn/Fe LDH (0.2 g/L)	7-298 °K	50000	-	-	8 h	151.37 mg/g As(V) 122.03 mg/g Sb(V)	Lu et al., 2015
Ironoxide coated rock (15 g/L) (Groundwater)	7.5-25°C	40	75 AsT	-	6 h	0.36 mg/g	Maji et al., 2011
Ironoxide coated perlite (10 g/L) (Syntetic water)	6.5-7	1000 As(V)	100 As(V)	-	5 min	0.39 mg/g	Mostafa et al., 2011
WTRs (1 g/L)	4.0	20000	-	-	5 h	132 mg/g As(III) 77 mg/g As(V)	Ocinski et al., 2016

Table 3.7 Continues

Adsorbent and dose	pH-temperature	Initial As/Sb Concentration (µg/l)	As Removal (%)	Sb Removal (%)	Contact Time	Adsorption Capacity	Reference
TiO ₂ media (0.2-22 g/L)	8.2	34.8 As(III) 142.5 As(V) 244.7 Sb(V)	100 AsT	99.4 (syntetic water) 100 (mining wastewater)	4 h	-	Qiu et al., 2019
Synthetic Manganite (0.4 g/L)	7-25°C	3.99-808 µmol/L	-	99.00	15 min	-	Wang et al., 2012
Goethite (1 g/L)	7-298°K	1000 Sb(III)	-	99 Sb(III)	24 h	-	Xi et al., 2013
Drinking water treatment sludges (DWTs-200) (1 g/L)	3	35 As 90 Sb	98.61	85.10	3 h	-	This study
Drinking water treatment sludges coated with zirconium (ZOC-DWTS) (1 g/L)	3	35 As 90 Sb	99.15	85.30	3 h	-	This study

Table 3.8 Performances of various materials in the literature (Column studies)

Material	As influent (mg/L)	Sb influent (mg/L)	Flow rate (ml/min)	Height (cm)	Diameter (cm)	Break through volume for As (L)	Break through volume for Sb (L)	Break through point for As (mg/L)	Break through point for Sb (mg/L)	Exhaust volume for As (L)	Exhaust volume for Sb (L)	Reference
Ironoxide coated sand	0.62	-	3	20	1.1	5.3	-	0.01	-	13	-	Arikan, 2016
Ironoxide coated sepiolite	0.514	-	3	20	1.1	23	-	0.01	-	46	-	Arikan, 2016
Iron modified activated carbon (UltraCarb)	0.04-0.06	-		13.5	0.5	31-34	-	0.01	-	-	-	Chen et al., 2007
Water treatment residual solids (TP-WTP)	0.043	-	2	20	2.5	2.587	-	0.01	-	-	-	Gibbons&Gagnon, 2010
Ironoxide coated zeolite	2.00	-	0.5	17	1.1	4.8	-	0.01	-	-	-	Jeon et al., 2009

Table 3.8 Continues

Material	As influent (mg/L)	Sb influent (mg/L)	Flow rate (ml/min)	Height (cm)	Diameter (cm)	Breakthrough volume for As (L)	Breakthrough volume for Sb (L)	Break through point for As (mg/L)	Break through point for Sb (mg/L)	Exhaust volume for As (L)	Exhaust volume for Sb (L)	Reference
Ironoxide coated cement	1.35	-	8.5	20	2	5.61	-	0.01	-	-	-	Kundu&Gupta, 2007
Drinking water treatment sludges (DWTS-200)	0.04	0.08	5	20	1.7	6004	640	0.01	0.005	9748	4564	This study
Drinking water treatment sludges coated with zirconium (ZOC-DWTS)	0.04	0.08	5	20	1.7	7444	820	0.01	0.005	13780	6004	This study

3.6 Granulation of DWTS

Powdered DWTS needs to be transformed granular DWTS to meet industrial demands, with high mechanical strength, improved hydraulic conductivity, and much slower clogging. Although, research on DWTS granulation remains scarce. Common technologies include;

- pelleting and sintering (Afarani et al., 2013; Hoffman-Caris et al., 2017; Zou et al., 2012),
- wood loading (Soleimanifar et al., 2016),
- gel entrapment (Jung et al., 2016; Li et al., 2018)

Li et al. (2018) mixed powdered DWTS (10 g) and 100 ml 2% sodium alginate solution and added the mixture into a $\text{FeCl}_3(2\%)$ solution using a syringe to form granular DWTS. The spheres were washed and air dried.

Afarani et al. (2013) realized synthesis of alumina granules and alumina was heated at 1400, 1500 and 1600°C. Increasing the sintering temperature reduced the surface area, pore size, and extent of attrition/breakage of the sintered granules during the attrition and bulk compression tests.

Hoffman-Caris et al. (2017) pelletized the material in order to improve handling of the sludge. At the laboratory this was done by dissolving a binder (carboxymethyl cellulose; CMC) into the wet sludge (ca. 10% solids). The material then was dried, crushed and sieved to obtain the desired particle sizes. When sludge had high solid matter capacity, cement and sodium water glass were used as binders.

3.7 Arsenic and Antimony Adsorption Mechanism on Metal Oxide Based Adsorbents

Metal oxide-based adsorbents can be procured as microparticles, nanoparticles, nanocomposites, or granules. Research in recent years has shown major progress in techniques of synthesis of metal oxide materials. Metal oxides, particularly iron and aluminum oxides, are also components of industrial wastes (like red mud), fly ashes, and WTRs from drinking water treatment (Ocinski et al., 2016). Among these wastes, WTRs are the most up and coming materials, because they are not hazardous, they are acquired from natural water operations, display neutral pH, and indicate a high capacity for the arsenic and antimony adsorption.

As speciation is determined primarily based on pH and redox potential (Eh) (Smedley & Kinniburgh., 2002). As can be seen Figure 3.1, in aqueous solution, As(V) exists as H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-} anions above pH 2, therefore, iron hydroxide that is attached to the adsorbent materials surfaces may remove these ions. On the contrary, As(III) is present as H_2AsO_3^- , HAsO_3^{2-} , AsO_3^{3-} anions above pH 9. H_3AsO_3 is dissociated between pH 6–9 as a small percentage. Hence, pH must be above 7 for an effective As(III) treatment.

The mechanism of arsenic removal by adsorption on metal oxide-based adsorbents that implies to the surface complexes formation between the surface hydroxyl groups and soluble arsenic species as arsenic attaches to the metal oxide sites of the material where arsenite and arsenate can be adsorbed easily. For this reason, using metal oxide especially iron-based waste materials is cheaper and effective than using metal oxides.

Ociński & Mazur (2020) reported a decline in maximum adsorption capacity (q_m) for As(V) on a Fe–Mn-based adsorbent (from 26.80 to 13.49 mg/g) as pH increased

from 6.0 to 8.5. Because the ratio of HAsO_4^{2-} to H_2AsO_4^- is higher at pH value of 8.5 than pH value of 6.0. Stronger pushing between As(V) and the Fe–Mn based adsorptive media performs at higher ratio.

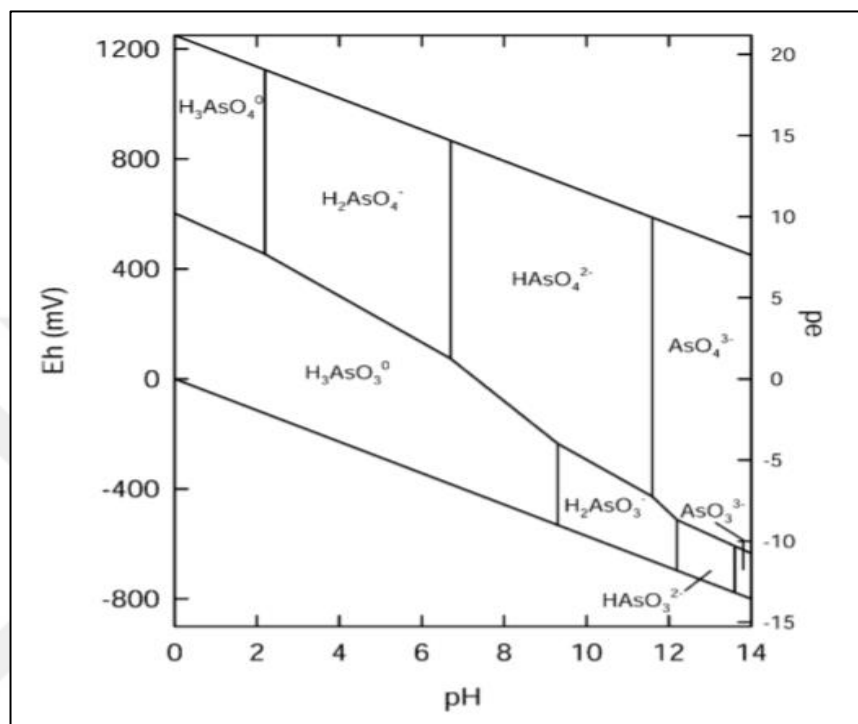


Figure 3.1 Eh-pH diagram for arsenic species in the As-O₂-H₂O system

Sb(V) occurs as $\text{Sb}(\text{OH})_6^-$ and is the dominant species in oxic waters. However, Sb(III) is more stable and occurs as $\text{Sb}(\text{OH})_3$ in anoxic solutions (Wang et al., 2012).

$\text{Sb}(\text{OH})_6^-$ is more soluble than $\text{Sb}(\text{OH})_3$ and adsorbs less well than $\text{Sb}(\text{OH})_3$ to metal (hydr)oxide surfaces. Thereby, the mobility of antimony is affected by oxidation processes.

$\text{Sb}(\text{OH})_6^-$ is less adsorbed onto metal hydroxides with increasing pH. It can be explained by i) when pH increases, less protonated surface sites, which are engaged by $\text{Sb}(\text{OH})_6^-$ by ligand exchange, ii) for ligand exchange, at higher pH values,

competition with OH^- ions and iii) when pH increases, increased electrostatic pushing between the $\text{Sb}(\text{OH})_6$ and the more negatively charged mineral surfaces (Verbeeck et al., 2019).

According to a study about antimony adsorption, when the pH raised from 3.0 to 10.0, the adsorption capacity of $\text{Sb}(\text{V})$ (at the pH of 3–10, exists $\text{Sb}(\text{OH})_6$ form) on the negatively charged modified iron filings decreased from 12.2 to 4.24 mg/g. Because higher pH value cause to higher ratio of $\text{Sb}(\text{OH})_6$ to $\text{Sb}(\text{OH})_5$, stronger pushing between the adsorbate and adsorbent happened (Zhang et al., 2019).

3.8 Desorption Behaviour of Arsenic and Antimony Loaded Adsorbents

The desorption of the adsorbent is essential in order to recover the used adsorbent. Release of adsorbed arsenic and antimony occur as a consequence of reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ via acid and alkaline washing depending on adsorbent surface charge (Giles et al., 2011). Surface hydroxyl groups transform negatively charged at high pH values. Therby, negatively charged arsenic and antimony species desorp from the adsorbent efficiently. Afterwards, adsorbent is rinsed with dilute hyrocloric acid solution and surface hydroxyl groups become pronated. So, the adsorbent material can be reuse for the next treatments (Arıkan, 2016).

Tufano et al. (2008) carried out a desorption study of arsenic from goethite, haematite and ferrihydrite coated sands to perform desorption of $\text{As}(\text{III})$ and $\text{As}(\text{V})$. Experiments gave the following order of competitious capacity: phosphate (PO_4^{3-}) > carbonate (CO_3^{2-}) > sulphate (SO_4^{2-}) > chloride (Cl^-).

Natale et al. (2013) aimed arsenic desorption from an activated carbon media and achieved more than 80% of arsenic recover using sodium chloride solution.

Helle et al. (2008) indicated that arsenic desorption from calcite complete within hours and was relatively fast. This study demonstrated that arsenic was not easily combined into the calcite crystal lattice.

3.9 Fixed Bed Column Design

In the adsorption system, various technique is occurred like batch, continuous moving and continuous fixed bed, pulsed bed and continuous fluidize bed. Fixed bed adsorption column is more feasible and preferable for removing different contaminants. Breakthrough curves represent the productivity of fixed bed adsorption column. Adsorption mechanism is hinged on numerous criteria, such as film diffusion resistance, equilibrium with the adsorbent, axial dispersion, and intraparticle diffusion resistance (Miralles et al., 2010).

The relation among the fixed bed adsorption and breakthrough curve was expressed using primary sorption zone and mass transfer zone. As seen in Figure 3.2, raw water is fed into the inlet of the column, and during the first stage of the process, the adsorbate is adsorbed effectively and rapidly by several top layers of the adsorbent. This was because of the higher amounts of adsorbent and lower amounts of adsorbate in these layers, facilitating the escape of adsorbate into the lower layer and not allowing adsorbate out of the adsorbent. Thus, mass transfer zone or primary adsorption zone is achieved near the upper of the column. Adsorbate concentration (C) is zero at this point, as is the effluent to initial concentration ratio. Then, the top adsorbent layer is slowly saturated by feeding the adsorbate solution into the column, making the adsorbent less effective. Primary adsorption zone tracks decrease to the fresher adsorbent part in the column. Moreover, the inclination suggests that higher amounts of adsorbate get out in the effluent in pursuant to points C_1/C_0 , C_2/C_0 , C_3/C_0 , and C_4/C_0 . The evolvement of this zone fundamentally increases with rising initial adsorbate concentration in comparison to the velocity of raw water. After a while (C_s), the column is exhausted and then, adsorption does not happen anymore. Herein,

C/C_0 ratio is 1 (one). In most instances of the column adsorption studies, breakthrough curves display a 'S' shape with varying plumbness degree (Patel, 2019).

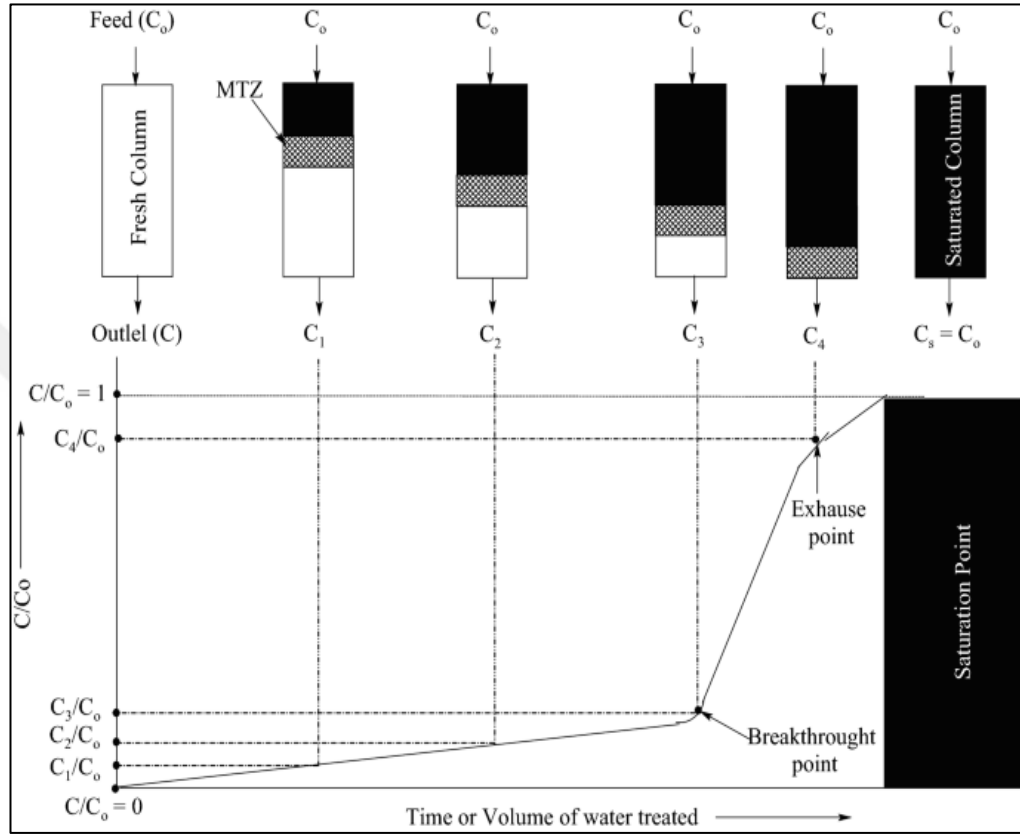


Figure 3.2 Presentation of breakthrough curve by motion of mass transfer zone

An ideal breakthrough curve was shown in Fig. (3.3). Hereby, V_x and V_b are the effluent volume corresponding to C_x called exhaustion point concentration and C_b called break point concentration, respectively.

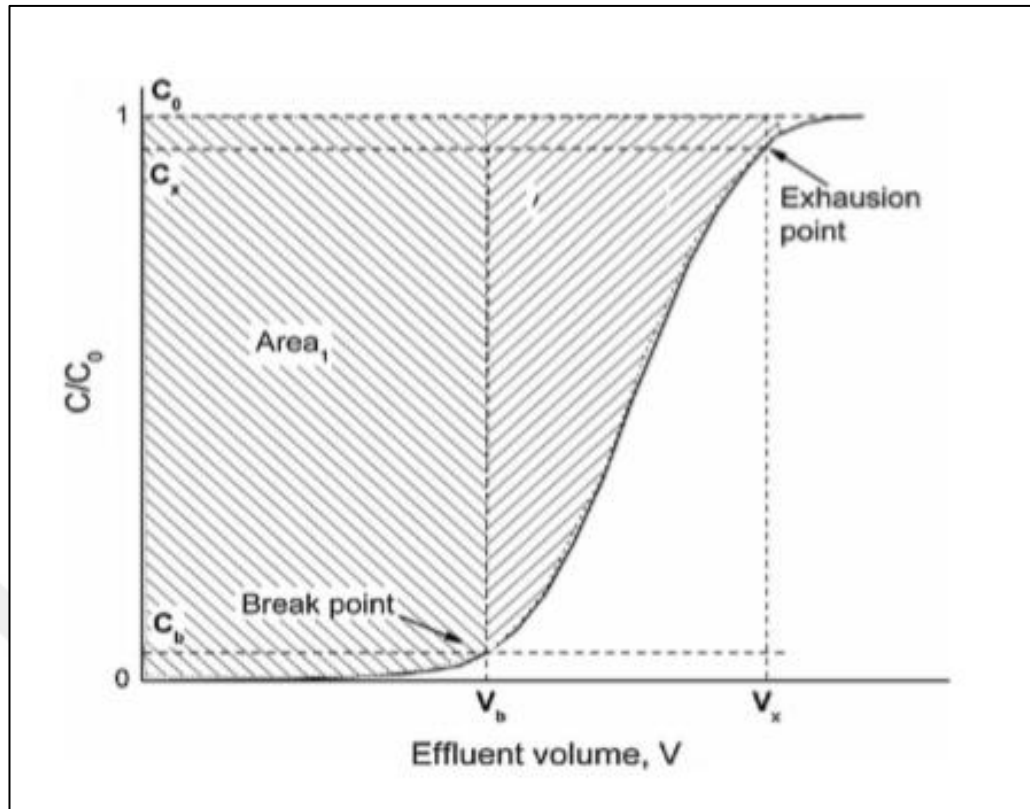


Figure 3.3 Ideal breakthrough curve

CHAPTER 4

MATERIALS AND METHODS

The main idea of the thesis is to develop efficient and economically competitive adsorbent by using drinking water treatment residuals (DWTS). Therefore, iron based drinking water treatment sludge was used as raw material, and it was modified by heating and coating processes. The modified materials were called as DWTS-200, DWTS-400, DWTS-600 and ZOC-DWTS.

The experimental works are broken down into number of sub tasks. These include;

- (i) modification of the DWTS using heat and zirconium oxide,
- (ii) characterization studies of the modified adsorbents
- (iii) equilibrium and kinetic studies for arsenic and antimony adsorption
- (iv) fixed-bed column studies for determining the adsorption capacity
- (v) regeneration studies.

4.1 Reagents

All chemicals used in the experiments were reagent grade. All solutions were prepared by deionized water. 1000 ± 6 $\mu\text{g/ml}$ concentration of arsenic and 1000 ± 4 $\mu\text{g/ml}$ concentration of antimony stock solutions were used and preserved with 2% HNO_3 for arsenic and 5% HNO_3 + 0.1% HF for antimony. 0.1 M NaOH and HCl were used to arrange pH.

4.2 Adsorbents

Drinking water treatment sludge was used as adsorbent in the experiments. The Fe-based drinking water treatment plant sludge sample was obtained from the Tahtali drinking-water treatment plant in Izmir, where iron salts were used as the coagulant. The sludge samples having 30-35% solid matter were obtained from a filter press unit. Raw DWTS was air-dried (Figure 4.1), ground, ground in a miller and sieved to a diameter of 0.250 mm-2 mm. Then, they were washed with deionized water as well as the water was colorless and dried at 105°C.



Figure 4.1 Air-dried drinking water treatment sludge (Personal archive, 2019)

Raw sludge samples were heated in order to lose their combined water and dehydration. To show the impact of heating on adsorption efficiency, material was heated at temperatures of 200, 400, and 600 °C in an oven for 1 and 4 hours according to the methods given by Chen et al., 2008, Li et al., 2014, and Wang et al., 2016. Then, heated materials were washed by deionized water to remove the dissolved organic matter from the DWTS, and then were kept in the oven at 100°C for drying.

Afterward, DWTS-200 having maximum As (T) removal efficiency (i.e. 92.1%) at 200°C, 1h duration, was coated using the technique described in Chaudhry et al. (2017b). Briefly, 125 ml 0.125 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution was poured in a 500 ml beaker and 25 g DWTS-200 was added. 0.1 M NaOH or HCl solution was added in drops so that the pH would be maintained at around 7.5. After stirring the mixture for 22 hours, the coated DWTS was left to age for 3 hours and filtered. The zirconium oxide-coated DWTS was dried in an oven at 105°C for 22 h and washed using distilled water a number of times to remove loose oxide particles. Then, it was left to dry in an oven for 3 hours at 105°C (Fig 4.2).



Figure 4.2 Zirconium Oxide Coated DWTS (ZOC-DWTS) (Personal archive, 2019)

4.3 Characterization of the Materials

4.3.1 Elemental and Phase Analyses

In the experiments, elemental composition of the materials were conducted with an EDS and X-ray diffraction (XRD) analysis (phase analysis) to determine the crystal structure and assign the components.

XRD analysis technique was employed to characterize materials in a scan range of 10-80° [2 θ]. The sample was kept rotating at 8.0°/min for better counting data by reflection geometry.

4.3.2 Surface Morphology

Surface morphology examination is an advanced type of high-resolution spatial imaging by sophisticated microscopes on exposed surfaces of samples for objects too small for the eye. In the study, surface morphology was investigated using a scanning electron microscope (SEM) and at 100x and 1000x magnifications.

4.3.3 Surface Area, Pore Volume and Bulk Density Analysis

Surface area and pore volume were determined using the Brunauer, Emmet and Teller (BET) analysis. This method is implemented in systems with multilayer adsorption, often using probing gases with no chemical reaction with the surfaces to measure the specific surface area. Since nitrogen is the most widely used gas for this purpose, BET analyses are usually carried out at the boiling temperature of N₂ (77 K).

Bulk density is calculated by dividing the masses of the particles by their total volume, which includes both inter-particle void volume, particle volume, and internal pore volume. Bulk density is not constant and can change upon handling (e.g., disturbing a cylinder containing a powder would move the powder particles closer and yield higher values of bulk density).

4.4 Arsenic and Antimony Measurements

Analysis for As, Sb and Fe was carried out using inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent 7700x, with HMI), with additional quality assurance operations. The continuing check verification standard solution was used to check the validity of the calibration curve during analysis. Samples were preserved by adding HNO_3 till pH was under 2.

4.5 Batch Adsorption Studies

Batch adsorption experiments were performed by mechanical shaker (WiseShake SHO-2D). The effect of pH, contact time, initial arsenic concentration, and dosage of adsorbent were investigated. Besides, mixtures of arsenic and antimony solutions with different ratios were prepared to simultaneous removal of the antimony ions with arsenic; and batch experiments were applied to determine the treatment performance. Finally, in order to demonstrate the effect of competing ions, groundwater was obtained from the wells and used in the experiments. In the experiments, arsenic containing water was put in erlenmeyer flasks at first, and adsorbents were (i.e. raw sludge, heated sludge and coated sludge) added to each flasks. After a predetermined contact time, shaking was stopped and the mixture in each flasks was settled. After settling, samples were separated out from a filter of $0.45\ \mu\text{m}$ dimension and prepared for arsenic measurements. Experiments were performed at room temperature ($23^\circ\text{C} \pm 2$) shaking the mixtures at 150 rpm, and repeated three times. The photograph of testing apparatus is shown in Figure 4.3.



Figure 4.3 Testing apparatus (Personal archive, 2019)

4.5.1 Impact of pH on Adsorption

In this study, the initial pH of solution was changed from 3 to 10. HCl and NaOH solutions (each of 0.1 M) were put into arsenic solutions to arrange pH, and pH meter was used to measure pH of the solutions. Experiments were realized using 50 ml samples of water. Arsenic concentration was prepared as 50 $\mu\text{g/L}$, and 1 g/L of adsorbents (DWTS-200 and ZOC-DWTS) was put into each flask. These solutions were shaken for 3 hours in a mechanical shaker at 150 rpm. After 3 hours, mixtures were settled and filtered to analyze arsenic concentration at the effluent.

4.5.2 Impact of Contact Time on Adsorption

Experiments were carried out at different contact times changing between 30 minutes and 8 hours. Adsorbent dosage (DWTS-200 and ZOC-DWTS) was 1 g/L and initial arsenic concentration was 50 $\mu\text{g/L}$. Experiments were done using 50 ml samples of water, pH of As solutions were adjusted as 7 by adding HCl and NaOH. These solutions were shaken at 150 rpm through preset periods (i.e. at the end of 30, 60, 120, 240 and 480 minutes); and after settling, samples were taken from supernatant by filtering from 0.45 μm to analyse arsenic concentration at the effluent.

4.5.3 Impact of Initial Arsenic Concentration on Adsorption

Adsorption experiments were performed at various initial arsenic concentrations, from 50 to 500 µg/L with 1 g/L dosage of adsorbents (DWTS-200 and ZOC-DWTS). 50 ml samples of water were used in the experiments. Based on previous experiments, pH of arsenic solutions was 3 and contact time was 3 hours. Following to 3 hours reaction period, each flask was settled and filtered, and samples were withdrawn from supernatant to analyze arsenic concentration at the effluent.

4.5.4 Impact of Adsorbent Dose on Adsorption

In order to determine the optimal adsorbent dose, various dosages (1 to 10 g/L) of the adsorbents (DWTS-200 and ZOC-DWTS) were put into the beakers. 50 µg/L was chosen as initial arsenic concentration in the experiments. 50 ml samples of water were used in the experiments. Based on the previous experiments, pH of arsenic solutions was adjusted as 3, and contact time was taken as 3 hours. Following to 3 hours reaction period, each flask was settled and filtered, and samples were withdrawn from supernatant to analyze arsenic concentration at the effluent.

4.5.5 Co-removal of Arsenic and Antimony Ions

To investigate the co-removal of antimony and arsenic, arsenic and antimony solutions were mixed certain rates (1, about 1/2 and 2). Initial arsenic and antimony concentration 35 and 90 µg/L (35 µg/L As+35 µg/L Sb, 90 µg/L As+90 µg/L Sb, 35 µg/L As+90 µg/L Sb and 90 µg/L As+35 µg/L Sb). Experiments were done using 50 ml samples of water. Based on the previous experiments, pH of arsenic solutions was taken as 3, 1 g/L was chosen as adsorbent dose and 3 hours was chosen as contact time. Following to 3 hours reaction period, each flask was settled and filtered, and

samples were withdrawn from supernatant to analyze arsenic concentration at the effluent.

4.5.6 Impact of Ions Existing in Groundwater on Adsorption

Arsenic and antimony including groundwater sample obtained from Bayındır/Izmir region was used to show the impact of other ions on arsenic and antimony adsorption. Major ions/anions measured in the groundwater sample are presented in Table 4.1. 1 g/L dose of DWTS-200 and ZOC-DWTS were used in the experiments at pH 3 at room temperature (25°C). Solutions were shaken for 3 hours in a mechanical shaker at 150 rpm. Then each flask was settled and filtered to analyze arsenic concentration at the effluent.

Table 4.1 Concentrations of ions/anions in the groundwater in Bayındır/Dernekli well

Ions/Anions	Groundwater concentration (mg/L)
Iron	0.3
Manganese	0.269
Phosphate	<0.4
TOC	0
Arsenic	0.0092
Antimony	0.0567

4.6 Column Studies

Plexiglass columns filled with adsorbents was operated in the column experiments. The inner diameter and height of a column was 1.7 cm and 80 cm,

respectively. Nozzles were placed to hold the adsorbents at the bottom of the column. DWTS-200 and ZOC-DWTS were studied simultaneously in lab-scale column experiments. A peristaltic pump (Thermo Fh100m) was used to get desired flow rate to each column. The columns were backwashed with tap water until exit water was colorless. Then, the columns were operated with distilled water at first till the stable media height was obtained. Afterwards, a peristaltic pump was used to feed arsenic and antimony solutions (40 ppb As and 80 ppb Sb) to the column. The reason for choosing these concentrations is the use of approximately the same values as those of the underground water well in Bayındır/Dernekli in terms of being close to reality. The water samples were taken from the outlet at certain time periods and measured for the remaining arsenic and antimony in order to determine the breakthrough and exhaustion volume. The schematic diagram and photograph of the experimental set up are illustrated in Figure 4.4 and 4.5.

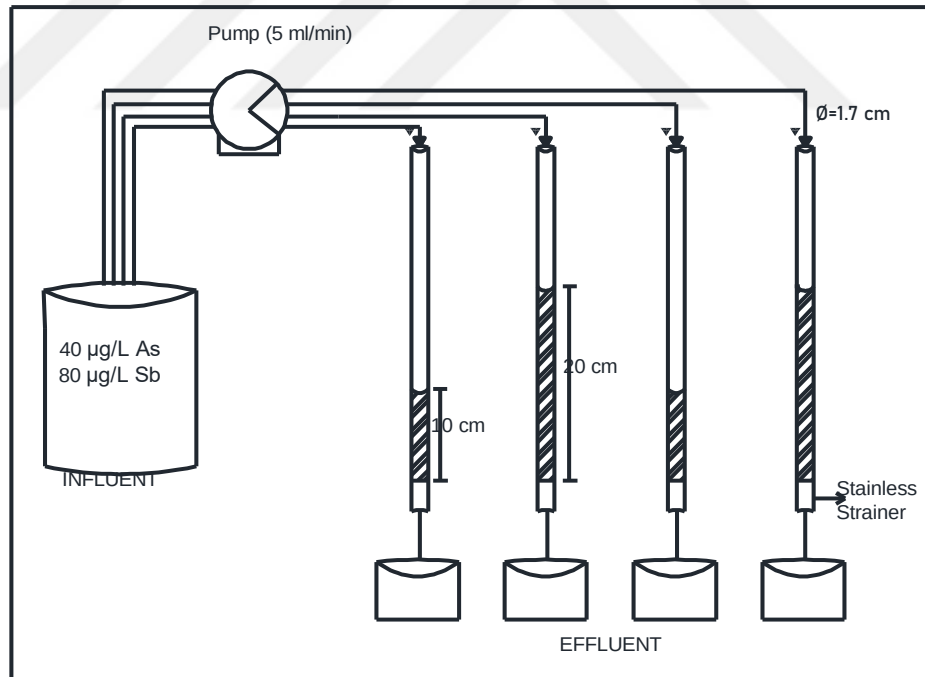


Figure 4.4 Schematic diagram of the testing apparatus



Figure 4.5 Photograph of the testing apparatus(Personal archive, 2019)

4.6.1 Effect of Bed Depth on Adsorption

Experiments were performed with two bed depths (i.e. 10 and 20 cm) at $25^{\circ}\text{C} \pm 2$. Firstly, columns were filled with media (DWTS-200 and ZOC-DWTS) at 10 cm and 20 cm heights. Arsenic and antimony solutions (app. $40 \mu\text{g/L}$ As and $80 \mu\text{g/L}$ Sb) were passed through the fixed-bed columns at a stable rate of flow of 5 mL/min . The solution pH 3, determined in previous batch experiments, was used in the column studies. Effluent samples were taken from bottom part of the columns in certain time intervals, arsenic and antimony measurements were done by ICP-MS to obtain breakthrough and exhaustion volume.

4.7 Regeneration of Adsorbents

Regeneration studies were performed by sodium hydroxide solution (NaOH) for the adsorbents. During the experiments, exhausted media were regenerated by 1% NaOH solutions. For regeneration, NaOH solution was fed with the same flow rate (5 ml/min) in down flow mode, and samples were collected from the column exit in certain time intervals and arsenic, antimony and iron measurements were performed. Feeding of NaOH solution was terminated when effluent arsenic concentration decreased to the standards ($<10\text{ }\mu\text{g/L}$). Then, dilute acid solution (HCl-pH 2 DI water) was fed to the column in order to provide protonated surface. After acid treatment, column was washed with distilled water (DI water) until the effluent pH was increased to 7.

Media was taken from the column and dried at 65°C for three days to specify adsorption capacity of regenerated media. Batch experiments were carried out at optimum conditions (1 g/L adsorption dose, 3 hours of contact time, pH of 3) obtained from previous batch experiments with raw media and regenerated media for two different initial concentrations (40 $\mu\text{g/L}$ As and 80 $\mu\text{g/L}$ Sb with 200 $\mu\text{g/L}$ As and 400 $\mu\text{g/L}$ Sb).

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Modification by Heat

After pre-treatment of the materials (air-dried, milling in a china mortar and sieving), heating and coating were performed. The experiments were carried out at pH 7, 5 g/L adsorbent dose, 50 µg/L initial arsenic concentration and 4 hours contact time and arsenic removal efficiencies of the materials were calculated. As can be seen from Figure 5.1, the maximum As(T) removal efficiency (i.e. 92.1%) was obtained at 200°C, 1h duration. Increasing the temperature from 200 °C to 400°C were resulted a decrease in the removal efficiency. When sludge sample heated at 400°C for a 1h, app. 87% of the As (T) was removed. Increasing the time did not cause the efficiency improvement; app. 84% As (T) removal was achieved. Heating at 600°C was resulted an increase at effluent arsenic concentrations; in fact, higher effluent arsenic concentrations from influent values were obtained. Increase of arsenic concentrations at effluent was explained with releasing the arsenic compound from DWTS at high temperatures. As a result, optimum temperature and time for thermal modification was decided as 200°C and 1hour. The optimal heating values determined for raw sludge were also used for zirconium coating process. And, thermally modified DWTS at 200 °C was coated by $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution, and called ZOC-DWTS.

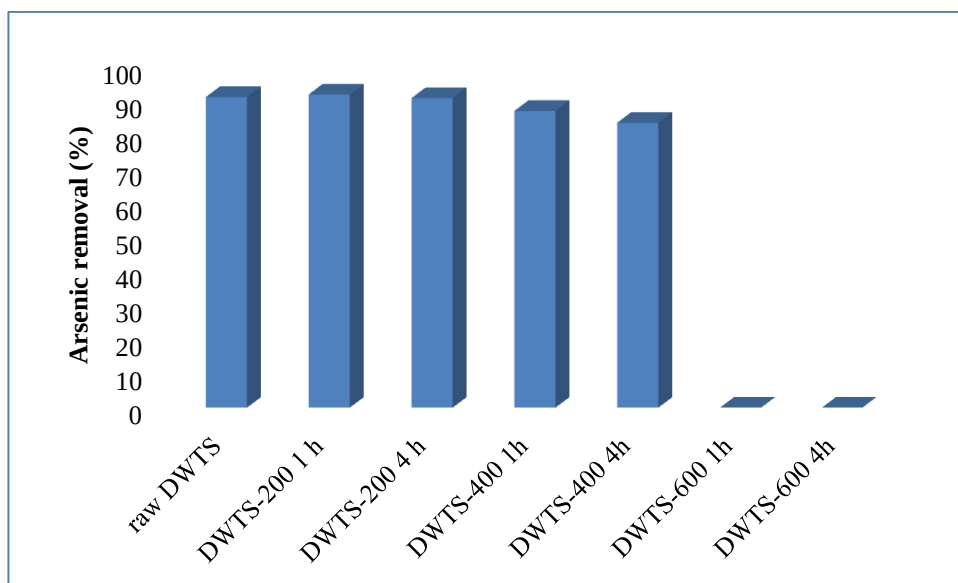


Figure 5.1 Effect of heating temperature on arsenic removal for DWTS

As it stated above, DWTS-600 released some arsenic to the water. In order to assess the behavior of the ZOC-DWTS under high temperature, it was heated to 600°C; and batch experiments were performed. We did not observe the arsenic release to the water. Furthermore, efficiency of arsenic removal was 100% at pH 3 and 89% at pH 7. This experiment revealed that zirconium oxide increases the strength of materials.

5.2 Characterization of the Materials

The experiments were performed using DWTS-200 and ZOC-DWTS. Batch experiments were carried out by powdered materials (Fig. 5.2 a-b) whereas column studies were conducted with granular DWTS-200 and ZOC-DWTS (Fig.5.2 c-d).

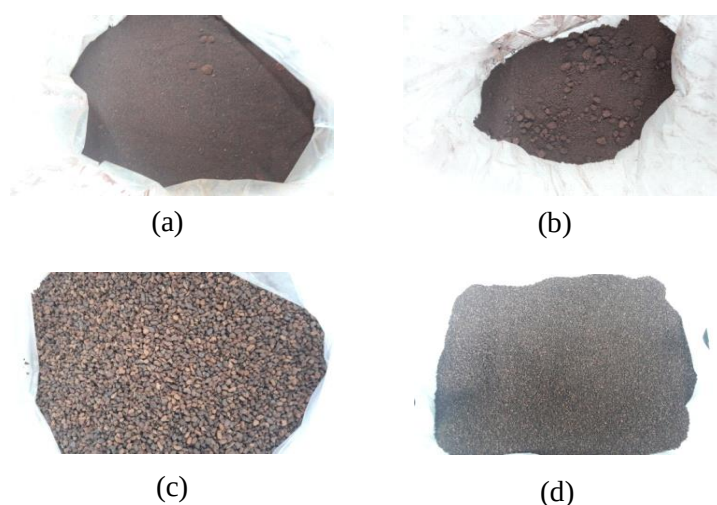


Figure 5.2 Photos of adsorbent materials a) DWTS-200(powder, <250 μm) , b) ZOC-DWTS(powder, <250 μm), c) DWTS-200(granule, 700 μm -2 mm), d) ZOC-DWTS (granule, 700 μm -2 mm)(Personal archive, 2019)

5.2.1 Elemental and Phase Analysis

The elemental analyses of the materials (raw sludge, DWTS-200, DWTS-400, DWTS-600 and ZOC-DWTS) conducted with an EDS are presented in Table 5.1 and Table 5.2. As it was expected, the major components of raw sludge were iron (52.2% for powder and 35.02% for granular), oxygen (26.4% for powder and 36.3% for granular), calcium (9.51% for powder and 20.51% for granular) and silica (5.75% for powder and %3.42 for granular). Oxygen (50.99 for powder and 46.35% for granular), iron (23.29% for powder and 26.08% for granular), calcium (5.57% for powder and 14.38% for granular) and silica (6.03% for powder and 3.51% for granular) were detected at DWTS-200 (1 h) samples. Oxygen (50.17 for powder and 38.80% for granular), iron (21.05% for powder and 38.93% for granular), calcium (20.69% for powder and 8.86% for granular) and silica (3.52% for powder and 7.29% for granular) were detected at DWTS-400 (1 h) samples. For DWTS-600 (1 h) samples, oxygen (32.65 for powder and 32.99% for granular), iron (38.84% for powder and 44.21% for granular), calcium (19.25% for powder and 11.04% for granular) and silica (4.24% for powder and 5.99% for granular) were detected.

The major component of ZOC-DWTS were iron (38.02% for powder and 32.74% for granular), oxygen (28.69% for powder and 38.32% for granular), zirconium (15.1% for powder and 11.93% for granular) and calcium (10.01% for powder and 6.29% for granular).

EDS analysis focuses to a phase randomly. So, these elemental percentages do not express a meaning exactly and do not be compared. But we have idea about elemental distribution.

Phase analysis of the materials were specified by XRD analysis and given in Figure 5.3-Figure 5.15. The (XRD) pattern were taken in the range of $10-80^\circ [2\theta]$ and turned in a step scan mode (at $8.0^\circ/\text{min}$ step size) to achieve preferable numbering statistics with the repercussion geometry. Regarding to XRD analysis from Figure 5.3 to Figure 5.15, the main occurring phases of the materials may be given as calcite, iron compounds, various silicates and quartz. The detailed information about the occurring phases related to XRD pattern was given as calcite 65%, quartz 25% and silicate 10% for Figure 5.3, calcite 33%, iron compound 33% and zeolite 33% for Figure 5.4, calcite 45%, calcium silicate 50% and zeolite 5% for Figure 5.5, calcite 45%, silica 45% and aluminium oxide hydroxide 10% for Figure 5.6, calcite 93%, iron compound 5% and silicate 2% for Figure 5.7, calcite 60%, alite 30% and iron compound 10% for Figure 5.8, calcite 90% and iron compound 10% for Figure 5.9, calcite 33%, quartz 33% and iron compound 33% for Figure 5.10, calcite 95% and quartz 5% for Figure 5.11, calcite 60%, calcium hydroxide 38% and quartz 2% for Figure 5.12, calcite 50%, quartz 12%, KOH 13% and iron compound 25% for Figure 5.13, calcite 60% and iron compound 40% for Figure 5.14 and quartz 70%, iron compound 25% and silicate 5% for Figure 5.15. Besides, since $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ has only been coated on the substrate of the material, zirconia phase has not been encountered in the ZOC-DWTS.

Table 5.1 Elemental analysis of powder raw sludge, DWTS-200, DWTS-400, DWTS-600 and ZOC-DWTS

	POWDER MATERIALS							
Component (wgt. %)	Raw Sludge	DWTS -200 1 h	DWTS -200 4 h	DWTS -400 1 h	DWTS -400 4 h	DWTS -600 1 h	DWTS -600 4 h	ZOC- DWTS
Fe	52.2	23.29	43.39	21.05	31.59	38.84	38.54	38.02
O	26.4	50.99	34.69	50.17	41.07	32.65	32.8	28.69
Ca	9.51	5.57	10.3	20.69	18.79	19.25	20.2	10.01
Si	5.75	6.03	6.1	3.52	4.02	4.24	3.49	3.16
Mn	2.82	1.12	1.77	0.97	1.65	1.96	2.57	3.04
Al	2.1	2.47	2.08	1.41	1.46	1.56	1.08	0.99
K	0.93	0.37	0.55	0.25	0.38	0.53	0.45	-
Na	0.18	1.51	0.74	1.2	0.69	0.58	0.59	0.7
Mg	0.12	0.85	0.38	0.76	0.36	0.39	0.27	0.29
C	-	7.8	-	-	-	-	-	-
Zr	-	-	-	-	-	-	-	15.1
S	-	-	-	-	-	-	-	-
Total	100	100	100	100.02	100	100	99.99	100

Table 5.2 Elemental analysis of granular raw sludge, DWTS-200, DWTS-400, DWTS-600 and ZOC-DWTS

	GRANULAR MATERIALS				
Component (wgt. %)	Raw Sludge	DWTS-200 1 h	DWTS-400 1 h	DWTS-600 1 h	ZOC- DWTS
Fe	35.02	26.08	38.93	44.21	32.74
O	36.3	46.35	38.8	32.99	38.32
Ca	20.51	14.38	8.86	11.04	6.29
Si	3.42	3.51	7.29	5.99	5.87
Mn	2.86	1.27	1.16	1.43	1.68
Al	1.21	1.32	2.8	2.07	1.58
K	-	-	0.42	0.46	0.25
Na	0.38	0.86	1.08	0.67	0.92
Mg	0.3	0.54	0.64	0.45	0.42
C	-	5.7	-	-	-
Zr	-	-	-	-	11.93
S	-	-	-	0.69	-
Total	100	100.01	99.98	100	100

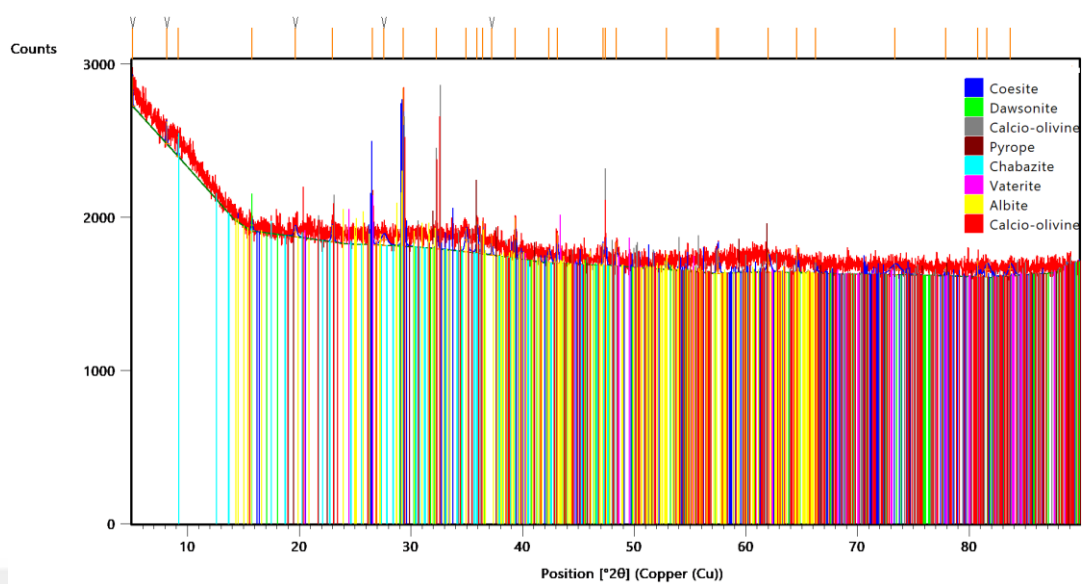


Figure 5.3 XRD analysis of raw sludge (grain size<250 μm)

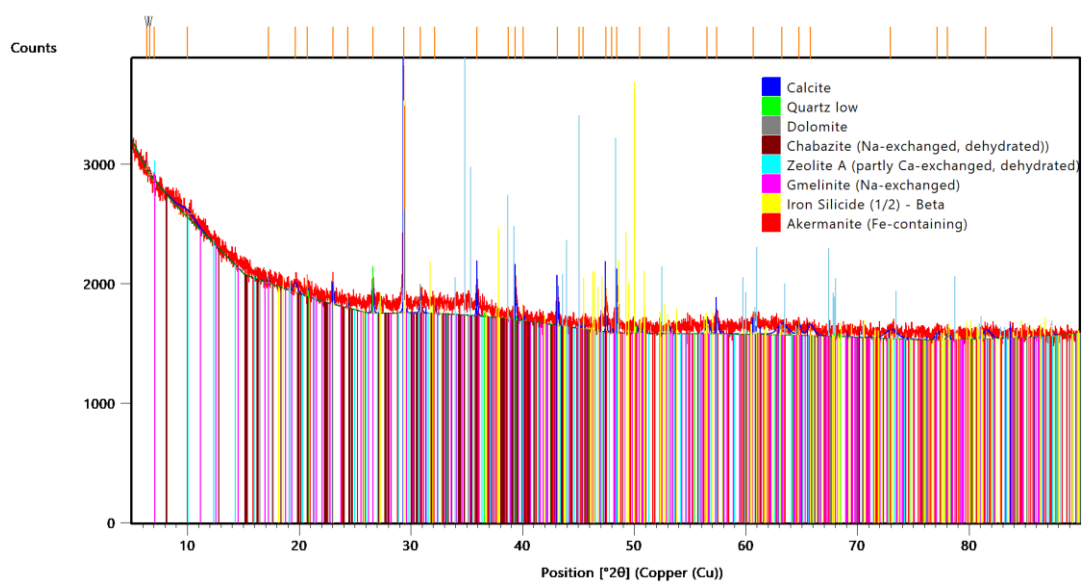


Figure 5.4 XRD analysis of DWTS-200-1h(grain size<250 μm)

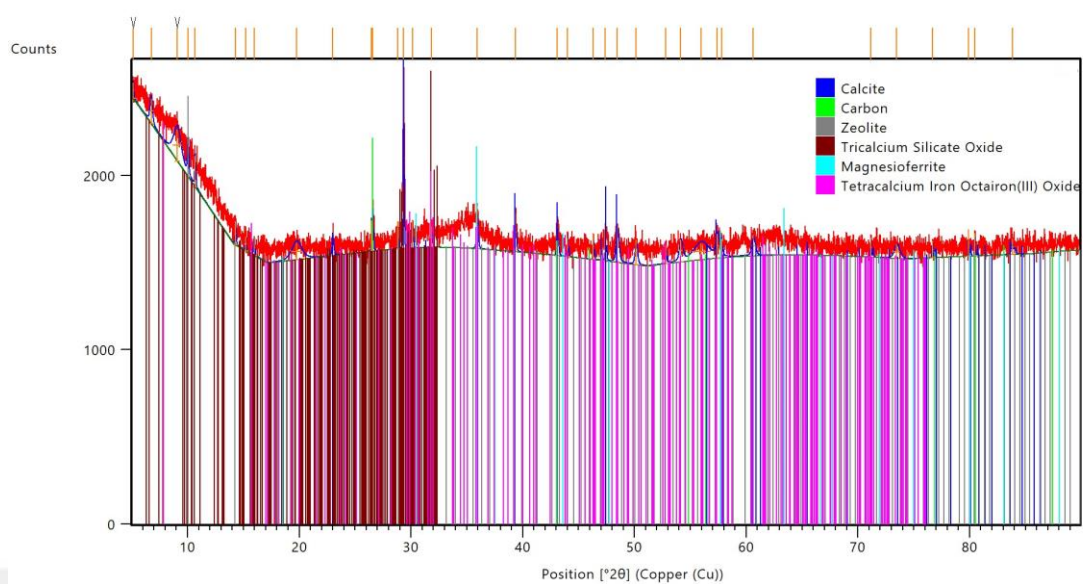


Figure 5.5 XRD analysis of DWTS-200-4h(grain size<250 μm)

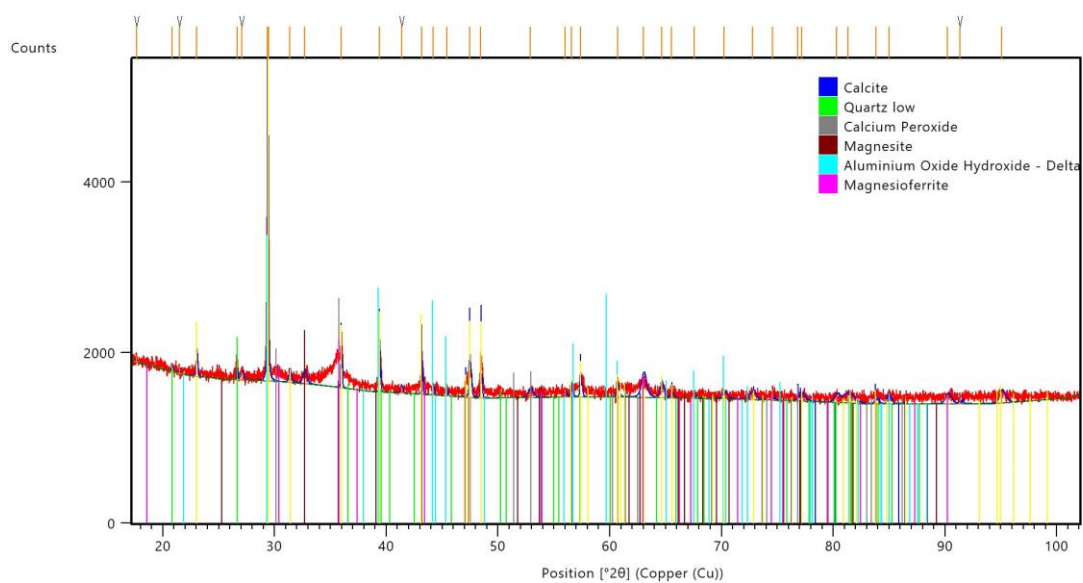


Figure 5.6 XRD analysis of DWTS-400-1h(grain size<250 μm)

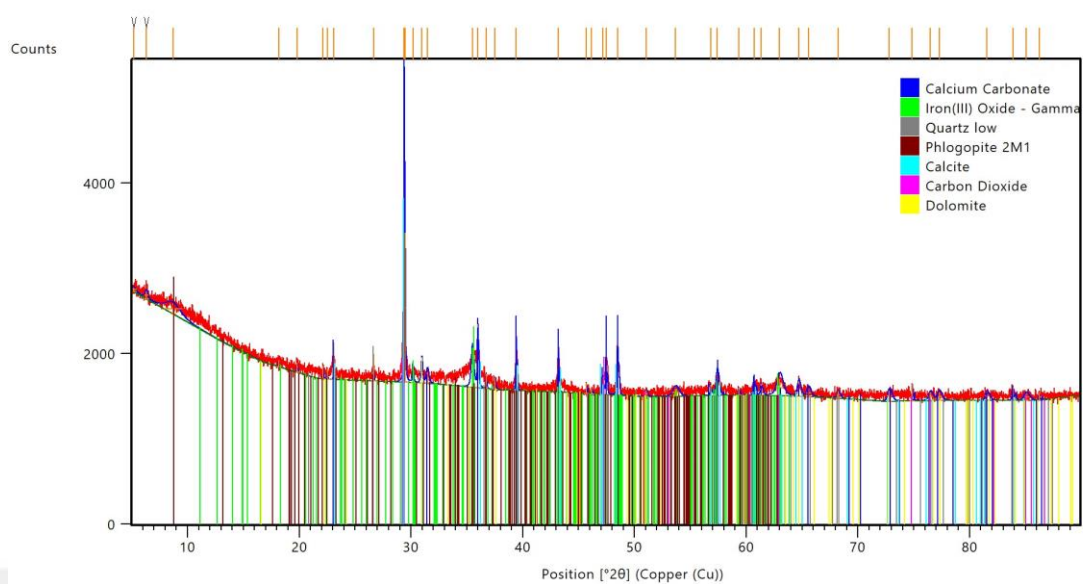


Figure 5.7 XRD analysis of DWTS-400-4h(grain size<250 μm)

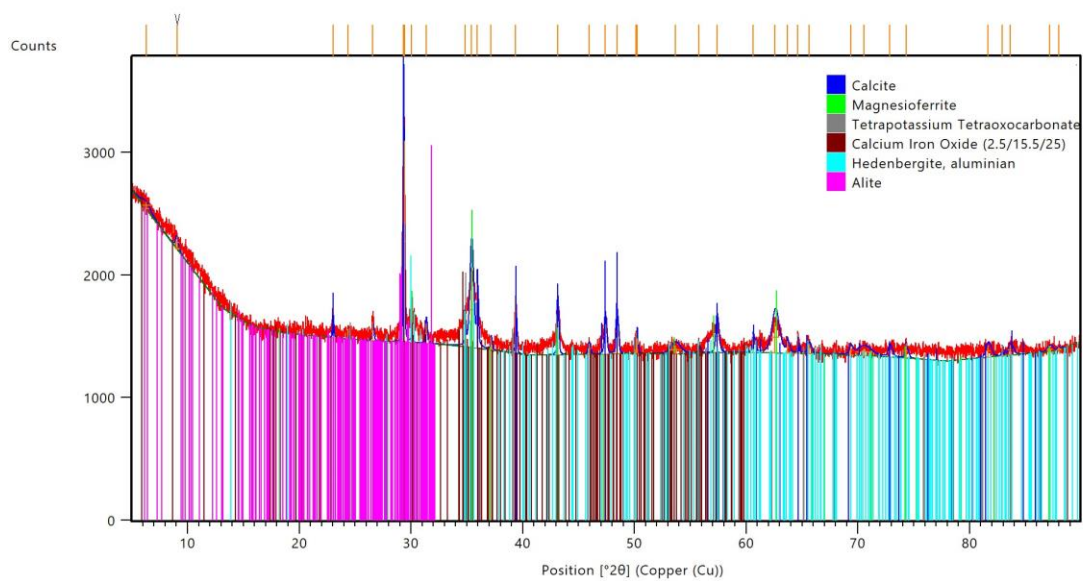


Figure 5.8 XRD analysis of DWTS-600-1h(grain size<250 μm)

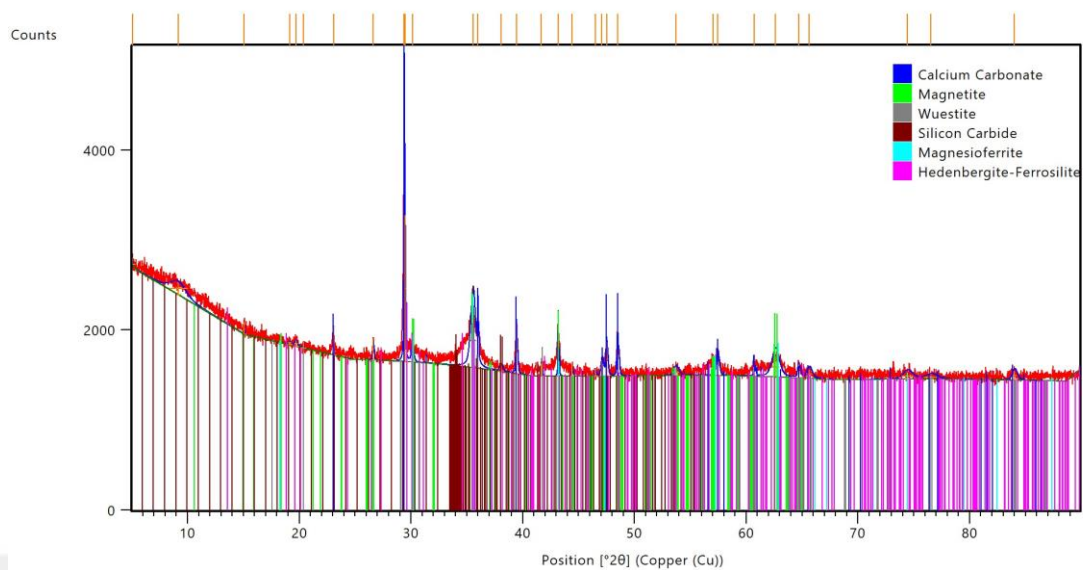


Figure 5.9 XRD analysis of DWTS-600-4h(grain size<250 μm)

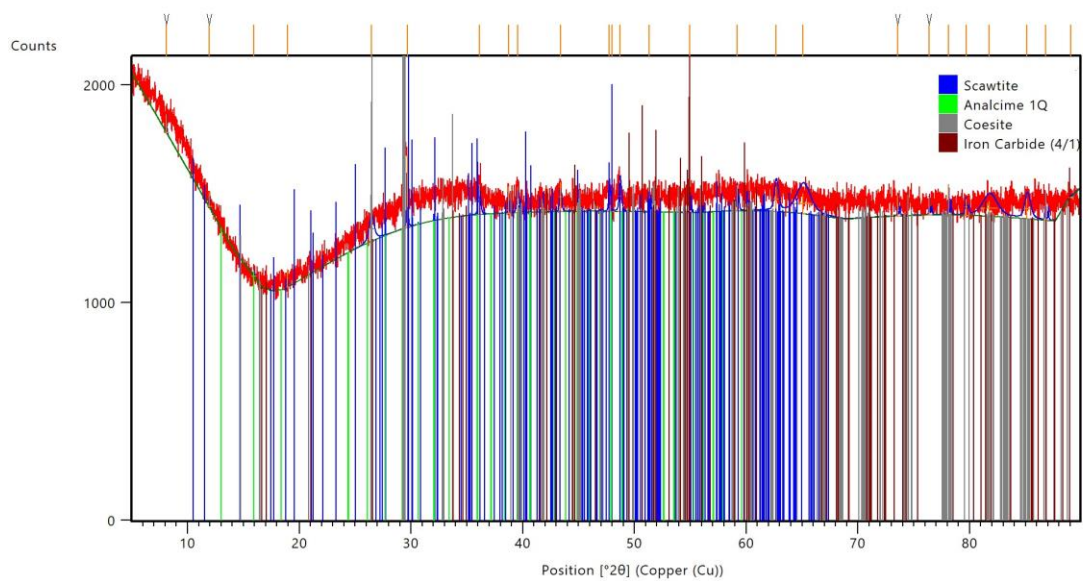


Figure 5.10 XRD analysis of ZOC-DWTS(grain size<250 μm)

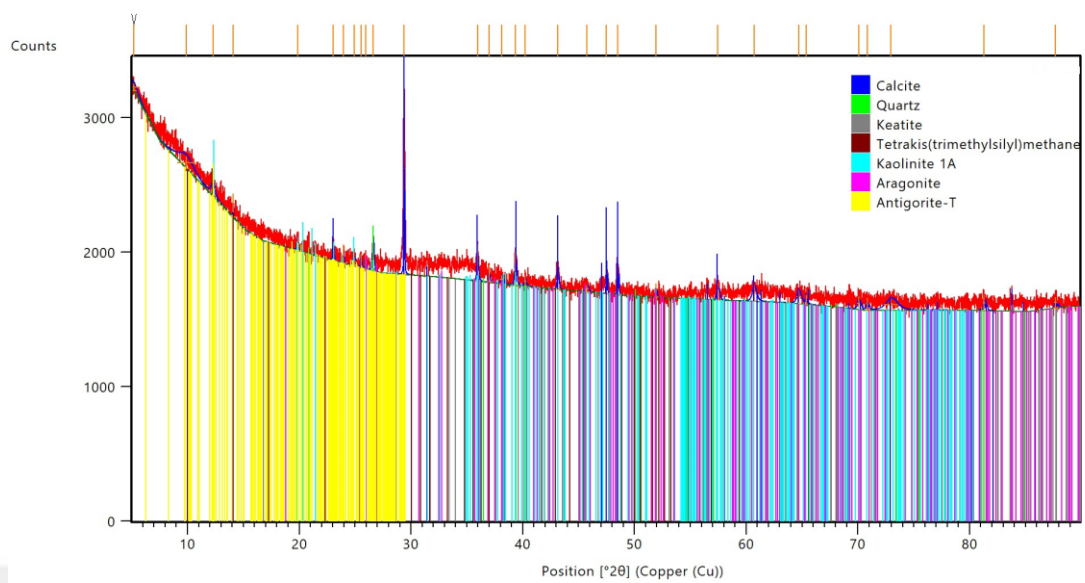


Figure 5.11 XRD analysis of raw sludge (grain size: 700 μm -2 mm)

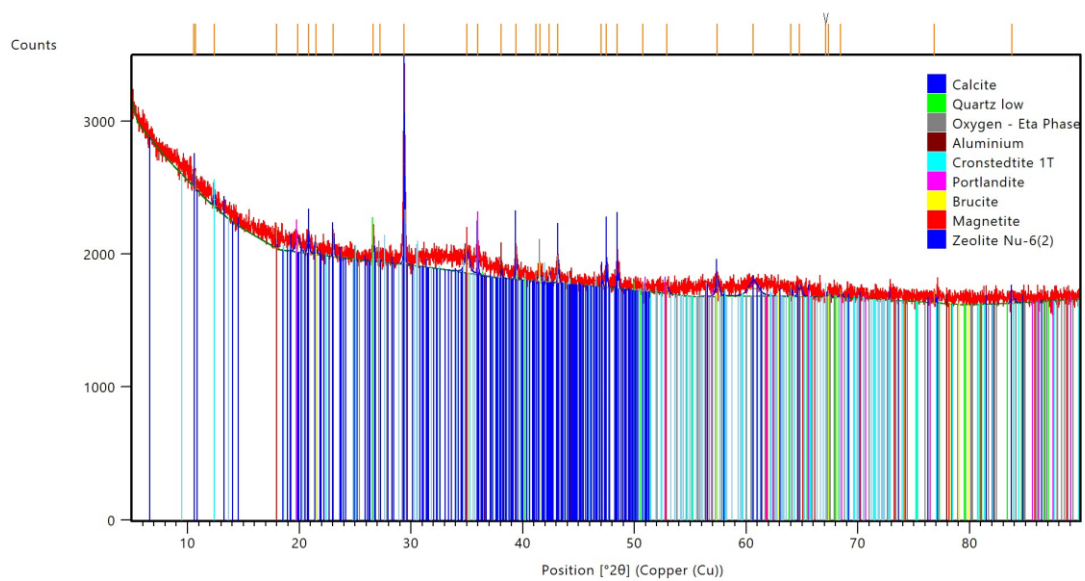


Figure 5.12 XRD analysis of DWTS-200-1h (grain size: 700 μm -2 mm)

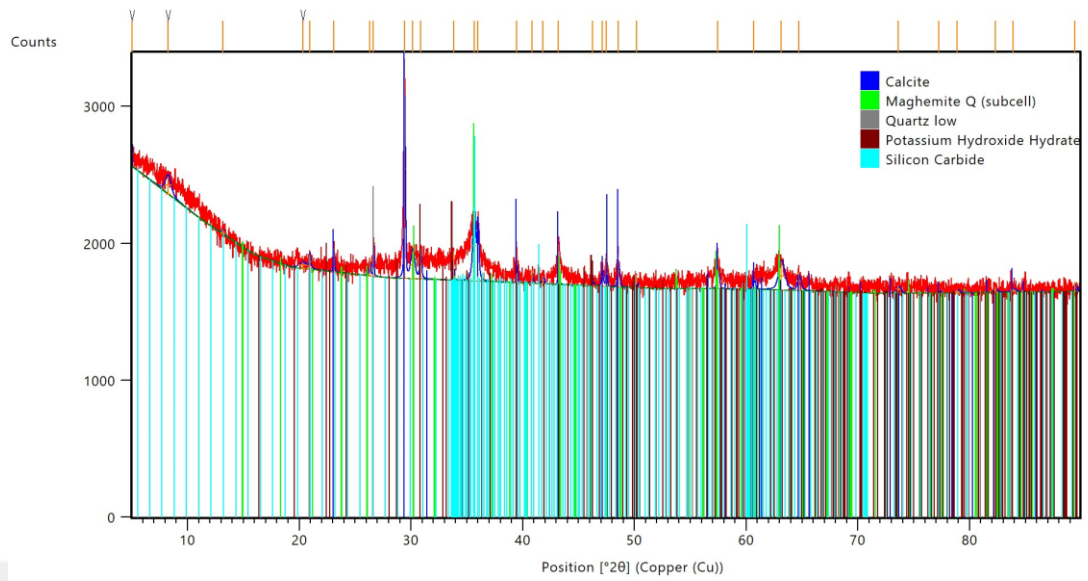


Figure 5.13 XRD analysis of DWTS-400-1h (grain size: 700 μm -2 mm)

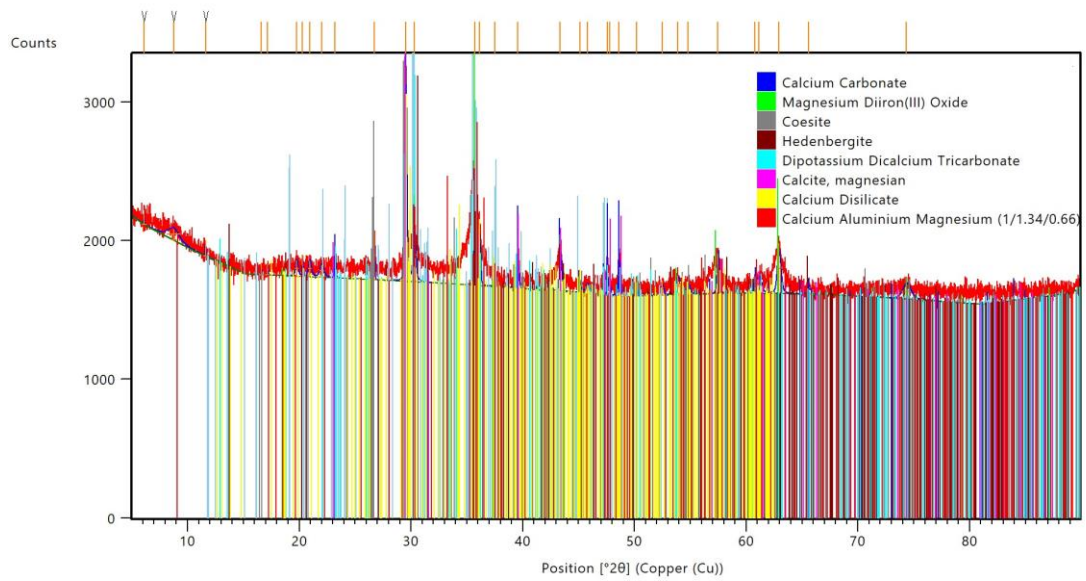


Figure 5.14 XRD analysis of DWTS-600-1h (grain size: 700 μm -2 mm)

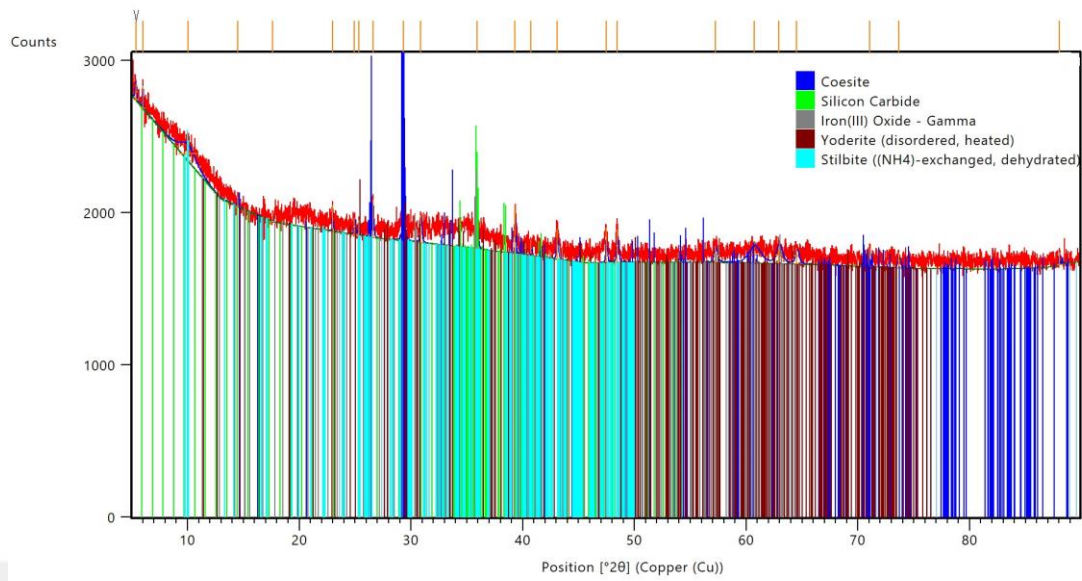
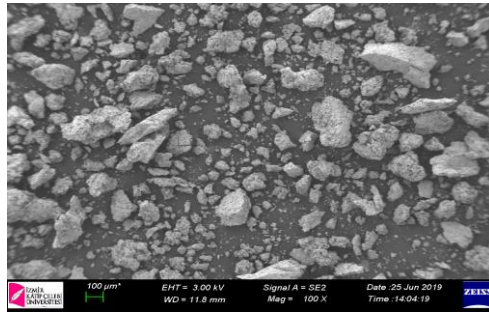


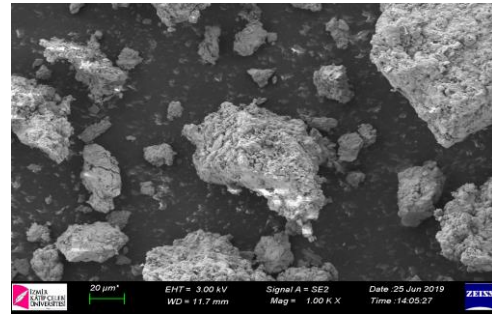
Figure 5.15 XRD analysis of ZOC-DWTS (grain size: 700 μm -2 mm)

5.2.2 Surface Morphology

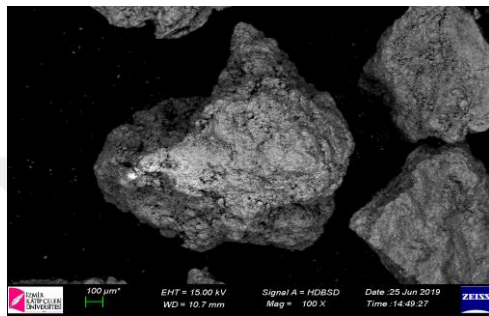
Figure 5.16- Figure 5.20 illustrates SEM images which were taken both at 100x and 1000x magnifications to observe the surface morphology of raw sludge, DWTS-200, DWTS-400, DWTS-600 and ZOC-DWTS, respectively. As seen in Figure 5.15- Figure 5.18, raw sludge and thermal treated sludges i.e. DWTS-200, DWTS-400, DWTS-600, have rough surfaces and heterogeneous. In addition, ZOC-DWTS images revealed that zirconium oxide growing on the surface of grain, causing a rather porous and heterogeneous appearance (Figure 5.19). Also, irregular structures were found to form on the coating because of the formless zirconium oxide. Moreover, coating with zirconium oxide caused an increase in the surface area (from 148 m^2/g to 156 m^2/g for materials grain size < 250 μm).



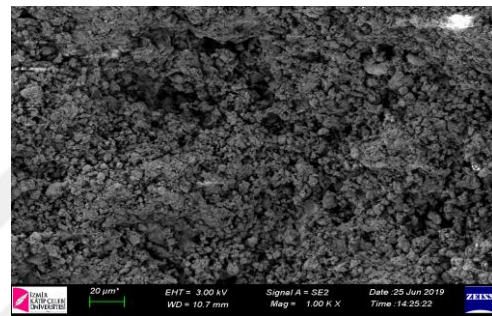
(a)



(b)

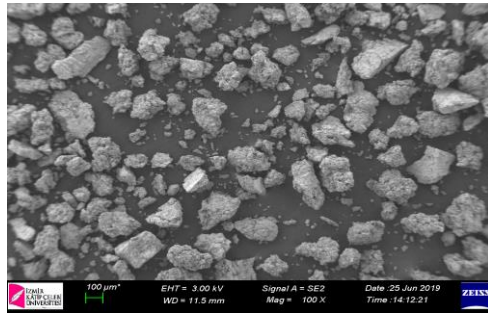


(c)

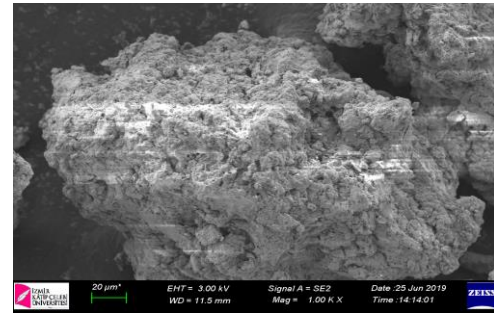


(d)

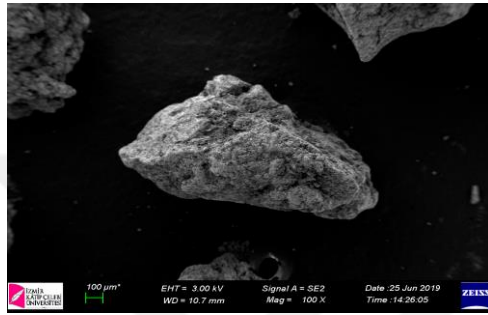
Figure 5.16 SEM displays of raw sludge(a) 100x magnification of raw sludge (grain size < 250 μm), (b) 1000x magnification of raw sludge (grain size < 250 μm), (c) 100x magnification of raw sludge (grain size: 700 μm -2 mm) and (d) 1000x magnification of raw sludge (grain size: 700 μm -2 mm)



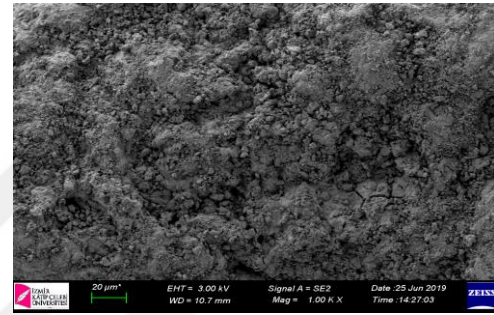
(a)



(b)

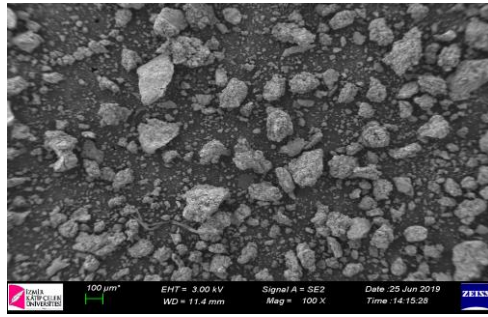


(c)

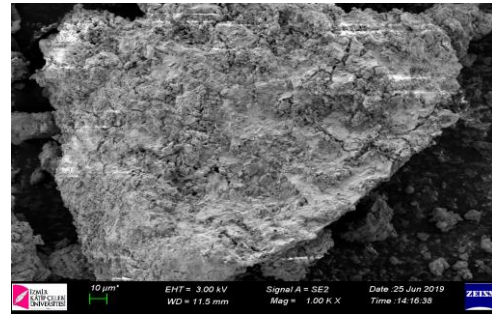


(d)

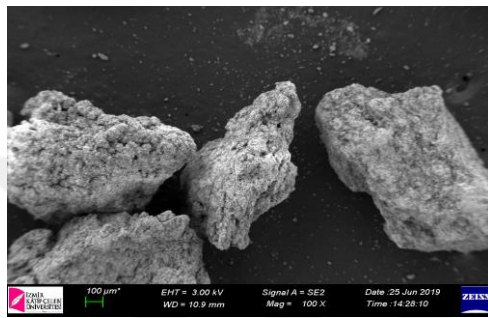
Figure 5.17 SEM displays of DWTS-200-1 h(a) 100x magnification of DWTS-200 (grain size<250 μm), (b) 1000x magnification of DWTS-200 (grain size<250 μm), (c) 100x magnification of DWTS-200 (grain size: 700 μm -2 mm) and (d) 1000x magnification of DWTS-200 (grain size: 700 μm -2 mm)



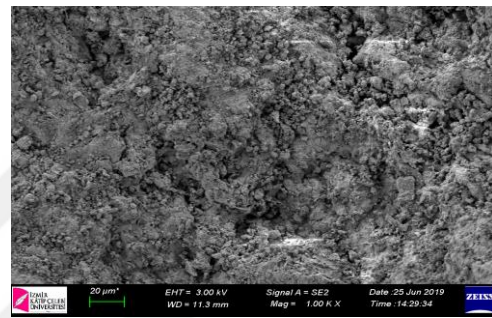
(a)



(b)

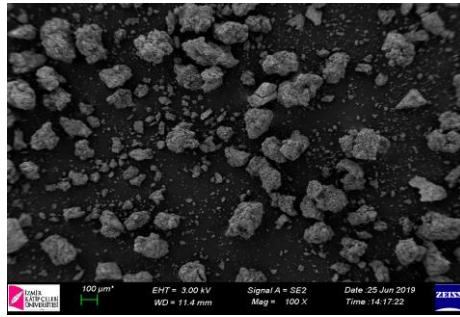


(c)

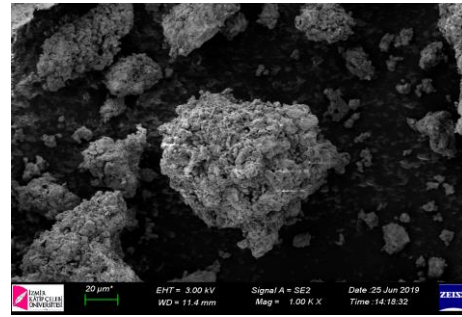


(d)

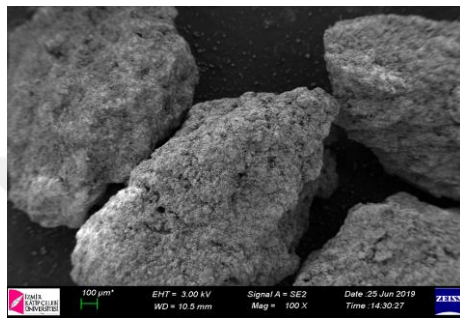
Figure 5.18 SEM displays of DWTS-400-1 h(a)100x magnification of DWTS-400 (grain size<250 μm), (b) 1000x magnification of DWTS-400 (grain size<250 μm), (c) 100x magnification of DWTS-400 (grain size: 700 μm -2 mm) and (d) 1000x magnification of DWTS-400 (grain size: 700 μm -2 mm)



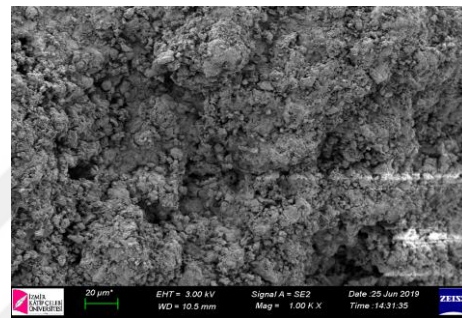
(a)



(b)



(c)



(d)

Figure 5.19 SEM displays of DWTS-600-1 h(a)100x magnification of DWTS-600 (grain size<250 μm), (b) 1000x magnification of DWTS-600 (grain size<250 μm), (c) 100x magnification of DWTS-600 (grain size: 700 μm -2 mm) and (d) 1000x magnification of DWTS-600 (grain size: 700 μm -2 mm)

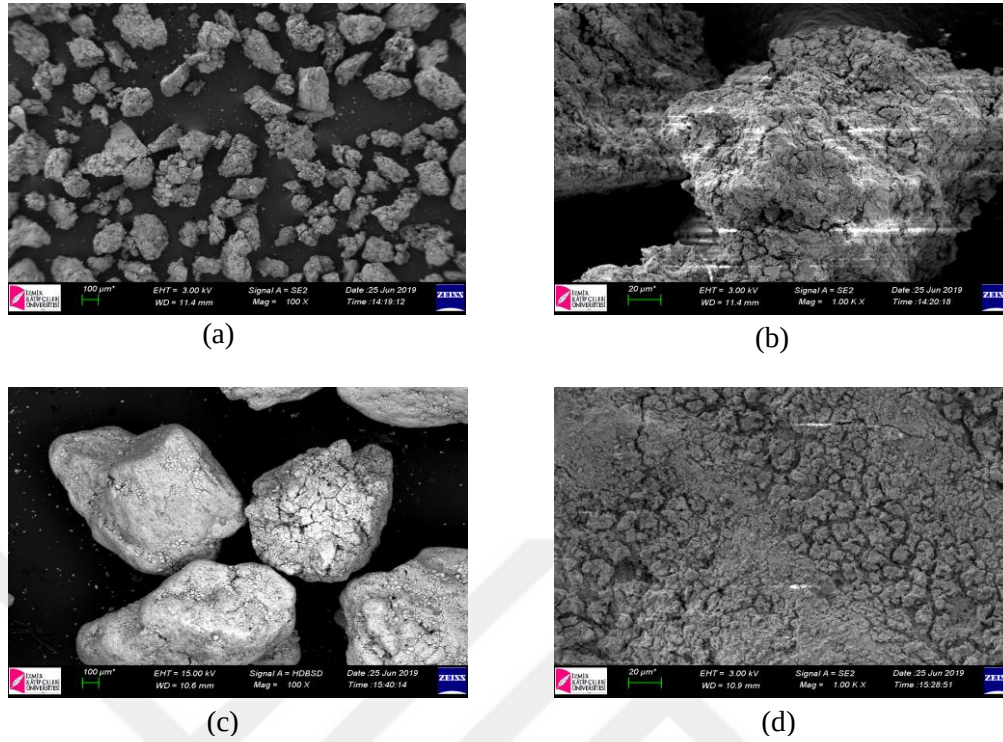


Figure 5.20 SEM displays of ZOC-DWTS(a)100x magnification of ZOC-DWTS (grain size<250 μm), (b) 1000x magnification of ZOC-DWTS (grain size<250 μm), (c) 100x magnification of ZOC-DWTS (grain size: 700 μm -2 mm) and (d) 1000x magnification of ZOC-DWTS (grain size: 700 μm -2 mm)

5.2.3 Surface Area, Pore Volume and Bulk Density Analysis

Surface area and pore volume of the materials were determined by BET analysis. Particles having <250 μm diameters were used in the batch experiments and having 700 μm -2 mm diameters were used in the column experiments. Results of the BET analyses are shown in Table 5.3. Surface area of the raw sludge which are smaller than 250 μm was measured as about 139 m^2/g . Heating to 200°C (1 h) was resulted an increase in the surface area, thus BET surface area was increased to about 149 m^2/g yielding 7% expansion for particles < 250 μm . Increasing heating temperature (i.e. 200°C, 1 h) resulted by a decrease in surface area. Similar results were obtained for iron oxide aerogel reported by Kun Yoo et. al. (2019). When the temperature was increased to 500°C, the BET specific surface areas were significantly decreased. The

rapid decrease in the specific surface area was explained with increased sinterability of the material.

In addition, granule form of adsorbents (700 μm -2 mm) has greater surface area than powder form (<250 μm). For powder form, zirconium oxid coating was resulted an increase in the surface area. For granule form, a significant change has not been observed. Pore volume has increased with increasing heating temperature till 600°C and average pore size has increased with increasing heating temperature, too. Micropore area of ZOC-DWTS was above 14 m^2/g , thus significant increase was observed when material was modified with zirconium oxid.

Bulk density of materials was ranged from 2.30-4.32. Bulk density of powder materials was bigger than granular materials because powder materials could be pressed more than granular form.

As conclusion, ZOC-DWTS was the material which has maximum micropore area and volume due to more porous structure. Thus, zirconium oxide coating caused a significant increase in micropore area and volume.

Table 5.3 Surface area, pore volume and size and bulk density of the materials used as of adsorbent

Material	Surface Area (m ² /g)		Pore Volume (cm ³ /g)		Avg. Pore Size (Å)	Bulk Density (g/cm ³)
	BET	Micropore Area	Total	Micropore Volume		
Raw sludge (<250µm)	138.898	10.289	0.113	0.004	32.56	24.588
DWTS-200 1 h (<250µm)	148.992	3.371	0.12	0.0038	32.225	34.119
DWTS-200 4 h (<250µm)	136.904	11.661	0.152	0.005	44.298	30.669
DWTS-400 1 h (<250µm)	95.168	5.755	0.16	0.0025	67.402	31.709
DWTS-400 4 h (<250µm)	92.978	12.93	0.155	0.0064	66.613	31.866
DWTS-600 1 h (<250µm)	38.074	6.363	0.103	0.0032	107.744	43.207
DWTS-600 4 h (<250µm)	36.684	11.519	0.0898	0.00599	97.94	34.383
ZOC-DWTS (<250µm)	156.562	14.826	0.1198	0.00634	30.601	26.252
Raw sludge (700µm-2 mm)	172.492	9.23	0.127	0.00316	29.342	23.061
DWTS-200 1 h (700µm-2 mm)	169.56	5.691	0.136	0.00128	32.005	25.204
DWTS-400 1 h (700µm-2 mm)	91.948	7.638	0.171	0.00326	74.236	41.671
DWTS-600 1 h (700µm-2 mm)	39.007	5.628	0.129	0.00282	132.721	36.145
ZOC-DWTS (700µm-2 mm)	167.512	14.372	0.128	0.00594	30.503	25.047

5.3 Batch Experiments

5.3.1 Impact of pH on Arsenic Removal

The impact of the pH on removal of As(T) is illustrated in Figure 5.21. The maximum As(T) removal efficiency was obtained at pH 3 for DWTS-200. Approximately 98% of initial As (T) were removed at acidic conditions. The As (T) removal rate was higher than 90% within pH range of 3 to 5. However, the efficiency was reduced remarkably when pH increased to 10. At alkaline conditions (i.e. pH 10) As (T) removal efficiency was obtained as 64%. Decreasing the As adsorption with an increasing pH values was also proven by various researchers (Elkhatib et. al., 2015; Zhang & Itoh, 2005). It is attributed to the increase of negative-charge sites on the adsorbent surface at high pH values. At $\text{pH} > 9$, HAsO_4^{2-} is the dominant As(V) species that may compete with negative site of the adsorbent surface to reduce the adsorption capability due to electrostatic repulsion.

The maximum As(T) removal efficiency (i.e. 99.1%) was obtained at pH 3 for ZOC-DWTS. Concentration of the material decreased from 44.8 $\mu\text{g/L}$ to 0.40 $\mu\text{g/L}$. Similarly to DWTS-200, efficiencies were decreased when pH increased. The removal rate was reduced to 93.3% for pH 5, 89.3% for pH 7 and 75.7% for pH 10.

The increase in As(T) uptake for ZOC-DWTS material is explained with increasing of positive surface charges and synergetic effect of bi-metal oxide (Fe and Zr). Adsorption occurred more effectively at acidic pH, and alkaline conditions were not favorable for As(T) uptake. Similarly, Ocinski et al. (2016) performed arsenic treatment via water treatment residuals at optimum pH 4.

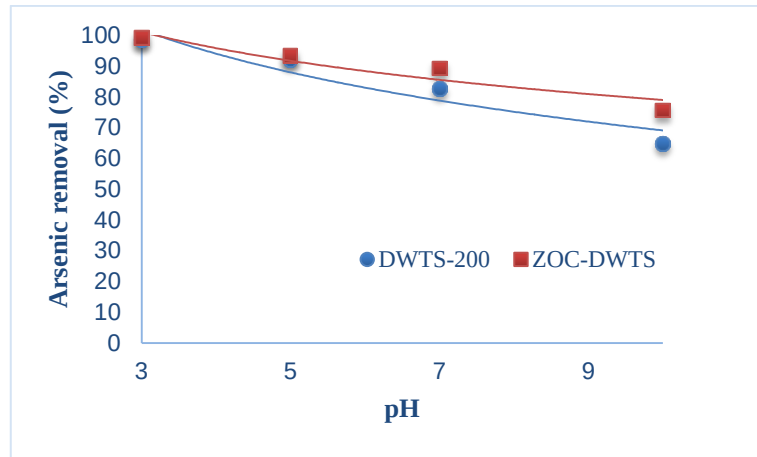


Figure 5.21 Impact of pH on arsenic removal for DWTS-200 and ZOC-DWTS

5.3.2 Impact of Contact Time on Arsenic Removal

The impact of contact time on removal of As(T) is illustrated in Figure 5.22.

For DWTS-200, approximately 65% of arsenic was removed within 30 minutes, and at the end of 2 hours removal rate increased to about 83%. After that, arsenic uptake slightly increased and reached to approximately 93% at the end of the 8 hours. Due to the availability of a large number of adsorption sites on the adsorbent, high removal rates were conducted at first. Since the increases in removal rates were not significant after 3 or 4 hours, optimum contact time was taken as 3 hours.

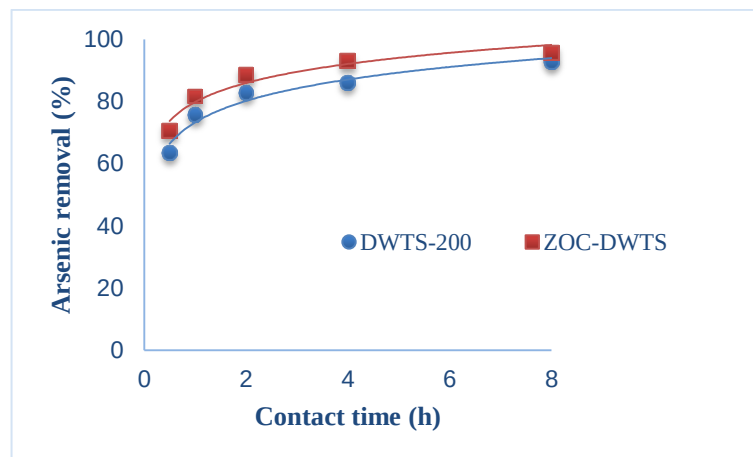


Figure 5.22 Impact of contact time on DWTS-200 and ZOC-DWTS

For ZOC-DWTS, approximately 71% of arsenic was removed within 30 minutes, and at the end of 2 hours removal rate increased to about 89%. After that, arsenic uptake slightly increased and reached to approximately 96% at the end of the 8 hours. Since the increases in removal rates were not significant after 3 or 4 hours, optimum contact time was taken as 3 hours, too.

5.3.3 Impact of Initial Concentration on Arsenic Removal

The effect of initial arsenic concentration on DWTS-200 and ZOC-DWTS adsorption was shown at Figure 5.23. For both materials, arsenic removal rates did not change significantly when initial arsenic concentration was raised. In the experiments the maximum arsenic adsorption was obtained as 98.6% for initial arsenic concentration of 44.2 and 94.18 $\mu\text{g/L}$ for DWTS-200. The maximum arsenic adsorption was obtained as 98.2% for initial arsenic concentration of 94.18 $\mu\text{g/L}$ for ZOC-DWTS. Concentration of the material decreased from 94.18 $\mu\text{g/L}$ to 1.76 $\mu\text{g/L}$.

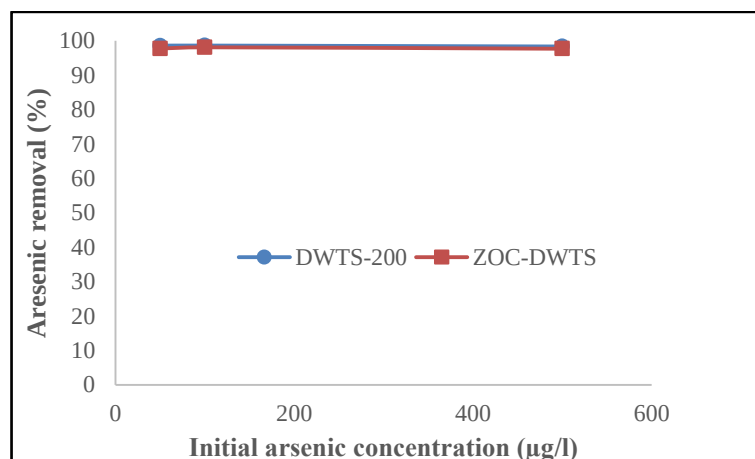


Figure 5.23 Impact of initial arsenic concentration on DWTS-200 and ZOC-DWTS

5.3.4 Impact of Adsorbent Dose on Arsenic Removal

Experiments were carried out with varied adsorbent dosages (1, 5 and 10 g/L) to determine the optimum adsorbent dose. As can be seen Figure 5.24, removal rates did not significantly change and reached to 99,5% for 1 g/L for ZOC-DWTS and 98,6% for 10 g/L for DWTS-200. The results showed that 1 g/L adsorbent dose is sufficient to obtain desired arsenic levels for 50 µg/L initial arsenic concentration.

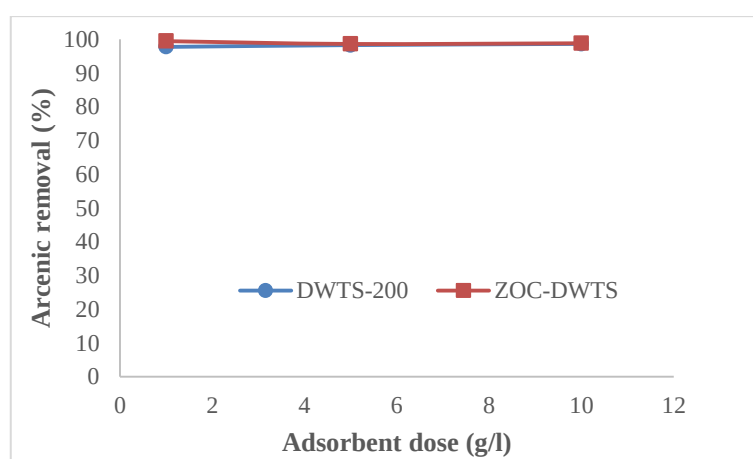


Figure 5.24 Impact of adsorbent dose on DWTS-200 and ZOC-DWTS

5.3.5 Co-removal of Arsenic and Antimony Ions

In order to simultaneously remove arsenic and antimony ions from water different mixtures were prepared. The mixtures used in the study were 90 $\mu\text{gAs/L}$ - 90 $\mu\text{gSb/L}$, 35 $\mu\text{gAs/L}$ - 35 $\mu\text{gSb/L}$, 90 $\mu\text{gAs/L}$ -35 $\mu\text{gSb/L}$, and 35 $\mu\text{gAs/L}$ - 90 $\mu\text{gSb/L}$. Using these mixtures, batch experiments were performed to specify the optimum As/Sb rate. As can be seen in Figure 5.25, coating with zirconium oxide is not effective for arsenic removal, removal rate of arsenic is nearly the same for DWTS-200 and ZOC-DWTS. When the concentration of arsenic is high (i.e. 90 $\mu\text{g/L}$), zirconium is efficient for removal of antimony. The treatment efficiency of ZOC-DWTS is higher than DWTS-200. Nevertheless, when the concentration of arsenic is low (i.e. 35 $\mu\text{g/L}$), zirconium isn't efficient at antimony removal.

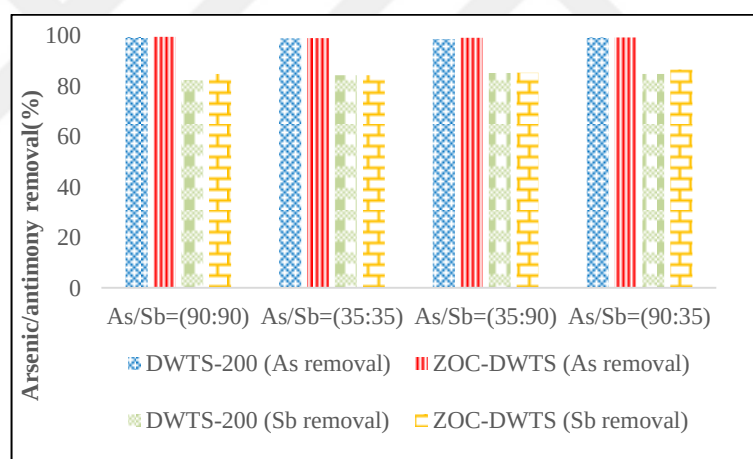


Figure 5.25 Effect of As/Sb ratios on DWTS-200 and ZOC-DWTS

5.3.6 Impact of Existing Ions in Groundwater on Adsorption

Real groundwater sample was used to show the impact of other ions on As adsorption. 1 g/L dose of DWTS-200 and ZOC-DWTS were used in the experiments at pH 3 at room temperature (25°C). The remaining concentrations of ions were measured after the adsorption process was completed and results are shown in Table 5.4. The concentration of arsenic, antimony and iron reduced after adsorption for

each materials by Table 5.4. Only manganese increased because DWTS released manganese.

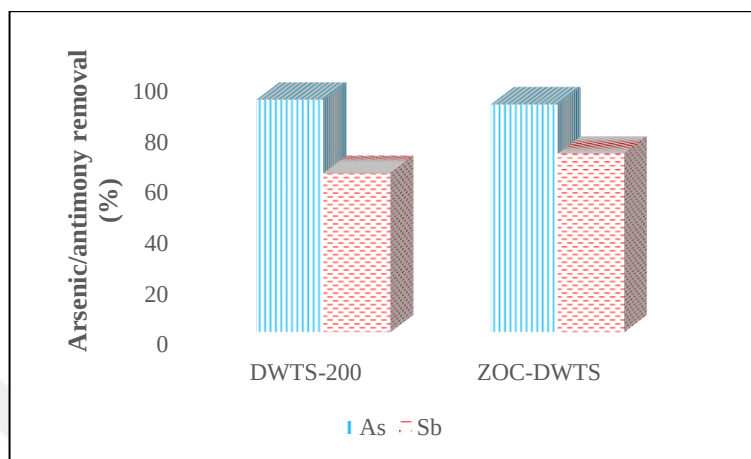


Figure 5.26 Effect of ions existing in groundwater sample on arsenic adsorption on DWTS-200 and ZOC-DWTS

Table 5.4 Concentrations of ions/anions in groundwater before and after adsorption

Ions/Anions	Groundwater	After DWTS-200 treatment	After ZOC-DWTS treatment
Fe($\mu\text{g/L}$)	300.29	15.36	14.73
Mn($\mu\text{g/L}$)	269.16	380.14	670.15
PO ₄ (mg/L)	<0.4	n.a	n.a
TOC (mg/L)	0	0.89	1.54
As ($\mu\text{g/L}$)	9.21	0.79	0.96
Sb ($\mu\text{g/L}$)	56.76	21.23	16.87

Figure 5.26 shows the effect of ions existing in groundwater sample on arsenic and antimony adsorption on DWTS-200 and ZOC-DWTS. In regard to Figure 5.26, approximately 91.5% of arsenic and 63% antimony treated from groundwater samples with DWTS-200 however when the synthetic water was used, the efficiency increased to 99% and 85% (Figure 5.25). For ZOC-DWTS, adsorption experiments with real groundwater samples were completed with 89.6% of arsenic and 70.3%

antimony removal efficiencies whereas 99.2% of arsenic and 85.3 antimony from synthetic water was effectively treated. The results gathered from experiments with real groundwater samples were shown that ions and anions have a significant impact on the treatment performance for both materials. Results indicated that existence of competing anions was resulted by decreasing in arsenic and antimony removal efficiency approximately 8% for arsenic and 22% for antimony for DWTS-200. For ZOC-DWTS, the reduction of percent removal was 9.6% for arsenic and 15% for antimony, comparing to synthetic water. Li et al. (2012) and Nekhunguni et al. (2017) found out that PO_4^{3-} had an inhibitory effect for As and Sb removal at high concentration. In this study PO_4^{3-} had insignificant effect on As and Sb removal because $<0.4 \text{ mg/L}$.

5.4 Kinetic Studies

Arsenic compounds removal rate from solution by an adsorbent is important issue for adsorption practices. The solute uptake rate can be calculated by using various contact time required for the adsorption process with the kinetic analysis. Therefore, kinetic studies were performed for 1 g/L adsorbent dose of DWTS-200 and ZOC-DWTS. The kinetic tests were performed for a period of 8 hours at the speed of 150 rpm. Studies were performed at various initial arsenic concentrations. These concentrations were 45.40, 107.50 and 515.20 $\mu\text{g/L}$. Samples were taken with various time intervals (i.e. 30, 60, 120, 240 and 480 minutes), arsenic measurements were done and adsorption capacity was calculated.

5.4.1 Results for DWTS-200

The kinetic data for As(T) sorption from DWTS-200 is shown in Figure 5.27. In this figure, q_e , which defines the quantity of adsorbed As(T) per unit amount of DWTS-200 at equilibrium, is depicted with respect to time.

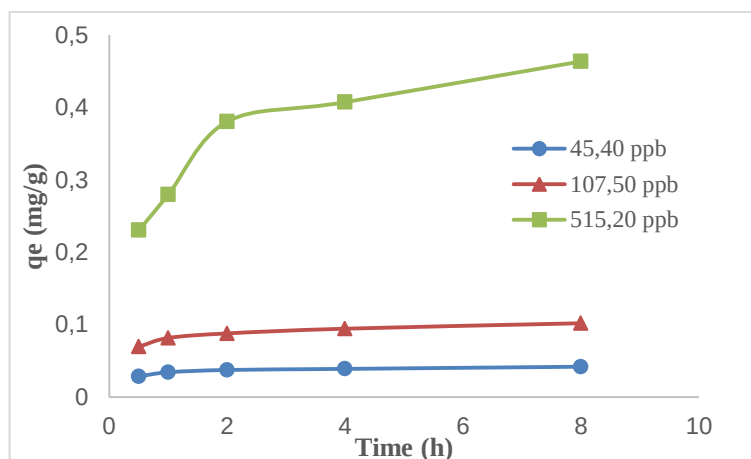


Figure 5.27 Adsorption kinetics of arsenic for DWTS-200

As seen in the Figure 5.27, for about 45.40 $\mu\text{g/L}$ initial arsenic concentration, the amount of arsenic adsorbed by DWTS-200 was 0.0391 mg/g within 4 hours yielding 86.12% removal efficiency. Adsorption capacity slightly increased at the end of the 8 hours of contact time and reached 0.0421 mg/g. Adsorption capacities reached to 0.1021 and 0.4636 mg/g for initial arsenic concentration of 107.50 and 515.20 $\mu\text{g/L}$. The conducted results revealed higher adsorption capacity for DWTS-200 with increasing initial arsenic concentrations since there was enough adsorption sites.

To analyze As(T) adsorption rates for DWTS-200 and ZOC-DWTS, the kinetic data was adapted to first order, pseudo-first order, second order, and pseudo-second order reaction kinetics, the linear models of which are given in Figures 5.28, 5.29, 5.30, and 5.31, respectively. Table 5.5 offers the equations for these kinetics, along with the coefficient of determination (R^2) values.

Table 5.5 Kinetic equations for DWTS-200

Kinetic of reaction	Initial concentration ($\mu\text{g/L}$)	Equation of reaction	R^2
First order	45.40	$\ln C_t = -0.2572t + 3.0161$	0.7398
	107.50	$\ln C_t = -0.3044t + 3.9136$	0.8217
	515.2	$\ln C_t = -0.2527t + 5.7999$	0.879
Pseudo-first-order	45.40	$\ln (q_e - q_t) = -1.5697t - 3.544$	0.9565
	107.50	$\ln (q_e - q_t) = -1.2627t - 2.7564$	0.8909
	515.2	$\ln (q_e - q_t) = -1.3211t - 0.92$	0.9846
Second order	45.40	$1/C_t = 0.0021t + 0.0022$	0.9852
	107.50	$1/C_t = 0.0208t + 0.0109$	0.9794
	515.2	$1/C_t = 0.0324t + 0.0434$	0.9738
Pseudo-second-order	45.40	$t/q_t = 23.078t + 6.8474$	0.9993
	107.50	$t/q_t = 9.481t + 3.1563$	0.9991
	515.2	$t/q_t = 2.0017t + 1.4096$	0.9980

As it was clarified in Chapter 3, first order reaction kinetic is predicated on the concentration of solution and given as Eq. 3.9. Linear model of first order reaction kinetics is graphed in Figure 5.28. The R^2 value was determined as 0.7398, 0.8217 and 0.879 for initial arsenic concentrations of 45.40, 107.50 and 515.20 $\mu\text{g/L}$ (Table 5.5).

As it was explained in Chapter 3.3.2, the pseudo-first order model is predicated on the solid capacity and defined in Eq. 3.11. Linear model of pseudo-first order kinetics is graphed in Figure 5.29. The R^2 was determined as 0.9565, 0.8909 and 0.9846 for initial arsenic concentrations of 45.40, 107.50 and 515.20 $\mu\text{g/L}$ (Table 5.5).

Kinetic parameters of the second order rate equation given in Eq. 3.13 are specified from the graph of $1/C_t$ against time at a specified initial concentration.

Linear model of second order kinetics is graphed in Figure 5.30. The R^2 value was determined as 0.9852, 0.9794 and 0.9738 for initial arsenic concentrations of 45.40, 107.50 and 515.20 $\mu\text{g/L}$ (Table 5.5).

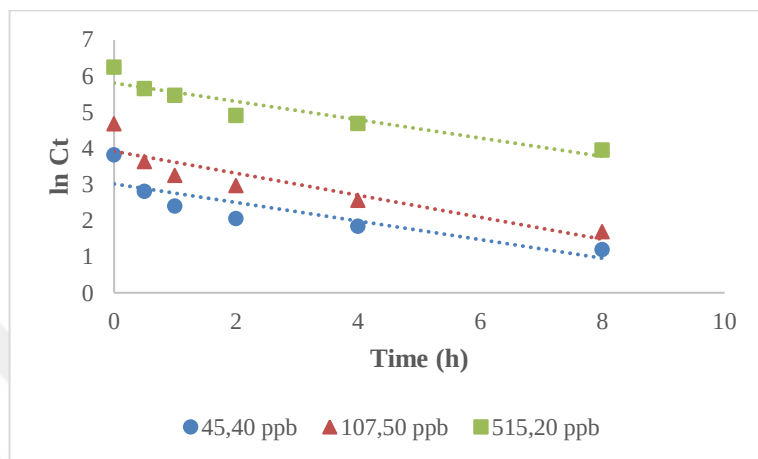


Figure 5.28 Linear model of first order reaction kinetics for DWTS-200

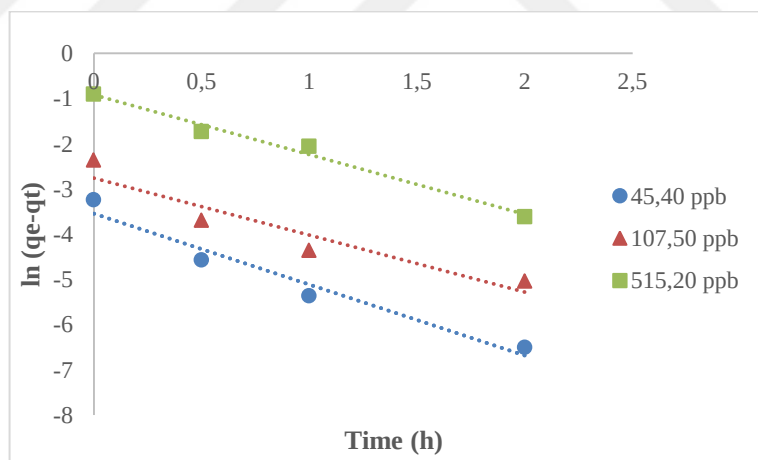


Figure 5.29 Linear model of pseudo first order reaction kinetics for DWTS-200

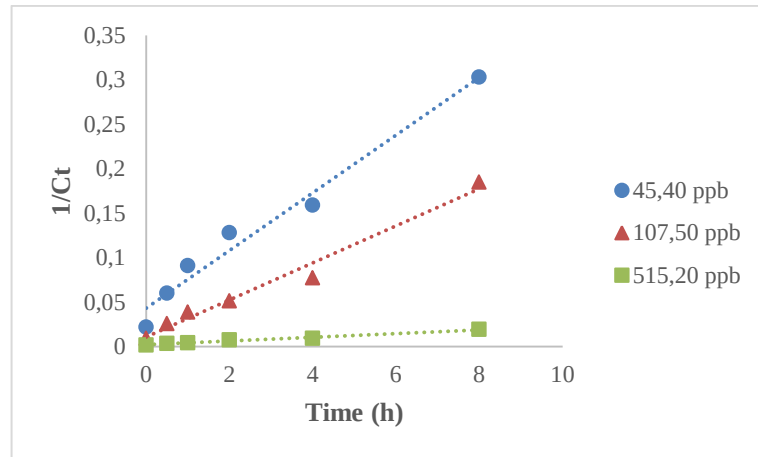


Figure 5.30 Linear model of second order reaction kinetics for DWTS-200

The expression of the pseudo-second order model is predicated on the capacity of adsorption and presented in Eq. 3.15. From the plotting the t/q_t versus t , Figure 5.31 is obtained. The highest R^2 values (>0.998) were calculated for the pseudo-second order reaction equation. In regard to R^2 , the adsorption process fitted better to the pseudo-second order kinetic than other models. This result agrees with previous literature, which outlines that the pseudo-second-order model represents a better adsorption kinetic (Kim et.al. 2022; Jeon et. al., 2018). This study was also revealed that the adsorption mechanism of arsenic on a metal oxide surface was a favorable chemical interaction between adsorbent and adsorbate. Similarly, Nandi et al. (2021) reported that arsenic removal with graphene nanoplatelets adsorbent material prepared from nail waste, were explained with the pseudo-second order reaction kinetics.

Adsorption rate is determined from the slope of lines and that is coefficient of time. The experiments proved that adsorption rate diminished with increased initial concentration in consequence of limited adsorption sites.

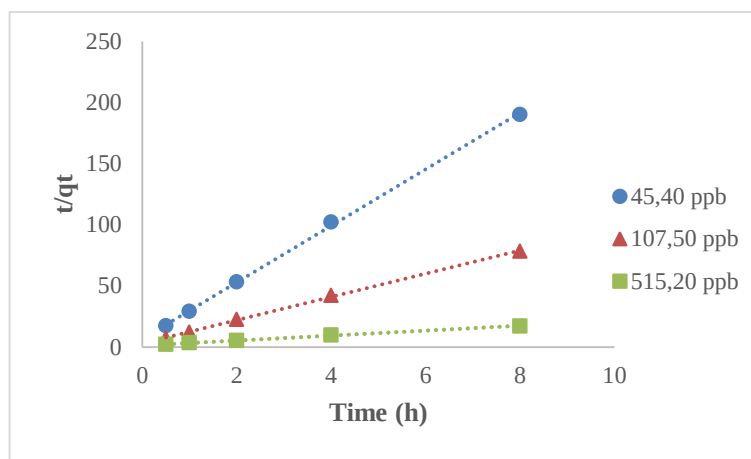


Figure 5.31 Linear model of pseudo-second order reaction kinetics for DWTS-200

5.4.2 Results for ZOC-DWTS

Adsorption kinetics of arsenic sorption from ZOC-DWTS is shown in Figure 5.32. In this figure, q_e , which defines the quantity of As(T) adsorbed per unit amount of ZOC-DWTS at equilibrium, is drew with respect to time. From this figure, it can be seen clearly for 45.40 $\mu\text{g/L}$ initial concentration, the amount of arsenic adsorbed by ZOC-DWTS was 0.0423 mg/g within 4 hours yielding 93.17% removal efficiency. Adsorption capacity slightly increased at the end of the 8 hours of contact time and reached 0.0434 mg/g. Adsorption capacities reached to 0.1038 and 0.4862 mg/g for initial arsenic concentration of 107.50 and 515.20 $\mu\text{g/L}$. The conducted results revealed that the adsorption capacity of ZOC-DWTS rised with rising initial arsenic concentrations due to the availability of sufficient adsorption sites.

The kinetic datum was applied to different models (first order, pseudo-first order, second order and pseudo-second order reaction models). Figure 5.33-Figure 5.36 show linear model of these four reactions kinetics for ZOC-DWTS. Also, the equations and R^2 values of these kinetic of reactions are presented in Table 5.6.

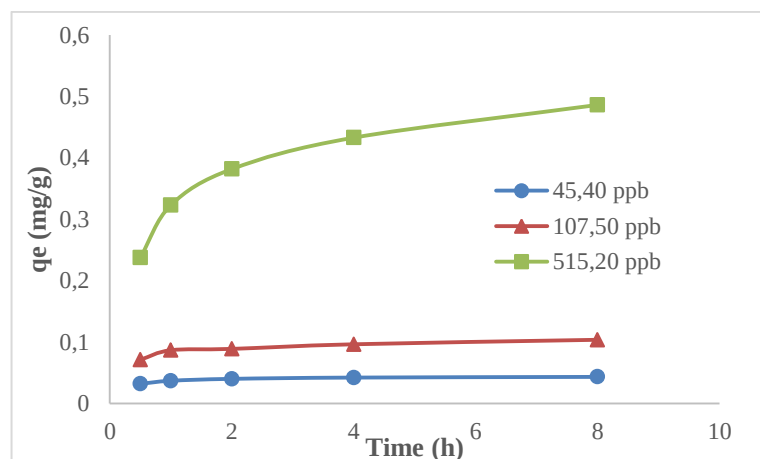


Figure 5.32 Adsorption kinetics of arsenic for ZOC-DWTS

Table 5.6 Kinetic equations for ZOC-DWTS

Kinetic of reaction	Initial concentration (µg/L)	Equation of reaction	R ²
First order	45.40	$\ln Ct = -0.3141t + 2.81$	0.715
	107.50	$\ln Ct = -0.3446t + 3.8768$	0.8398
	515.2	$\ln Ct = -0.3218t + 5.7979$	0.9314
Pseudo-first-order	45.40	$\ln (q_e - qt) = -1.4194t - 3.548$	0.9184
	107.50	$\ln (q_e - qt) = -1.2151t - 2.8238$	0.8044
	515.2	$\ln (q_e - qt) = -1.0398t - 1.0024$	0.9677
Second order	45.40	$1/Ct = 0.0586t + 0.0538$	0.9796
	107.50	$1/Ct = 0.031t + 0.0032$	0.9537
	515.2	$1/Ct = 0.004t + 0.0006$	0.9619
Pseudo-second-order	45.40	$t/qt = 22.487t + 4.5263$	1.000
	107.50	$t/qt = 9.3496t + 2.9217$	0.999
	515.2	$t/qt = 1.9141t + 1.2932$	0.999

The linear model for the first order reaction is graphed in Figure 5.33. The value of R^2 was determined as 0.7150, 0.8398 and 0.9314 for initial arsenic concentrations of 45.40, 107.50 and 515.20 µg/L (Table 5.6).

The parameters for the pseudo-first order model can be achieved from the graph of $\ln(q_e - qt)$ versus time at a given initial concentration. The linear model for the pseudo-first order reaction is graphed in Figure 5.34. The value of R^2 was determined as 0.9184, 0.8044 and 0.9677 for initial arsenic concentrations of 45.40, 107.50 and 515.20 $\mu\text{g/L}$ (Table 5.6).

The parameters for the second order model can be achieved from the graph of $1/Ct$ versus time at a specified initial concentration. The linear model for the second order reaction is graphed in Figure 5.35. The value of R^2 was determined as 0.9796, 0.9537 and 0.9619 for initial arsenic concentrations of 45.40, 107.50 and 515.20 $\mu\text{g/L}$ (Table 5.6).

For the pseudo-second order model, thereby graphing the t/qt against time, Figure 5.36 is obtained. The highest R^2 values (>0.999) for the pseudo-second order reaction equation were measured. Considering the R^2 values, the adsorption was found to best fit the pseudo-second order model.

Adsorption rate is specified from the slope of lines and that is coefficient of time. The experiments demonstrated that the rate of adsorption diminished with increased initial concentration because of limited adsorption sites.

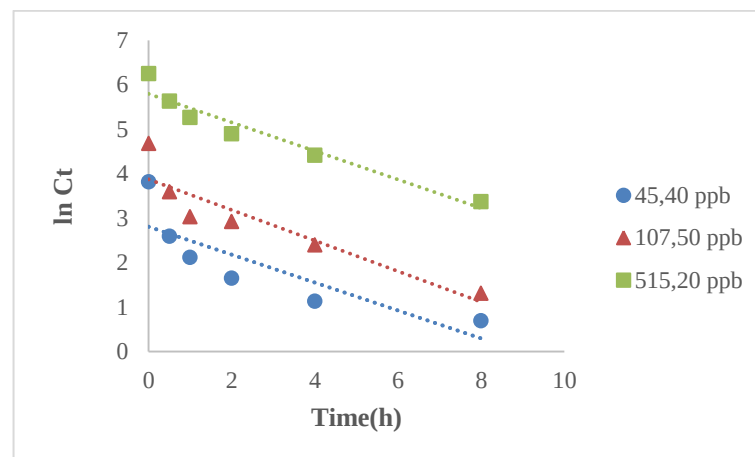


Figure 5.33 Linear model of first order reaction kinetics for ZOC-DWTS

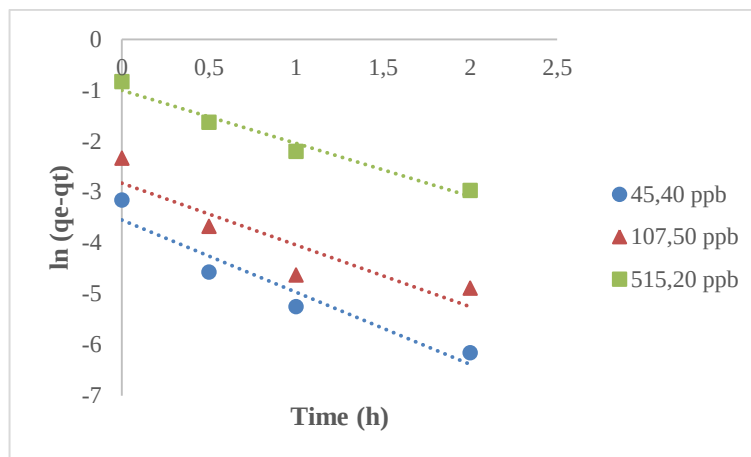


Figure 5.34 Linear model of pseudo-first order reaction kinetics for ZOC-DWTS

Evaluation of the results showed that the adsorption process adapted the pseudo-second order model preferable than the other models for both DWTS-200 and ZOC-DWTS (Table 5.5 and 5.6). For DWTS-200, the pseudo-second order adsorption rate constants (k) was calculated as 78.125 g/mgmin, 28.465 g/mgmin and 2.843 g/mgmin for 45.40, 107.50 and 515.20 $\mu\text{g/L}$ initial arsenic concentrations, respectively. For ZOC-DWTS, the pseudo-second order adsorption rate constants (k) was calculated as 111.607 g/mgmin, 30.030 g/mgmin and 2.841 g/mgmin for 45.40, 107.50 and 515.20 $\mu\text{g/L}$ initial arsenic concentrations, respectively (Table 5.7).

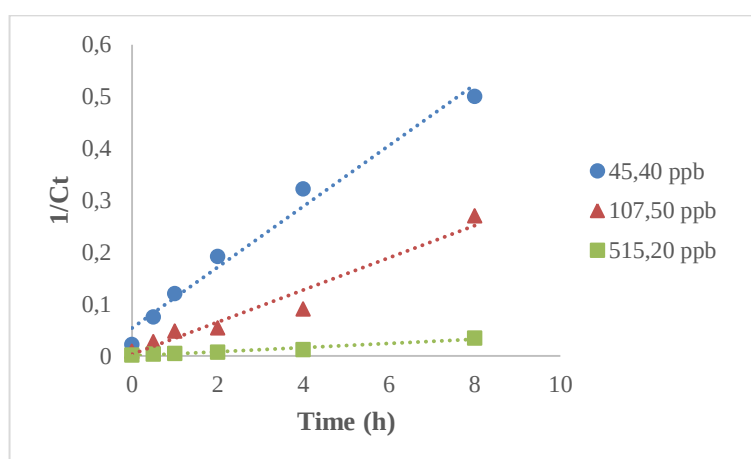


Figure 5.35 Linear model of second order reaction kinetics for ZOC-DWTS

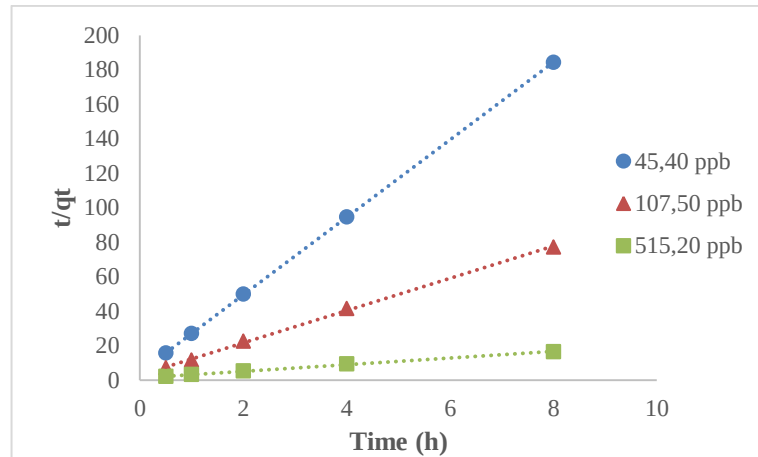


Figure 5.36 Linear model of pseudo-second order reaction kinetics for ZOC-DWTS

For both DWTS-200 and ZOC-DWTS materials, the kinetic data was defined by the pseudo-second order kinetic equation, which suggests that kinetics are determined by the lots of arsenic ions in the solution and the lotsof adsorption sites on the adsorbent surface (Chaudhry et al., 2017). The removal of arsenic can be controlled by both physi- and chemi-sorption processes, and that the removal process involves electron exchanges between anions and adsorbents (Lee et al., 2018). The formation of chemical bonds between the adsorbate and the adsorbent at suitable sites are the rate-limiting step (Arıkan, 2016; Chaudhry et al., 2017). Similar results for arsenic removal were obtained by Arıkan (2016), Chaudhry et al. (2017), Mostafa et al. (2011) and Nandi et al. (2021).

Table 5.7 The pseudo-second order adsorption rate constant for DWTS-200 and ZOC-DWTS

Material	Initial Concentration (µg/L)	Equation of reaction	qe (mg/g)	k (g/mg.min)
DWTS-200	45.40	$t/qt = 23.078t + 6.8474$	0.0433	78.125
	107.50	$t/qt = 9.481t + 3.1563$	0.1055	28.465
	515.2	$t/qt = 2.0017t + 1.4096$	0.4996	2.843
ZOC-DWTS	45.40	$t/qt = 22.487t + 4.5263$	0.0445	111.607
	107.50	$t/qt = 9.3496t + 2.9217$	0.1069	30.030
	515.2	$t/qt = 1.9141t + 1.2932$	0.5220	2.841

5.5 Isotherm Studies

Fitting adsorption findings to various isotherms is required for modeling in both theory and practice. Also, the correlation of the findings regarding the equilibrium is essential to optimize adsorption. Here, the experimental adsorption findings were described using the Langmuir, Temkin, and Freundlich isotherm equations.

In this study, isotherm studies were performed for DWTS-200 and ZOC-DWTS to investigate the adsorption characteristics and adsorption capacities. Varying adsorbent dosages (1-10 g/L) were used with fixed initial arsenic concentration. Experiments were performed for a period of 3 hours at a speed of 150 rpm. Samples were received after three hours and analysed for arsenic. Adsorption capacity was calculated as the quantity of adsorbed adsorbate in milligrams per one gram of adsorbent at a given temperature.

5.5.1 Isotherm Results for DWTS-200

Langmuir, Freundlich and Temkin isotherms were studied to determine the isotherm constants. Figure 5.37, 5.38 and 5.39 show Langmuir, Freundlich and Temkin isotherms for DWTS-200. Additionally, isotherm constant are presented in Table 5.8.

Table 5.8 Langmuir, Freundlich and Temkin isotherm constant at 25°C for DWTS-200

Adsorbent	Adsorbent dose (g/L)	Langmuir			Freundlich			Temkin		
		q _{max} (mg/g)	b (L/mg)	R ²	1/n	k _f (mg/g)	R ²	A _T (L/g)	b _T (kJ/mol)	R ²
DWTS-200	1	13.089	3.84	0.955	0.648	6.527	0.982	0.02	0.21	0.658
	5	0.205	65.8	0.904	0.841	9.119	0.973	0.29	0.395	0.681
	10	0.071	120.48	0.837	1.01	21.32	0.970	0.507	0.637	0.656

The linear form of Langmuir isotherm can be depicted by plotting the $1/q_e$ against $1/C_e$ values. Langmuir constants $q_{\max}$ and b are found from the point where the linear equation cuts the Y-axis and the slope of the curve.

The linearized form of Freundlich isotherm is drawn by plotting the $\ln C_e$ values vs. $\ln q_e$. Freundlich constants $1/n$ and k_f are found from the breakpoint and the slope of the straight line.

The linearized form of Temkin isotherm is drawn by plotting the $\ln C_e$ values vs. q_e . A_T and b_T , called the Temkin constants, are found from the slope and intercept of the straight line.

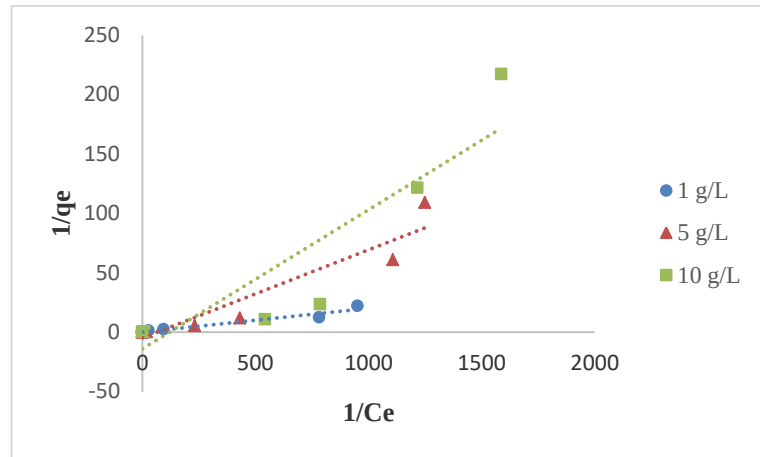


Figure 5.37 Langmuir isotherm for DWTS-200

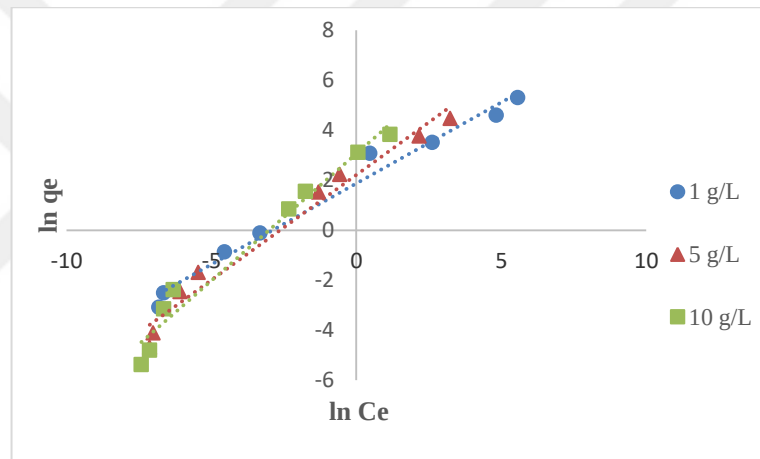


Figure 5.38 Freundlich isotherm for DWTS-200

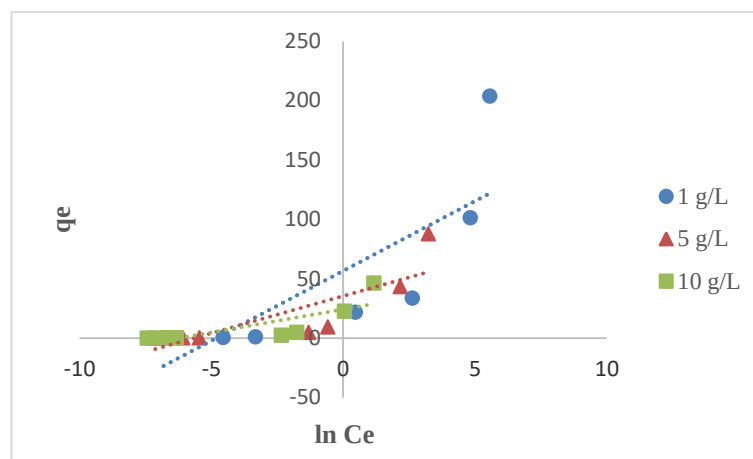


Figure 5.39 Temkin isotherm for DWTS-200

Freundlich model was fitted better than other models (Langmuir and Temkin models) with relatively higher R^2 values 0.982, 0.973 and 0.970 for 1, 5 and 10 g/L dosages of DWTS-200. The maximum adsorption capacity determined by Freundlich model was about 21.32 mg/g for 10 g/L adsorbent dose of DWTS-200 (Table 5.8). Freundlich constant, n , is the exponent that stands for intensity of adsorption or heterogeneity of the surface. This value is preferred to be between 1-10 for convenient adsorption. A value of 1 indicates that the separation is independent of the concentration, while values above 1 indicate normal adsorption and values below 1 show cooperative adsorption. In this study the $1/n$ values were 0.648, 0.841 and 1.01 for 1, 5 and 10 g/L adsorbent doses, therefore 1 g/L and 5 g/L dosages were favourable adsorption phenomenon. 10 g/L adsorbent doses were overdose and unfavourable adsorption.

Similar results were also presented in various studies by Chaudhry et al. (2017), Gang et al. (2010) and Thirunavukkarasu et al. (2001).

5.5.2 Isotherm Results for ZOC-DWTS

Datum of isotherm models for ZOC-DWTS are illustrated in Figures 5.40, 5.41 and 5.42. Table 5.9 shows isotherm constants and the co-efficient of determination values (R^2).

Table 5.9 Langmuir, Freundlich and Temkin isotherm constant at 25°C for ZOC-DWTS

Adsorbent	Adsorbent dose (g/L)	Langmuir			Freundlich			Temkin		
		q_{max} (mg/g)	b (L/mg)	R^2	$1/n$	k_f (mg/g)	R^2	A_T (L/g)	bt (kJ/mol)	R^2
ZOC-DWTS	1	0.842	182	0.913	0.62	7.38	0.972	0.196	0.243	0.726
	5	0.722	22.2	0.991	0.85	8.36	0.98	0.242	0.39	0.703
	10	0.137	68.5	0.979	1.03	18.47	0.989	0.435	0.643	0.627

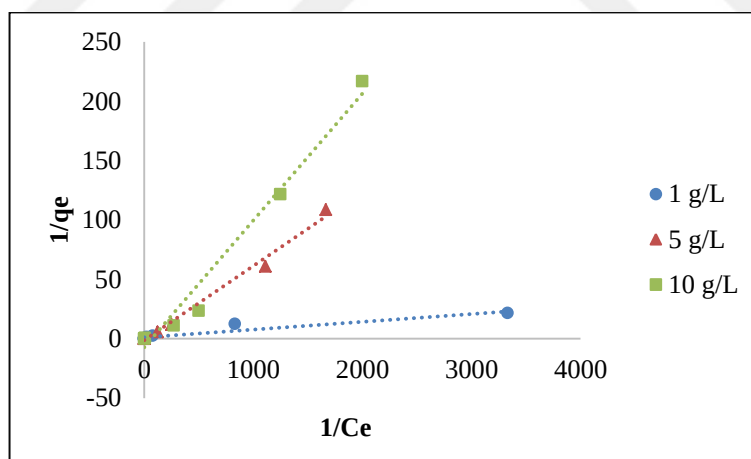


Figure 5.40 Langmuir isotherm for ZOC-DWTS

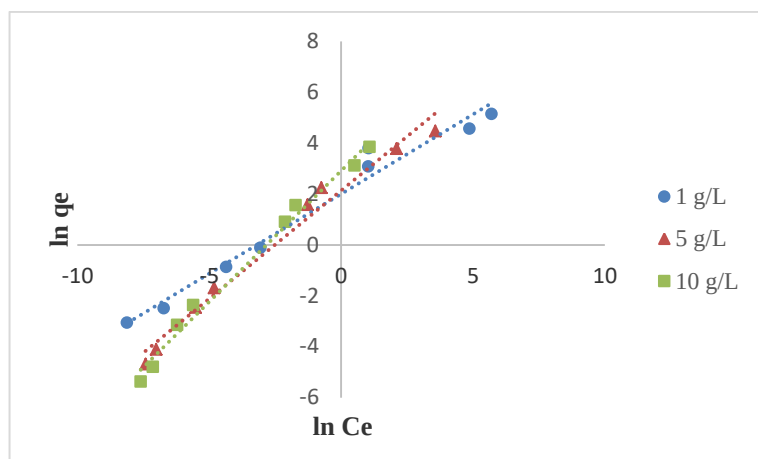


Figure 5.41 Freundlich isotherm for ZOC-DWTS

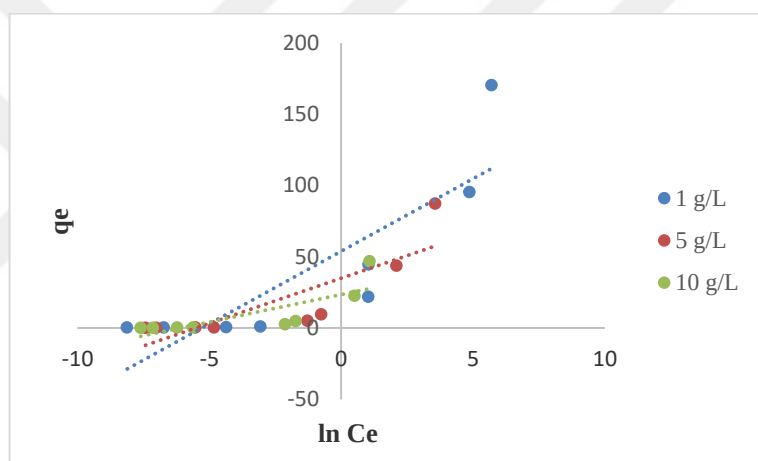


Figure 5.42 Temkin isotherm for ZOC-DWTS

R^2 values proved that the Freundlich model was more proper to explain the results than the other models especially Temkin model. The values of R^2 were 0.972, 0.980 and 0.989 for 1, 5 and 10 g/L dosages of ZOC-DWTS. The maximum capacity of adsorption was calculated as 18.47 mg/g for 10 g/L dose of ZOC-DWTS (Table 5.9). The $1/n$ values were 0.62, 0.85 and 1.03 for 1, 5 and 10 g/L adsorbent doses, therefore 1 g/L and 5 g/L dosages were favourable adsorption phenomenon.

The results showed that DWTS-200 and ZOC-DWTS have superior adsorption capacity than most of the iron contained or modified materials in the literature such

as ironoxide coated rock 0.36 mg/g (Maji et al., 2011), iron oxide coated sand 0.142 mg/g and iron oxide coated sepiolite 0.0501 mg/g (Arıkan, 2016), ironoxide coated perlite 0.39 mg/g (Mostafa et al., 2011). The isotherm data of each material (i.e. DWTS-200 and ZOC-DWTS) Sb(III) were better fitted by Freundlich model demonstrating that the adsorption of As on material is a multilayer process.

5.6 Column Studies

5.6.1 Impact of Bed Depth on Arsenic Adsorption in Column Studies

The aggeration of contaminant (arsenic) in a column depends on the amount of adsorbent filled in the fixed bed column. Each material was filled into the columns to investigate the impact of bed depth at two different bed heights, i.e. 10 and 20 cm. The effluent arsenic concentrations were depicted against volumes for each depth in Figures 5.43 and 5.44. In addition, breakthrough curves obtained at various depths (i.e. 10 cm and 20 cm) are shown in Figures 5.45 and 5.46 for DWTS-200.

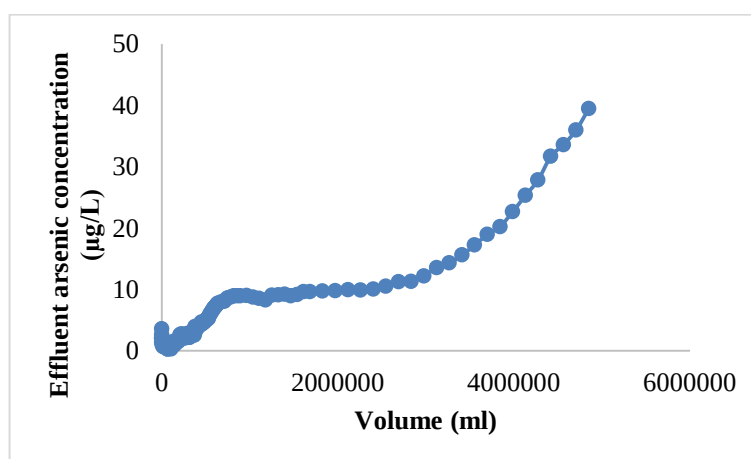


Figure 5.43 Variation of arsenic effluent concentration by treated volume for 10 cm bed depth of DWTS-200

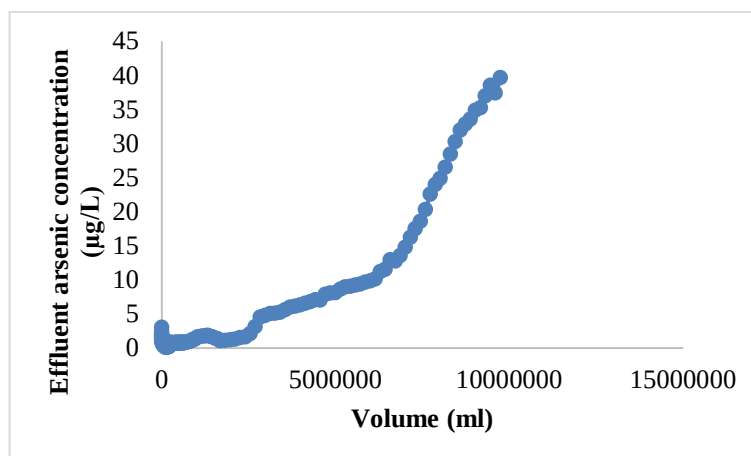


Figure 5.44 Variation of arsenic effluent concentration by treated volume for 20 cm bed depth of DWTS-200

As depicted by Figure 5.45 and 5.46, the breakthrough volumes varied with bed height. The breakthrough ($C_e/C_0=0,25$) was obtained as 2404 L for 10 cm bed depth whereas it was increased to 6004 L for 20 cm depth of bed. The breakthrough volume increased with a rising bed height from 10 to 20 cm. The binding sites were limited at low bed depths, where the arsenic compounds failed to adsorb on the surface of the DWTS-200, causing a decline in breakthrough. On the contrary, increased bed depth led to increased retention time, allowing the contaminants to penetrate deeper into the DWTS-200.

The ratio of effluent to influent arsenic concentration (C_e/C_0) increased after breakthrough point and reached to exhaustion at 4852 L of effluent volumes for 10 cm bed depth. For 20 cm bed depth, about 9748 L of feed water passed through the column until exhaustion point. Thus, the results showed that increasing bed depth caused more active adsorption site providing additional treated volume until exhaustion point.

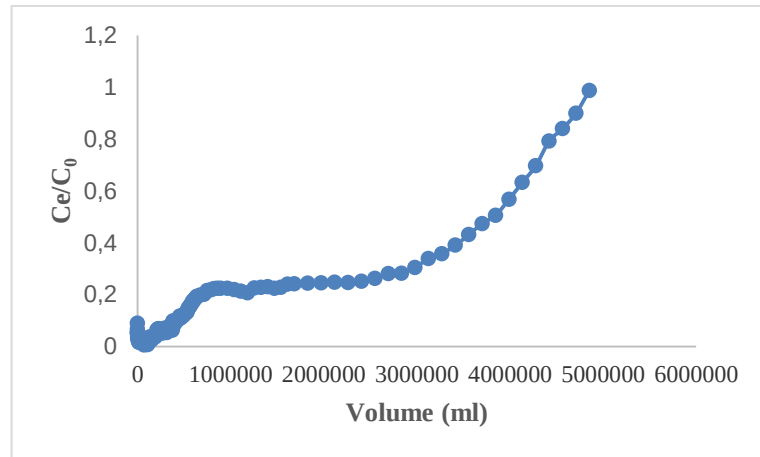


Figure 5.45 The arsenic breakthrough curve of 10 cm bed depth of DWTS-200

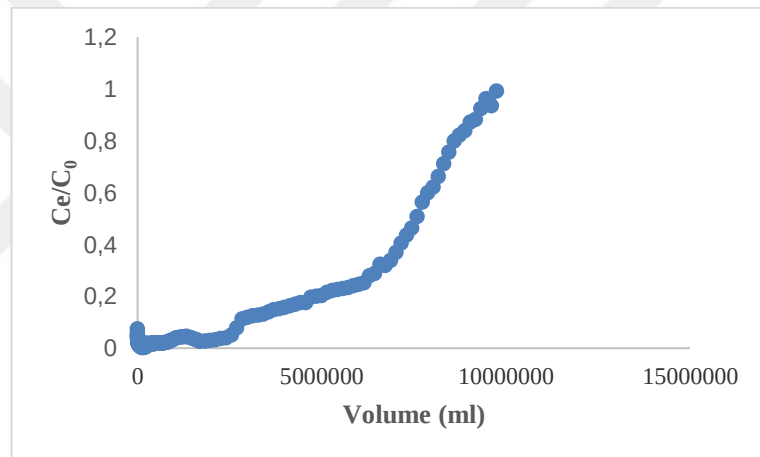


Figure 5.46 The arsenic breakthrough curve of 20 cm bed depth of DWTS-200

For ZOC-DWTS, the effluent arsenic concentrations are also plotted against effluent volumes, at different bed depths, i.e. 10 cm and 20 cm, and presented in Figures 5.47 and 5.48. Additionally, breakthrough curves acquired for arsenic adsorption onto ZOC-DWTS at various depths are shown in Figures 5.49 and 5.50.

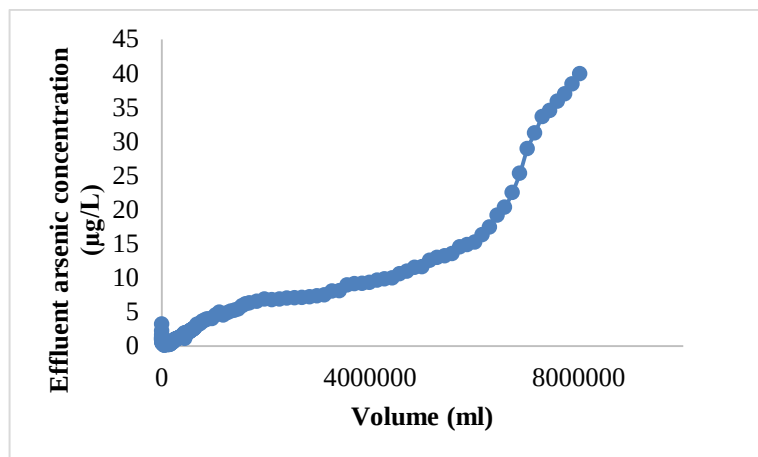


Figure 5.47 Variation of arsenic effluent concentration by treated volume for 10 cm bed depth of ZOC-DWTS

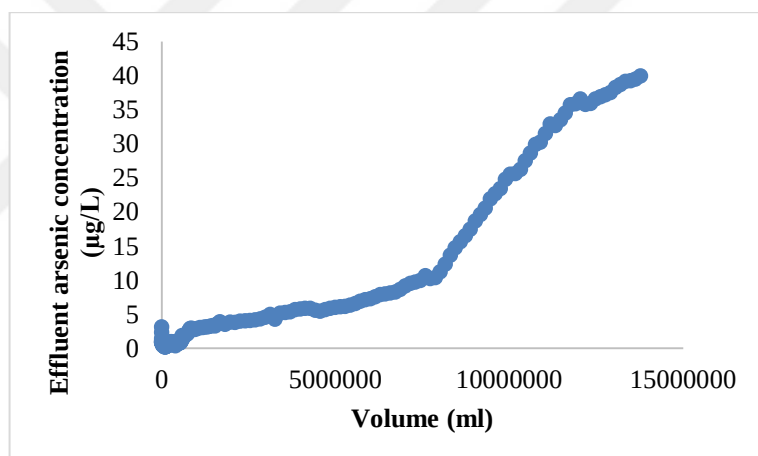


Figure 5.48 Variation of arsenic effluent concentration by treated volume for 20 cm bed depth of ZOC-DWTS

As can be seen Figure 5.49, approximately 4420 L of feed water was treated to below 10 µg/L effluent arsenic concentration. Thereby, breakthrough point ($C_e/C_0 = 0.249$) occurred at 4420 L of effluent volume and after this point, C_e/C_0 value increased up to 8020 L. It can be explained that the adsorption zone was nearly completely exhaust ($C_e/C_0 = 0.99$).

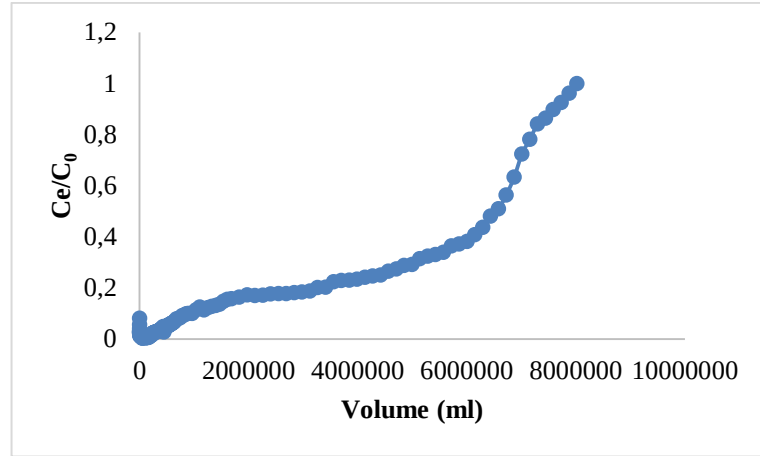


Figure 5.49 The arsenic breakthrough curve of 10 cm bed depth of ZOC-DWTS

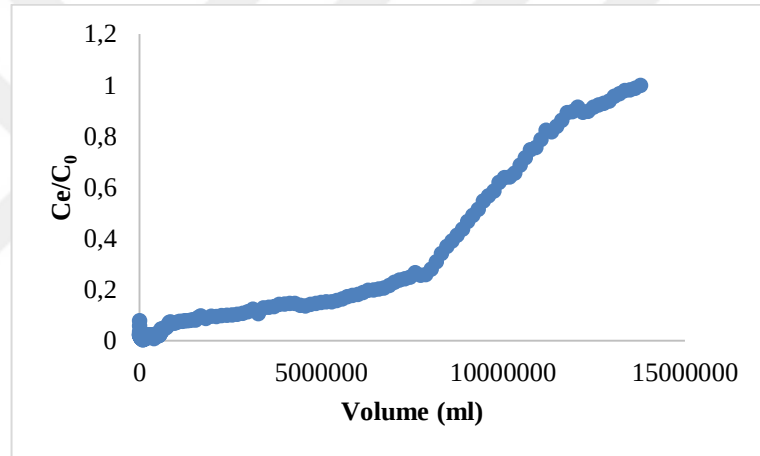


Figure 5.50 The arsenic breakthrough curve of 20 cm bed depth of ZOC-DWTS

The breakthrough volume increased 4420 L to 7444 L with a rising bed depth from 10 to 20 cm. $C_e/C_0 = 0.25$ was taken as breakthrough point which indicates 10 $\mu\text{g/L}$ arsenic concentration in the effluent. Column started to exhaust after 7444 L and effluent arsenic concentration increased to 39.9 $\mu\text{g/L}$ at 13780 L volume. The C_e/C_0 value was 0.99 at the exhaustion point (i.e. 13780 L effluent volume); and then no further arsenic adsorption was observed.

5.6.2 Impact of Bed Depth on Antimony Adsorption in Column Studies

The materials i.e. DWTS-200 and ZOC-DWTS were filled into the columns at two different bed heights, i.e. 10 and 20 cm to investigate the impact of bed depth for antimony removal. The effluent antimony concentrations were depicted against volumes for each depth in Figures 5.51 and 5.52. Breakthrough curves were acquired for antimony adsorption onto DWTS-200 at various depths (i.e. 10 cm and 20 cm) and the results are shown in Figures 5.53 and 5.54.

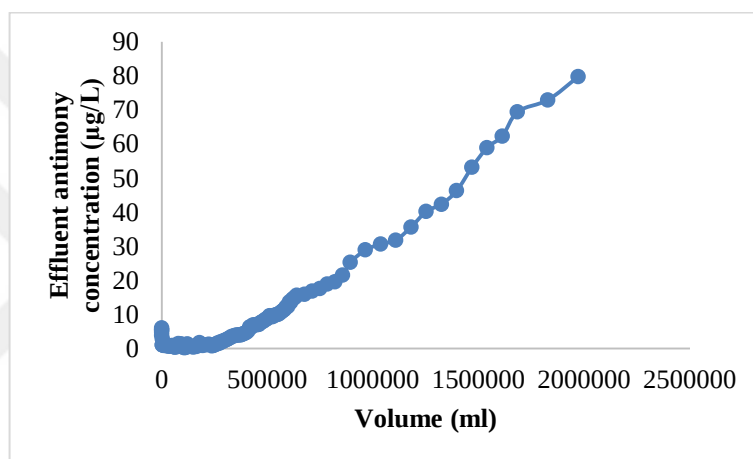


Figure 5.51. Variation of antimony effluent concentration by treated volume for 10 cm bed depth of DWTS-200

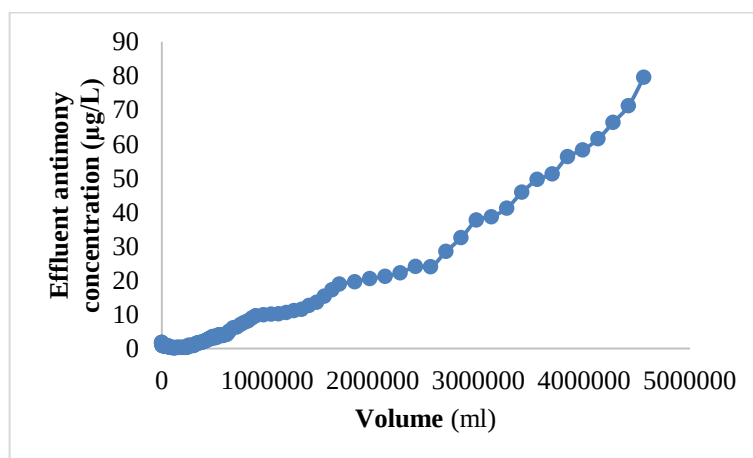


Figure 5.52. Variation of antimony effluent concentration by treated volume for 20 cm bed depth of DWTS-200

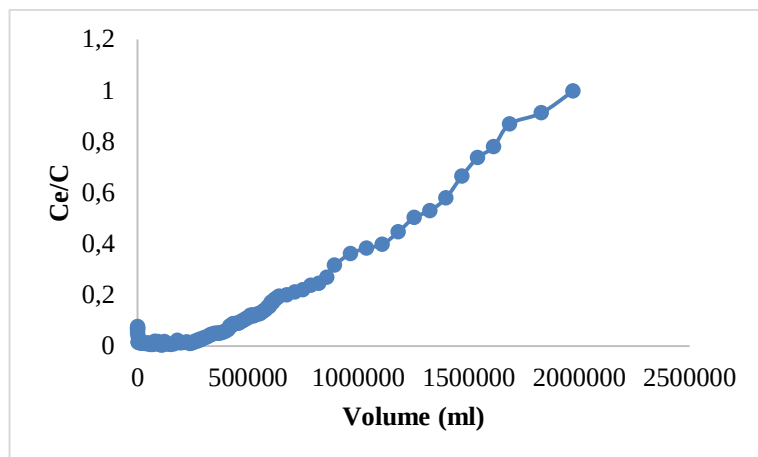


Figure 5.53 The breakthrough curve of 10 cm bed depth of DWTS-200

As depicted in Figure 5.53 and 5.54, the breakthrough volumes varied with bed height. The breakthrough ($C_e/C_0=0.0625$) was obtained as about 410 L for 10 cm bed depth whereas it was increased to 640 L for 20 cm depth of bed. The breakthrough volume reduced with a decreasing bed depth from 20 to 10 cm. At low bed depths, the binding sites were limited and the antimony ions failed to diffuse into the surface of the DWTS-200, causing a decline in breakthrough. On the contrary, increased bed depth allowed increased retention time in the column, so that the antimony ions diffuse deeper into the DWTS-200.

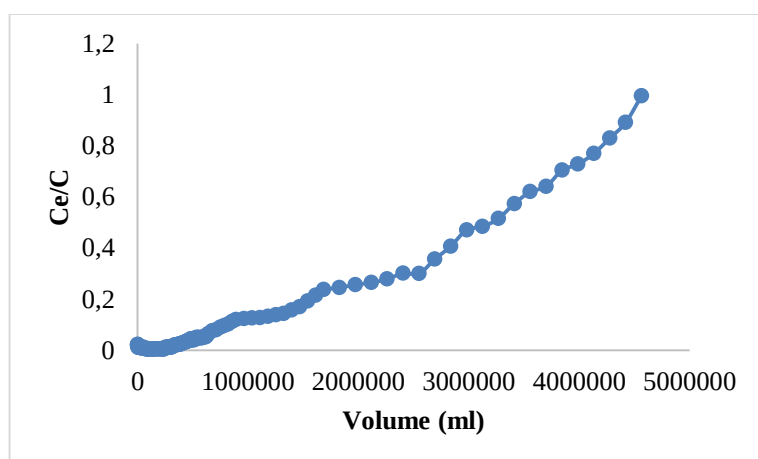


Figure 5.54 The breakthrough curve of 20 cm bed depth of DWTS-200

For 10 cm bed depth, the ratio of effluent to influent antimony concentration (C_e/C_0) rapidly increased after breakthrough point and reached to exhaustion at 1972 L of effluent volumes. Nevertheless, about 4564 L of feed water passed through the column until exhaustion point for 20 cm bed depth. Therefore, the results revealed that increasing bed depth caused more active adsorption site providing additional treated volume until exhaustion point.

For ZOC-DWTS, the effluent antimony concentrations are also plotted against effluent volumes, at different bed depths, i.e. 10 cm and 20 cm, and presented in Figures 5.55 and 5.56. Additionally, breakthrough curves acquired for antimony adsorption onto ZOC-DWTS at various depths are shown in Figures 5.57 and 5.58.

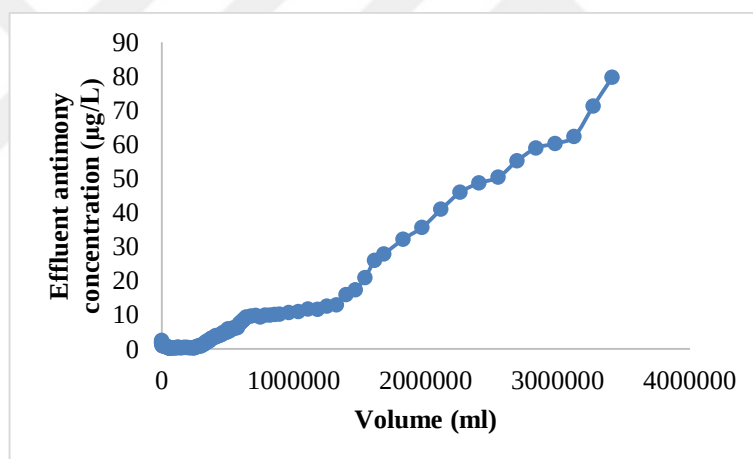


Figure 5.55 Variation of antimony effluent concentration by treated volume for 10 cm bed depth of ZOC-DWTS

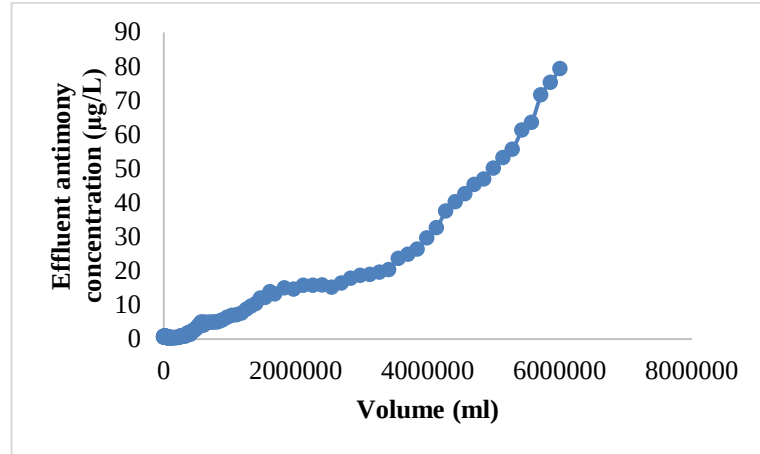


Figure 5.56 Variation of antimony effluent concentration by treated volume for 20 cm bed depth of ZOC-DWTS

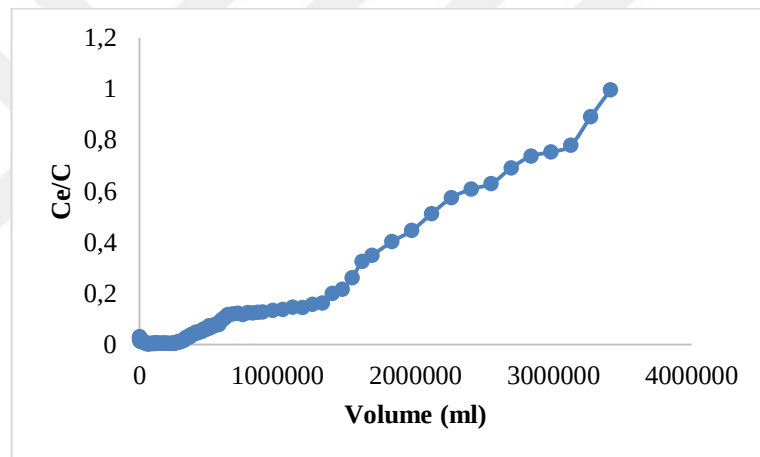


Figure 5.57 The breakthrough curve of 10 cm bed depth of ZOC-DWTS

As can be seen in Figure 5.55, approximately 504 L of feed water could be treated to below 5 µg/L effluent antimony concentration. Thus, breakthrough point ($C_e/C_0 = 0.0625$) occurred at 504 L of effluent volume and after the breakthrough point, C_e/C_0 value increased rapidly up to 3412 L. It can be explained that the adsorption zone was almost completely exhaust ($C_e/C_0 = 0.99$).

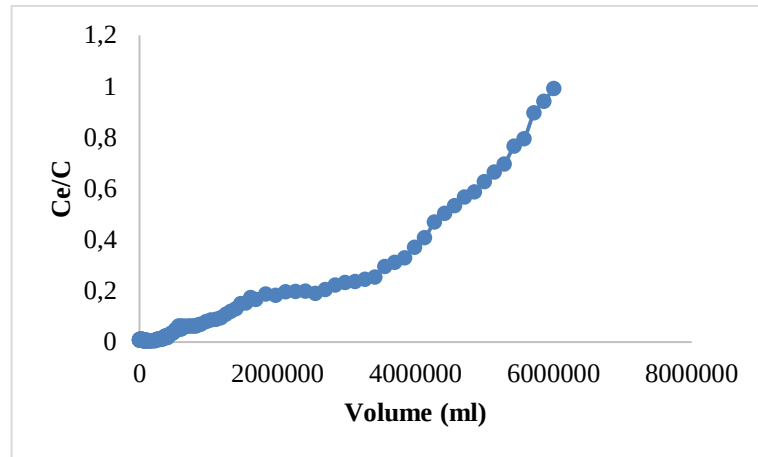


Figure 5.58 The breakthrough curve of 20 cm bed depth of ZOC-DWTS

The breakthrough volume increased with a rising bed depth from 10 to 20 cm. $C_e/C_0 = 0.0625$ was taken as breakthrough point which indicates $5 \mu\text{g/L}$ antimony concentration in the effluent. The column reached to breakthrough point at 8208 L of effluent volume. Column started to exhaust rapidly after 8208 L and effluent arsenic concentration increased to $79 \mu\text{g/L}$ at 6004 L volume. The C_e/C_0 value was 0.99 at the exhaustion point (i.e. 6004 L effluent volume), and after that no further antimony adsorption was observed.

5.7 Modeling of Fixed-Bed Adsorption

Fixed-bed adsorption is an easy and effective process that is commonly used for separation and purification, with great focus on its optimum operation conditions. The costly and time-consuming nature of adsorption performance experiments under different conditions, predicting fixed-bed adsorption using mathematical models becomes a necessity. Efforts on such models aim to provide accurate breakthrough estimation and detailed assessment of the impact of numerous variables (Xu et al., 2013).

Dynamic adsorption models often involve a macroscopic mass conservation equation, an uptake rate equation, and an isotherm. Adsorption systems involve numerous elements and mostly require accurate estimations through simplified models for practicality. This makes it difficult to propose models for general use, albeit crucial. Models are often based on certain assumptions, meaning they mostly allow to describe the conditions for a restricted number of cases. Here, we used some of the most common models to estimate the adsorption of arsenic and antimony using DWTS-200 and ZOC-DWTS. The models we used were the Thomas Model, the Bohart& Adams Model, the Yoon Nelson Model, and the Clark Model.

5.7.1 Thomas Model

The Thomas Model is one of the most widely used mathematical model to estimate the column performance (Ghribi&Chlendi, 2011; Rozada et al., 2007). The mathematical expression is defined by the equation below:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{Th}.q_0.M}{Q} - k_{Th}.C_0.t\right)} \quad (5.1)$$

And linearized form is:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}.q_0.M}{Q} - K_{Th}.C_0.t \quad (5.2)$$

where C_t stands for the effluent concentration at a specific time (mg/L), C_0 for the influent concentration (mg/L), K_{Th} for the Thomas rate constant (L/min.mg), q_0 for equilibrium uptake per gram of adsorbent (mg/g), M for the amount of adsorbent in the column, t for time (min), and Q for flowrate (L/min). Using linear regression, we can obtain K_{Th} and q_0 from the plot of $\ln(C_0/C_t - 1)$ versus time (t) at a given flow rate.

5.7.1.1 Application of Thomas Model to DWTS-200

The values of the model parameters on arsenic and antimony for DWTS-200, i.e., K_{Th} and q_0 were calculated using the slope and intercept of the graphs of $\ln(C_0/C_t-1)$ against time. Table 5.10 gives the relevant findings and the Appendix include the linear forms of the graphs. Coefficients of determination values indicated a fit between the Thomas model and the findings, with R^2 values ranging from 0.76-0.90 for arsenic and 0.84-0.87 for antimony.

Table 5.10 Thomas model constant for arsenic and antimony adsorption by DWTS-200 for varied bed depths

Contaminant	h (cm)	Q (ml/min)	C_0 (mg/L)	k_{Th} (L/min.mg)	q_0 (mg/g)	R^2
Arsenic	10	5	0.04	0.125	5.72	0.7631
	20	5	0.04	0.075	6.53	0.9033
Antimony	10	5	0.08	0.25	4.3	0.8373
	20	5	0.08	0.1	5.21	0.8659

According to Table 5.10, maximum adsorption capacity, q_0 increased with higher bed depths from 10 to 20 cm. Adsorption capacity, q_0 , obtained 5.72 mg/g and 6.53 mg/g for 10 and 20 cm bed depths for arsenic and 4.3 mg/g and 5.21 mg/g for the same bed depths for antimony. Besides, when bed depth increased, adsorption capacity, q_0 , also increased, however, Thomas rate constant, k_{Th} , decreased from 0.125 to 0.075 L/min.mg for arsenic and 0.25 to 0.1 L/min.mg for antimony.

Breakthrough curves obtained experimental data and predicted values using Thomas model for different bed heights are shown in Figure 5.59 and 5.60 for arsenic and Figure 5.61 and 5.62 for antimony.

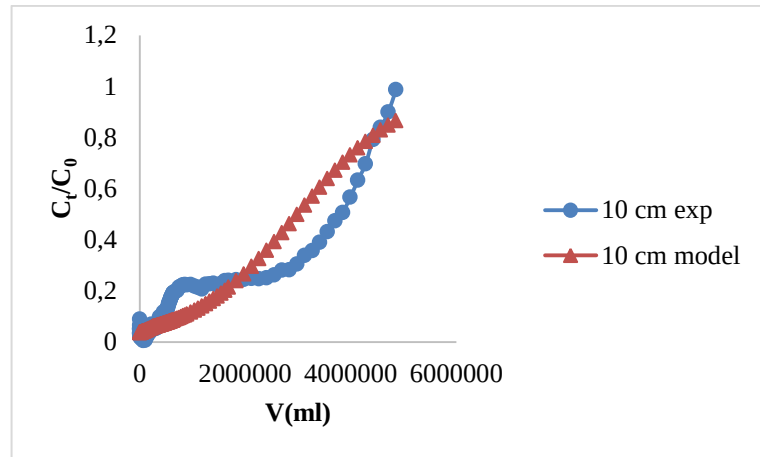


Figure 5.59 Experimental and simulating breakthrough curves on arsenic for 10 cm bed depth (DWTS-200-Thomas model)

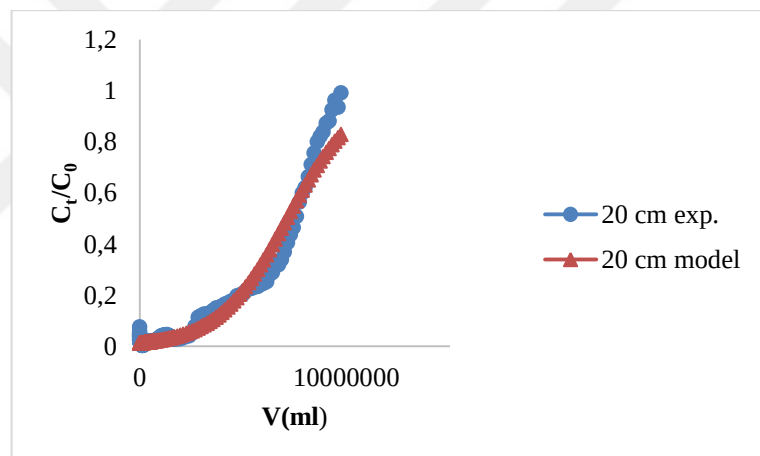


Figure 5.60 Experimental and simulating breakthrough curves on arsenic for 20 cm bed depth (DWTS-200-Thomas model)

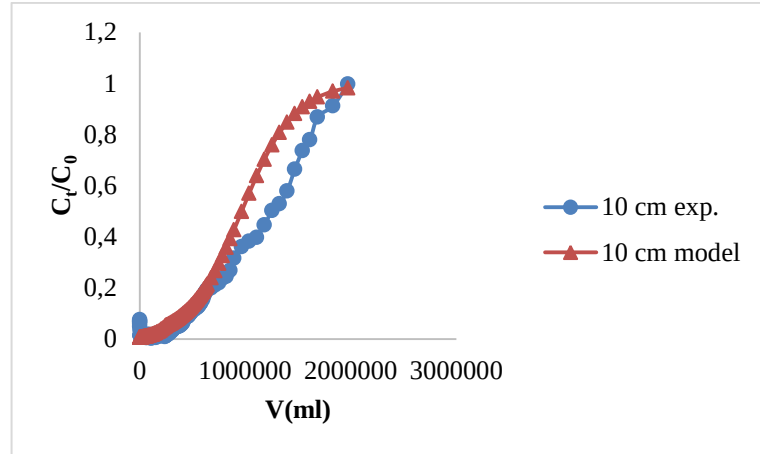


Figure 5.61 Experimental and simulating breakthrough curves on antimony for 10 cm bed depth (DWTS-200-Thomas model)

Figure from 5.59 to 5.62 show that the differences among the values obtained from the model and from the experiment were negligible especially for 20 cm bed depths. Thus, higher correlation coefficients (i.e. 0.90 for arsenic and 0.86 for antimony) were obtained for higher bed depth of 20 cm.

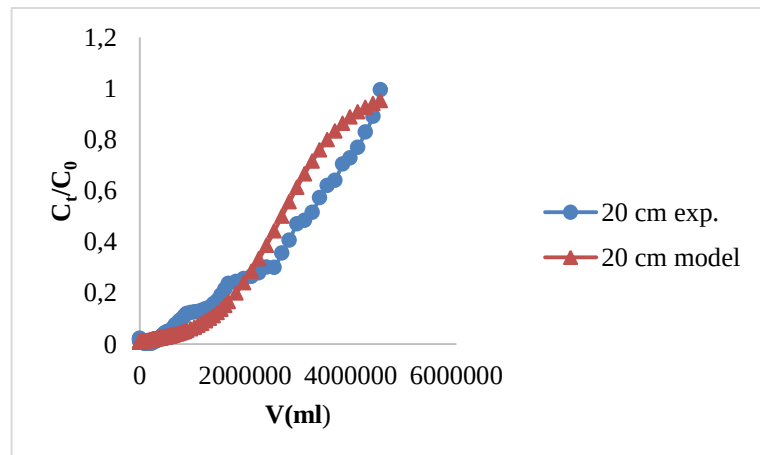


Figure 5.62 Experimental and simulating breakthrough curves on antimony for 20 cm bed depth (DWTS-200-Thomas model)

5.7.1.2 Application of Thomas Model to ZOC-DWTS

The values of the model parameters on arsenic and antimony for ZOC-DWTS, i.e. K_{Th} and q_0 were also found from the slope and breakpoint of the graphs of $\ln(C_0/C_t-1)$ against time. The results are shown in Table 5.11 and the linear forms of the graphs are presented in the Appendix.

Table 5.11. Thomas model constant for arsenic and antimony adsorption by ZOC-DWTS for varied bed depths

Contaminant	h (cm)	Q (ml/min)	C_0 (mg/L)	k_{Th} (L/min.mg)	q_0 (mg/g)	R^2
Arsenic	10	5	0.04	0.1	8.74	0.8035
	20	5	0.04	0.05	9.13	0.9179
Antimony	10	5	0.08	0.125	8.67	0.8331
	20	5	0.08	0.075	6.82	0.8766

Adsorption capacities determined from the graphs were much higher than the DWTS-200 column. For arsenic, lower bed depths resulted with a reduction in the adsorption capacities. But for antimony, adsorption capacity was lower for 20 cm bed depth for ZOC-DWTS.

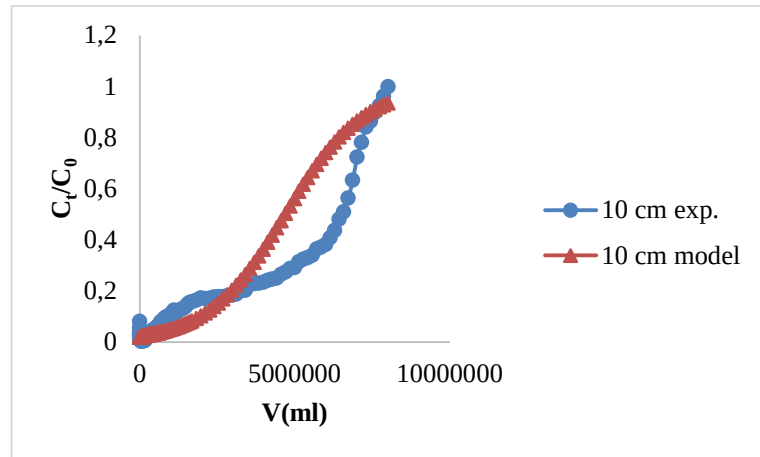


Figure 5.63 Experimental and simulating breakthrough curves on arsenic for 10 cm bed depth (ZOC-DWTS-Thomas model)

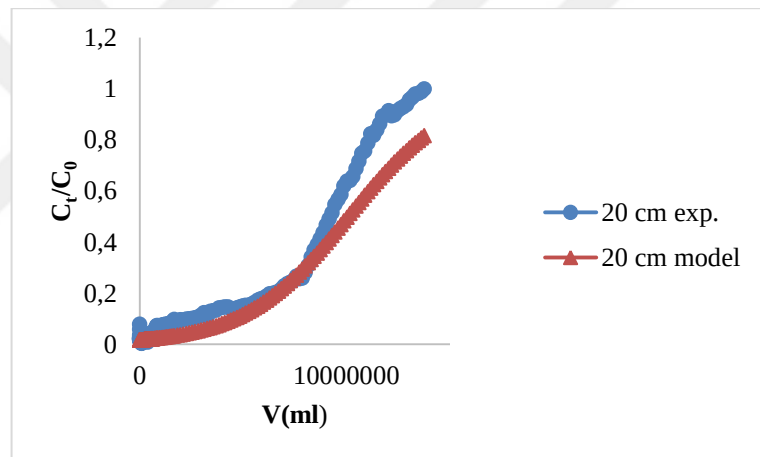


Figure 5.64 Experimental and simulating breakthrough curves on arsenic for 20 cm bed depth (ZOC-DWTS-Thomas model)

As can be seen from the breakthrough curves, the differences between the experimental and predicted data were insignificant for all operating parameters especially for 20 cm bed height for arsenic and 10 cm bed height for antimony. The experimental data of ZOC-DWTS fitted well with the Thomas model for varied bed depths and correlation coefficients ranged from 0.8035 to 0.9179. Adsorption capacity relatively decreased for antimony and increased for arsenic for increased bed depths. For arsenic, adsorption capacities increased from 8.74 to 9.13 mg/g when

bed depth was increased from 10 cm to 20 cm while for antimony, adsorption capacities decreased from 8.67 to 6.82 mg/g.

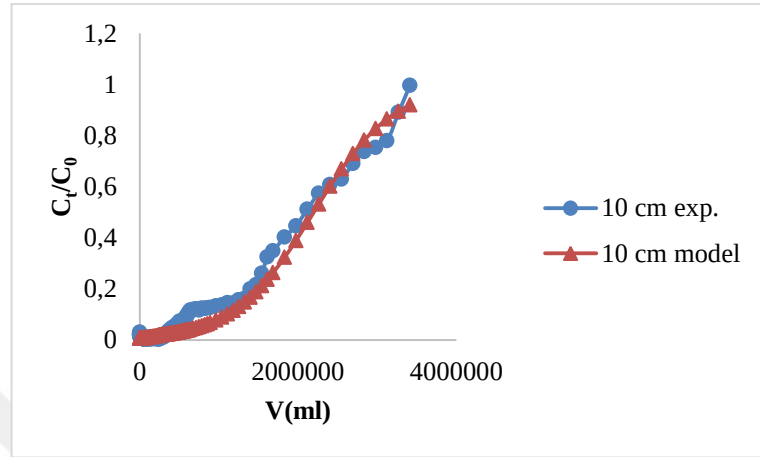


Figure 5.65 Experimental and simulating breakthrough curves on antimony for 10 cm bed depth (ZOC-DWTS-Thomas model)

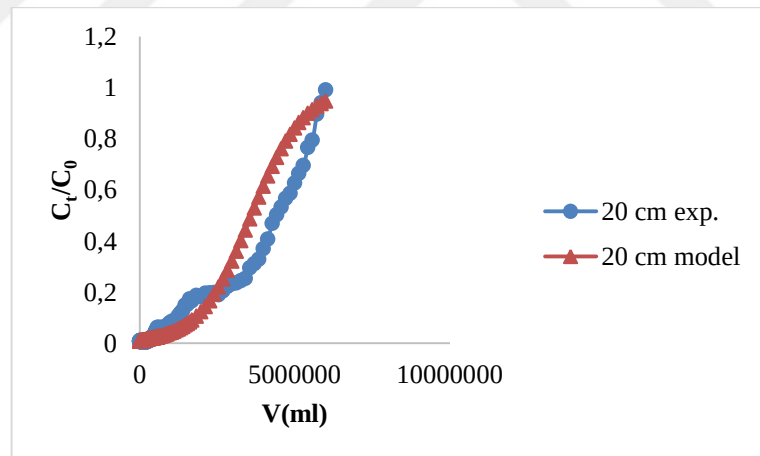


Figure 5.66 Experimental and simulating breakthrough curves on antimony for 20 cm bed depth (ZOC-DWTS-Thomas model)

The adsorption capacities found from the experimental results were compared with the literature data. Dhanasekaran&Sahu (2021) studied arsenate removal from groundwater by sawdust impregnated ferric hydroxide and active alumina (SFAA) and found 0.10 mg/g adsorption capacity for As(V) at pH 6.5. Zambrano Guisela et al. (2022) studied adsorption of arsenic anions using modified

lignocellulosic adsorbents and found the maximum adsorption capacity of total arsenic ions as 0.944 mg/g at pH 6. Mohan et al. (2019) used guava leaves, mango peel and sugar cane bagasse to remove As(III) from water and achieved adsorption capacity as 1.05 mg/g at pH 6, 1.25 mg/g at pH 6.5 and 1.35 mg/g at pH 7.5, respectively. Babazad et al. (2021) used macromolecule-carbonized rice husks for arsenic removal from water and found arsenic removal efficiency as 86% at pH 9 and 100 µg/L initial concentration.

5.7.2 Bohart&Adams (B&A) Model

Bohart and Adams (1920) developed this model by hypothesizing that the rate of chlorine uptake would be proportional to the chlorine concentration in bulk fluid and the residual adsorption capacity of charcoal. The basic equations defining the connection there among C_t/C_0 and time in a continuous system was determined by this model. B&A model is expressed as:

$$\frac{C_t}{C_0} = \exp(k_{BA} \cdot C_0 \cdot t - \frac{k_{BA} \cdot N \cdot Z}{Q}) \quad (5.3)$$

A linearized version of the B&A analytical solution is given by:

$$\ln \left(\frac{C_0}{C_t} \right) = k_{BA} \cdot C_0 \cdot t - \frac{k_{BA} \cdot N \cdot Z}{Q} \quad (5.4)$$

where C_t is the solution concentration at the column outlet at time t (mg/L), C_0 is the initial concentration (mg/L), k_{BA} is the B&A rate constant (L/mg.min), N is the adsorption capacity of the adsorbent per unit volume of the bed (mg/L), Z is the total bed depth (cm), Q is the linear flow rate (ml/min) and t is time (min). From Equation 4, N and k_{BA} are got by the y-intercept and slope of the plot, respectively.

5.7.2.1 Application of B&A Model for DWTS-200

The values of B&A model parameters for DWTS-200 were determined from the slope and the point where it intersects the y-minus of the graphs of $\ln(C_0/C_t-1)$ against time at various column depths. The results are shown in Table 5.12 and the linear forms of the graphs are presented in the Appendix.

Table 5.12 B&A model constant for arsenic and antimony adsorption by DWTS-200 for varied bed depths

Contaminant	h (cm)	Q (ml/min)	C_0 (mg/L)	K_{BA} (L/min.mg)	N (mg/L)	R^2
Arsenic	10	5	0.04	0.1	15756	0.6535
	20	5	0.04	0.05	21427	0.8786
Antimony	10	5	0.08	0.125	18120	0.7733
	20	5	0.08	0.075	15087	0.7809

In Table 5.12, coefficient of determination values, R^2 , was in the range of 0.6535 to 0.8786 for varying bed depths. Saturation concentration, N, increased with increasing bed depth for arsenic, but decreased for antimony. For arsenic, saturation concentration obtained as 15756 mg/L for 10 cm bed depth, it was increased to 21427 mg/L for 20 cm. But for antimony, N decreased from 18120 to 15087 mg/L with increasing bed depth. B&A rate constant, k_{BA} , decreased from 0.1 to 0.05 for arsenic and from 0.125 to 0.075 for antimony when bed depths increased from 10 to 20 cm.

Breakthrough curves obtained experimental and predicted values at different bed depths are illustrated in Figures from 5.67 to 5.70.

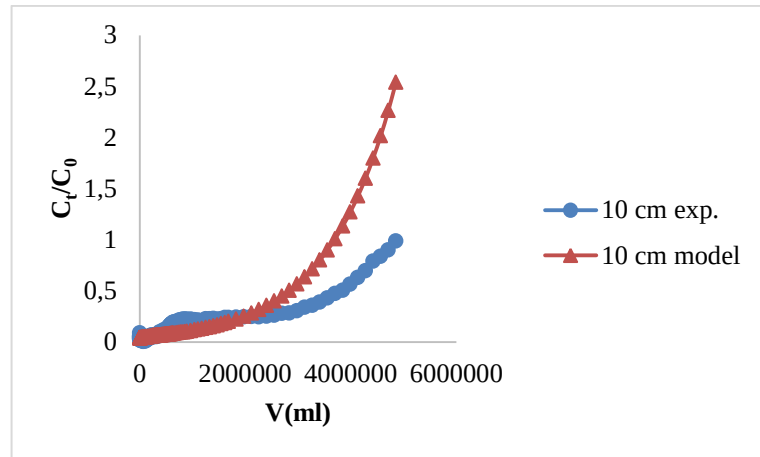


Figure 5.67 Experimental and simulating breakthrough curves on arsenic for 10 cm bed depth (DWTS-200-B&A model)

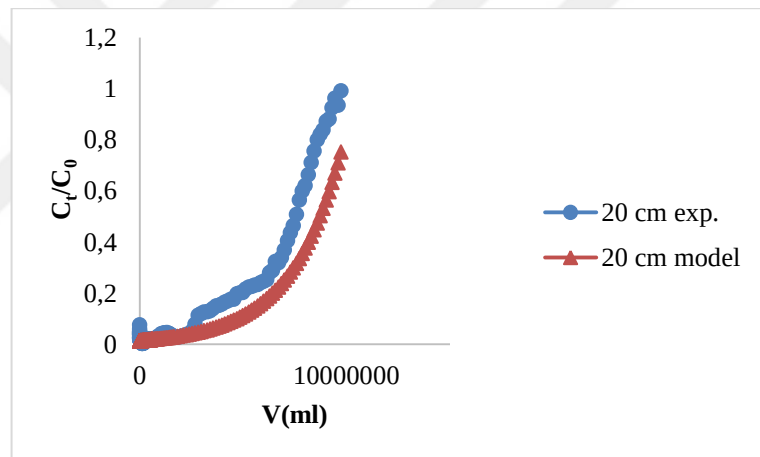


Figure 5.68 Experimental and simulating breakthrough curves on arsenic for 20 cm bed depth (DWTS-200-B&A model)

B&A model agreed not bad with 10 cm and 20 cm bed depths by DWTS-200 with 0.65 for arsenic, 0.77 for antimony and 0.87 for arsenic, 0.78 for antimony coefficient of determination, respectively.

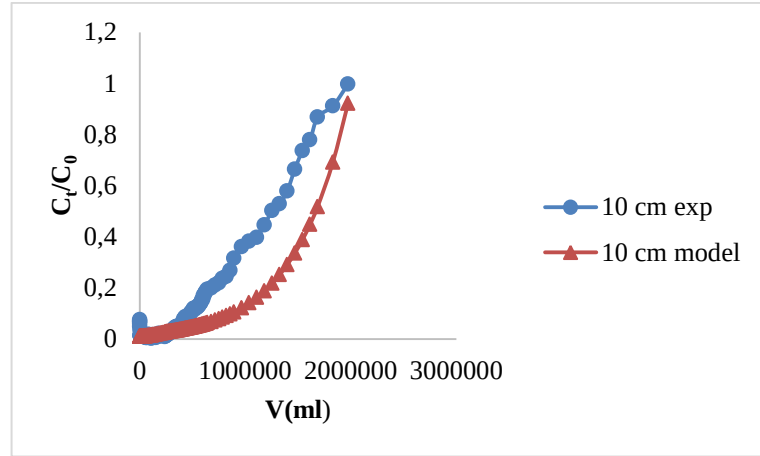


Figure 5.69 Experimental and simulating breakthrough curves on antimony for 10 cm bed depth (DWTS-200-B&A model)

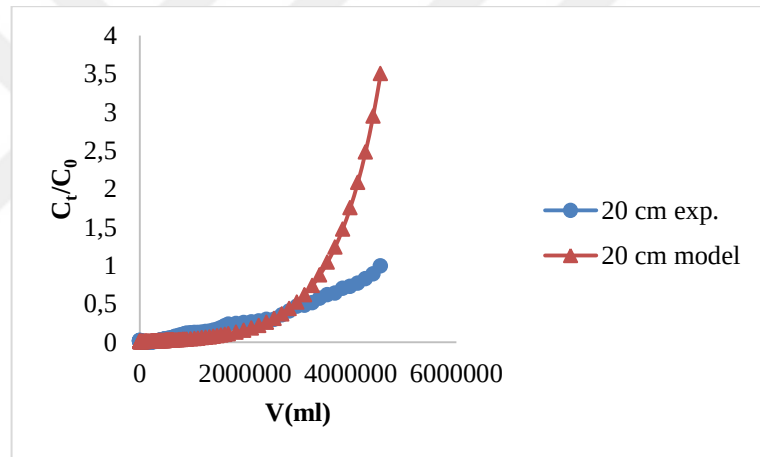


Figure 5.70 Experimental and simulating breakthrough curves on antimony for 20 cm bed depth (DWTS-200-B&A model)

5.7.2.2 Application of B&A Model for ZOC-DWTS

The values of B&A model parameters for ZOC-DWTS were detected from the slope and the point where it intersects the y-minus of the graphs of $\ln (C_0/C_t - 1)$ against time at various column depths. The kinetic constants and saturation concentrations were showed in Table 5.13 and the linear forms of the graphs were presented in the Appendices. As seen from the Table 5.13, the correlation coefficient R^2 was in the range of 0.7286 to 0.8722 for various bed depths. The k_{BA} values

decreased from 0.075 to 0.05 L/min.mg when column depth rised from 10 to 20 cm for arsenic and decreased 0.1 to 0.05 L/min.mg for antimony.

Table 5.13. B&A model constant for arsenic and antimony adsorption by ZOC-DWTS for varied bed depths

Contaminant	h (cm)	Q (ml/min)	C₀ (mg/L)	K_{BA} (L/min.mg)	N (mg/L)	R²
Arsenic	10	5	0.04	0.075	25499	0.7424
	20	5	0.04	0.05	19621	0.8722
Antimony	10	5	0.08	0.1	23270	0.7286
	20	5	0.08	0.05	22389	0.8011

In Table 5.13, saturation concentration obtained 25499 mg/L and 19621 mg/L for 10 and 20 cm bed depths for arsenic and 23270 mg/L and 22389 mg/L for the same column heights for antimony. Increasing in bed depths resulted by decreasing in saturation concentrations for both arsenic and antimony.

Breakthrough curves obtained experimental and predicted values at different bed depths are illustrated in Figures from 5.71 to 5.74. Experimental data and model values were fitted well yielding moderately high coefficient of determination values (from 0.72 to 0.87) for different bed depths.

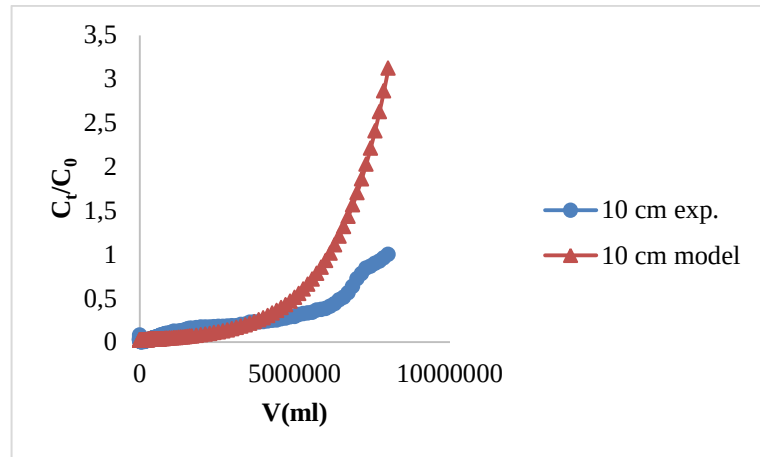


Figure 5.71 Experimental and simulating breakthrough curves on arsenic for 10 cm bed depth (ZOC-DWTS-B&A model)

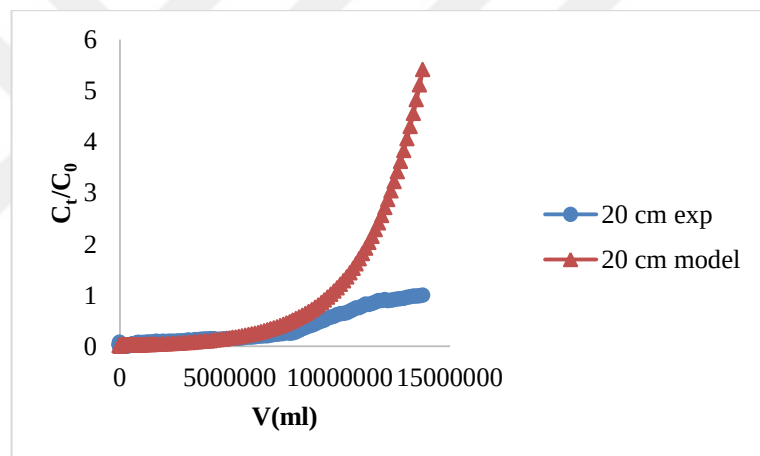


Figure 5.72 Experimental and simulating breakthrough curves on arsenic for 20 cm bed depth (ZOC-DWTS-B&A model)

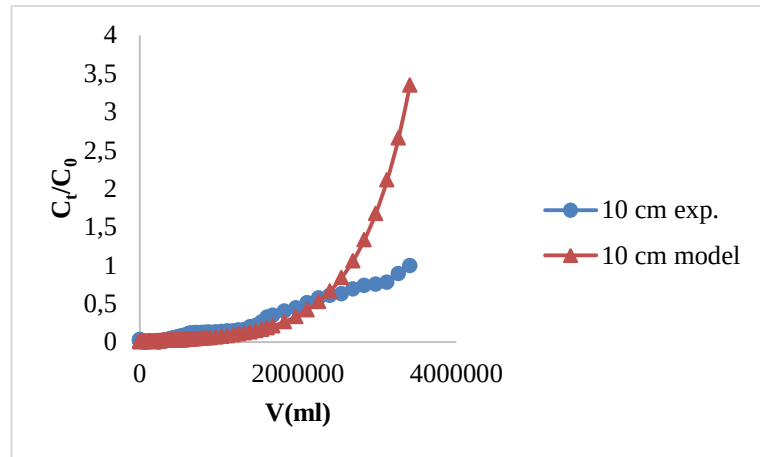


Figure 5.73 Experimental and simulating breakthrough curves on antimony for 10 cm bed depth (ZOC-DWTS-B&A model)

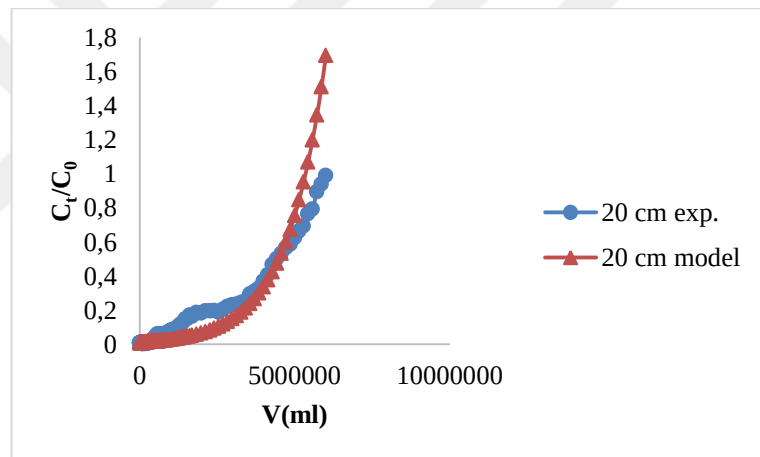


Figure 5.74 Experimental and simulating breakthrough curves on antimony for 20 cm bed depth (ZOC-DWTS-B&A model)

5.7.3 Clark Model

A model was developed to provide for the performance of granular active carbon-organic compounds adsorption system by Clark in 1987. This model associates the mass transfer notion with the Freundlich equation:

$$\ln \left[\left(\frac{C_0}{C_t} \right)^{n-1} - 1 \right] = -rt + \ln B \quad (5.5)$$

where n is the Freundlich constant, B is the constant of the Clark model (min), and r is the sorption rate (mg/L.min). $\ln[(C_0/C_t)^{n-1}-1]$ is plotted against time and r is found from the slope of the graph, and B from the intercept.

5.7.3.1 Application of Clark Model for DWTS-200

It was confirmed that the Freundlich model could be used to define the arsenic sorption on the DWTS-200 in a previous batch research. Therefore, the parameters of the Clark model was estimated with the Freundlich constant 1/n (0.648, 25°C) determined in the batch experiments. The values of B and r of the Clark model were calculated by Eq.(5.5) via linear regression analysis. These values are shown in Table 5.14 whereas the linear forms of the graphs are presented in the Appendix.

Table 5.14 Clark model constant for arsenic adsorption by DWTS-200 for varied bed depths

Contaminant	h (cm)	Q (ml/min)	C₀ (mg/L)	B (min)	r (mg/L.min)	R²
Arsenic	10	5	0.04	7.63	0.000004	0.7845
	20	5	0.04	17.84	0.000003	0.8951

As the bed depth increased, the constant of the Clark model (B) increased and the values of the sorption rate (r) decreased. The breakthrough curves predicted by the Clark model according to Eq.(5.5) were shown in Figure 5.75 and Figure 5.76.

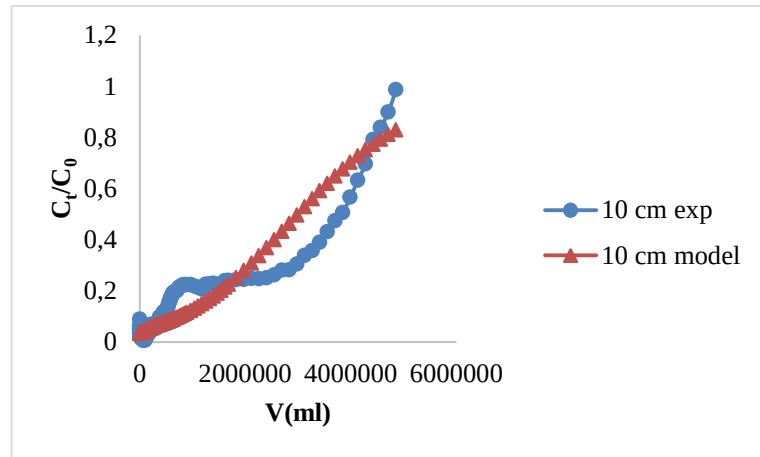


Figure 5.75 Experimental and simulating breakthrough curves on arsenic for 10 cm bed depth (DWTS-200-Clark model)

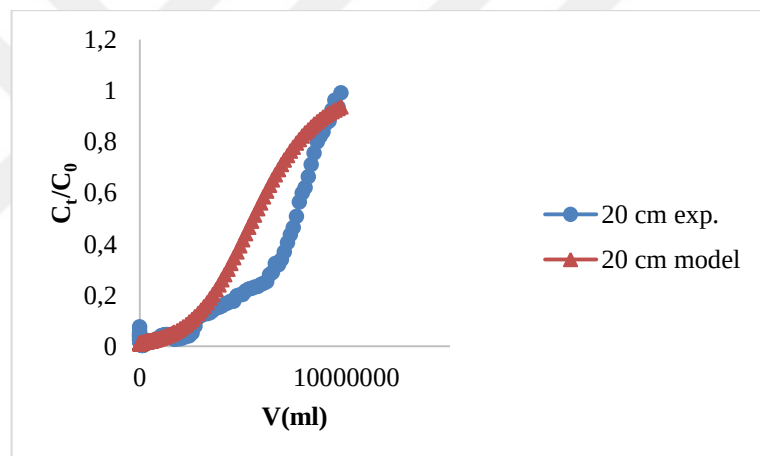


Figure 5.76 Experimental and simulating breakthrough curves on arsenic for 20 cm bed depth (DWTS-200-Clark model)

Coefficient of determination values indicated that Clark model fitted well to the experimental data and R^2 values ranging from 0.7845 to 0.8951, i.e., the fact shows that the forecast values are moderately close to the measured ones.

5.7.3.2 Application of Clark Model for ZOC-DWTS

The parameters of the Clark model was estimated with the Freundlich constant $1/n$ (0.85, 25°C) determined in the batch experiments for ZOC-DWTS. B and r values which are the constants of the Clark model were calculated via linear regression analysis. The outcomes are summarized in Table 5.15 whereas the linear forms of the graphs are presented in the Appendix.

Table 5.15 Clark model constant for arsenic adsorption by ZOC-DWTS for varied bed depths

Contaminant	h (cm)	Q (ml/min)	C_0 (mg/L)	B (min)	r (mg/L.min)	R^2
Arsenic	10	5	0.04	28.959	0.000003	0.8041
	20	5	0.04	34.02	0.000002	0.9151

As the bed depth increased, the constant of the Clark model (B) increased and the values of the sorption rate (r) decreased for ZOC-DWTS. The breakthrough curves determined by the Clark model according to Eq.(5.5) were shown in Figure 5.77 and Figure 5.78.

A comparison of the data regression with the experimental results demonstrated that the Clark model gave good correlation on the effects of the bed depths ($R^2=0.8041$ to 0.9151).

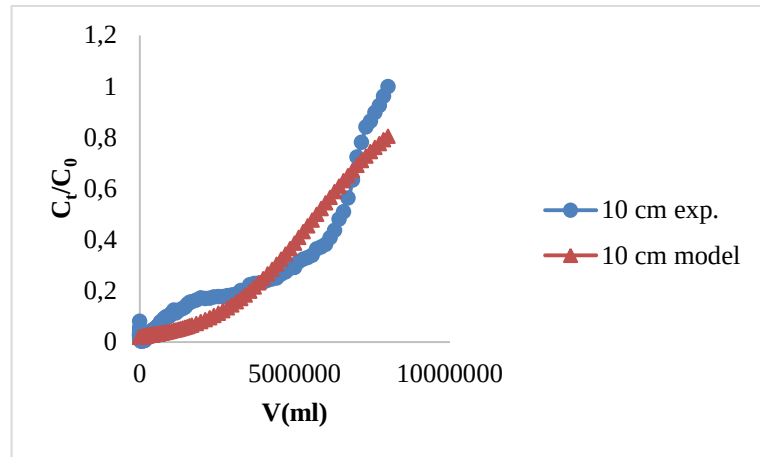


Figure 5.77 Experimental and simulating breakthrough curves on arsenic for 10 cm bed depth (ZOC-DWTS-Clark model)

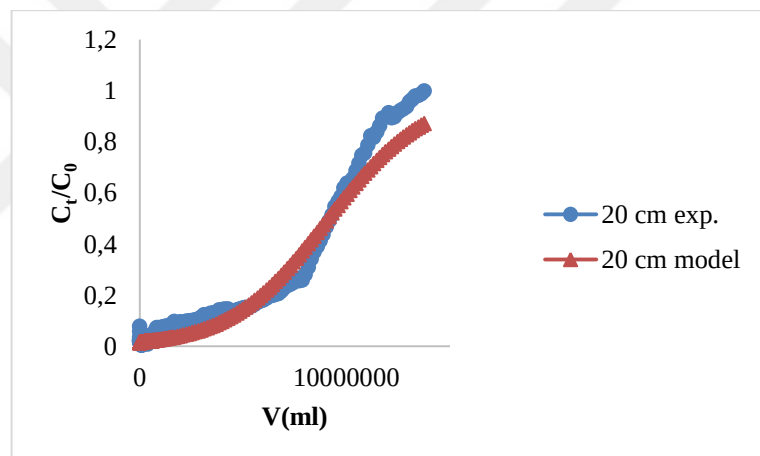


Figure 5.78 Experimental and simulating breakthrough curves on arsenic for 20 cm bed depth (ZOC-DWTS-Clark model)

5.7.4 Yoon&Nelson Model

This model simply assumes that for each adsorbate, the decline in the probability to be adsorbed is proportional to its probability of adsorption and breakthrough on the adsorbent (Yoon&James, 1984). The model, which is considered to be a simple theoretical model since less column data is required to construct the model, was used

to explore the breakthrough character of the arsenic and antimony sorption onto DWTS-200 and ZOC-DWTS. Yoon&Nelson model is expressed as:

$$\ln \frac{C_t}{C_0 - C_t} = K_{YN}t - t_{1/2}K_{YN} \quad (5.6)$$

where K_{YN} is the Yoon&Nelson rate constant and $t_{1/2}$ is the time required for 50% adsorbate breakthrough (min). By plotting $\ln \frac{C_t}{C_0 - C_t}$ vs time, K_{YN} and $t_{1/2}$ are calculated.

5.7.4.1 Application of Yoon&Nelson Model for DWTS-200

The values of Yoon&Nelson model parameters for DWTS-200 were determined from the slope and intercept of the graphs of $\ln (C_t/C_0 - C_t)$ versus time at various bed depths. The results are shown in Table 5.16 and the linear forms of the graphs are submitted in the Appendix.

Table 5.16 Yoon&Nelson model constant for arsenic and antimony adsorption by DWTS-200 for varied bed depths

Contaminant	h (cm)	Q (ml/min)	C ₀ (mg/L)	K _{YN} (min ⁻¹)	t _{1/2} (h)	R ²
Arsenic	10	5	0.04	0.000005	10784	0.7631
	20	5	0.04	0.000003	24594	0.9033
Antimony	10	5	0.08	0.00002	4057	0.8373
	20	5	0.08	0.000008	9817	0.8659

In Table 5.16, coefficient of determination values, R^2 , was in the range of 0.7631 to 0.9033 for varying bed depths. Yoon&Nelson rate constant, K_{YN} , decreased whereas the 50% adsorbate breakthrough time, $t_{1/2}$, increased with increasing bed depths. For arsenic, $t_{1/2}$ obtained as 10784 h for 10 cm bed depth, it was increased to 24594 h for 20 cm. For antimony, $t_{1/2}$ increased from 4057 to 9817 h with increasing bed depth. Yoon&Nelson rate constant, k_{YN} , decreased from 0.000005 to 0.000003 for arsenic and from 0.00002 to 0.000008 for antimony when bed depths increased from 10 to 20 cm.

Breakthrough curves obtained experimental and predicted values at different bed depths are illustrated in Figures from 5.79 to 5.82.

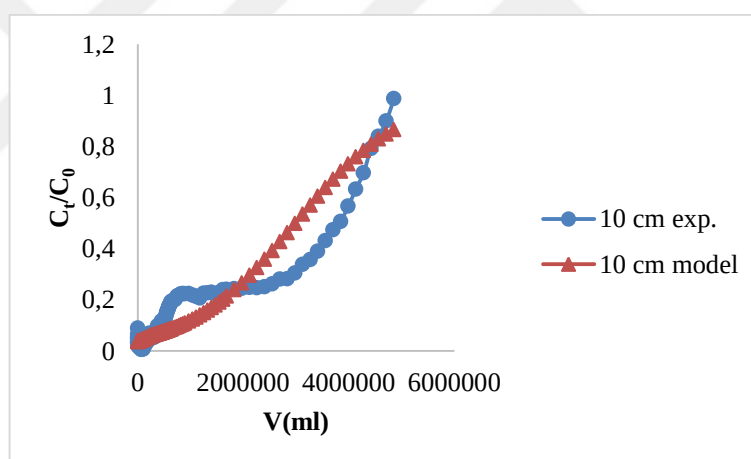


Figure 5.79 Experimental and simulating breakthrough curves on arsenic for 10 cm bed depth (DWTS-200- Yoon&Nelson model)

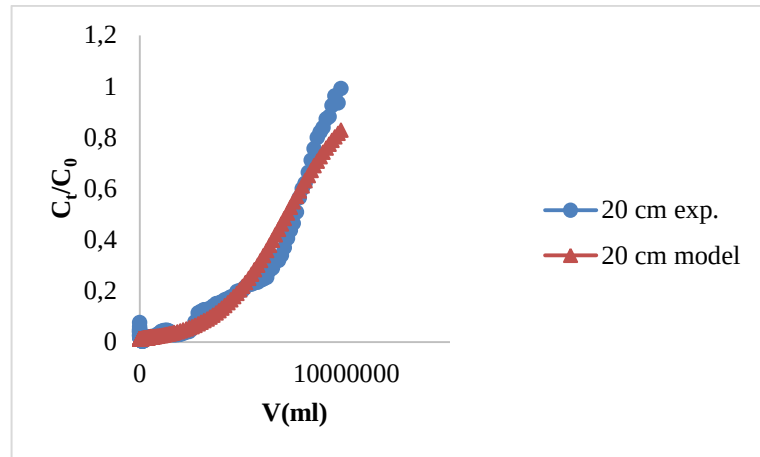


Figure 5.80 Experimental and simulating breakthrough curves on arsenic for 20 cm bed depth (DWTS-200- Yoon&Nelson model)

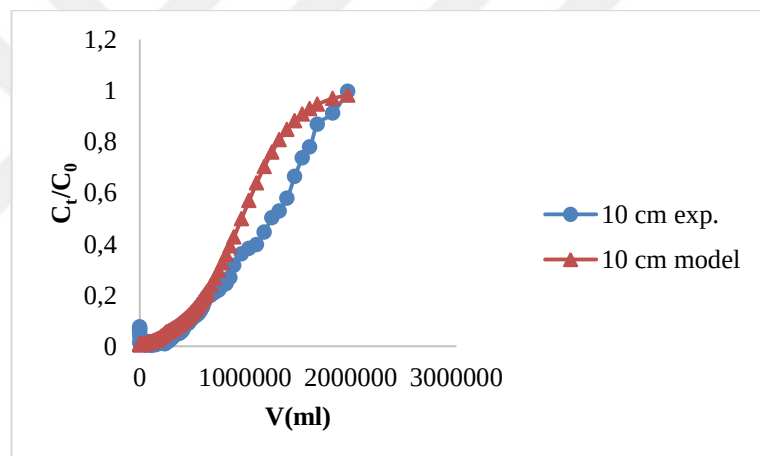


Figure 5.81 Experimental and simulating breakthrough curves on antimony for 10 cm bed depth (DWTS-200- Yoon&Nelson model)

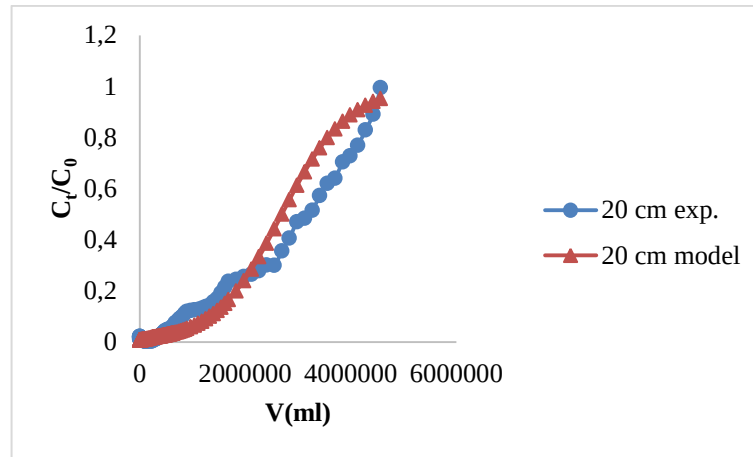


Figure 5.82 Experimental and simulating breakthrough curves on antimony for 20 cm bed depth (DWTS-200- Yoon&Nelson model)

High correlation coefficients ($R^2=0.83$ to 0.90) indicate that the experimental data could be well fitted by using the Yoon and Nelson model except for 10 cm bed depth on arsenic ($R^2=0.76$). Table 5.16 shows that the correlation coefficient (R^2) of Yoon-Nelson equation is same as that of Thomas equation.

5.7.4.2 Application of Yoon&Nelson Model for ZOC-DWTS

The values of this model parameters on arsenic and antimony for ZOC-DWTS, i.e. K_{YN} and $t_{1/2}$ were also calculated from the slope and intercept of the graphs of $\ln(C_t/C_0 - C_t)$ versus time. The results are summarized in Table 5.17 and the linear forms of the graphs are presented in the Appendix.

Table 5.17. Yoon&Nelson model constant for arsenic and antimony adsorption by ZOC-DWTS for varied bed depths

Contaminant	h (cm)	Q (ml/min)	C ₀ (mg/L)	K _{YN} (min ⁻¹)	t _{1/2} (h)	R ²
Arsenic	10	5	0.04	0.000004	16478	0.8035
	20	5	0.04	0.000002	34396	0.9179
Antimony	10	5	0.08	0.00001	8163	0.8331
	20	5	0.08	0.000006	12848	0.8766

In Table 5.17, coefficient of determination values, R², was in the range of 0.8035 to 0.9179 for varying bed depths. Yoon&Nelson rate constant, K_{YN}, decreased whereas the 50% adsorbate breakthrough time, t_{1/2}, increased with increasing bed depths. For arsenic, t_{1/2} obtained as 16478 h for 10 cm bed depth, it was increased to 34396 h for 20 cm. For antimony, t_{1/2} increased from 8163 to 12848 h with increasing bed depth. Yoon&Nelson rate constant, k_{YN}, decreased from 0.000004 to 0.000002 for arsenic and from 0.00001 to 0.000006 for antimony when bed depths increased from 10 to 20 cm. For ZOC-DWTS, t_{1/2} values were higher than DWTS-200, because ZOC-DWTS removal efficiencies were higher than DWTS-200.

Breakthrough curves obtained experimental and predicted values at different bed depths are illustrated in Figures from 5.83 to 5.86

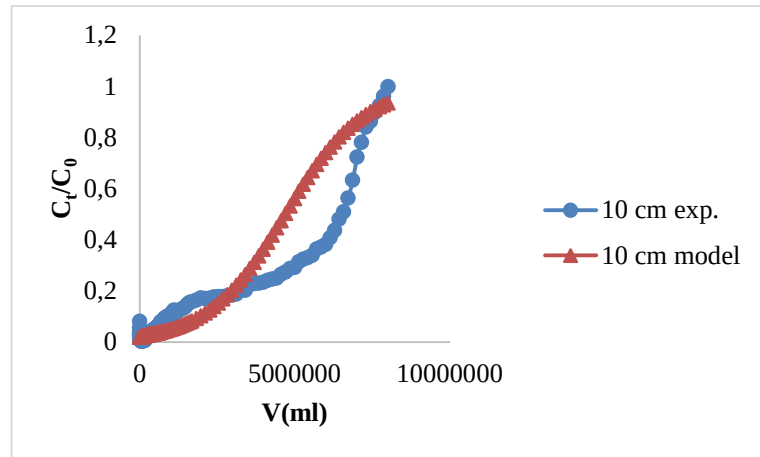


Figure 5.83 Experimental and simulating breakthrough curves on arsenic for 10 cm bed depth (ZOC-DWTS- Yoon&Nelson model)

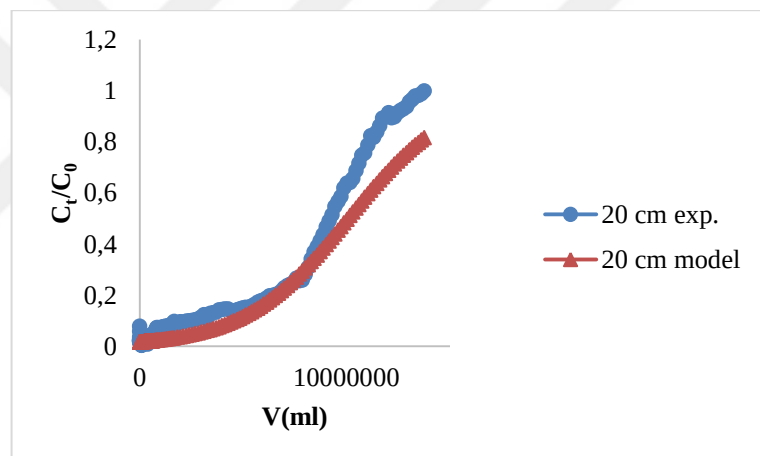


Figure 5.84 Experimental and simulating breakthrough curves on arsenic for 20 cm bed depth (ZOC-DWTS- Yoon&Nelson model)

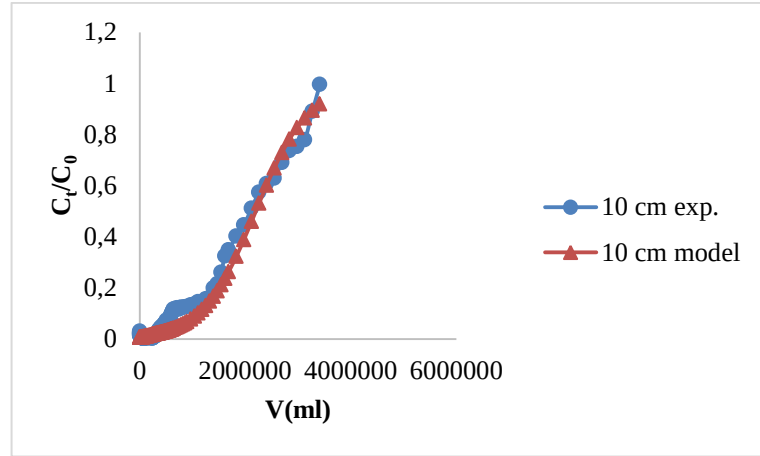


Figure 5.85 Experimental and simulating breakthrough curves on antimony for 10 cm bed depth (ZOC-DWTS- Yoon&Nelson model)

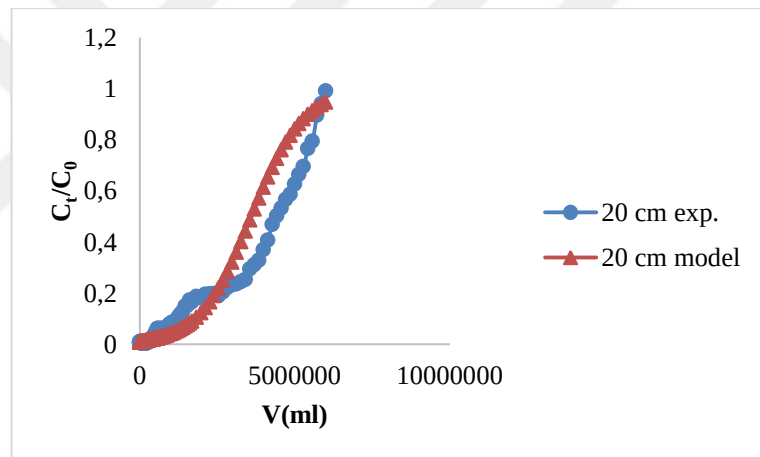


Figure 5.86 Experimental and simulating breakthrough curves on antimony for 20 cm bed depth (ZOC-DWTS- Yoon&Nelson model)

High correlation coefficients ($R^2=0.80$ to 0.91) indicate that the experimental data could be well fitted by using the Yoon&Nelson model. Table 5.17 shows that the correlation coefficient (R^2) of Yoon&Nelson equation for ZOC-DWTS is same as that of Thomas and Clark equation.

5.8 Column Regeneration Studies

Regeneration studies were performed by 1% sodium hydroxide solution for adsorbents. During regeneration, sodium hydroxide were fed into the column, and samples were taken from outlet of the column in certain time intervals and arsenic, antimony and iron measurements were performed.

For DWTS-200, effluent arsenic, antimony and iron concentrations were illustrated in Figure 5.87.

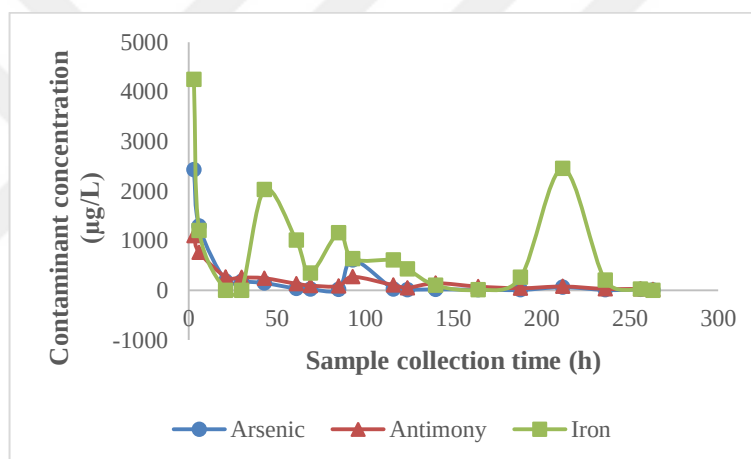


Figure 5.87 Eluent concentrations in regeneration of DWTS

After the regeneration studies, media was taken from the column and dried at 65°C for three days. Batch experiments were performed at optimum conditions (1 g/L adsorption dose, 3 hours of contact time, pH of 3) with raw and regenerated media in order to determine reuse potential of regenerated media.

Removal efficiencies of arsenic and antimony were compared for DWTS-200 and regenerated DWTS-200 and showed in Figure 5.88. Besides, concentrations of heavy metals released from media submitted in Table 5.18.

As is seen Figure 5.88, arsenic removal efficiency of regenerated DWTS-200 is approximately as the same as DWTS-200, but antimony removal efficiency is higher than DWTS-200. But, regenerated DWTS-200 released iron, manganese, copper and lead non-standard (according to TS 266) (Table 5.18). DWTS-200 released only manganese. Moreover, regeneration of DWTS -200 continued 11 days and 79.2 L wastewater composed. This period was accepted too long for regeneration. Because 3504 bed volume wastewater was formed. Otherwise, physical endurance, particle size and quantity of DWTS-200 decreased after regeneration.

Table 5.18 Concentrations of heavy metals released from DWTS-200 and regenerated DWTS-200 after adsorption

Heavy metals	Raw water I (40 ppb As+80 ppb Sb)	Raw water II (800 ppb As+1600 ppb Sb)	After DWTS-200 treatment		After regenerated DWTS-200 treatment	
			Raw water I	Raw water II	Raw water I	Raw water II
As(ppb)	31.02	605.67	0.38	4.01	0	0.12
Sb(ppb)	69.38	1514.03	21.52	359.93	0.22	6.26
Fe(ppb)	38.77	14.34	26.14	19.86	55.66	239.74
Mn(ppb)	0	-	173.41	616.38	347.18	454.17
Cd(ppb)	0.06	-	0	0.01	0.11	0.14
Cr(ppb)	0.02	-	1.03	0.09	0.16	0.77
Cu(ppb)	0.21	-	1.25	1.65	84.42	141.65
Ni(ppb)	0	-	0	2.82	0.89	1.97
Pb (ppb)	2.61	-	0	0.26	6.69	11.6
Zn (ppb)	9.72	-	51.42	315.5	297.09	371.85

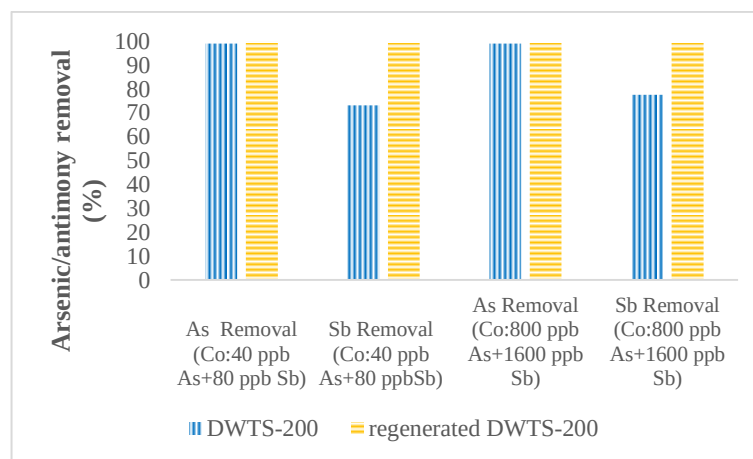


Figure 5.88 Effect of regeneration on arsenic and antimony removal for DWTS-200

Regeneration studies were done by alkaline solution (1% NaOH) for ZOC-DWTS, too. Regeneration continued for 12 days, but arsenic and antimony concentrations were not decrease desired level. 86.4 L (approximately 3823 bed volume) wastewater was formed. Also, clogging problem occurred during regeneration. Therefore, ZOC-DWTS column could not be reused for arsenic and antimony removal.

In a study performed by Saleh et al. (2022) on the regeneration of adsorbents, arsenic adsorption was carried out using newly prepared polymer modified perlite adsorbent and the results demonstrated that the produced adsorbent had reusability performance until seven cycles.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

In this thesis, arsenic and antimony adsorption performance of two materials (DWTS-200 and ZOC-DWTS) were investigated and compared with commercial adsorbents. Materials were prepared from drinking water treatment sludges and utilized as low cost efficient adsorbents for the arsenic and antimony removal in batch and fixed bed column system. In this scope, batch experiments were carried out to acquire optimum adsorption parameters like pH, contact time, initial concentration, adsorbent dose and existing ions in water. Thuswise, kinetic and isotherm studies were conducted and adsorption capacities and adsorption rates of the adsorbents were calculated. Then, fixed bed column studies were performed for DWTS-200 and ZOC-DWTS for two bed depths. Kinetic models which can estimate characteristic parameters and describe the dynamics of adsorption in column were applied to design and operate column successfully.

Results acquired from batch experiments demonstrated that optimum pH was 3 for arsenic and antimony on DWTS-200 and ZOC-DWTS. Over 98% removal rate was obtained for 50 µg/L initial arsenic concentration for 3 hours contact time and 1 g/L adsorbent dose.

Optimum contact time was found 3 hours operation at pH 3 and 1 g/L adsorbent dose to obtain effluent concentration below 10 µg/L for 50 µg/L initial arsenic concentration for both two adsorbents. Although experiments were conducted at pH 3, it should be noted that, to adjust the pH to 3 requires additional operation. In real conditions, since pH of raw water is around 7, operation has to be conducted at pH 7. In that case, it should be considered that a small descended in efficiency could be achieved.

Approximately 50, 100 and 500 $\mu\text{g/L}$ initial arsenic concentrations could be treated below 10 $\mu\text{g/L}$ at pH 3, 3 hours of contact time and 1 g/L adsorbent dose for both two adsorbents.

Optimum dose was 1 g/L for both adsorbents at pH 3, 3 hours of contact time and 50 $\mu\text{g/L}$ initial arsenic concentration.

To investigate the co-removal of antimony and arsenic, arsenic and antimony solutions were mixed certain rates (1, about 1/2 and 2). For all experiments, arsenic and antimony removal efficiencies were above 95% and 80%, respectively at pH 3, 3 hours of contact time and 35 and 90 $\mu\text{g/L}$ initial arsenic and antimony concentrations.

Arsenic and antimony removal rates, in case of existing competing ions (using real groundwater) were obtained 91.5% for arsenic and 63% for antimony on DWTS-200 and 89.6% for arsenic and 70.3% for antimony on ZOC-DWTS, at pH 3, 3 hours of contact time and 50 $\mu\text{g/L}$ initial arsenic concentration. Ions and anions in groundwater affected arsenic and antimony removal performance for both materials. Existence of competing anions was resulted by decreasing in arsenic and antimony removal efficiency approximately 8% for arsenic and 22% for antimony for DWTS-200. For ZOC-DWTS, the reduction of percent removal was 9.6% for arsenic and 15% for antimony, comparing to synthetic water.

Adsorption mechanisms were best described by Freundlich isotherm for DWTS-200 and ZOC-DWTS. Adsorption capacities of arsenic were calculated through these isotherms and obtained 6.527 mg/g and 7.38 mg/g at 1 g/L adsorbent doses for DWTS-200 and ZOC-DWTS, respectively. Adsorption rate of adsorbents fitted well with pseudo second order reaction kinetic model for both DWTS-200 and ZOC-DWTS.

Column experiments were performed using optimum pH (pH 3) obtained in batch experiments. Column experiments indicated that column utilization is more effective at higher bed depths (20 cm) for both adsorbents. For DWTS-200, at 20 cm bed depth, 40 µg/L and 80 µg/L arsenic and antimony concentrations, approximately 6000 L water could be treated at breakthrough point with desired levels (<10 µg/L) for arsenic whereas approximately 640 L water could be treated at breakthrough point with desired levels (<5 µg/L) for antimony. At same conditions, 7444 L water could be effectively treated below 10 µg/L for arsenic and 820 L water could be treated below 5 µg/L for antimony by ZOC-DWTS.

Column design parameters were utilized for various bed depths by applying Thomas model, Bohart&Adams model, Clark model and Yoon&Nelson model to experimental data. Among the four models, the correlation coefficients (R^2) for the Thomas model were the same as those for the Yoon& Nelson and Clark model for ZOC-DWTS and for DWTS-200, the Thomas model were the same as those for the Yoon& Nelson model, but the Clark model had very close values with the Thomas and Yoon& Nelson models. The correlation coefficients (R^2) for the Bohart&Adams model were lower than the other models. In a comparison of the experimental data and the predicted curves, the Thomas, Yoon&Nelson and Clark models could be used to describe the behavior of the sorption process, but the B&A model did not give the best results. At 5 ml/min flow rate and 20 cm bed depth with 40 µg/L arsenic and 80 µg/L antimony concentrations, Thomas model parameters; Thomas rate constants, K_{Th} , and adsorption capacities, q_0 , obtained 0.075 L/mg.min and 6.53 mg/g for arsenic and 0.1 L/mg.min and 5.21 mg/g for antimony by DWTS-200, and 0.05 L/mg.min and 9.13 mg/g for arsenic and 0.075 L/mg.min and 6.82 mg/g for antimony by ZOC-DWTS, respectively. At same conditions, B&A model parameters, B&A rate constants, K_{BA} and adsorption capacities, N , obtained 0.05 L/mg.min and 21427 mg/L for arsenic and 0.075 L/mg.min and 15087 mg/L for antimony by DWTS-200, and 0.05 L/mg.min and 19621 mg/L for arsenic and 0.05 L/mg.min and 22389 mg/L for antimony by ZOC-DWTS, respectively. Clark model parameters, Clark rate constants, B and r , obtained 17.84 min^{-1} and $0.000003 \text{ mg/L.min}$ for arsenic by DWTS-200, and 34.02 min^{-1} and $0.000002 \text{ mg/L.min}$ for

arsenic by ZOC-DWTS, respectively. Yoon&Nelson model parameters, Yoon&Nelson rate constants, K_{YN} and time required for 50% adsorbate breakthrough, $t_{1/2}$, obtained $0.000003 \text{ min}^{-1}$ and 24594 h for arsenic and $0.000008 \text{ min}^{-1}$ and 9817 h for antimony by DWTS-200, and $0.000002 \text{ min}^{-1}$ and 34396 h for arsenic and $0.000006 \text{ min}^{-1}$ and 12848 h for antimony by ZOC-DWTS, respectively.

Regeneration and then reuse of the DWTS-200 could be possible without efficiency loss even better removal efficiency of antimony. But, regenerated media released some heavy metals (iron, manganese, copper and lead) non-standard (according to TS 266). Moreover, regeneration period was too long (263 hours) and too much wastewater was formed. ZOC-DWTS could be regenerated by same method, but after 289 hours, arsenic and antimony concentrations were assigned not to decrease desired levels. And, because of the ZOC-DWTS column clogging, operation problems were existed.

Experimental results show that DWTS-200 and ZOC-DWTS are high performance materials to remove arsenic and antimony by adsorption. Adsorption capacities of the materials was compete with commercial adsorbents which are bought from abroad with an expensive costs. GEH₁₀₂ is high performance adsorbent uses effectively in As removal facilities. The data given in the catalog of GEH₁₀₂ is compared herein with the results obtained in this study. Iron content of the GEH₁₀₂ is reported as 60% whereas 26% and 33% for DWTS-200 and ZOC-DWTS for the granules less than 2mm. Ferric oxide loading is responsible form high iron content of GEH₁₀₂ than DWTS-200 and ZOC-DWTS. However, although DWTS-200 and ZOC-DWTS has relatively lower iron content, their adsorption capacities competes with the GEH₁₀₂. Adsorption capacity of GEH₁₀₂ is determined as 2-10 mg/g while DWTS-200 and ZOC-DWTS adsorption capacities are 6.53 mg/g and 9.13 mg/g for arsenic, respectively. Specific surface area of GEH₁₀₂ is $220 \text{ m}^2/\text{g}$ while the surface areas of DWTS-200 and ZOC-DWTS are approximately $170 \text{ m}^2/\text{g}$ and $166 \text{ m}^2/\text{g}$, respectively. Specifications reported for GEH₁₀₂ and developed material in this study

are comparable. However, DWTS-200 and ZOC-DWTS offers an advantage in terms of Sb removals.

Cost is one of the most important operational parameters in selecting the adsorbent material. In real applications, it is essential to use the effective and low-cost adsorbent. The commercial adsorbent used in the package treatment plants in Izmir (e.g. GEH₁₀₂) has costs around 5-6 Euro/kg. The cost of the DWTS-200 and ZOC-DWTS could not be determined because the studies conducted in this thesis were lab scale. In order to determine the cost of the materials, all the processes in preparation and modification should be specified, and the unit cost of the material should be calculated considering the expenditures of energy for drying, chemicals, labour works, etc. However, it is considered that it might be more economic as the materials are not imported from abroad and saving in waste disposal costs is obtained.

Besides that, in circular economy (CE), waste materials, by products, residues have tremendous potential for general use. Recycle and recovery of substances from water and wastewater treatment plants and reuse them in different areas are important issues in CE model. Therefore, within the context of this thesis, using the drinking water treatment plant sludge as a raw material will represent an economic and financial benefit that contributes to the sustainability of the systems.

Recommendations for future studies:

Drinking water contamination by arsenic is of concern in various countries all over the world. This study focused on to develop low-cost adsorbent material that are produced from waste sludge and to use it in package treatment systems especially in rural areas. Based on the results found in this study the modified adsorbent material seems promising in removing both arsenic and antimony from groundwater. To find a comprehensive solution in removing arsenic the following points should be considered for future work:

- A pilot scale study needs to be performed in order to obtain more accurate operational data for commercial use of the DWTS-200 and ZOC-DWTS adsorbents
- The cost analysis needs to be done in order to justify the economic feasibility of the adsorption process
- To find the best match of the experimental data other mathematical models need to be examined or developed.
- The column needs to be operated with real contaminated water to find out the effect of other impurities on adsorption, and to be operated at neutral pH range avoiding the extra pH adjustment.
- The impact of the competing ions could be investigated in more detail. In this context, column studies could be achieved by both synthetic and real groundwater sample. The ions competing both with As and Sb could be studied more comprehensively.
- Different metals such as manganese, copper, titanium and lanthanum could be used for coating, and adsorption performance could be examined.
- Lab-scale column studies could be carried out pilot scale operation and evaluated surface hydraulic loading.
- In the column experiments to be carried out with groundwater, the columns can be operated in series, and the competing ions can be kept highly in the first column called a filtration column. Thus, the load of the adsorption column containing adsorbent material will decrease and the arsenic and antimony removal efficiency will increase.

REFERENCES

- Afarani, M.S., Samimi, A., & Yekta, E.B. (2013). Synthesis of alumina granules by high shear mixer granulator: Processing and sintering. *Powder Technology*, 237, 32-40.
- Alpaslan, M.N., Dolgen, D., Boyacıoglu, H., & Sarptas, H. (2010). İçme suyundan kimyasal yöntemlerle arsenic giderimi. *The Journal of ITU*, 20(1), 15-25.
- An, Y.J., & Kim, M. (2009). Effect of antimony on the microbial growth and the activities of soil enzymes. *Chemosphere*, 74(5), 654-659.
- Arıkan, S. (2016). *Investigation of arsenic adsorption performance of the modified natural materials*. [Unpublished doctoral dissertation]. University of Dokuz Eylül.
- Asan, U. (2011). *Madencilik çalışmalarının toplum sağlığına etkileri*. [Unpublished doctoral dissertation]. University of Ege.
- Babazad, Z., Kaveh, F., Ebadi, M., Mehrabian, R.Z., & Juibari, M.H. (2021). Efficient removal of lead and arsenic using macromolecule-carbonized rice husks. *Heliyon*, 7, e06631.
- Bhattacharya, P., Chatterjee, D., & Jacks, G. (2010). Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, Eastern India: Options for safe drinking water supply. *International Journal of Water Resources Development*, 13, 79-92.

- Biswas, B.K., Inoue, J., Kawakita, H., Ohto, K., & Inoue, K. (2009). Effective removal and recovery of antimony using metal-loaded saponified orange waste. *Journal of Hazardous Materials*, 172(2-3), 721-728.
- Caporale, A.G., Pigna, M., Dynes, J.J., Cozzolino, V., Zhu, J., & Violante, A. (2011). Effect of inorganic and organic ligands on the sorption/desorption of arsenate on/from Al–Mg and Fe–Mg layered double hydroxides. *Journal of Hazardous Materials*, 198, 291-298.
- Caporale, A.G., Punamiya, P., Pigna, M., Violante, A., & Sarkar, D. (2013). Effect of particle size of drinking water treatment residuals on the sorption of arsenic in the presence of competing ions. *Journal of Hazardous Materials*, 260, 644-651.
- Chaudhry, S.A., Khan, T.A., & Ali, A. (2017a). Zirconium oxide-coated sand based batch and column adsorptive removal of arsenic from water: Isotherm, kinetic and thermodynamic studies. *Egyptian Journal of Petroleum*, 26, 553-563.
- Chaudhry, S.A., Zaidi, Z., & Siddiqui, S.I. (2017b). Isotherm, kinetic and thermodynamics of arsenic adsorption onto Iron-Zirconium Binary Oxide-Coated Sand (IZBOCS): Modelling and process optimization. *Journal of Molecular Liquids*, 229, 230-240.
- Chaudhry, S.A., Khan, T.A., & Ali, A. (2017c). Equilibrium, kinetic and thermodynamic studies of Cr(VI) adsorption from aqueous solution onto manganese oxide coated sand grain (MOCSG). *Journal of Molecular Liquids*, 236, 320-330.

- Chen, W., Parette, R., Zou, J., Cannon, F.S., & Dempsey, B.A. (2007). Arsenic removal by iron-modified activated carbon. *Water Research*, 41, 1851-1858.
- Chen, B., Zhou, D., & Zhu, I. (2008). Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science & Technology*, 42, 5137-5143.
- Chen, R.Z., Zhang, Z.Y., Yang, Y.N., Lei, Z.F., Chen, N., Guo, X., Zhao, C., & Sugiura, N. (2011). Use of ferric-impregnated volcanic ash for arsenate (V) adsorption from contaminated water with various mineralization degrees. *Journal of Colloid and Interface Science*, 353(2), 542-548.
- Chen, A.S.C, Sorg, T.J., & Wang, L. (2015). Regeneration of iron based adsorptive media used for removing arsenic from groundwater. *Water Research*, 77, 85-97.
- Choong, T.S.Y., Chuah, T.G., Robiah, Y., Koay, F.L.G., & Azni, I. (2007). Arsenic toxicity, health hazards and removal techniques from water: an overview. *Desalination*, 217(1-3), 139-166.
- Chuang, C.L., Fan, M., Xu, M., Brown, R.C., Sung, S., Saha, B., & Huang, C.P. (2005). Adsorption of arsenic (V) by activated carbon prepared from oat hulls. *Chemosphere*, 61(4), 478-483.
- Dada, A.O., Olalekan, A.P., Olatunya, A.M., & Dada, O. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. *Journal of Applied Chemistry*, 3, 38-45.

Dambies, L. (2004). Existing and prospective sorption technologies for the removal of arsenic in water. *Separation Science and Technology*, 39(3), 603-627.

Demir, E. (2008). *Isıl işlemin bir bentonitin katyon değiştirme kapasitesi, adsorpsiyon, gözenekliliği, yüzey alanı ve yüzey asitliği gibi bazı fizikokimyasal özelliklerine etkisi*. [Unpublished doctoral dissertation]. University of Ankara.

Deng, B.L., Caviness, M., & Gu, Z.M. (2005). Arsenic removal by activated carbon-based materials. *Advances in Arsenic Research*, 915, 284-293.

Dhanasekaran, P., & Sahu, O. (2021). Arsenate and fluoride removal from groundwater by sawdust impregnated ferric hydroxide and activated alumina (SFAA). *Groundwater for Sustainable Development*, 12, 100490.

Elkhatib, E., Mahdy, A., Sherif, F., & Hamadeen, H. (2015). Evaluation of a novel water treatment residual nanoparticles as a sorbent for arsenic removal. *Journal of Nanomaterials*, 912942. <http://dx.doi.org/10.1155/2015/912942>

EPA, (2003). *Arsenic treatment technology evaluation handbook for small systems*. Retrieved 2019, from https://cfpub.epa.gov/safewater/arsenic/arsenictradeshows/Pubs/handbook_arsenic_treatment-tech.pdf.

Filella, M., Belzile, N., & Chen, Y.W. (2002). Antimony in the environment: a review focused on natural waters I. Occur. *Earth Science Reviews*, 57(1-2), 125-176.

Filella, M., Williams, P.A., & Belzile, N. (2009). Antimony in the environment: knowns and unknowns. *Environmental Chemistry*, 6(2), 95-105.

Fiella, M., Belzile, N., & Lett, M.C. (2007). Antimony in the environment: a review focused on natural waters. III. Microbiota relevant interactions, *Earth-Science Reviews*, 80, 195-217.

Gang, D.D., Deng, B.L., & Lin, L.S. (2010). As(III) removal using an iron-impregnated chitosan sorbent. *Journal of Hazardous Materials*, 182, 156-161.

Ghribi, A., & Chlendi, M. (2011). Modeling of fixed bed adsorption: Application to the adsorption of organic dye. *Asian Journal of Textile*, 1(4), 161-171.

Ghurye, G., & Clifford, D. (2001). Laboratory Study on the Oxidation of As(III) to As(V). EPA 600R01021, Prepared under contract 8CR311-NAEX for EPA ORD, March 2001.

Gibbons, M.K., & Gagnon, G.A. (2010). Adsorption of arsenic from a Nova Scotia groundwater onto water treatment residual solids. *Water Research*, 44, 5740-5749.

Giles, D.E., Mohapatra, M., Issa, T.B., Anand, S., & Singh, P. (2011). Iron and aluminium based adsorption strategies for removing arsenic from water. *Journal of Environmental Management*, 92, 3011-3022.

Gregor, J. (2001). Arsenic removal during conventional aluminium-based drinking water treatment. *Water Research*, 35, 1659-1664.

- Gu, Z.M., Fang, J., & Deng, B.L. (2005). Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Environmental Science & Technology*, 39(10), 3833-3843.
- Guo X.J., Wu, Z.J., & He, M.C. (2009). Removal of antimony (V) and antimony (III) from drinking water by coagulation-flocculation-sedimentation (CFS). *Water Research*, 43(17), 4327-4335.
- Guo, X., Wu, Z., He, M., Meng, X., Jin, X., Qiu, N., & Zhang, J. (2014). Adsorption of antimony onto iron oxyhydroxides: Adsorption behavior and surface structure. *Journal of Hazardous Materials*, 276, 339-345.
- Gupta, K., & Ghosh, U.C. (2009). Arsenic removal using hydrous nanostructure iron(III)-titanium(IV) binary mixed oxide from aqueous solution. *Journal of Hazardous Materials*, 161(2-3), 884-892.
- Gupta, V.K., Saini, V.K., & Jain, N. (2005). Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *Journal of Colloid and Interface Science*, 288(1), 55-60.
- Helle, U.S., Postma, D., Jakobsen, R., & Larsen, F. (2008). Sorption and desorption of arsenate and arsenite on calcite. *Geochimica et Cosmochimica Acta*, 72, 5871-5884.
- Hofman-Caris, R., Ahmad, A., Siegers, W., Rahn, S., Voort, J.W., & van der Kolk, O. (2017). Pelletized drinking water treatment residuals for the removal of arsenic and phosphate from water. KWR 2017.036, Project number: 400986-001.

Hofman-Caris, R., Siegers, W., Hofman, J., Elings, J., van der Kolk, O. & de Jong, A.(2015). Granular iron(hydr)oxide for phosphate removal from water, KWR *Watercycle Research Institute*, 88.

Ippolito, J. A., Barbarick, K.A., & Elliott, H.A. (2011). Drinking water treatment residuals: A review of recent uses. *Journal of Environmental Quality*, 40(1), 1-12.

Iqbal, M., Saeed, A., & Edyvean, R.G.J. (2013). Bioremoval of antimony (III) from contaminated water using several plant wastes: optimization of batch and dynamic flow conditions for sorption by green bean husk (*Vigna radiata*). *Chemical Engineering Journal*, 225, 192-201.

Jekel, M., & Amy, G.L. (2006). Interface science in drinking water treatment. In: Newcombe, G., Dixon, D. (Eds.). Elsevier, pp.

Jeon, C.S., Baek, K., Park, J.K., Oh, Y.K., & Lee, S. D. (2009). Adsorption characteristics of As(V) on iron-coated zeolite. *Journal of Hazardous Materials*, 163(2-3), 804-808.

Jeon, E.K., Ryu, S., Park, S.W., Wang, L., Tsang, D., & Baek, K. (2018). Enhanced adsorption of arsenic onto alum sludge modified by calcination. *Journal of Cleanear Production*, 176, 54–62.

Jimenes-Cedillo, M.J., Olguin, M.T., Fall, C., & Colin, A. (2011). Adsorption capacity of iron-or iron-manganese-modified zeolite-rich tuffs for As(III) and As(V) water pollutants. *Applied Clay Science*, 54(3-4), 206-216.

- Jung, K.W., Hwang, M.J., Jeong, T.U., Chau, D.M., Kim, K., & Ahn, K.H. (2016). Entrapment of powdered drinking water treatment residues in calcium-alginate beads for fluoride removal from actual industrial wastewater. *Journal of Industrial and Engineering Chemistry*, 39, 101-111.
- Kang, M., Kamei, T., & Magara, Y. (2003). Comparing polyaluminum chloride and ferric chloride for antimony removal. *Water Research*, 37(17), 4171-4179.
- Kang, M., Kawasaki, M., Tamada, S., Kamei, T., & Magara, Y. (2000). Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. *Desalination*, 131(1-3), 293-298.
- Kim, L., Thanh, N.T., Toan, P.V., Minh, H.V.T., & Kumar, P. (2022). Removal of arsenic in groundwater using Fe(III) oxyhydroxide coated sand: A case study in Mekong Delta, Vietnam. *Hydrology*, 9(1), 15. <https://doi.org/10.3390/hydrology9010015>
- Kolbe, F., Weiss, H., Morgenstern, P., Wennrich, R., Lorenz, W., Schurk, K., Stanjek, H., & Daus, B. (2011). Sorption of aqueous antimony and arsenic species onto akagenite. *Journal of Colloid and Interface Science*, 357, 460-465.
- Kun-Yoo, J., Jin-Kong, H., Wagle, R., Hyun Shon, B., Ki Kim, I., & Ho Kim, T. (2019). A study on the methods for making iron oxide aerogel. *Journal of Industrial and Engineering Chemistry*, 72, 332-337. <https://doi.org/10.106/j.jiec.2018.12.033>

- Kundu, S., & Gupta, A.K. (2007). As(III) removal from aqueous medium in fixed bed using iron oxide coated cement (IOCC): Experimental and modeling studies. *Chemical Engineering Journal*, 129, 123-131.
- Lan, B., Wang, Y., Wang, X., Zhou, X., Kang, Y., & Li, L. (2016). Aqueous arsenic (As) and antimony (Sb) removal by potassium ferrate. *Chemical Engineering Journal*, 292, 389-397.
- Lee, S.H., Tanaka, M., Takahashi, Y., & Kim, K.W. (2018). Enhanced adsorption of arsenate and antimonate by calcined Mg/Al layered double hydroxide: Investigation of comparative adsorption mechanism by surface characterization, *Chemosphere*, 211, 903-911.
- Lehr, C.R., Kashyap, D.R., & McDermott, T.R. (2007). New insight into microbial oxidation of antimony and arsenic. *Applied and Environmental Microbiology*, 73(7), 2386-2389.
- Lenoble, V., Bouras, O., Deluchat, V., Serpaud, B., & Bollinger, J.-C. (2002). Arsenic adsorption on to pillared clays and iron oxides. *Journal of Colloid and Interface Science*, 255, 52-58.
- Li, X.H., Dou, X.M., & Li, J.Q. (2012). Antimony (V) removal from water by iron-zirconium bimetal oxide: performance and mechanism. *Journal of Environmental Science China*, 24(7), 1197-1203.
- Li, F., Cao, X., Zhao, I., Wang, J., & Ding, Z. (2014). Effects of mineral additives on biochar formation: carbon retention, stability and properties. *Environmental Science Technology*, 48, 11211-11217.

- Li, X., Cui, J., & Pei, Y. (2018). Granulation of drinking water treatment residuals as applicable media for phosphorus removal. *Journal of Environmental Management*, 213, 36-46.
- Li, Z.H., Jean, J.S., Jiang, W.T., Chang, P.H., Chen, C.J., & Liao, L.B. (2011). Removal of arsenic from water using Fe-exchanged natural zeolite. *Journal of Hazardous Materials*, 187(1-3), 318-323.
- Lin, T.F., & Wu, J.K. (2001). Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics. *Water Research*, 35(8), 2049-2057.
- Liu, B., Jian, M., Wang, H., Zhang, G., Liu, R., Zhang, X., & Qu, J. (2018). Comparing adsorption of arsenic and antimony from single-solute and bi-solute aqueous systems onto ZIF-8. *Colloids and Surfaces A*, 538, 164-172.
- Liu, D., Deng, S., Maimaiti, A., Wang, B., Huang, J., Wang, Y., & Yu, G. (2018). As(III) and As(V) adsorption on nanocomposite of hydrated zirconium oxide coated carbon nanotubes. *Journal of Colloid and Interface Science*, 511, 277-284.
- Lu, H., Zhu, Z., Zhang, H., Zhu, J., & Qiu, Y. (2015). Simultaneous removal of arsenate and antimonate in simulated and practical water samples by adsorption onto Zn/Fe layered double hydroxide. *Chemical Engineering Journal*, 276, 365-375.
- Lunge, S., Singh, S., & Sinha, A. (2014). Magnetic iron oxide (Fe_3O_4) nanoparticles from tea waste for arsenic removal. *Journal of Magnetism and Magnetic Materials*, 356, 21-31.

- Maji, S.K., Kao, Y.H., & Liu, C.W. (2011). Arsenic removal from real arsenic bearing groundwater by adsorption on iron-oxide-coated natural rock (IOCNR). *Desalination*, 280(1-3), 72-79.
- Miralles, N., Valderrama, C., Casas, I., Martinez, M., & Florido, A. (2010). Cadmium and lead removal from aqueous solution by grape stalk wastes: Modeling of a fixed bed column. *Journal of Chemical&Engineering Data*, 55(9): 3548-3554.
- Mohan, D., Markandeya, Dey, S., Dwivedi, S.B., & Shukla, S.P. (2019). Adsorption of arsenic using low cost adsorbents: guava leaf biomass, mango bark and bagasse. *Current Science*, 117, 649-661.
- Molgora, C.C., Dominguez, A.M., Avila, E.M., Drogui, P., & Buelna, G. (2013). Removal of arsenic from drinking water: a comparative study between electrocoagulation-microfiltration and chemical coagulation- microfiltration processes. *Separation Purification Technology*, 118, 645-651.
- Mondal, P., Bhowmick, S., Chatterjee, D., Figoli, A., & Van der Bruggen, B. (2013). Remediation of inorganic arsenic in groundwater for safe water supply: a critical assesment of technological solutions. *Chemosphere*, 92(2), 157-170.
- Mostafa, M.G., Chen, Y.H., Jean, J.S., Liu, C.C., & Lee, Y.C. (2011). Kinetics and mechanism of arsenate removal by nanosized iron oxide-coated perlite. *Journal of Hazardous Materials*, 187(1-3), 89-95.

Nagar, R., Sarkar, D., Makris K.C. & Data, R. (2010). Effect of solution chemistry on arsenic sorption by Fe- and Al-based drinking-water treatment residuals. *Chemosphere*, 78(8), 1028-1035.

Nandi, D., Ghosh, S.K., Ghosh, A., Siengchin, S., Roy, A., Gupta, K., Parameswaranpillai, J., Bhowmick, A.K. & Ghosh, U.C. (2021). Arsenic removal from water by graphene nanoplatelets prepared from nail waste: A physicochemical study of adsorption based on process optimization, kinetics, isotherm and thermodynamics. *Environmental Nanotechnology, Monitoring&Management*, 16, 100564.

Natale, F.D., Erto, A., & Lancia, A. (2013). Desorption of arsenic from exhaust activated carbons used for water purification. *Journal of Hazardous Materials*, 260, 451-458.

Nishiyama, S.Y., Saito, K., Saito, K., Sugita, K., Sato, K., Akiba, M., Saito, T., Tsuneda, S., Hirata, A., Tamada, M., & Sogo, T. (2003). High speed recovery of antimony using chelating porous hollow-fiber membrane. *Journal of Membrane Science*, 214(2), 275-281.

Nouh, E.S.A., Amin, M., Gouda, M., & Abd-Elmagid, A. (2015). Extraction of uranium (VI) from sulfate leach liquor after iron removal using manganese oxide coated zeolite. *Journal of Environmental Chemical Engineering*, 3, 523-528.

Ocinski, D., Jacukowicz-Sobala, I., Mazur, P., Raczyk, J., & Kociolek-Balawejder, E. (2016). Water treatment residuals containing iron and manganese oxides for arsenic removal from water- characterization of physicochemical properties and adsorption studies. *Chemical Engineering Journal*, 294, 210-221.

Ocinski, D., & Mazur, P. (2020). Highly efficient arsenic sorbent based on residual from water deironing-sorption mechanism and column studies. *Journal of Hazardous Materials*, 382, 121062.

Pallier, V., Feuilleade-Cathalifaud, G., Serpaud, B., & Bollinger, J.C. (2010). Effect of organic matter on arsenic removal during coagulation/flocculation treatment. *Journal of Colloid Interface Science*, 342(1), 26-32.

Patel, H. (2019). Fixed-bed column adsorption study: a comprehensive review. *Applied Water Science*, 9(45), 1-17. <https://doi.org/10.1007/s13201-019-0927-7>

Pattanayak, J., Mondal, K., Mathew, S., & Lalvani, S.B. (2000). A parametric evaluation of the removal of As(V) and As(III) by carbon-based adsorbents. *Carbon*, 38(4), 589-596.

Qiu, S., Yan, L., & Jing, C. (2019). Simultaneous removal of arsenic and antimony from mining wastewater using granular TiO₂: Batch and field column studies. *Journal of Environmental Sciences*, 75, 269-276.

Rahaman, M.S., Basu, A., & Islam, M.R. (2008). The removal of As(III) and As(V) from aqueous solutions by waste materials. *Bioresourch Technology*, 99(8), 2815-2823.

Ranjan, M.B., Soumen, D., Sushanta, D., & De Chand, G.U. (2003). Removal of arsenic from groundwater using crystalline hydrous ferric oxide (CHFO). *Water Quality Research Journal*, 38(1), 193-210. <https://doi.org/10.2166/wqrj.2003.013>

Ritchie, V.J., Ilgen, A.G., Mueller, S.H., Trainor, T.P., & Goldfarb, R.J. (2013). Mobility and chemical fate of antimony and arsenic in historic mining environments of the Kantishna Hills district, Denali National Park and Preserve, Alaska, *Chemical Geology*, 335, 172-188. <https://doi.org/10.1016/j.chemgeo.2012.10.016>

Rozada, F., Otero, M., Garcia, A.I., & Moran, A. (2007). Application in fixed bed systems of adsorbents obtained from sewage sludge and discharged tyres. *Dyes and Pigments*, 72(1), 47-56. <https://doi.org/10.1016/j.dyepig.2005.07.016>

Saito, T., Tsuneda, S., Hirata, A., Nishiyama, S., Saito, K., Saito, K., Sugita, K., Uezu, K., Tamada, M., & Sogo, T. (2004). Removal of antimony (III) using polyol-ligand-containing porous hollow-fiber membranes. *Separation Science and Technology*, 39(13), 3011-3022. <https://doi.org/10.1081/SS-200033727>

Saleh, T.A., Tuzen, M., Sarı, A., & Altunay, N. (2022). Factorial design, physical studies and rapid arsenic adsorption using newly prepared polymer modified perlite adsorbent. *Chemical Engineering Research and Design*, 183, 181-191.

Samsuri, A.W., Sadegh-Zadeh, F., & Seh-Bardan, B.J. (2013). Adsorption of As(III) and As(V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk. *Journal of Environmental Chemical Engineering*, 1(4), 981-988. <https://doi.org/10.1016/j.jece.2013.08.009>

Saqip, A.N.S., Waseem, A., Khan, A.F., Mahmood, Q., Khan, A., Habib, A., & Khan, A.R. (2013). Arsenic bioremediation by low cost materials derived from Blue Pine (*Pinus wallichiana*) and Walnut (*Juglans regia*). *Ecological Engineering*, 51, 88-94. <https://doi.org/10.1016/j.ecoleng.2012.12.063>

Sasaki, T., Iizuka, A., Watanabe, M., Hongo, T., & Yamasaki, A. (2014). Preparation and performance of arsenate (V) adsorbents derived from concrete wastes. *Waste Management*, 34(10), 1829-1835. <http://dx.doi.org/10.1016/j.wasman.2014.01.001>.

Shih, M.C. (2005). An overview of arsenic removal by pressure-driven membrane processes. *Desalination*, 172(1), 85-97.

Singh, T.S., & Pant, K.K. (2004). Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. *Separation and Purification Technology*, 36(2), 139-147. [https://doi.org/10.1016/S1383-5866\(03\)00209-0](https://doi.org/10.1016/S1383-5866(03)00209-0)

Smedley, P.L., & Kinniburgh, D.G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17, 517–568.

Soleimanifar, H., Deng, Y., Wu, L., & Sarkar, D. (2016). Water treatment residual (WTR)-coated wood mulch for alleviation of toxic metals and phosphorus from polluted urban stormwater runoff. *Chemosphere*, 154, 289-292.

Tan, G., Wu, Y., Liu, Y., & Xiao, D. (2018). Removal of Pb(II) ions from aqueous solution by manganese oxide coated rice straw biochar –A low-cost and highly effective sorbent. *Journal of the Taiwan Institute of Chemical Engineers*, 84, 85-92.

Tchobanoglous, G. & Burton, F.L. (1991). *Wastewater engineering: treatment, disposal and reuse* (3rd ed.). New York: Metcalf&Eddy, Inc., McGraw-Hill.

Thirunavukkarasu, O.S., Viraraghavan, T., & Subramanian, K.S. (2001). Removal of arsenic in drinking water by iron-oxide coated sand and ferrihydrite-Batch studies. *Water Quality Research Journal of Canada*, 36(1), 55-70.

Thirunavukkarasu, O.S., Viraraghavan, T., & Subramanian, K.S. (2003). Arsenic removal from drinking water using granular ferric hydroxide. *Water SA*, 29(2), 161-170.

Tuna, A.O.A., Ozdemir, E., Simsek, E.B., & Beker, U. (2013). Removal of As(V) from aqueous solution by activated carbon-based hybrid adsorbents: impact of experimental conditions. *Chemical Engineering Journal*, 223, 116-128. <https://doi.org/10.1016/j.cej.2013.02.096>

Ungureanu, G., Santos, S., Boaventura, R., & Botelho, C. (2015). Arsenic and antimony in water and wastewater: overview of removal techniques with special reference to latest advances in adsorption. *Journal of Environmental Management*, 151, 326-342.

USEPA, (2001). *Fact Sheet: Drinking Water Standard for Arsenic*. http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations_factsheet.cfm.

Uslu, H., Datta, D., & Azizian, S. (2016). Separation of chromium (VI) from its liquid solution using new montmorillonite supported with amine based solvent. *Journal of Molecular Liquids*, 215, 449-453.

Verbeecka, M., Warrinniera, R., Gustafssonb, J.P., Thiryc, Y., & Smoldersa, E. (2019). Soil organic matter increases antimonate mobility in soil: An Sb(OH)₆ sorption and modelling study. *Applied Geochemistry*, 104, 33-41.

- Vieira, B.R.C., Pintor, A.M.A., Boaventura, R.A.R., & Botelho, C.M.S. (2017). Arsenic removal from water using iron-coated seaweeds. *Journal of Environmental Management*, 192, 224-233.
- Wang, C., Jiang, H., Yuan, N., Pei, Y., & Yan, Z. (2016). Tuning the adsorptive properties of drinking water treatment residue via oxygen-limited heat treatment for environmental recycle. *Chemical Engineering Journal*, 284, 571-581.
- Wang, C., Wu, Y., Bai, L., Zhao, Y., Yan, Z., Jiang, H., & Liu, X. (2018a). Recycling of drinking water treatment residue as an additional medium in columns for effective P removal from eutrophic surface water. *Journal of Environmental Management*, 217, 363-372.
- Wang, C., Wu, Y., Wang, Y., Bai, L., Jiang, H., & Yu, J. (2018b). Lanthanum-modified drinking water treatment residue for initial rapid and long-term equilibrium phosphorus immobilization to control eutrophication. *Water Resource*, 137, 173-183.
- Wang, Y.R., Tsang, & D.C.W. (2013). Effects of solution chemistry on arsenic (V) removal by low-cost adsorbents. *Journal of Environmental Science China*, 25(11), 2291-2298.
- Wang, X., He, M., Lin, C., Gao, Y., & Zheng, L. (2012). Antimony (III) oxidation and antimony (V) adsorption reactions on synthetic manganite. *Geochemistry*, 72(4), 41-47. <https://doi.org/10.1016/j.chemer.2012.02.002>

Weber, W.J., McGinley, P.M., & Katz, L.E. (1991). Sorption phenomena in subsurface systems: Concepts, models, and effects on contaminant fate and transport. *Water Research*, 25(5), 499-528.

World Health Organization. (2006). *World Health Organization (WHO), Guidelines for Drinking Water Quality*, vol. 1. http://www.who.int/water_sanitation_health/dwq/GDW12rev1and2.pdf. http://www.who.int/water_sanitation_health/WHO_WWD2010_guidelines_2010_6_en.pdf, pp. 306-308b.

Wolfe-Simon, F., Davies, P.C.W., & Anbar, A.D. (2009). Did nature also choose arsenic? *International Journal of Astrobiology*, 8, 69-74.

Wu, D., Sun, S.P., He, M., Wu, Z., Xiao, J., Chen, X.D., & Wu, W.D. (2018). As(V) and Sb(V) co-adsorption onto ferrihydrite: synergistic effect of Sb(V) on As(V) under competitive conditions. *Environmental Science and Pollution Research*, 25, 14585-14594.

Wu, Z.J., He, M.C., Guo, X.J., & Zhou, R.J. (2010). Removal of antimony (III) and antimony (V) from drinking water by ferric chloride coagulation: competing ion effect and mechanism analysis. *Separation and Purification Technology*, 76(2), 184-190.

Xi, J.H., He, M.C., & Lin, C.Y. (2011). Adsorption of antimony (III) and antimony (V) on bentonite: kinetics, thermodynamics and anion competition. *Microchemical Journal*, 97(1), 85-91. <https://doi.org/10.1016/j.microc.2010.05.017>

- Xi, J.H, He, M.C., Wang, K.P., & Zhang, G.Z. (2013). Adsorption of antimony (III) on goethite in the presence of competitive anions. *Journal of Geochemical Exploration*, 132, 201-208.
- Xu, W., Wang, H.J., Liu, R.P., Zhao, X., & Qu, J.H. (2011). The mechanism of antimony(III) removal and its reactions on the surfaces of Fe–Mn Binary Oxide. *Journal of Colloid and Interface Science*, 363, 320-326.
- Xu, Z., Cai, J., & Pan, B. (2013). Mathematically modeling fixed-bed adsorption in aqueous systems. *Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)*, 14(3), 155-176.
- Yadav, L.S., Mishra, B.K., Kumar, A., & Paul, K.K. (2014). Arsenic removal using bagasse fly-iron coated and sponge iron char. *Journal of Environmental Chemical Engineering*, 2, 1467-1473. <https://dx.doi.org/10.1016/j.jece.2014.06.019>.
- Yan, L., Yin, H.H., Zhang, S., Leng, F.F., Nan, W.B., & Li, H.Y. (2010). Biosorption of inorganic and organic arsenic from aqueous solution by *Acidithiobacillusferrooxidans* BY-3. *Journal of Hazardous Materials*, 178(1-3), 209-217.
- Zambrano Guisela, B., De Almailda Ohana, N., Duarte Dalvani, S., Velasco Fermin, G., Luzardo Francisco, H.M., & Nieto-Gonzalez, L. (2022). Adsorption of arsenic anions in water using modified lignocellulosic adsorbents. *Results in Engineering*, 13, 100340.
- Zhang, F.S. & Itoh, H. (2005). Iron oxide-loaded slag for arsenic removal from aqueous system. *Chemosphere*, 60(3), 319–325.

Zhang, C., Jiang, H.Y., Deng, Y.M., & Wang, A.H. (2019). Adsorption performance of antimony by modified iron powder. *RSC Advances*, 9, 31645-31653.

Zhang, G.S., Ren, Z.M., Zhang, X.W., & Chen, J. (2013). Nanostructured iron(III)-copper(II) binary oxide: a novel adsorbent for enhanced arsenic removal from aqueous solutions. *Water Research*, 47(12), 4022-4031.

Zhang, G.S., Qu, J.H., Liu, H.J., Liu, P.R., & Wu, R.C. (2010). Preparation and evaluation of a novel Fe-Mn binary oxide adsorbent for effective arsenite removal. *Water Research*, 44, 1921-1928.

Zhu, J., Pigna, M., Cozzolino, V., Caporale, A.G., & Violante, A. (2011). Sorption of arsenite and arsenate on ferrihydrite: Effect of organic and inorganic ligands. *Journal of Hazardous Materials*, 189, 564-571.

Zou, J.L., Xu, G.R., Pan, K., Zhou, W., Dai, Y., Wang, X., Zhang, D., Hu, Y., & Ma, M. (2012). Nitrogen removal and biofilm structure affected by COD/NH₄⁺-N in a biofilter with porous sludge-ceramsite. *Separation and Purification Technology*, 94, 9-15.

Zouboulis, A., & Katsoyiannis, I. (2002). Removal of arsenates from contaminated water by coagulation-direct filtration. *Separation Science and Technology*, 37(12), 2859-2873. <https://doi.org/10.1081/SS-120005470>

APPENDIX

APPENDIX-1: Thomas Model for Arsenic(DWTS-200)

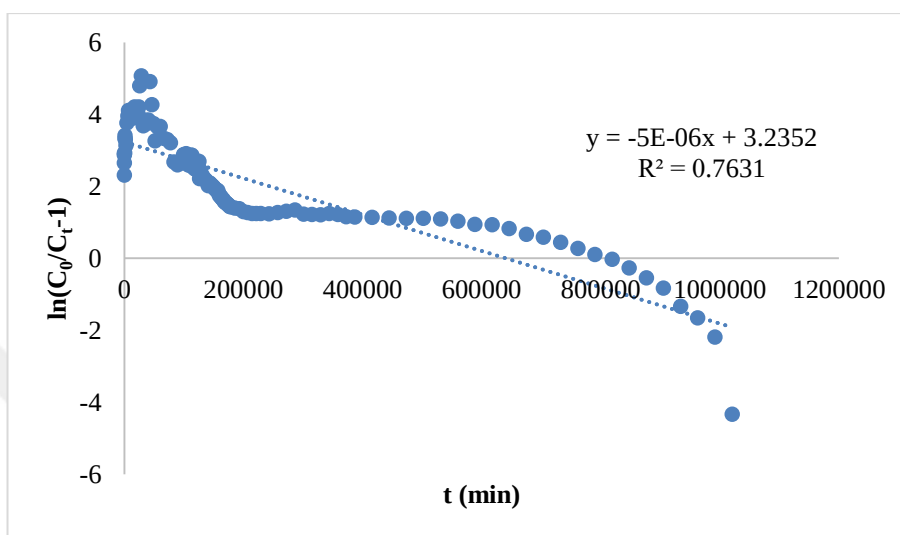


Figure A.1 Arsenic adsorption on DWTS-200 for 10 cm bed depth according to Thomas model

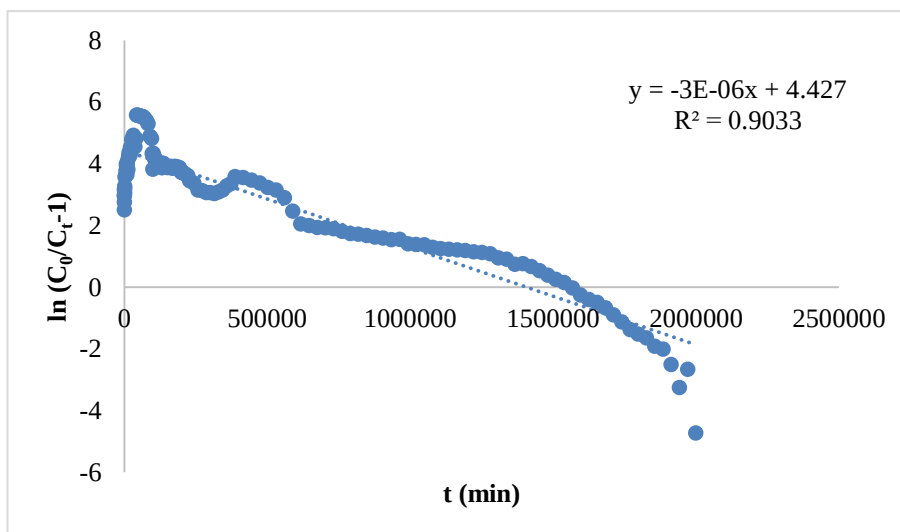


Figure A.2 Arsenic adsorption on DWTS-200 for 20 cm bed depth according to Thomas model

APPENDIX -2: Thomas Model for Antimony (DWTS-200)

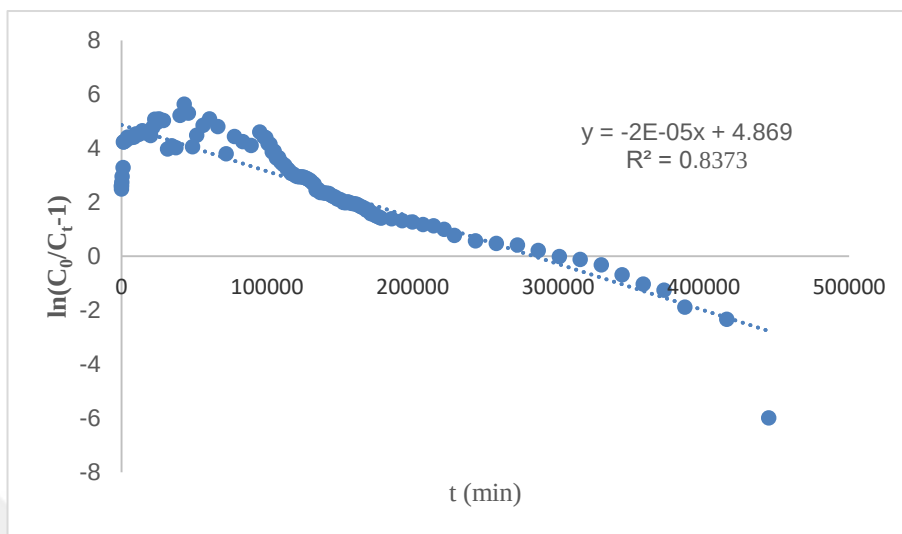


Figure A.3 Antimony adsorption on DWTS-200 for 10 cm bed depth according to Thomas model

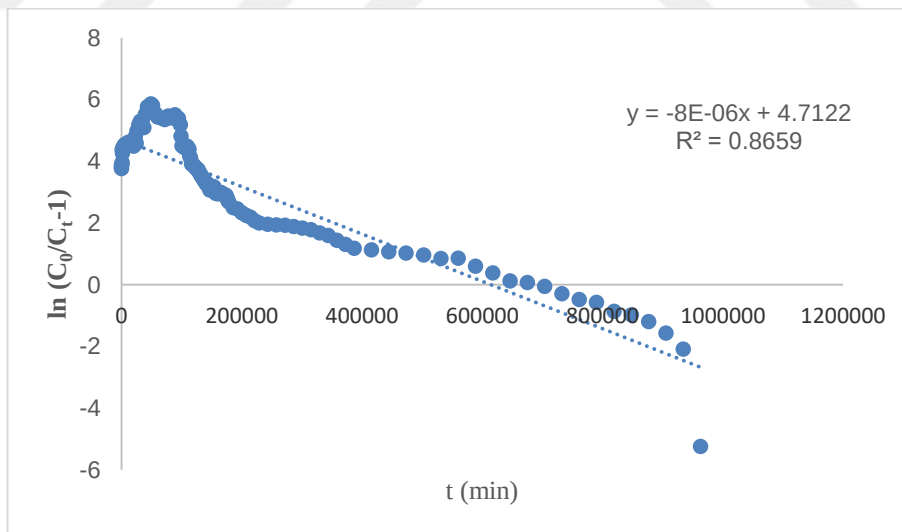


Figure A.4 Antimony adsorption on DWTS-200 for 20 cm bed depth according to Thomas model

APPENDIX-3: Thomas Model for Arsenic (ZOC-DWTS)

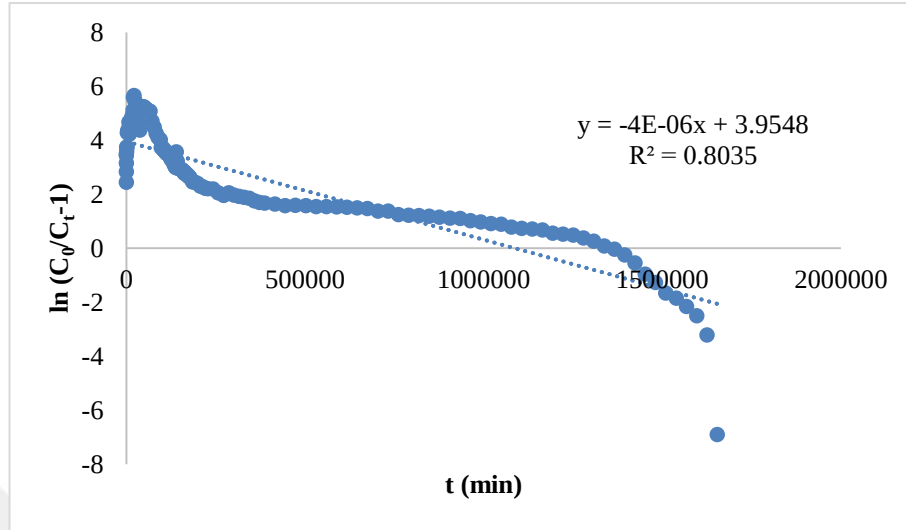


Figure A.5 Arsenic adsorption on ZOC-DWTS for 10 cm bed depth according to Thomas model

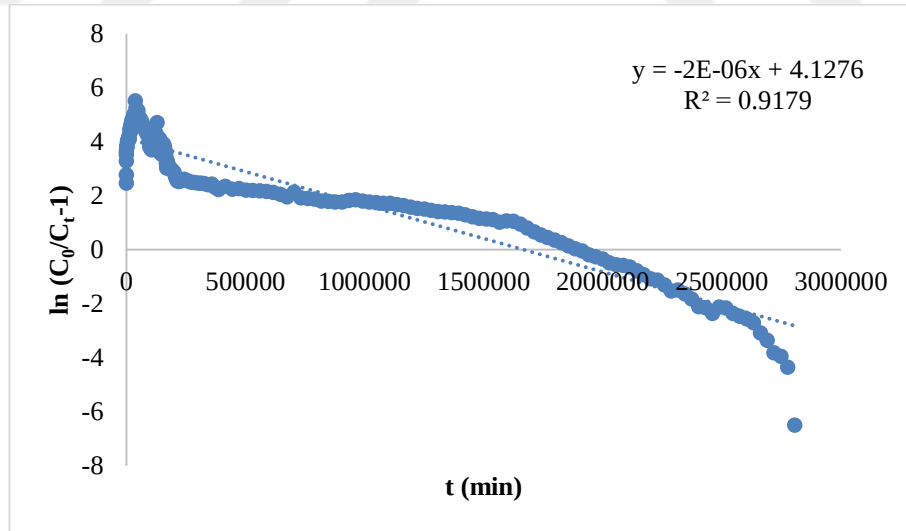


Figure A.6 Arsenic adsorption on ZOC-DWTS for 20 cm bed depth according to Thomas model

APPENDIX-4: Thomas Model for Antimony (ZOC-DWTS)

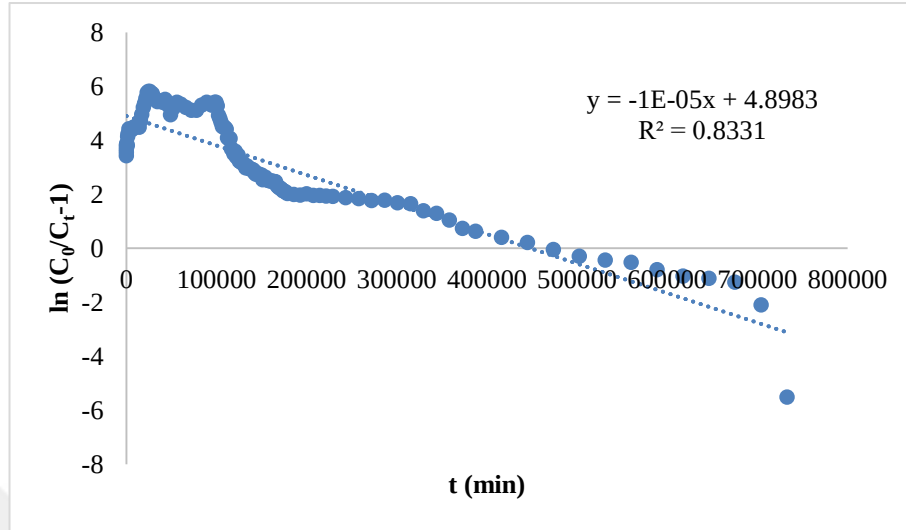


Figure A.7 Antimony adsorption on ZOC-DWTS for 10 cm bed depth according to Thomas model

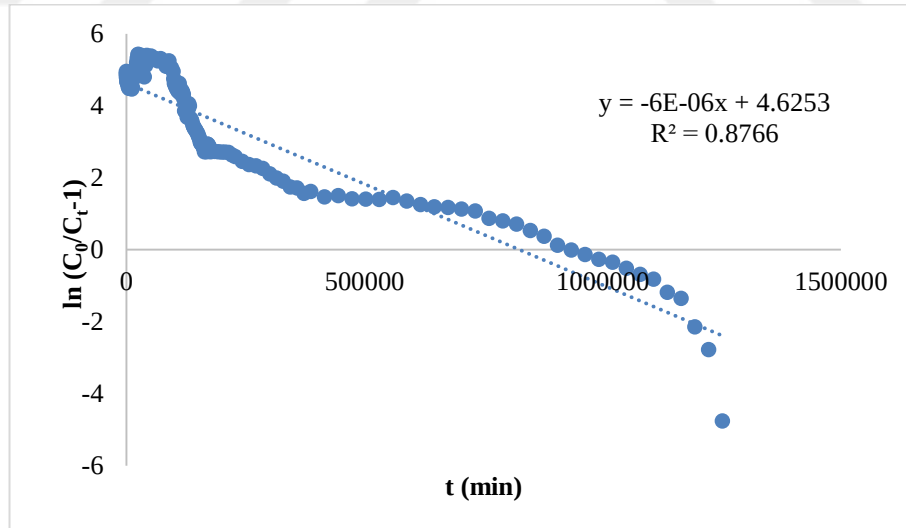


Figure A.8 Antimony adsorption on ZOC-DWTS for 20 cm bed depth according to Thomas model

APPENDIX-5: B&A Model for Arsenic(DWTS-200)

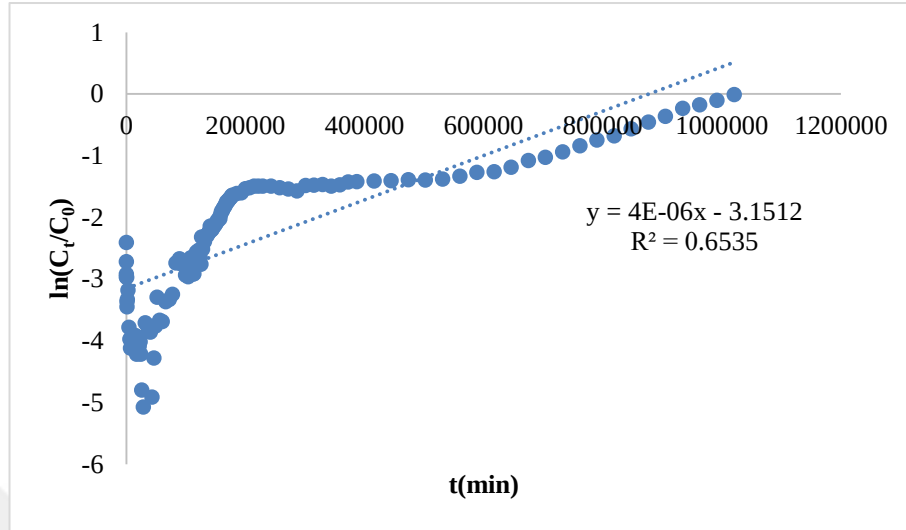


Figure A.9 Arsenic adsorption on DWTS-200 for 10 cm bed depth according to B&A model

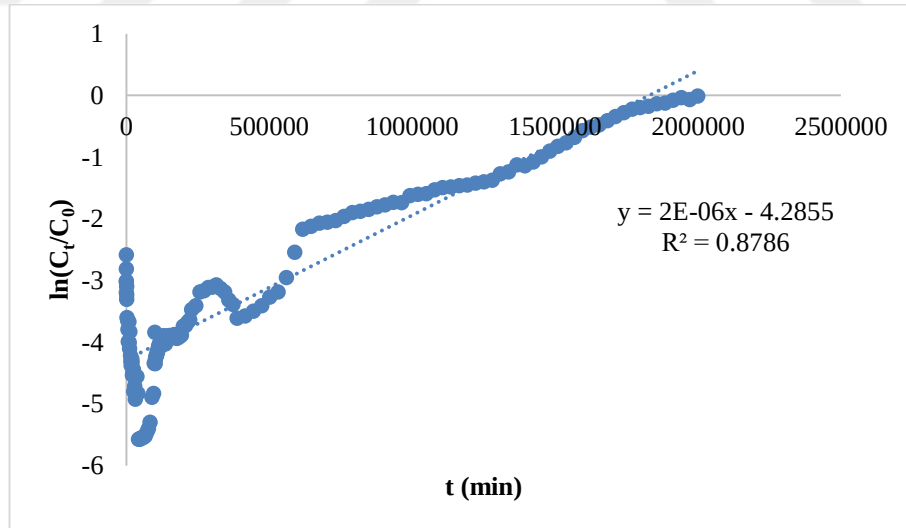


Figure A.10 Arsenic adsorption on DWTS-200 for 20 cm bed depth according to B&A model

APPENDIX-6: B&A Model for Antimony (DWTS-200)

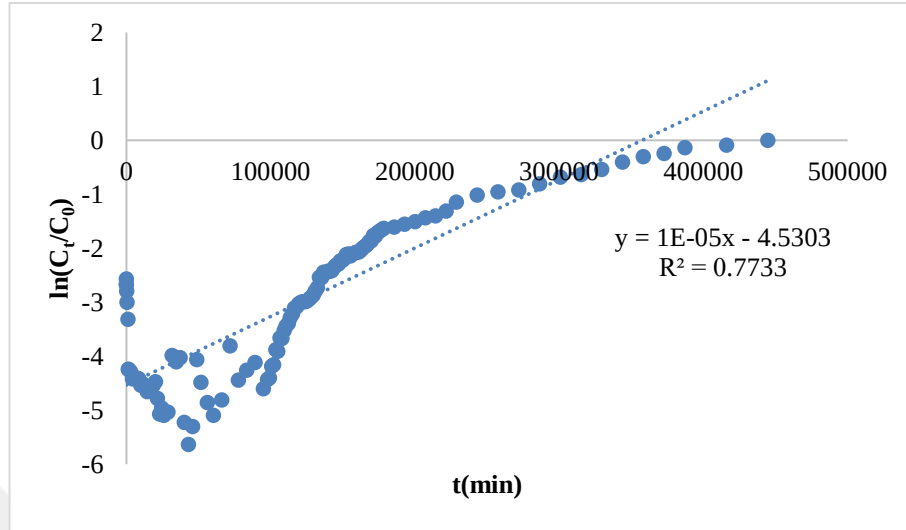


Figure A.11 Antimony adsorption on DWTS-200 for 10 cm bed depth according to B&A model

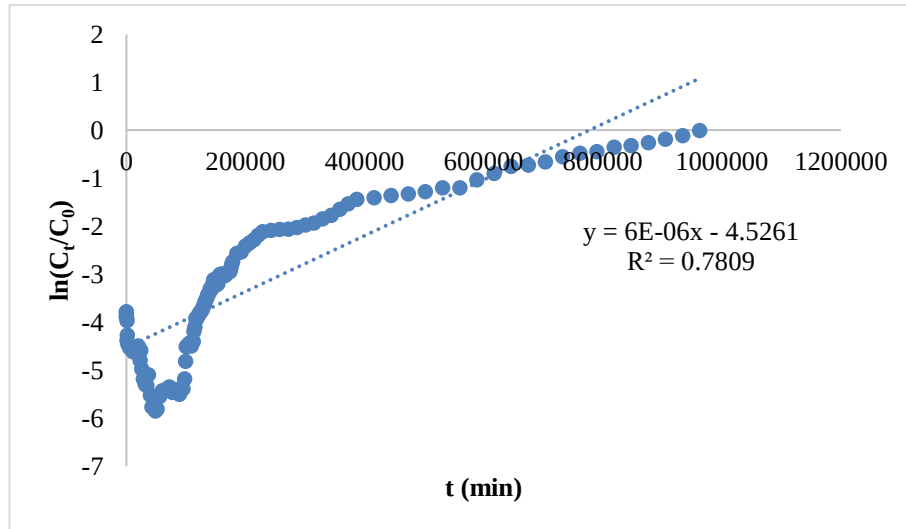


Figure A.12 Antimony adsorption on DWTS-200 for 20 cm bed depth according to B&A model

APPENDIX-7: B&A Model for Arsenic (ZOC-DWTS)

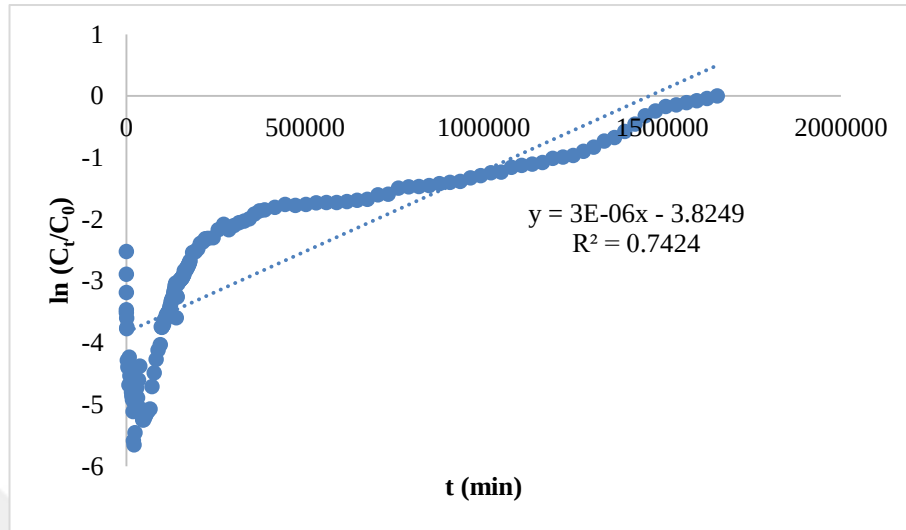


Figure A.13 Arsenic adsorption on ZOC-DWTS for 10 cm bed depth according to B&A model

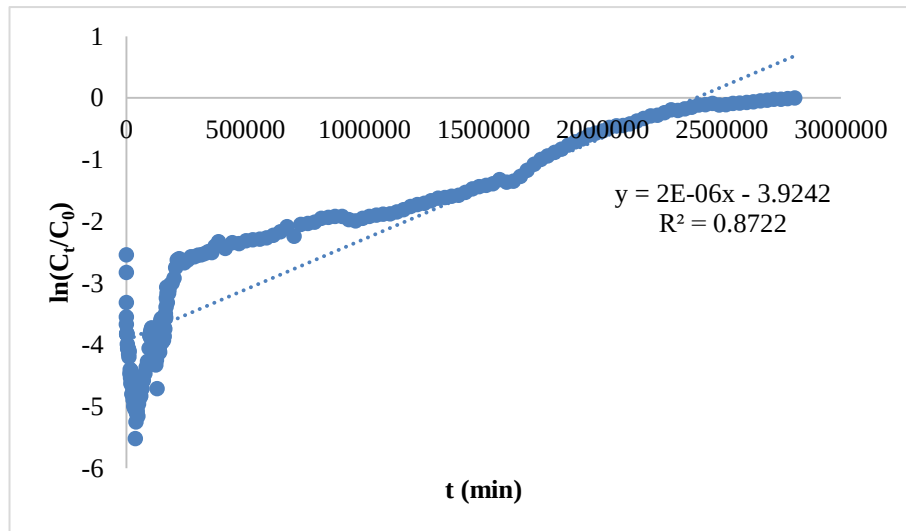


Figure A.14 Arsenic adsorption on ZOC-DWTS for 20 cm bed depth according to B&A model

APPENDIX-8: B&A Model for Antimony (ZOC-DWTS)

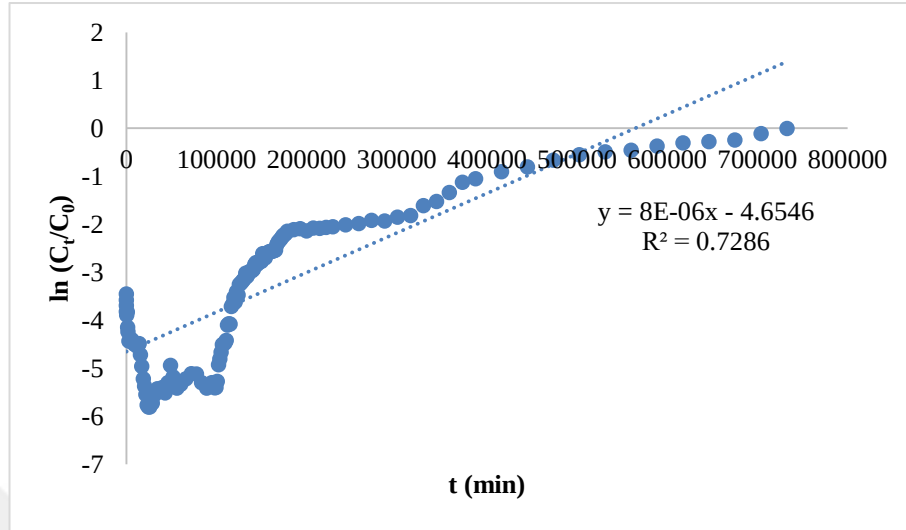


Figure A.15 Antimony adsorption on ZOC-DWTS for 10 cm bed depth according to B&A model

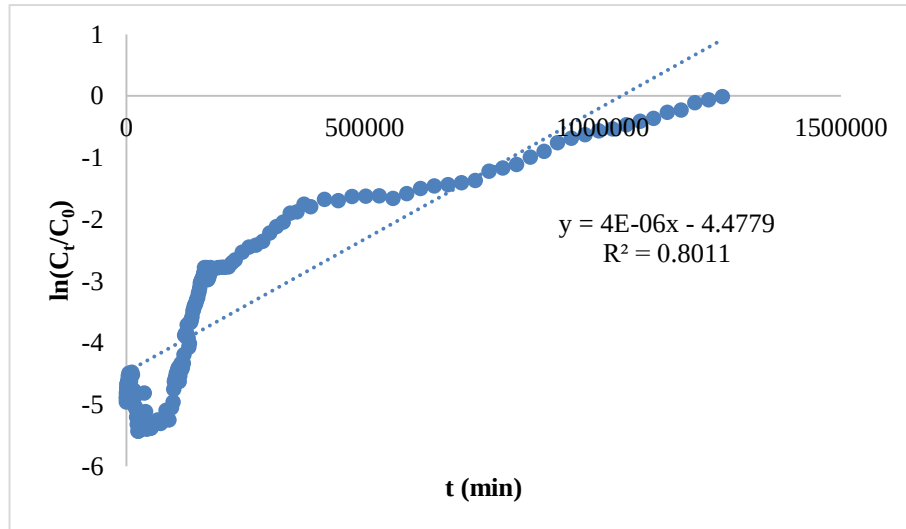


Figure A.16 Antimony adsorption on ZOC-DWTS for 20 cm bed depth according to B&A model

APPENDIX-9: Clark Model for Arsenic(DWTS-200)

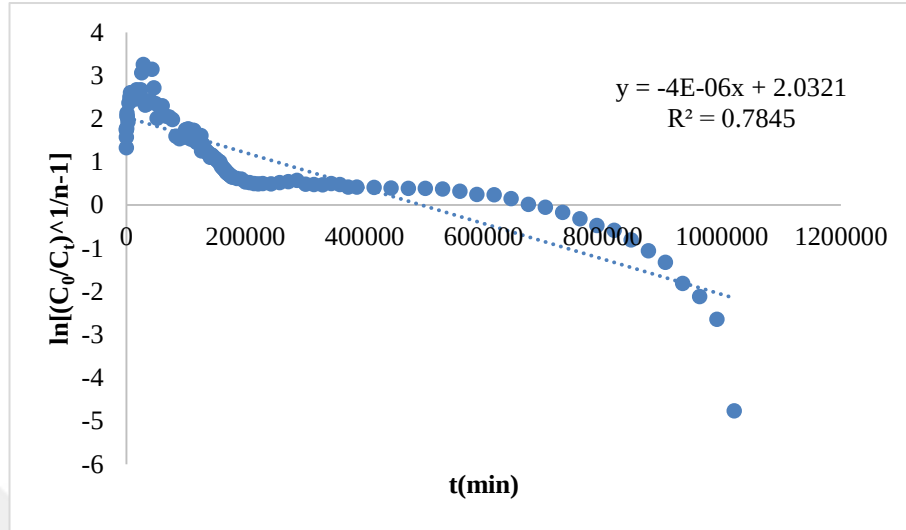


Figure A.17 Arsenic adsorption on DWTS-200 for 10 cm bed depth according to Clark model

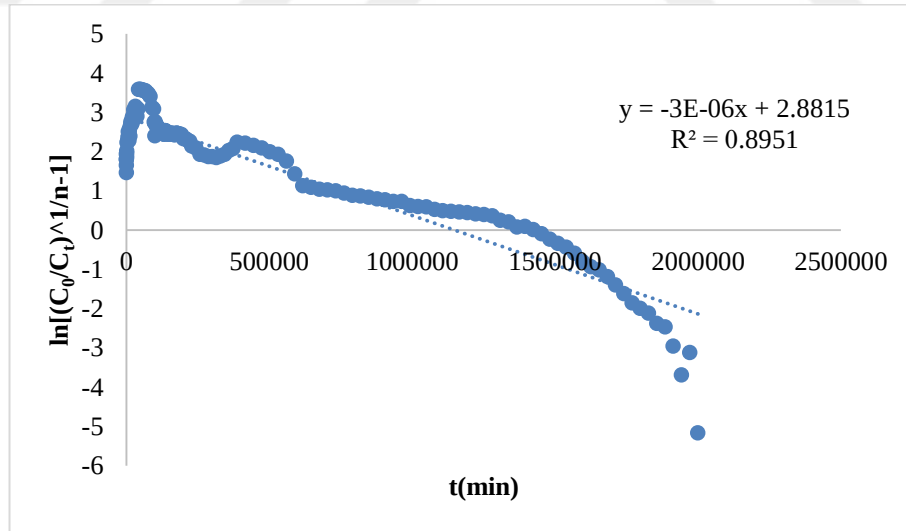


Figure A.18 Arsenic adsorption on DWTS-200 for 20 cm bed depth according to Clark model

APPENDIX-10: Clark Model for Arsenic (ZOC-DWTS)

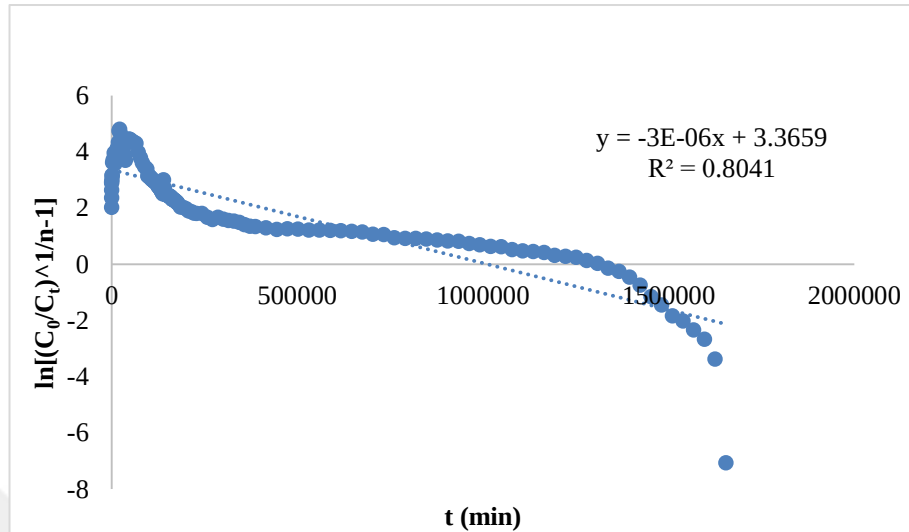


Figure A.19 Arsenic adsorption on ZOC-DWTS for 10 cm bed depth according to Clark model

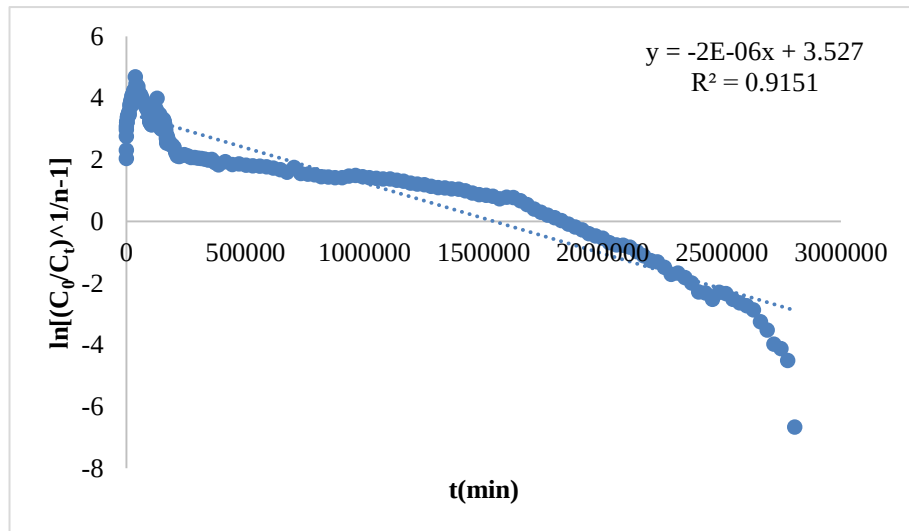


Figure A.20 Arsenic adsorption on ZOC-DWTS for 20 cm bed depth according to Clark model

APPENDIX-11: Yoon-Nelson Model for Arsenic(DWTS-200)

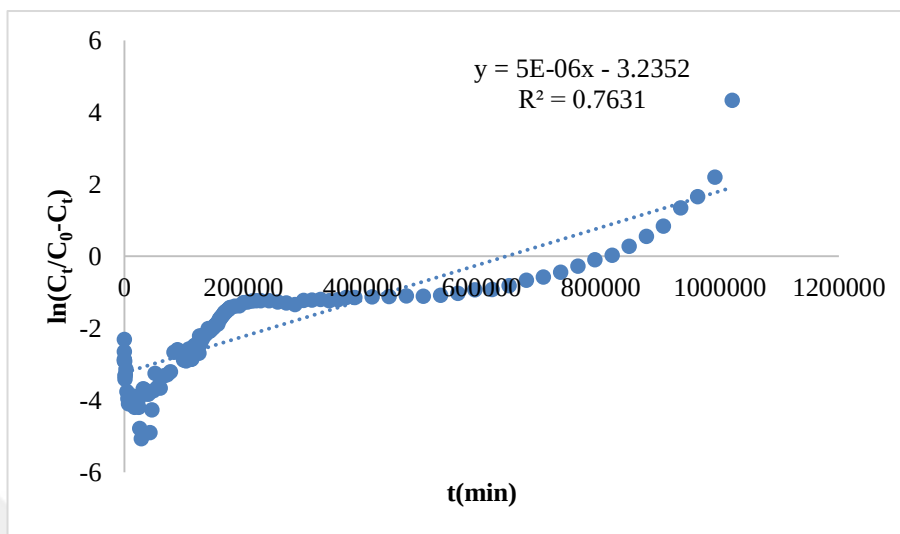


Figure A.21 Arsenic adsorption on DWTS-200for 10 cm bed depth according to Yoon-Nelson model

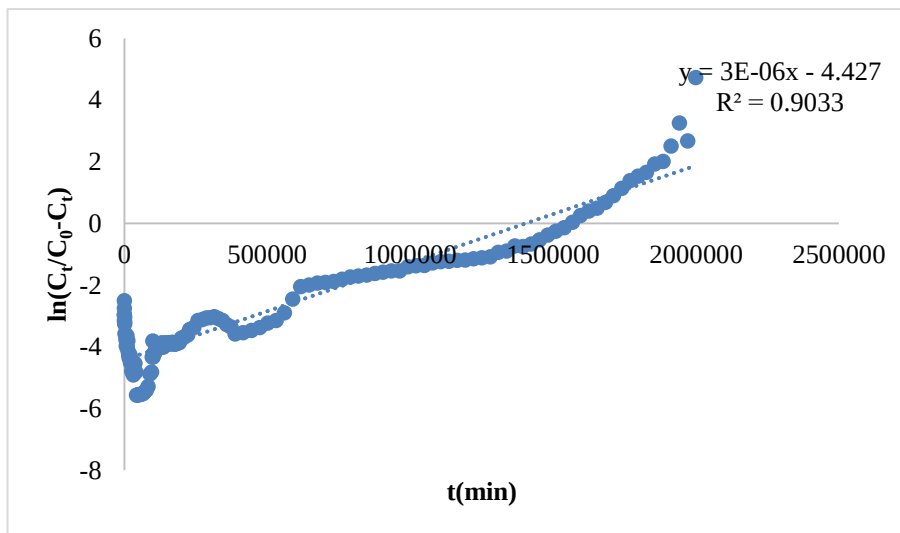


Figure A.22 Arsenic adsorption on DWTS-200for 20 cm bed depth according to Yoon-Nelson model

APPENDIX-12: Yoon-Nelson Model for Antimony (DWTS-200)

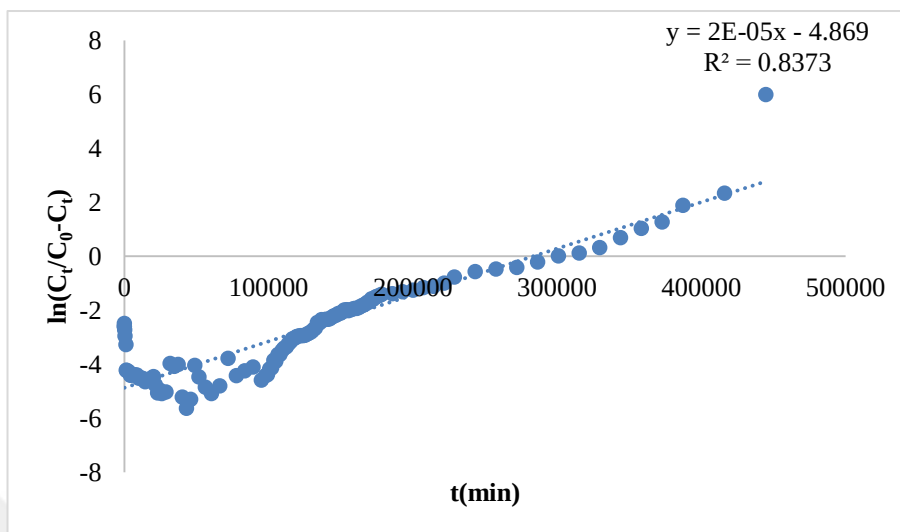


Figure A.23 Antimony adsorption on DWTS-200 for 10 cm bed depth according to Yoon-Nelson model

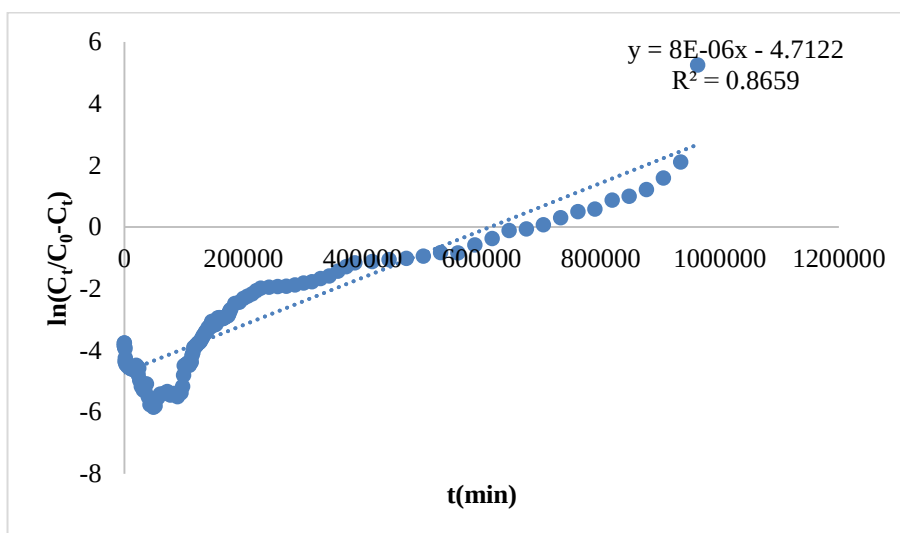


Figure A.24 Antimony adsorption on DWTS-200 for 20 cm bed depth according to Yoon-Nelson model

APPENDIX-13: Yoon-Nelson Model for Arsenic (ZOC-DWTS)

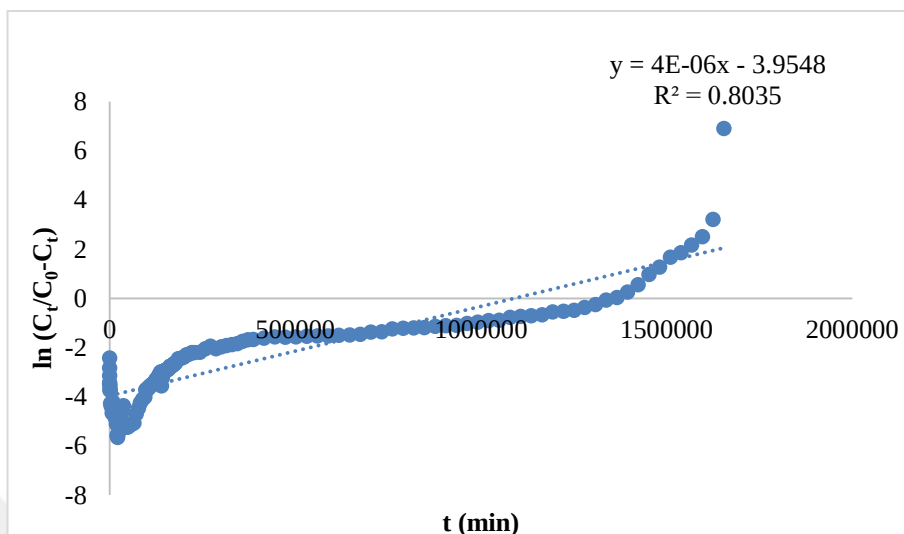


Figure A.25 Arsenic adsorption on ZOC-DWTS for 10 cm bed depth according to Yoon-Nelson model

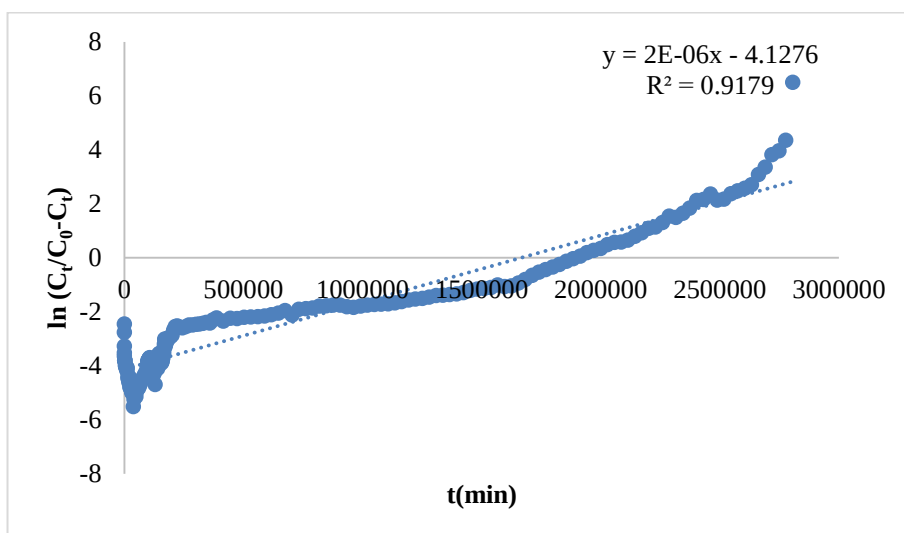


Figure A.26 Arsenic adsorption on ZOC-DWTS for 20 cm bed depth according to Yoon-Nelson model

APPENDIX-14: Yoon-Nelson Model for Antimony (ZOC-DWTS)

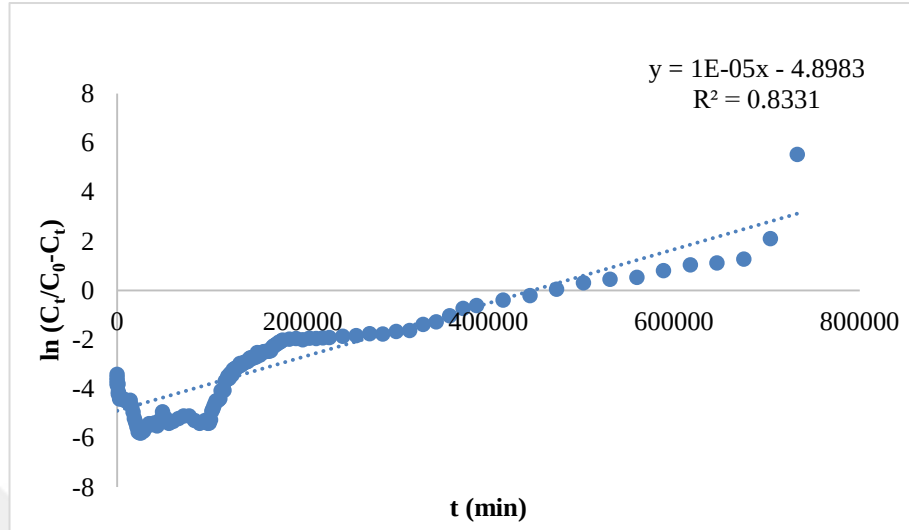


Figure A.27 Antimony adsorption on ZOC-DWTS for 10 cm bed depth according to Yoon-Nelson model

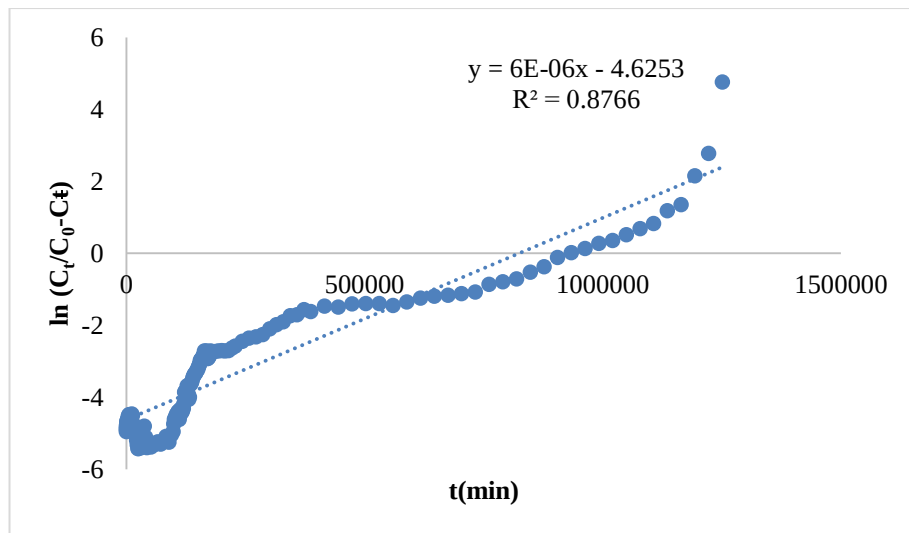


Figure A.28 Antimony adsorption on ZOC-DWTS for 20 cm bed depth according to Yoon-Nelson model