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Surname, Initial(s). (2012). Title of the thesis or dissertation (Doctoral Thesis / Master's Dissertation). Johannesburg: University of Johannesburg. Available from:
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**THE REMOVAL OF CHROMIUM(VI) FROM WATER USING FUNCTIONALISED
MORINGA OLEIFERA LEAVES**

By

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Mini dissertation in fulfilment of the requirement for the degree



MASTER

In

NANOSCIENCE

**UNIVERSITY
in the
JOHANNESBURG**

FACULTY OF SCIENCE

at the

UNIVERSITY OF JOHANNESBURG

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JANUARY, 2020

DEDICATION

I dedicate this work to my lovely mother (Mokgatla Masekela) and my late dad (Joseph Masekela).

May your soul rest in peace MOKWENA!!!



ACKNOWLEDGEMENTS

First of all I would like to thank the almighty God who has given me strength from my younger age and until where I am right now. Again I would like to thank the following people and institution for their assistance:

- I would like to express my deepest appreciation to my supervisor Dr N. Mabuba and Co-supervisor Dr N.C. Hintsho-mbita for their support, guidance and encouragement throughout the year. This research would have not been possible if it wasn't for them.
- Special thanks to the electrochemistry group (Luthando Tshwenya, Colani Fakude, Thabo Matthew, Katlego Raseruthe, Blessie Wessel, Abongile Damba, Molebogeng Malemela, Elelwani Ramudzwagi) for being there for me when I needed any assistance.
- I take this opportunity to express my gratitude to our lab technician (Solomon Pole) for helping me with characterization of the prepared materials using TGA, BET and Zeta potential. Again I would like to thank Lebogang Manamela for assisting me with SEM characterization.
- I wish to express my love and gratitude to my beloved family (Masekela K.C, Masekela M.F, Masekela N.M) for their support, understanding and endless love through the duration of my studies.
- Special thanks to my closest friends (Dineo Constance Letsoalo, Peter Kganyago, Lesego Malepe, Ngoako Waleng) for their encouragement and support extended to me.
- I would like to thank University of Johannesburg and Department of Chemical Sciences, previously known as Department of Applied Chemistry for giving me the opportunity to pursue my master's degree. Finally, I would like to thank Department of Science and Technology (DST) for financial assistance.

PUBLICATIONS AND PRESENTATIONS

The work presented in this dissertation has been presented at University and international conferences.

Conference Presentations

- ❖ **Masekela D.**, Hintsho-Mbita N.C., and Mabuba N. *The removal of chromium(VI) from water using functionalised Moringa Oliefera and detection by Uv-vis spectrophotometer.* Shot-gun presentation. 3rd International Caparica Conference on Pollutant Toxic Ions and Molecules, Portugal , Lisbon, 03-07-November-2019
- ❖ **Masekela D.**, Hintsho-Mbita N.C., and Mabuba N. *The removal of chromium(VI) from water using functionalised Moringa Oliefera and detection by Uv-vis spectrophotometer.* Oral presentation. Department of Applied Chemistry, University of Johannesburg, Johannesburg, 29-March-2019

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ABSTRACT

The presence of heavy metals such as arsenic, lead, zinc, cadmium and chromium etc. poses serious health challenges worldwide. These metals are disposed into water systems due to rapid growth of industries like chrome tanning, mining and electroplating. Drinking water containing high concentration of chromium(VI) above the allowed limit (0.05 mg/L) can cause lung cancer, liver and kidney damages. Therefore, this study is investigating the application of functionalised *Moringa oleifera* (FMO) and magnetic functionalised *Moringa oleifera* ($\text{Fe}_3\text{O}_4/\text{FMO}$) as adsorbents for the removal of chromium(VI) from aqueous solution. *Moringa oleifera* was functionalised with amine groups to enhance its adsorption capacity towards Cr(VI) removal. The functionalised *Moringa oleifera* was incorporated with Magnetite (Fe_3O_4) nanoparticles as to form magnetic composites ($\text{Fe}_3\text{O}_4/\text{FMO}$) which can be recovered from aqueous media. The adsorbents were characterized using FTIR, XRD, SEM, BET and TGA. The introduction of amine groups on the surface of *Moringa oleifera* (MO) was confirmed by FTIR. It was worth noticing that the peak at 1351 cm^{-1} for C-N stretching indicated successful grafting of amino groups into MO surface. For $\text{Fe}_3\text{O}_4/\text{FMO}$, the new developed sharp intense peak at 685.6 cm^{-1} indicated Fe-O stretching, suggesting successful incorporation of Fe_3O_4 onto FMO. The BET results showed that successful incorporation of magnetite nanoparticles onto FMO resulted in a huge increase of surface area of composite ($\text{Fe}_3\text{O}_4/\text{FMO}$) from 1.0942 to $30.6387\text{ m}^2/\text{g}$.

The adsorption of Cr(VI) on both adsorbents (FMO and $\text{Fe}_3\text{O}_4/\text{FMO}$) was conducted by optimizing the following parameters: pH, dosage, contact time and initial Cr(VI) concentration. The highest Cr(VI) removal percentages by FMO and $\text{Fe}_3\text{O}_4/\text{FMO}$ at pH 2 were 88.15 and 90.1 %, respectively. From co-existing ion studies, it was noticed that both adsorbents (FMO and $\text{Fe}_3\text{O}_4/\text{FMO}$) were selective towards Cr(VI) in the presence of metal cations (Ni^{2+} , Zn^{2+} , and Cu^{2+}). In the presence of anions (NO_3^- , Cl^- and SO_4^{2-}) the Cr(VI) removal was slightly affected more especially at high

concentrations like 100 mg/L of SO_4^{2-} . The reusability studies showed that FMO can be reused for 3 adsorption cycles without losing its stability, whereas for $\text{Fe}_3\text{O}_4/\text{FMO}$ it was only for 2 adsorption cycles. Therefore, this study showed that both FMO and $\text{Fe}_3\text{O}_4/\text{FMO}$ are promising adsorbents for removal of Cr(VI) from wastewater. Antibacterial activity of FMO was also tested using pond, river, tap and sewage water against several bacterial strains. It was found that the FMO was active against *E. coli*, *Staphylococcus aureus* and total coliforms. Based on the data obtained this study has shown that environmentally safe adsorbents can be used as multifunctional materials for the treatment of water.



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LIST OF ABBREVIATIONS

AC	: Activated carbon
AS	: 3-aminopropylthethoxyline
BET	: Brunauer-Emmett-Teller
CNTs	: Carbon nanotubes
DMF	: Dimethylformamide
DETA	: Diethylenetriamine
DPC	: Diphenylcarbazine
DTG	: Derivative thermalgravimetric
EDA	: Ethylenediamine
EDS, EDX	: Energy dispersive X-ray spectroscopy
FAO	: Food and Agriculture Organization
FE-SEM	: Field Emission Scanning Electron Microscope
FMO	: Functionalised <i>Moringa oleifera</i>
FTIR	: Fourier-Transform Infrared
IUPAC	: International Union of Pure and Applied Chemistry
MEUF	: Micellar enhanced ultrafiltration
MF	: Microfiltration

MO	: <i>Moringa oliefera</i>
MWCNTs	: Multi-walled carbon nanotubes
NF	: Nanofiltration
PEI	: Polyethylenimine
PEUF	: Polymer enhanced ultrafiltration
RO	: Reverse Osmosis
SAB	: South Africa Bureau of Standards
SWCNTs	: Single-walled carbon nanotubes
TETA	: Triethylenetetramine
TGA	: Thermal Gravimetric Analysis
UF	: Ultrafiltration
USEPA	: United States Environmental Protection Agency
UV-vis	: Ultraviolet visible
WHO	: World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Background

The presence of heavy metals like nickel, zinc, mercury, cadmium, copper, lead, arsenic and chromium in water has become a serious problem worldwide[1]. Due to rapid industrialization and urbanization, these heavy metals are released into the environment [2]. The released heavy metals tend to accumulate within human bodies since they are non-biodegradable. All these heavy metals ions are toxic and carcinogenic even if they are present in low levels in aqueous solution. Amongst most of these heavy metals, chromium is considered as one of the most toxic pollutants in the environment [3]–[5]. It occurs in concentrations greater than >0.25 mg/L in industrial wastewater caused by electroplating, paints, dyes, chrome tanning and paper industries. [6].

In the aquatic environment, chromium tends to exist in two forms as hexavalent Cr(VI) and trivalent Cr(III). Trivalent chromium is less toxic compared to hexavalent chromium since it is one of the trace elements required by humans and plants for metabolic activities [7]. On the other hand, hexavalent chromium is the most highly toxic element due to high mobility and solubility in water. The United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) have set the allowed limit of Cr(VI) to be 0.25, 0.1 and 0.05 mg/L in industrial wastewater, surface water and drinking water, respectively [6], [8]. Drinking water with high concentration of Cr(VI) above the permissible limit can result in several health problems including lung cancer, stomach upsets as well as kidney and liver damages [9], [10].

Therefore, new developments of highly efficient methods that can remove or reduce high concentrations of Cr(VI) present in contaminated media below the allowable

levels as to provide safe drinking water to the environment are required. The current study is based on the application of functionalised *Moringa oleifera* and magnetic functionalised *Moringa oleifera* as sorbents for the removal of hexavalent chromium from water.

1.2 Problem statement

Long term exposure to hexavalent chromium tends to cause serious health issues like chronic skin disorders, lung cancer, kidney and liver damages [9], [10]. Therefore, this toxic heavy metal ion needs to be removed from water. Several methods such as precipitation, membrane separation, ion exchange, reverse osmosis and many more were employed for remediation of water containing Cr(VI) [11]–[13]. However, most of these methods are associated with several shortcomings that prevent their applications for removal of Cr(VI) in aqueous solution. The disadvantages of these methods include incomplete removal of Cr(VI), require expensive equipment and the production of secondary waste such as toxic sludge that involve additional treatment [11]–[13]. Besides these techniques, adsorption has been considered as the most reliable method for Cr(VI) removal as it is less expensive, highly efficient, easy to operate and has a regeneration ability [14], [15].

1.3 Rationale and Motivation

There are various agricultural waste materials that have been utilized as sorbents for heavy metals remediation from aqueous solution, these include rice husk/bran, wheat bran/straw, sugarcane bagasse and coconut shells [16]–[19]. The major advantage of these waste materials for sorption of heavy metals consist of good adsorption capacity (even at low concentrations), easy accessibility in large amount, being environmentally friendly, selectivity and accessible at low cost [20]. However, these raw materials as adsorbent have been reported to have a poor adsorption capacity towards anionic metals [21]. Several studies have shown that through

chemical modification with quaternary ammonium and amine groups, their adsorption capacity can be enhanced [21].

Wartelle and Marshall [22] prepared anion exchangers by quaternizing various agricultural waste-materials including rice hulls, corn stoves and almond shell with N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride. The prepared anion exchangers were utilized for removing phosphate, arsenate, selenite and chromate from wastewater. Based on their results, the quaternized corn stover gave a good adsorption uptake for selenite, arsenate and chromate, respectively [21]. The modified corn stover adsorbed more than 90 % of all anionic contaminants at pH 7. Another study conducted by Orlando *et al.*, modified two waste materials (i.e. Sugarcane bagasse and rice hull) by grafting epichlorohydrin and dimethylamine on to them for nitrate remediation from aqueous solution [16], [23], [24]. The highest psugarcane bagasse and rice hull, respectively. Also, Chen *et al.*[25] prepared an anion exchange by reacting corn stalk material with epichlorohydrin and triethylamine using diethylenetriamine (DETA) as a modifying agent. The modified corn stalk (MCS) had a higher point zero charge value (P_{zcc}) of 6.5 compared to the raw corn stalk (RCS), suggesting an increase of more positively charged groups on the MCS surface. The MCS was even more effective in removing Cr(VI) ions at neutral pH, as opposed to RCS which was effective in acidic media (pH 2).

The present study was aimed to use functionalised *Moringa oleifera* as adsorbent for Cr(VI) remediation from wastewater. *Moringa oleifera* is a plant tree which tend to have nutritional, medicinal, antimicrobial and water treatment properties [26]. For example, *Moringa oleifera* leaves can be added to any meal to increase vitamin, proteins and mineral content. Many African countries including South Africa uses this plant tree as a traditional medicine for treating malaria and malnutrition. In this present study, a new affordable anionic adsorbent was prepared by reacting *Moringa oleifera* powder with epichlorohydrin and triethylamine using diethylamine as a modifying agent for removing Cr(VI) from aqueous solution. To address the challenge of recovering adsorbents from the treated water, the iron oxide (magnetite) was incorporated into the functionalised *Moringa oleifera*. The magnetite (Fe_3O_4) nanoparticles have been shown to have magnetic properties,

thus making them a viable option as they can be easily separated from aqueous media by use of an external magnet [27]. Thus, in this work the functionalised *Moringa oleifera* was incorporated with iron oxide nanoparticles (Fe_3O_4) to form a magnetic composite that can be separated/recovered from water by use of an external magnet.

1.4 Aim and Objectives

➤ Aim:

- To remove chromium(VI) from water samples using functionalised *Moringa oleifera* and functionalised *Moringa oleifera* incorporated with magnetite nanoparticles.

➤ Objectives:

- Functionalization of *Moringa oleifera* with amine groups
- Synthesize magnetite (Fe_3O_4) nanoparticles using co-precipitation method
- Incorporate Fe_3O_4 nanoparticles into functionalised *Moringa oleifera*
- Characterise the synthesized materials using FTIR, SEM-EDS, TEM, VSM, BET, TGA, XRD and Zeta potential.
- To study the impact of parameters like pH, dosage, contact time, initial concentration and co-existing ions for the removal of Cr(VI) from standard solutions
- Conduct reusability studies of the FMO and Fe_3O_4 /FMO for Cr(VI) removal
- To treat real water samples
- To test the antibacterial activity of FMO and Fe_3O_4 /FMO

1.5 Dissertation outline

This highlight a brief summary of the topics that has been covered in the chapters. In this study experimental methodology were separated as different chapters. Here, results and discussions were reported as different chapters in the form of manuscripts for publication purpose. Each chapters (Chapter 4 and 5) had separate experimental methodologies. The experimental methodology reported in chapter 3 gave a brief review on the background of each instrumental techniques used in this study and their sample preparations for analysis.

Chapter 2

The literature review chapter will provide an insight on the background of the heavy metals in the environment, their toxicity and applications. This chapter also gives a brief summary of the conventional methods used for removing poisonous metals, more especially Cr(VI). Agricultural waste materials as sorbent for removal of heavy metals are also discussed in this chapter

Chapter 3

In this chapter, all characterization techniques used for confirmation of the prepared adsorbents are discussed. The sample preparation for analysis and the procedures used to conduct batch adsorption experiment are explained in this chapter.

Chapter 4

This chapter gives information about the batch adsorption experiments conducted using funtionalised *Moringa olefeira* as an adsorbent. Various parameters like the effect of dosage, pH, contact time and initial concentration are discussed. The effect of co-existing ions that could interfere with Cr(VI) removal are also discussed. Kinetics models such as pseudo first order model, pseudo second order and intraparticle diffusion are argued in details in this chapter. Lastly, the activity of FMO against four bacterial strains and real water samples are also investigated.

Chapter 5

The main purpose of this chapter is for removal of Cr(VI) from aqueous solution using $\text{Fe}_3\text{O}_4/\text{FMO}$. Here, the magnetic adsorbent ($\text{Fe}_3\text{O}_4/\text{FMO}$) will be used for Cr(VI) remediation. The effect of parameters like pH, dosage, time and initial concentration which might affect Cr(VI) removal will also be discussed. The kinetics models such as pseudo first order and second order for this magnetic adsorbent will also be revealed.

Chapter 6

All conclusions, recommendations and future work are mentioned in this chapter.



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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the presence of heavy metals such cadmium, arsenic, mercury and more especially chromium in the environment will be discussed. Their toxicity, discharging sources and allowed limits in the environment will also be discussed. This chapter will also cover several conventional methods used for removal of toxic metals, more especially for Cr(VI) removal. Agricultural waste materials used as sorbent for removal of heavy metals will be conversed in this chapter.

2.2 Heavy metals in the environment

Heavy metals are classified as elements with high atomic number greater than 20.0, with density of more than 5.0 g/cm^3 [1]. Most of these heavy metals such as arsenic, lead, nickel, zinc, cadmium, copper, mercury and chromium are known to be toxic. Even though copper, zinc, iron, manganese and cobalt are required by our bodies for metabolic activities, their high concentration in water can cause serious health problems. Other heavy metals like chromium, lead, mercury, cadmium and arsenic are known to be toxic even at low concentrations (ppb). As opposed to other pollutants, these heavy metals are non-biodegradable, therefore tend to accumulate in our bodies [2], [3]. Excessive accumulation of these metal ions in our bodies can cause several health problems such as bone diseases, cardiovascular, kidney and liver damage as well as lung cancer [3]. Therefore, the development of new effective technologies for the removal heavy metals from water is required to provide clean water. Industries like mining, pharmaceuticals, metal plating, fertilizer and painting are the major sources of the existence of these heavy metals in the environment [4], [5]. Due to the rapid increment of these industries, these heavy metals are released into the environment thus leading to the contamination of water from the rivers, ocean or lakes.

2.2.1 Cadmium

Cadmium is a chemical element with symbolic term Cd and atomic number 48. This element is highly unstable and thus can be found in two oxidation states as Cd^{2+} and Cd^{+1} , but usually exists in the form of Cd^{2+} [6].

Cadmium is known to be the most toxic heavy metal among others [7]. It is normally found in wastewater due to anthropogenic activities [8]. Wastewater from industry contains different concentrations of cadmium. Industrial wastewater from electroplating process generally consist of about 17.5 mg/L cadmium [8]. According to the Food and Agriculture Organization (FAO) the allowed limit for cadmium is set to be 0.01 mg/L, in which industrial wastewater exceeds that amount [9].

According to the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA), the allowed limit of cadmium is 0.03 and 0.01 mg/L, respectively in drinking water [10]. Drinking water with cadmium exceeding the allowed limit can cause disorders in endocrine system and can also affect cardiovascular, neurological, pulmonary and immunological systems [11]–[14]. Several technologies were used for removing this toxic element from water. These include membrane filtration, coagulation, reverse osmosis, precipitation, adsorption and many more [15], [16].

2.2.2 Arsenic

Arsenic is a metalloid which exists in a metallic state in three forms namely, black, grey and yellow; with grey predominating. It is the 20th most abundant element on the earth's crust. It is known to be toxic and exists as an oxide or in anionic form. In water, arsenic normally exists in two oxidation states as As(V); arsenate and AS(III); arsenite. Arsenite is more toxic compared to arsenate due to its high solubility. However, arsenate tends to be more mobile and toxic at low pH [17].

The main sources of arsenic in the environment are mining industries. In the mining industries, arsenic rich minerals (arsonopyrite, cobaltite, enargite and others) are

brought to the earth's surface where they easily interact with water during rainfalls thus increasing the concentration of arsenic in water [18]. Organic fertilisers contain low amounts of arsenic and are used in agricultural field to provide the required elements by soil. Therefore, this promotes the leaching effect of arsenic into ground water system [18].

The World Health Organization (WHO) have set the allowed safe drinking water for arsenic content to be below 0.01 mg/L [19]. Drinking water with high content of arsenic above the set limit can result in several health issues such as lung, bladder, and skin cancer, diabetes and cardiovascular diseases [19]–[22].

2.2.3 Mercury

Mercury is the second most poisonous metal in the world. It exist in three different forms either as metallic, organic or inorganic complexes [23], [24]. Among these three forms, the organic form has been reported to be the most toxic since it can affect our immune systems, alter with genetic systems, and damage the human nervous system [25].

The recommended maximum allowed limit of mercury in drinking water by WHO is 0.001 mg/L. For humans there is no safe level of mercury because even in very small amounts (<1.0 ppb) below the allowed limit in drinking water can cause some serious health problems [25]. There are several sources which can lead to the discharge of mercury into water bodies like rivers, oceans and lakes. The main discharging sources are industries like manufacturing, paper and mining's [25].

2.2.4 Chromium

Cr is the 24th element in the periodic table and it is found in group 6. The name chromium is derived from greek word called chroma, which means color because most of the chromium compounds are colored. Amongst the elements on earth, chromium is the 21st most abundant element in the world [26]. It is one of the important trace elements needed by plants and animals for metabolic activities. It is

usually a natural occurring element that is found mainly in plants, animals, soil and rocks.

Chromium can be used in various ways in many industries, such as chrome plating steel production and corrosion resistance [27]. There are many sources of chromium such as crocoite (PbCrO_4) and chrome ochre (Cr_2O_3) but the main source is mining chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$). These industries release large amounts of chromium into water, ranging between 0.5 to 270,000 mL^{-1} . Therefore, it means that industrial wastewater contains a huge amounts of chromium.

Chromium normally exist in four different oxidation states as Cr(0), Cr(II), Cr(III) and Cr(VI) [28]. Among these states of chromium, Cr(VI) compounds are commercially important and are produced industrially by heating Cr(III). Chromium(VI) can exist as chromate (CrO_4^{2-}) ion, dichromate ($\text{Cr}_2\text{O}_7^{2-}$) or bichromate (HCrO_4^-) in aqueous solution depending on the concentration and acidity [29]. $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- are predominant at pH between 2 and 6 while CrO_4^{2-} is predominant in basic media, at $\text{pH}>6$ as displayed in **Figure 2.1** [56].

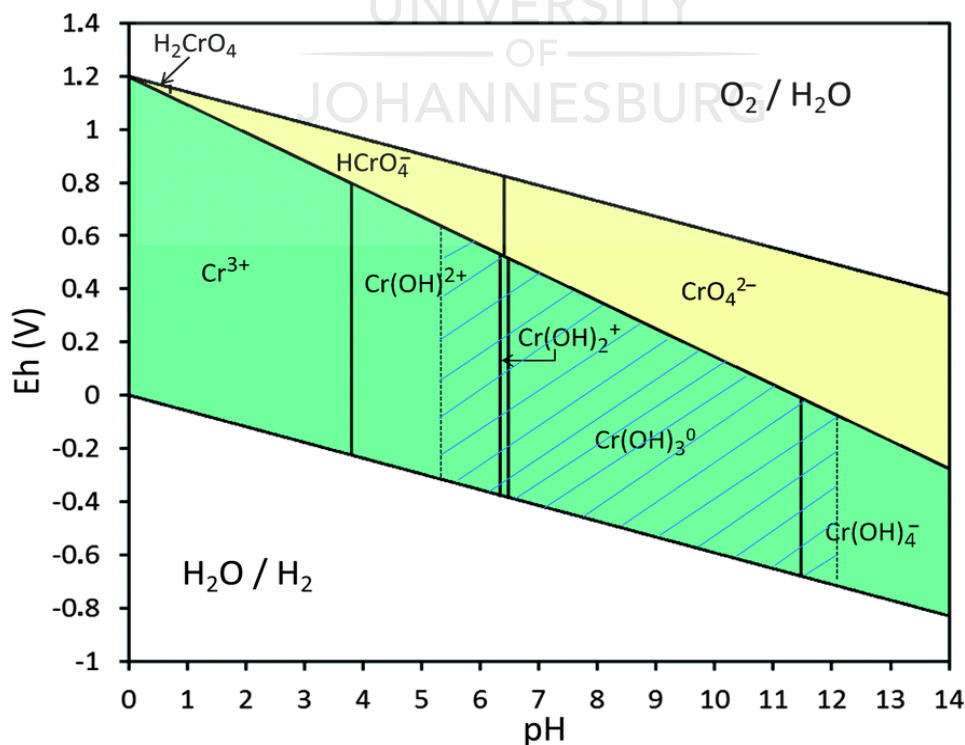


Figure 2. 1 : Chromium speciation in aqueous solution

Chromium(VI) and chromium(III) differ in toxicity, chromium(VI) is more than 500 times more toxic than chromium(III) due to its high mobility and solubility [31]. Chromium(III) is an important trace element for both human and animals at low concentrations, but its high consumption can be toxic [31]. Chromium(III) compounds are insoluble in water, while most of the chromium(VI) compounds dissolve (soluble) completely in water. Chromium(VI) is known to be harmful, carcinogenic to human and animal life's [32]. Hence, there is need to reduce or remove chromium(VI) present in water to provide safe drinking water.

Drinking water with high content levels of chromium can create many health issues like lung cancer, diarrhoea, kidney damage and also respiratory problems. According to WHO and South African Bureau of Standards (SAB) the maximum allowed limit of chromium(VI) in drinking water is 0.05 mg/L [32], [33] .**Table 2.1** shows the allowed permissible limit of a few selected heavy metals in drinking water by WHO and USEPA including their health effects.

Table 2. 1: Summary of the allowed limits and health effects of several toxic heavy metals

Heavy metals	The allowed limits in drinking water(mg/L)			Health effects	Ref
	WHO	USEPA	SAB		
Cadmium	0.003	0.005	0.005	Drinking water with cadmium exceeding permissible limit can cause disorders in endocrine system and can also affect neurological, pulmonary and immunological systems	[10], [34], [35], [36]
Arsenic	0.01	0.01	0.01	Long term exposure of arsenic from contaminated water can cause lung, bladder and skin	[19], [37], [38], [36]

				cancer, diabetes and cardiovascular diseases	
Mercury	0.001	0.002	-	Drinking water exceeding the allowed limit can cause neurological damages of the human body.	[25], [39]
Lead	-	0.01	0.1	Health effects associated with lead includes nervous system damage, and also kidney, reproductive and liver damages	[40], [41], [36]
Zinc	3.0	5.0	3.0	Drinking water with high content of zinc can cause vomiting, nausea, stomach cramps, skin irritations, and anaemia.	[42] – [44], [36]
Copper	1.5	1.3	1.0	Vomiting, stomach cramps and convulsions.	[45], [46], [36]
Nickel	2.0	1.3	-	High consumption of nickel exceeding the allowed limit can cause lung and kidney damages, also skin dermatitis and pulmonary fibrosis	[47], [48]

The next section highlight several techniques used for removal of heavy metals from aqueous especially Cr(VI). Their operational methods, advantages and disadvantages were discussed in details.

2.3 Remediation

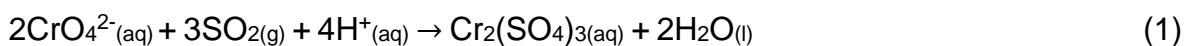
Several treatment processes were developed for removing chromium from aqueous solution. These include ion exchange [49], solvent extraction [50], precipitation [51], filtration [52], reverse osmosis and adsorption. Majority of these methods has several disadvantages including high costs, sludge generation, low selectivity and incomplete removal [53]. Adsorption on the other hand is the most attractive method used for removing chromium from water due to the fact that is less expensive, versatile and user friendly (ease of operation) [54].

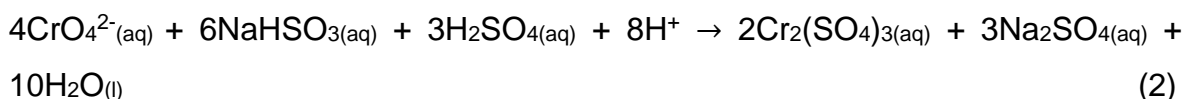
2.3.1 Precipitation

Chemical precipitation is a method that tends to remediate the heavy metals from aqueous solution through chemical reaction between the precipitating agents and the heavy metals. The chemical reaction results into a solid insoluble form called precipitates, which is separated at later stage from aqueous solution by a process called sedimentation or filtration [55], [56]. The removal of Cr(VI) by this method involves several steps:

1. The first step is the reduction of Cr(VI) to Cr(III)
2. Precipitation of less toxic form Cr(III) to insoluble form Cr(OH)₃ at basic conditions (pH>8)
3. Sedimentation of the solid insoluble precipitate Cr(OH)₃
4. The final process includes the disposal of the dewatered sludge through landfill

The removal of Cr(VI) from water by the precipitation method involves its reduction from aqueous solution into a solid insoluble form Cr(OH)₃. There are several precipitation methods for remediation of Cr(VI), the most widely used precipitation methods includes the reduction of Cr(VI) into Cr(III) using sulphur precipitating agents such as sodium bisulphate or sulphur dioxide gas as shown on the following equations (1) and (2) below [56], [57].





Even though this method has been applied for remediation of toxic metals from aqueous solution, the major disadvantages associated with these methods involves the use of expensive precipitating agents to treat small amounts of Cr(VI), generation of sludge which causes secondary pollution, poor sedimentation and slow metal precipitation [58].

2.3.2 Membrane technology

Membrane process can be classified into nanofiltration (NF), ultrafiltration (UF), microfiltration (MF) and reverse osmosis (RO) based on selectivity, pore size and driven force as shown in **Figure 2.1** [59].

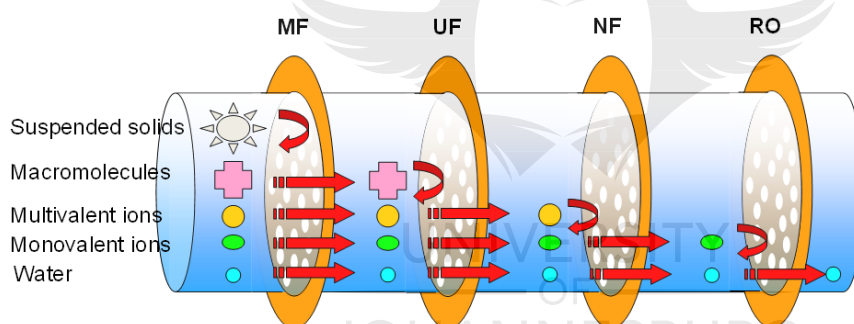


Figure 2. 2: Classification of membrane technology

All these techniques use the pressure that is greater than the natural occurring osmotic pressure to remove a large majority of contaminants from water. The applied pressure tends to force the water to infiltrate semi-permeable membrane. The semi-permeable membrane then allows certain molecules or atoms to infiltrate through, while blocking others to pass through [60]. Reverse osmosis membranes are more advantageous compared to microfiltration, ultrafiltration and nanofiltration membranes, in the sense that it uses high pressures between 20 and 80 MPa that tends to reject the smallest contaminants and also monovalent ions from solutions [60]. Reverse osmosis membranes can also remove all contaminants that microfiltration, ultrafiltration and nanofiltration membranes cannot remove.

In 1980, Scamehorn *et al.* [61] introduced both polymer enhanced ultrafiltration (PEUF) and micellar ultrafiltration (MEUF) for the removal of dissolved inorganic and organic compounds from aqueous media. Different membranes and surfactants were utilized for removal of various metals from water such as Cr(VI), Zn(II), Cd(II), Ni(II), Pb(II) and Cu(II). **Table 2.2** below shows the removal of heavy metals by MEUF and PEUF.

Table 2. 2: Heavy metal ions remediation by MEUF and PEUF.

UF type	Membrane	Surfactant/complexing agent	Heavy metals	Optimum pH	Removal efficiency (%)	Ref
MEUF	Ceramic	Dodecylbenzenesulfonic acid, dodecylamine	Pb ²⁺ , AsO ₄ ⁻	7.47	Pb: >99%, As: 19%	[62]
MEUF	Polysulfone	SDS	Cd ²⁺ , Zn ²⁺	NA	92–98	[63]
MEUF	Amicon regenerated cellulose	SDS	Cd ²⁺ , Zn ²⁺	NA	99	[64]
MEUF	Polycarbonate	Sodium lauryl ether sulfate	Ni ²⁺	7	98.6	[65]
PEUF	AMICON 8400	Sodium polyacrylate, PEI	Cr(III), Cr(VI)	6–7, 5–6	82–100	[66]
PEUF	Ceramic	Poly(acrylic acid) sodium	Cu ²⁺	5.5	99.5	[67]
PEUF	Polysulfone	Poly(ammonium acrylate)	Cd(II)	6.32	99	[68]
PEUF	Polyethersulfone	PEI	Cu ²⁺ , Ni ²⁺	pH > 6.0, pH > 8.0	94, 100	[69]

PEUF	Polyethersulfone	Carboxy methyl cellulose	Cu ²⁺ , Cr ³⁺ , Ni ²⁺	7.0	97.6, 99.5, 99.1	[70]
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2.3.4 Ion exchange

This method is used for the removal of dissolved contaminants from aqueous solution. Ion exchange resins are made of polymers that have the capability of exchanging particular ions with pollutant ions in aqueous solution. The dissolved contaminants form ions in water and these ions, their electrical charge can either be positive (+) or negative (-). Contaminants which have positive charge are called cations and tend to be removed using ion exchange media called cation exchange resin. The negative charge contaminants are known as anions, and are removed by ion exchange media called anion exchange resin. Ion exchange is frequently used to soften water containing calcium (Ca²⁺) and magnesium (Mg²⁺) as indicated in **Figure 2.3** [71]. Both ion exchangers (cation exchange and anion exchange media) have some drawbacks such as high operational cost for large scale treatment of water. In water treatment, the IE method has limitations in terms of removing solid particles from water since they tend to be clogged by the treatment media [71], thus this has led to a lot of research conducted within the scientific field.

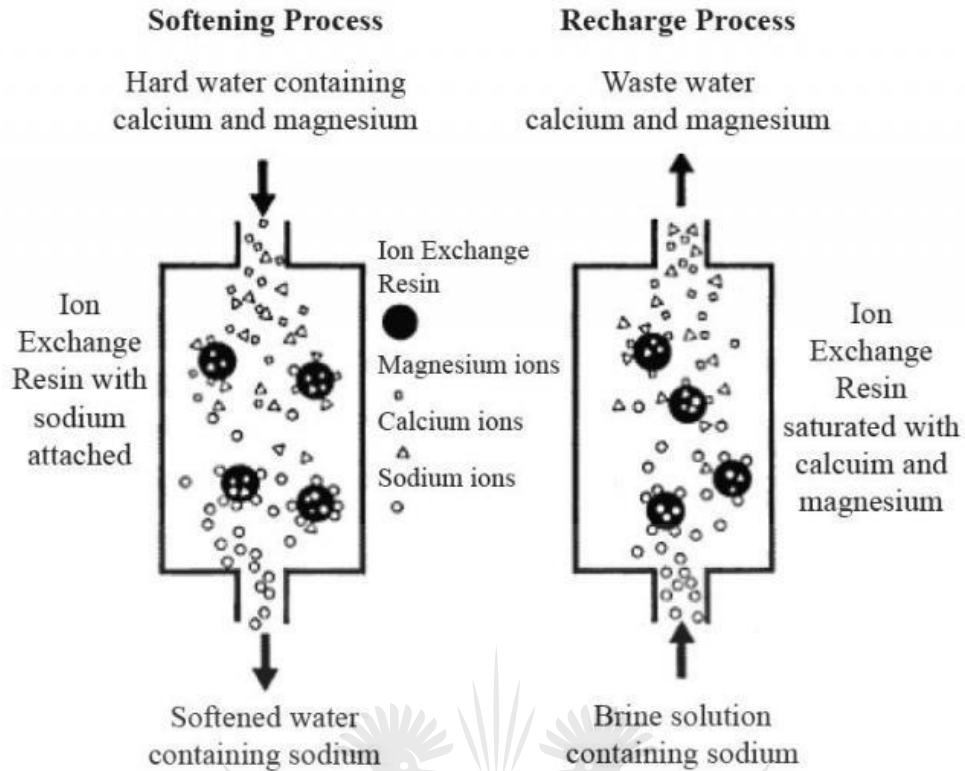


Figure 2. 3: Ion exchange process for water softening

Rengaraj *et al.* [50] carried out batch adsorption experiments to investigate the activity of both SKN1 and IRN77 cation exchange resins for removal of Cr(VI) from wastewater. The cation exchange resins removed more than 95% of Cr(VI) under optimum conditions. The maximum adsorption capacities for SKN1 and IRN77 cation exchange resins obtained from Freundlich isotherms were found to be 46.34 and 35.38 mg/g, respectively.

Another study reported by Bhatti *et al.* [72] used modified Amberlite XAD-4 (MAX-4) resin for removing toxic chromium from water. From the obtained results, the modified resin removed chromium(VI) best at pH 6.9 with highest adsorption capacity of 0.97 mmol/g. Misra *et al.* [73] did a study, where they investigated on the removal of several pollutants from wastewater such as Cr(VI), Pb(II), Cd(II) and Ni(II) using iminodiacetic acid functionalized cation exchange resin. The cation exchange resin was more effective in removing Cr(VI) than other metals. The maximum percentage removals obtained were 99.7, 65.0, 59.0, and 28 % for chromium, nickel and cadmium, respectively at optimum conditions.

2.3.5 Adsorption technology

This method describes how molecules of fluids such as gases, vapors and liquids interact with the solids surface into forming an interface between any two phases such as liquid-liquid, gas-liquid, or liquid-solid interfaces [74], [75]. Molecules that tend to be adsorbed by solid material are called adsorbates while the solid material (porous) which adsorb the adsorbate are called adsorbents. Adsorption method has been considered as a promising technique for heavy metal remediation from aqueous solution due to the following advantages, cost effective (less expensive), easy to operate (user friendly), can operate over wide range pH ranges, highly efficient, regenerability , selectivity, no sludge generation, can operate at high temperatures (4-90 °C) and turn metal pollutants to more useful metal product.

There are two types of adsorptions namely physical and chemical adsorption. For physical adsorption, there is a physical interaction between adsorbate molecules and the solid materials (adsorbents) via intermolecular forces (Van der Waals force). In this process, the adsorption is rapid and the interaction can be reversed [76]. Whereas, in chemisorption; chemical interaction is involved between adsorbate molecules or ions and adsorbents (solid material). Here, the adsorption rate can be slow and the interaction is irreversible [76]

2.4 Nanomaterials for adsorption

Various nanomaterials have been utilized as sorbents for removing toxic metals present in aqueous media, these include carbon nanotubes, graphene and metal oxides. For nanomaterials to be used as adsorbents for water treatment, they should be nontoxic, have high adsorption capacities, also be selective towards various pollutants and infinitely recycled or regenerated if possible. Also, the adsorbed pollutants on the surface of the adsorbent should be removed easily.

Some of the other nanomaterials that satisfy these criteria comprise of iron oxide nanoparticles, carbon based nanomaterial such as active carbons especially derived from agricultural waste materials, graphene, carbon nanotubes, cellulose nanomaterials and metals [77]–[81]. These nanomaterials have been widely used

as nanosorbent for the removal of water pollutants due to their distinctive properties such as high surface area, high porosity, and small sizes [82]–[84]. As opposed to other common materials, their unique properties makes them better adsorbents for adsorption of many pollutants from water.

2.4.1 Iron oxide nanoparticles

The utilization of iron oxide nanoparticle as nanosorbents for heavy metals remediation from aqueous solution has drawn a lot of attention [85]. This is due to their high specific area, biocompatibility, low solubility, magnetic properties, reusability, and low cost. Iron oxide tends to exist in different forms, as magnetite (Fe_3O_4), hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$). Both magnetite and maghemite iron oxides display ferrimagnetism while maghemite and hematite have low saturation magnetization [86], [87]. Magnetite nanoparticles can easily be oxidized in air to form maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) at different temperatures. According to literature, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) normally forms at 110–230 °C while hematite ($\alpha\text{-Fe}_2\text{O}_3$) forms at temperature above 250 °C [86], [87].

Lasheen *et al.* [88] synthesized magnetite nanoparticles via the co-precipitation method and investigated it as a nanosorbent for the removal of Cr(VI) from wastewater. TEM was used to investigate the average size of magnetite and it was found to be ranging between 2-7 nm. The average surface area determined using BET was 125 m²/g. The effect of pH, amount of dose, contact time, and initial concentration were investigated for Cr(VI) removal. It was found that the adsorption equilibrium was reached at 30 min, at pH 5.5 for both 20 and 100 mg/L Cr(VI) initial concentration, with a maximum removal efficiency of 88 and 95%, respectively.

Ajouyed *et al.* [89] conducted studies on Cr(VI) removal from wastewater using different commercial adsorbents (goethite, hematite and α alumina). Important parameters that might affect Cr(VI) removal like effect pH, ionic strength and initial Cr(VI) concentration were investigated. It was found that the ionic strength of hematite and goethite had a minimal effect, while the pH played a major role. For, α

alumina both the pH and the ionic strength played a major role in removing Cr(VI) present in aqueous media. The maximum percentage removal was obtained at $\text{pH} \leq 3$ for goethite (92.9%), ≤ 5 for hematite (99.9%), and ≤ 5.5 for α alumina (93.0 %). Thus leading to hematite having the highest removal percentage of Cr(VI) when compared to the other oxy-hydroxides.

2.4.2 Carbon based materials

In recent decades carbon based nanomaterials have been used as sorbents for the removal of heavy metals due to their exceptional high surface area, porosity and sorption capacities.

2.4.2.1 Carbon nanotubes

Carbon nanotubes (CNTs) such as single-walled carbon nanotubes (SWCNTs) and Multi-walled carbon nanotubes (MWCNTs) have been widely utilized as sorbents for removing many pollutants metals since these materials have high adsorption, porosity and large specific area (**Figure 2.4**) [90]. SWCNTs can be defined as one single layer of folded graphene, whereas MWCNTs consist of multi-layers of graphene. According to literature, the adsorption by CNTs depends mainly on their surface functional groups and also the type of the adsorbate [91]. The major problem with carbon nanotubes in adsorption process is that they tend to agglomerate in aqueous media due to poor dispersion, therefore resulting in reduction of surface area for adsorption.

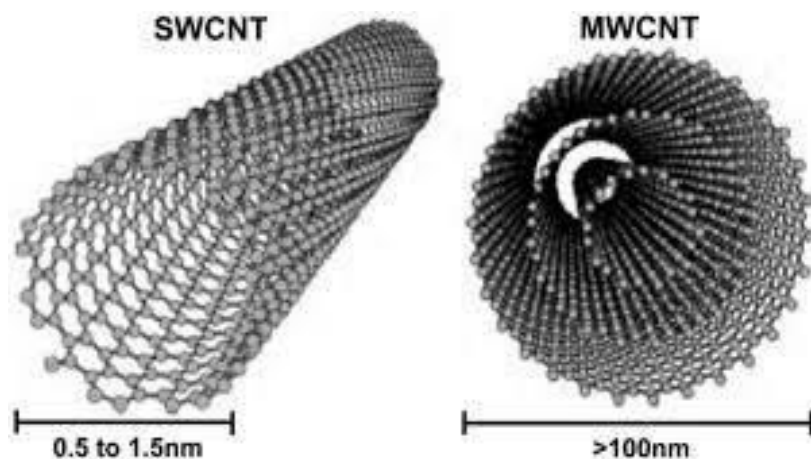


Figure 2. 4: Schematic diagram of SWCNTs and MWCNTs

Dehghani *et al.* [92] reported the removal of hexavalent chromium using both SWCNTs and MWCNTs as sorbents. Based on the results, the BET surface areas of MWCNTs and SWCNTs were obtained to be 270 and 700 m²/g, respectively. The maximum adsorption capacities for both adsorbents was found at pH 2.5, for SWCNTs (2.35 mg/g) and MWCNTs (1.26 mg/g). In acidic media, the surface hydroxyly groups of both adsorbents are protonated and tend to be positively charged which therefore electronically attract the negatively charged Cr(VI) ions. For both adsorbents, the adsorption equilibrium was attained after 60 min. It was also observed that pH played a major role for Cr(VI) uptake from aqueous using both adsorbents. The Cr(VI) removal efficiency decreased with an increase in the pH solution. The experimental adsorption kinetics followed pseudo second order, suggesting chemisorption mechanisms.

A new effective adsorbent, chitosan based functional gel consisting of multiwall carbon nanotube (MWNT)–poly (acrylic acid) (PAA)–poly (4-amino diphenyl amine) (PADPA) was investigated for removal of Cr(VI) from aqueous solution by Kim *et al* [93]. These new adsorbent (FG) was synthesized via polymerization and cross-linking reactions. The adsorption mechanism of Cr(VI) by FG was determined using X-ray absorption spectroscopy, FTIR spectroscopy, and XPS. Based on the adsorption results, the functional groups on the surface of FG played a huge role for Cr(VI) removal. The results also showed that new adsorbent (FG) was very stable and recyclable. The removal efficiency of Cr(VI) was found to be 85% after three adsorption cycles.

2.4.2.2 Graphene

Graphene is another type of carbon material which is mainly used as a nanosorbent for the adsorption of heavy metal ions present in wastewater. It has a 2D structure which consist of one or many atomic layers of graphites that have good mechanical, thermal and optical properties [94]. Zhao *et al.* [95] conducted sorption studies of Cd(II) and Co(II) onto graphene oxide (GO) sheets which was synthesized via the modified hummers method. The results showed that heavy metal removal depended on pH solution and ionic strength of the GO nanosheets. The Oxygen-containing functional groups on the GO sheets surface had a huge impact on heavy metal adsorption. The maximum sorption capacities of cadmium(II) and cobalt(II) were obtained to be 106.3 and 68.2 mg/g, respectively at pH 6.0 ± 0.1 and temperature ($T= 29.85$ °C).

He *et al.* [96] modified GO with 3-aminopropyltriethoxysilane (AS) to enhance the adsorption capacity towards Cr(VI) removal from water. The introduction of functional groups (amine and Si-OH groups) did not only improve adsorption capacity but also reduced the agglomeration of GO nanosheets. From the BET results, the modified GO had a larger surface area of (160.69 m²/g) compared to unmodified GO (146.17 m²/g). In their studies, the adsorption of Cr(VI) onto GO-AS was described well by pseudo second order model and Langmuir isotherm. The highest adsorption capacity was 215.1 mg/g for Cr(VI) at pH 2 and temperature (328K). The results from co-existing ions revealed that anions like NO₃⁻, PO₄³⁻ and Cl⁻ had a minimal effect on Cr(VI) except for SO₄²⁻ which had a huge impact.

2.4.2.3 Activated carbons

Activated carbon is a popular adsorbent which is mostly used for removing many pollutants including organic and inorganic pollutants from water due to their exceptional high specific area ranging between 250 and 300 m²/g and porosity. Activated carbons can be prepared from carbonaceous materials such as carbon nanotubes [97], graphene [98], graphene oxides [99], and glucose [100]. However, preparing activated carbons from these non-renewable precursors is highly

expensive and large scale treatment of water requires a lot of activated carbon. In recent decades, a lot of researchers have used renewable precursors such as potato peel, coconut shells, rice bran, sugar bagasse and other waste materials for the production of activated carbon [101].

Solgi *et al.* [102] prepared activated carbon from agricultural waste called medlar seeds following chemical activation method, potassium hydroxide was used as activating agent. Different temperatures, 450, 550, 650 and 750°C were used during carbonization. The prepared activated carbon (AC) was used as a sorbent to remove Cr(VI) from water. Parameters such as the effect of pH, dosage, contact time, temperature and concentration were investigated for Cr(VI) removal. Based on the investigation outcomes, the pH was the most vital parameter that played an important role for the removal of chromium(VI) from water. The highest percentage removal was 89.8 % at pH 2. The experimental data was described using Langmuir isotherm and pseudo second order kinetic model, with maximum adsorption capacity of 200 mg/g for Cr(VI).

Valentin-Reyes *et al.* [103] modified the surface of activated carbon through oxidation with nitric acid, ammonia treatment and heating under inert atmosphere. The activated carbon was modified for adsorption capacity enhancement towards the removal of Cr(VI) species from contaminated aqueous media. The adsorption experiments were studied at different initial Cr(VI) concentrations (10–500 mg/L) at room temperature and pH 6. Based on their findings, acid functional groups played an important role in the adsorption of Cr(VI). High transformation of highly toxic Cr(VI) to less toxic form Cr(III) was observed when using an oxidized adsorbent, heat treatment achieved low reduction of 50% , and ammonia modified activated obtained the lowest reduction (20%). The best adsorption capacity was obtained when using heat-treatment activated carbon as sorbent and was 48 mg/g for Cr(VI).

Karnib *et al.* [3] conducted adsorption studies to investigate the ability of activated carbon for removing toxic metals like cadmium, lead, chromium, nickel and zinc from wastewater. The removal percentage was high at low heavy metal concentration. At low heavy metal concentrations (30ppm), activated carbon was able to remove 86% cadmium, 90% nickel, 83.6 % zinc, 50.6% chromium and 83.0% lead from water.

The use of carbon based materials (Graphene, Carbon nanotubes and graphene) as adsorbents for removal of heavy metals is highly expensive, for instance it requires a lot of activated carbon to treat a large scale of wastewater. Graphene and carbon nanotubes are not effective in removing oxo-anions in aqueous system due their acid functional groups. Therefore, a lot of researchers nowadays uses agricultural waste materials as low cost adsorbents for heavy metal remediation.

2.5 Agricultural waste materials for adsorption

Several waste materials have drawn a lot of attention as adsorbents for removing toxic metal ions from water. The advantages of these raw waste materials as metal adsorbents include distinctive chemical composition, their availability in large amounts, renewability and less expensive [104]. These have shown good adsorption capabilities towards cationic and metal pollutants. The good adsorption towards cationic metals is because they have a large amounts of negatively charged groups on their surface, e.g. the hydroxyl and carboxyl group which have affinity to cations (positively charged ions) during adsorption. These raw materials also have small amounts of positively charged groups on their surface, which might also lead to the uptake of different anions during adsorption.

2.5.1 Wheat bran

Wheat bran is lignocellulosic agricultural material which is mostly applied to remove both inorganic and organic materials from wastewater. Singh *et al.* [105] conducted batch experiments to remove Cr(VI) from water. In their studies, parameters like effect of dosage, pH, temperature, uptake time and initial concentrations for removing Cr(VI) were investigated. Based on their findings, pH was the most important parameter that played a major role for removal of chromium from water. At $\text{pH} \leq 2$, there was a high electrostatic interaction of positively charged wheat bran and negatively charged Cr(VI) ions. The maximum adsorption was obtained to be

310.58 mg/g at optimum conditions (at pH 2, temperature 40 °C and initial concentration of 200 mg/L Cr(VI)).

Kaya *et al.* [106] modified wheat bran with tartic acid to enhance the adsorption capacity of the natural wheat bran for removal of heavy metals. The batch experiment were carried out to investigate the performance of raw wheat bran and the modified wheat bran towards removing Cr(VI) present in aqueous solution. The highest Cr(VI) removal was obtained at pH 2.0 and it was 51.0% and 90.0% for raw wheat brand and modified wheat bran, respectively. The maximum adsorption capacities were 4.53 and 5.28 mg/g Cr(VI) using raw wheat bran and modified wheat bran, respectively.

2.5.2 Wheat straw

Song *et al.* [107] used wheat straw and *Eupatorium adenophorum* as low cost adsorbents for removing chromium(VI) present in wastewater. Both these adsorbents were prepared through simple carbonization process. Parameters like dosage, pH, contact time, temperature and adsorbate concentration were investigated for Cr(VI) removal. The highest removal Cr(VI) was obtained to be 99.9% at acidic solution (pH 1.0). At pH less than 2, the surface of both adsorbent (wheat straw and *Eupatorium adenophorum*) tends to be protonated, hence making the adsorbents surface to be positively charged. Therefore, the highest Cr(VI) removal at low pH was due to electrostatic interaction between the positively charged adsorbent and negatively charged Cr(VI) ions. The maximum adsorption capacity was 89.22 mg/g Cr(VI) using both wheat straw and *Eupatorium adenophorum* as sorbents. The adsorption kinetics for this study followed pseudo second order model.

Xu *et al.* [108] modified wheat straw with amine groups using three different modifying agents, triethylenetetramine (TETA), diethylenetriamine (DETA) and ethyldiamine (EDA). The three modified wheat straw (MWS) were used as adsorbent for removing phosphate ions present in aqueous solution. Based on the results, wheat straw modified with EDA as a modifying agent had the largest

phosphate capacity (22.91 mg/g) compared to the other MWS. Dong *et al.* [109] reported Cu(II) removal from aqueous solution using modified wheat straw. The wheat straw was modified with polyethylenimine (PEI) for adsorption capacity enhancement towards the removal of Cu(II). The adsorption studies were carried out at batch mode and in a fixed bed column mode. The results showed that Cu(II) removal efficiency increased with an increase in pH of Cu(II) solution. The adsorption capacity was obtained to be 48.6 mg/g of Cu(II)/g at 293 K for PEI-WS. The experimental adsorption data fitted well with the elovich kinetic model, suggesting chemisorption mechanism between the Cu(II) and PEI-WS.

In addition to wheat straw (WS), another study was carried out by Xu *et al.* [110] where this agricultural waste material (WS) was cross linked with amine groups and used as an adsorbent for the removal of phosphate and chromium (VI) from wastewater. From the obtained results, 0.99 mmol/g was the highest adsorption capacity for Cr(VI) at pH 2. The amine cross-linked wheat straw (AC-WS) consists of amine groups on its surface which get protonated at low pH to enable the electrostatic interaction between HCrO_4^- and AC-WS. On the other hand, the maximum adsorption capacity for phosphate was obtained to be 1.19 mmol/g at pH 6. Both the uptake of phosphate and chromium(VI) by AC-WS fitted well with Langmuir isotherm model, suggesting possible ion exchange mechanism for the adsorption process.

2.5.3 Rice bran

Rice bran which is known to be a valuable by product of rice milling plant has been explored for removing many pollutants from water. Montanher *et al.* [111] conducted batch adsorption experiments to evaluate the performance of raw rice bran for adsorption of Cd(II), Cu(II), Pb(II) and Zn(II) from aqueous solutions. The maximum removal was obtained around pH 5–6 for all investigated metal ions, with the pH playing a major role in adsorption. At low pH value (<2), the overall surface of the raw wheat bran was positively charged hence making it impossible to attract positively charged metal cations. At high pH value (>6), the surface of the raw wheat

bran tends to become more negatively charged due to hydroxylation, hence increasing the removal efficiency of cation metals.

Singh *et al.* [112] investigated rice bran as an inexpensive adsorbent for Cr(VI) adsorption from wastewater. In this study, the effect of pH, dosage, contact time, temperature and initial concentration were investigated for Cr(VI) removal. The results revealed that the highest Cr(VI) removal was 99.4 % at pH 2, with initial Cr(VI) concentration 200 mg/L and temperature 20 °C. The adsorption kinetics fitted best with pseudo second order model with the correlation value (R^2) of 0.99. From the desorption studies, Cr(VI) was removed completely from the adsorbent surface at pH 9.5. At pH >9, the surface of rice bran is negatively charged and tends not to be attracted with negatively charged chromium(VI) ions.

Oliveira *et al.* [113] studied the adsorption of heavy metals like Cr(III), Cr(VI) and Ni(II) from water using raw rice bran as a natural adsorbent. Based on their studies, the highest Ni(II) and Cr(III) removals were obtained at pH values 5-6. The maximum efficiency for Cr(VI) was achieved at lower pHs between 1.5 and 2.0. The adsorption mechanism of Cr(VI) species by rice bran was via electrostatic interaction.

2.5.4 Rice husk

Another valuable by product of rice milling is rice husk. Hubadillah *et al.* [114] fabricated ceramic fiber membrane (CHFM) from rice husk ash as an adsorbent-separator for heavy metals removal from aqueous media. In their studies, the removal of toxic metals such as zinc(II), lead(II) and nickel(II) were investigated using CHFM as an adsorbent-separator. Based on the results, CHFM removed more than 90% of the metals at pH 5. Bansal *et al.* [115] also conducted their own study using boiled and formaldehyde treated rice husk for Cr(VI) removal. Based on their findings, boiled treated rice husk was able to remove 71.0% of Cr(VI) while formaldehyde treated rice husk removed 76.5% at pH 2. Experimental data was analysed using three different isotherms models including Langmuir, Dubinin-Radushkevich (D-R) and Freundlich isotherms. Based on the outcome of the results, only D-R models and Freundlich models were used to describe experimental data.

2.5.5 Coconut shell

Chandana *et al.* [116] reported the removal of Cr(VI) from wastewater using activated carbon derived from coconut shell. In their studies, the production of AC was done through physical activation method using carbon dioxide (CO₂), ozone (O₃) and steam (H₂O) as activating agents. Based on their results the maximum removal efficiency (94%) was obtained at pH 2. The high removal percentage in acidic medium was due to more of H⁺ on the surface of adsorbent AC, hence making the surface of the adsorbent more positively charged at pH 2. Therefore at low pHs, there's a strong electrostatic interaction between adsorbent (AC) and Cr(VI) ions. The equilibrium adsorption of Cr(VI) on AC followed Langmuir adsorption isotherm and pseudo second order kinetics.

Another study by Acheampong *et al.* [117] they studied Cu(II) removal in a fixed-bed column system using coconut shell as a biosorbent. The coconut was shown to be more effective in sorbing Cu(II) ion from water at pH 7. It was also found that bisorption of Cu(II) in a fixed column performed very well at 10 ppm inlet concentration Cu(II), flow rate 10 mL/min and bed depth 20 cm .

de Lima *et al.*[118] modified coconut shell fibers with ammonium quaternary salt (2-hydroxypropyltrimethyl ammonium chloride) to enhance adsorption capacity towards the removal of inorganic anions (PO₄³⁻, SO₄²⁻ and NO₃⁻) from water. The maximum adsorption capacities were obtained to be 200, 31.2 and 33.7 mg/g for phosphate, sulfate and nitrate, respectively at pH 7. In their studies, three kinetic models including pseudo-first order, pseudo-second order and intraparticle diffusion models were investigated to examine the kinetic adsorption of all anionic species. Based on the investigation outcomes, pseudo second order model was the only model which fitted well with the experimental data.

2.5.6 Sugarcane bagasse

Cronje *et al.*[119] studied the activity of activated carbon derived from renewable precursor called sugarcane bagasse as an adsorbent for removing Cr(VI) present in

aqueous solution. The activated carbon was produced using chemical activation method whereby ZnCl was an activating agent. For the determination of optimum parameters (pH, dosage, temperature, initial Cr(VI) concentration), batch adsorption studies were conducted. Based on their findings, the optimum dose, pH, temperature and initial concentration were 6.85 g/L, 8.58, 40 °C and 77.5 mg/L, respectively. The highest Cr(VI) removal was found to be 87% at optimum conditions.

Carvalho *et al.*[120] reported sorption studies for the removal of phosphate from aqueous media using carboxymethylated sugarcane fibers and raw sugarcane fibers doped with Fe²⁺ ion as sorbents. Based on the results, it was found that when 4% of Fe²⁺ ion was incorporated on the sugarcane fibers, the carboxymethylated and noncarboxymethylated- fibers adsorbed 97 and 94% of phosphate, respectively. The equilibrium adsorption of phosphate fitted well with both Langmuir and Freundlich isotherm models. The measured monolayer adsorption in Langmuir revealed that the presence of Fe²⁺ on the surface enhanced the adsorption capacity towards the removal of phosphate by about 45%. The maximum adsorption capacity of phosphate was found to be 152 mg/g.

2.5.7 Tea waste

Nigam *et al.*[121] investigated the removal of hexavalent chromium from wastewater in a batch system using inexpensive adsorbent called tea waste (TW). Parameters such as dosage, pH, temperature and contact time were investigated. It was found that the highest removal percentage was obtained to be almost 97% at a dose of 6.0 g/l, pH 3.9, 240 min and at a temperature of 303 K. In this study, the adsorption isotherms and kinetics were described using both Langmuir and pseudo second order model.

Ahsan *et al.*[122] investigated the sulfonated tea waste (STW) as a less expensive adsorbent for Cr(VI), methylene blue(MB) and tetracycline(TC) remediation from water. The tea waste was sulfonated to enhance the adsorption capacity towards various water pollutants. The maximum adsorption capacities were obtained to be

438.18, 1007.61 and 381 mg/g for Cr(VI), MB and TC, respectively. Another study reported by Fan *et al.*[123] obtained 75.76 mg/g Cr(VI) as the maximum adsorption capacity using magnetic tea waste composite as sorbent. Based on their findings, the magnetic tea waste tends removed chromium(VI) better as compared to raw tea waste[111].

As shown in **the Table 2.3**, it is worth noting that the removal of Cr(VI) by these less expensive adsorbent is more effective at low pH, especially pH <2.0. This was mainly due to electrostatic interaction between the negatively charged Cr(VI) oxy-anions and positively charged functional groups on the surface of the adsorbents.

Table 2. 3: Summary of bioadsorbents for removal of heavy metals present in aqueous solution.

Adsorbent	Heavy metals	Optimum pH	Adsorption capacity(mg/g)	Ref
Wheat bran	Cr(VI)	2.0	310.58	[105]
	Hg(II), Pb(II), Cd(II), Cu(II) & Ni(II)	4-6	70.0, 62.0, 2.0, 15.0 & 12.0	[124]
Sawdust	Cr(VI)	2.0	41.5	[125]
	Cu(II), Ni(II) & Zn(II)	>4.0	4.5, 4.0 & 2.0	[126]
Tea waste	Cr(VI)	3.9	438.18	[122]
	Ni(II) & Cu(II)	5.0	10.8 & 14.9	[127]
Rice husk	Cr(VI)	2.0	8.50	[128]
	As(VI) & As(III)	4.0 & 7	0.147 & 0139	[129]
Rice bran	Cr(VI)	5.0	0.15	[111]
	Cd(II),Cu(II), Pb(II) & Zn(II)	5-6	0.61, 0.21, 2,62, & 1,34	[111]
Wheat straw	Cr(VI)	2.0	89.22	[107]
	Cu(II)	6.0	24.89	[130]
Sugarcane bagasse	Cr(VI)	2.0	2.33	[131]
	Cd(II)	6.0	19.4	[132]

<i>Moringa oleifera</i>	Cr(VI),Ni(II) & Cu(II)	-	5.49, 5.53 & 6.07	[133]
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2.5.8 *Moringa oleifera*

Moringa oleifera is a versatile plant that is mostly cultivated in Asia, Africa and Latin America. It grows fairly at temperatures between 25-35°C, altitudes below 600m (2000ft) but cannot tolerate prolonged flooding or poor drainage [85]. Out of all the perennial plants, *Moringa oleifera* is the most useful tree in the world since it can be consumed as food and can be used as source of energy because of their nutritional contents [134].

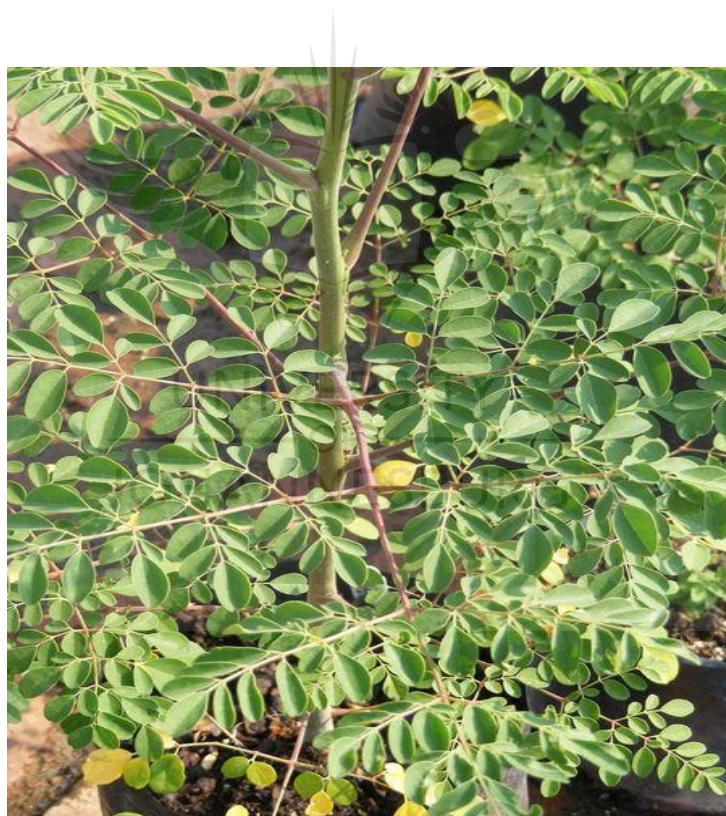


Figure 2.5: *Moringa oleifera* plant tree

The plant tree "*Moringa oleifera*" consist of *tannins, steroids, saponins, alkaloids, flavones aglycones, anthracenoside, triterpenoids* and *couramins* substances which are responsible for biological activities [135]. *Flavonoids* are found in high content in many plant trees, are effective antioxidant and antimicrobial substances. *Tannin* substance present within *moringa oleifera* tend to be responsible for killing

microorganisms. On the other hand, *steroids* and *terpenoids* are reported to be active against bacteria's and be used for cancer treatment [136], [137]. The nitrogen-containing compounds "*alkaloids*" present in *Moringa oleifera* have antimicrobial activities.

Moringa oleifera has acquired so much attention in recent years as a less expensive adsorbent for the removal organic and inorganic pollutants from water. Timbo *et al.* [138] reported on *moringa oleifera* leaves as a cheap adsorbent for Cr(VI) uptake from water. Based on their results, the highest removal of Cr(VI) percentage and maximum adsorption capacity were $99\% \pm 1\%$ and 33.9 mg/g, respectively at pH 2 after 60 minutes of contact time and initial Cr(VI) concentration of 100 mg/L.

Ghebremichael *et al.* [139] investigated the ability of different *Moringa oleifera* seeds, including whole seed powder (WSP), activated carbon (AC) derived from *Moringa oleifera* seed husk, and the residue after coagulant extraction (raCE) as biosorbents for removing Cr(VI) and Cr(III) present in wastewater. Based on their results, the maximum percentage removals for Cr(III) were obtained to be 99.9, 97 and 94 % using AC, WSP and RaCE, respectively at pH 7-8. For Cr(VI) removal, the highest percentages were 83.2 and 47.0 % using AC and RaCE, respectively.

In this study, *Moringa oleifera* leaves was modified with amine groups to enhance the adsorption capacity towards Cr(VI) removal from water. Diethylamine was used as a modifying agent and epichlorohydrin as cross-linking agent. For recovery process, magnetite nanoparticles (Fe_3O_4) were incorporated to the modified *Moringa oleifera* leaves to form magnetic adsorbent. The adsorbent was recovered from aqueous solution using external magnet.

2.6 Conclusions

In this review, several techniques such as chemical precipitation, membrane technology, ion exchange and adsorption were discussed for removal of heavy metals. Adsorption was the most effective method for removal of heavy metals due to the fact that it is less expensive, versatile and user friendly (ease of operation). The review was extended to the use of agricultural waste materials for adsorption of

heavy metals from water. Based on the results obtained when removing chromium(VI) using various agricultural waste materials, it was noticed that these materials were effective in removing Cr(VI) at low pH (<2). This was due to the fact that at acidic medium, these materials get protonated and hence become more positively charged which then interact with the negatively charged oxyanions of Cr(VI). Therefore, based on this literature review it can be concluded that there's a great potential of using waste materials as adsorbents for removal of heavy metals in the future.



2.7 References

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CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Introduction

In this chapter all characterization techniques used for confirmation of the prepared adsorbent will be discussed in details. The discussion also involves all methods used for analysis of Cr(VI), preparation of Cr(VI) stock solution, batch adsorption and microbiological evaluation studies.

3.2 Experimental procedures

3.2.1 Preparation of Cr(VI) solution

Cr(VI) stock solution of 1000 mg/L was prepared by dissolving 2.83 g of $K_2Cr_2O_7$ in a 1000 mL volumetric flask with deionised water.

3.2.2 Preparation of 1.5 Diphenylcarbazide (DPC) solution and Cr(VI) analysis

The Diphenylcarbazide (DPC) solution was prepared by dissolving 0.125 g of 1.5-Diphenylcarbazide powder in 25 mL of methanol (99.8%). Thereafter, the solution mixture was then added into 132 mL of 5.2 % sulphuric acid (H_2SO_4) in 250 mL volumetric flask. The solution was diluted with deionised water to 250 mL mark.

For Cr(VI) analysis, the DPC solution was mixed with Cr(VI) sample 1:3 ratio. The solution mixture turned into a violet coloured complex which absorbed at wavelength of 520 nm on the UV-vis spectrophotometer.

3.3 Analytical characterisation techniques

3.3.1 Field Emission Scanning Electron Microscope (FE-SEM)

Scanning Electron Microscope (SEM) is a high-resolution technique which uses beam of electrons to create images of the external surfaces of the solid materials. In comparison to light microscope, this technique has higher resolving power and magnification [1]. These properties make it very useful to detect much smaller objects in a material. The basic principle is based on the interaction of electron beam with the specimen. The electron beam generated from field emission gun or tungsten filament accelerates with high voltage in the range (0.1-3.0 keV) and pass through a series of electromagnetic lenses to interact with the specimen as indicated in **Figure 3.1** [2]. The interaction of the specimen and electron beam results in the ionization of the sample. For the detector to create images, it collects the secondary electrons emitted from the specimen. From the resulted micrographs (images), information about the texture, size and shape of the samples can be obtained.

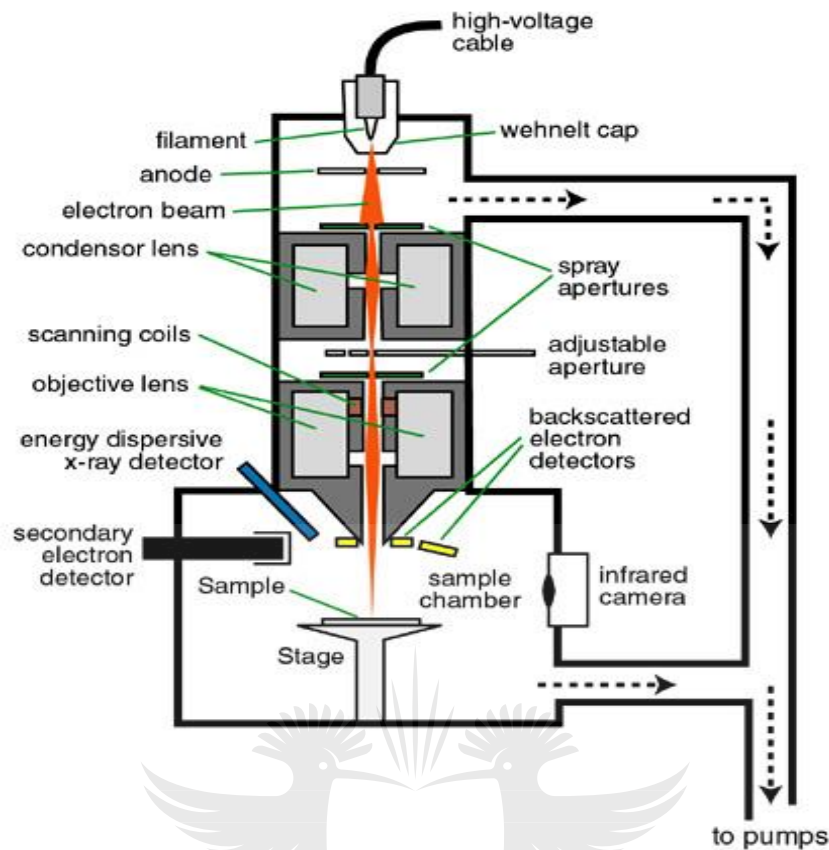


Figure 3. 1: Schematic representation of SEM.

SEM is frequently coupled with energy dispersive spectroscopy (EDS) also known as energy dispersive X-rays (EDX) to provide information about the elemental composition of the materials [3]. In this study, this technique was employed for determination the shape, size and elemental composition of the prepared materials.

3.3.1.1 Sample preparation for FE-SEM analysis

A small amount of fine powder material was introduced on a carbon sticker which was placed on top of the specimen holder, the specimen was then ready for analysis using SEM instrument. In this study, SEM was coupled with EDS which was used for elemental composition analysis.

The Instrumental set up conditions that are used for FE-SEM analysis are in Table 3.1.

Table 3. 1: Instrumental details for FE-SEM and EDS.

The name of instrument	Zeiss Crossbeam 540, United Kingdom
Parameters	
Voltage applied	3.0 keV
Magnification	Depended on each experimental analysis
Resolution	Depended on each experimental analysis

3.3.2 X-ray diffraction (XRD)

X-ray diffraction is a powerful technique which can be employed to analyse many different types of materials. This technique is mainly applied to identify the crystalline phases of the materials [4]. Some common uses of the XRD machine includes, analysing crystal structure, quantitative analysis of phase identification, determination of crystallite sizes and micro strains, identification of defects within samples, and the determination of texture orientation [4]. The XRD technique is not limited on identifying crystalline materials; it can also be used to identify amorphous materials e.g. metallic glasses and polymers. As opposed to other analytical instruments, XRD can provide information on the chemical composition as well their structures, which can be defined by atomic arrangements. The basic principle of the XRD technique is based on the constructive interference of monochromatic x-rays generated from the cathode sample with the crystalline samples (**Figure 3.2**). The diffracted x-rays from the sample in the x-ray tube then pass through the detector which gives out x-ray diffraction patterns [5]. In this work, XRD was used to identify the phases and the purity of all prepared materials.

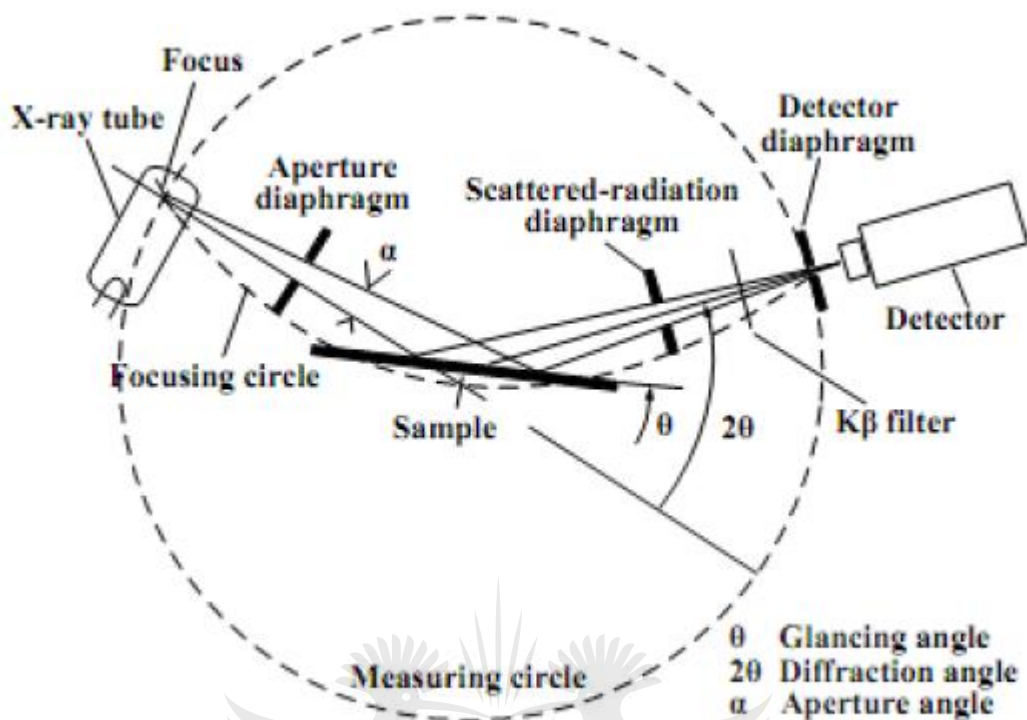


Figure 3. 2: X-ray diffraction (XRD) schematic diagram and basic components

3.3.2.1 Sample preparation for XRD analysis

A certain amount of FMO and $\text{Fe}_3\text{O}_4/\text{FMO}$ were crushed into fine powder using pestle and mortar. The spatula was used to introduce the fine powder material on the sample holder, the fine powder was well spread on the surface of the sample holder. Thereafter, the fine powder material was analysed using X-ray diffractometer (XRD). **Table 3.2** below shows some experimental conditions used for analysis.

Table 3. 2: Experimental condition of XRD analysis.

The name of the instrument	Ultima IV-Rigaku, Japan
Parameters	
Voltage generator	40 kV
Current generator	30 mA
2 theta range	10-90 °
Scan time	0.5°/min

3.3.3 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique that is mostly used to determine the functional groups which are present in the samples (**Figure 3.3**). The basic principle of this instrument is based on the interaction of the infrared light with sample [6]. During the interaction, the sample absorb IR light while some passes through and reaches the detector. The IR spectrum is obtained by irradiating the sample with infrared light, the light will interact with the compounds in the sample and reach the detector [7]. The resultant IR spectrum indicates the presence of different functional groups and chemical bonds present in the sample. The IR frequencies are measured in the range between 400 and 4000 cm^{-1} as wavenumbers. **Figure 3.3** shows some basic components of the FTIR.

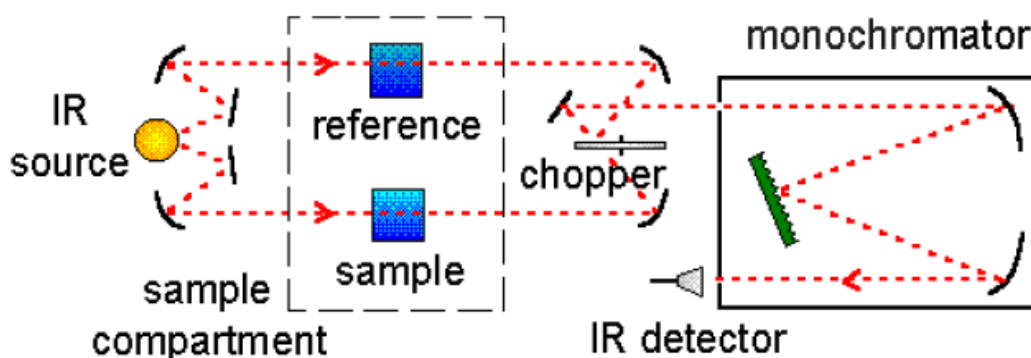


Figure 3. 3: Schematic diagram of FTIR with some basic components

In this study, this technique was used to determine functional groups present within the prepared materials and also those that were responsible for adsorption of chromium(VI).

3.3.3.1 Sample preparation for FTIR analysis

An approximately amount of 150 mg of potassium bromide (KBr) was mixed with about 1 mg of the sample. The mixture was crushed using pestle and mortar, thereafter a small amount of the crushed fine powder was loaded into three pieces of the pellet press using spatula. The three pieces of the pellet press was transferred to hydraulic press for compression for about 2 minutes. The resulted pellets were introduced into FTIR instrument for analysis. The experimental condition for FTIR analysis are shown in **Table 3.3**.

Table 3. 3: Experimental conditions for FTIR analysis.

Name of the instrument	Bruker-Alpha, Germany
Parameter	
Scan range	500-4500 cm ⁻¹

3.3.4 Brunauer-Emmett-Teller (BET)

Brunauer-Emmett-Teller (BET) is an analytical instrument mainly used to for determination of average surface area, pore size and volume of the materials [8]. BET analysis is based on the adsorption multilayer of nitrogen, which is measured when the sample is exposed to relative low pressure gas [9] . Before any analysis the sample should be prepared first. The sample consist of adsorbed contaminants such as water and atmospheric carbon dioxide which must be desorbed from the surface. For sample preparation, the sample has to be degassed under high temperature and vacuum conditions for a certain time to remove any contaminants that could interfere with analysis. After sample preparation, nitrogen gas was

introduced at low temperature (77 K). In this study, the samples were degassed at 100 ° C for 24 hours.

3.3.4.1 Sample preparation for BET analysis

An amount of approximately 200 mg of the sample was loaded into BET tube and degassed at 100 °C under nitrogen flow for 24 hours. The whole sample preparation was to remove any contaminants adsorbed on the surface of the sample. To obtain information about the porosity and surface area of the materials, the sample was introduced to nitrogen gas at very low temperature (77K).

3.3.5 Thermal gravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) is an analytical tool which is employed to determine the amount of weight loss by the material as function of temperature in the presence of helium or nitrogen gas. This technique gives information about the decomposition, adsorption, vaporization and adsorption of the materials [10]. Materials which can be analysed by TGA include polymeric materials such as plastics, thermoplastics ceramics, and composite materials. The technique can be used to analyse samples with mass between 1 mg and 150 mg, and temperatures of up to 1500 °C can be reached. TGA requires an inert (nitrogen is usually used) and oxidative (oxygen is used) gas flow rates which provide the appropriate environments for the analysis [10]. One of the disadvantages of this analytical technique includes its destructiveness to the sample after analysis. In this study, TGA was used to determine thermal stability of Fe₃O₄, FMO and Fe₃O₄/FMO composites.

3.3.5.1 Sample preparation for TGA analysis

The TGA normally require no sample preparation. In this study an approximately amount of 10 mg of the sample was loaded into TGA ceramic crucible and introduced to TGA instrument for analysis. **Table 3.4** below shows experimental conditions for TGA analysis.

Table 3. 4: Experimental set up conditions for TGA analysis.

Instrument's name	Hitachi-STA7200RV, Japan
Parameters	
Temperature range	30-650 °C
Nitrogen flow	20 ml/min
Heating rate	10 °C/min
Holding time	3 min

3.3.6 Zeta potential analyzer

Zeta potential analyzer is an analytical instrument used to predict long term stability of particles. Particles with zeta potential of less than sixty millivolts (-60 mv) or above sixty millivolts (60 mv) tends to have excellent stability. Conversely, particles with zeta potential between negative ten (-10 mv) and positive ten (+10 mv) millivolts suffer from rapid agglomeration unless protected with polyethylene glycol ligands [11]. Another important use of zeta potential includes the determination of surface charge of the materials. Materials with positive zeta potential (+mv) have positive charge on their surface, while materials with negative zeta potential (- mv) tends to be negatively charged. In this study, the surface charge of the prepared materials (MO, FMO and Fe₃O₄/FMO) were measured as a function of zeta potential (mV) at various pH solution (2-10) using Malvern Zetasizer Nano.

3.3.6.1 Sample preparation for surface charge analysis

In this study, zeta potential was measured at different pH solutions (2-10). For sample preparation, a certain amount of 0.1 g of the sample was added to each 50 mL conical flask containing a solution of certain pH value. The flask were agitated for 24 hrs using water shaker bath at 25 °C. The mixture solution was then analysed using Malvern Zetasizer Nano.

3.4 Batch adsorption experiments

The batch adsorption studies were conducted for the optimization purpose of important parameters such as pH, amount of dose, uptake time and initial concentration. Another purpose of the study was to determine adsorption mechanism of Cr(VI) using different adsorbents (FMO and Fe₃O₄/FMO). All adsorption experimental work was carried out using the water shaker bath shown in **Figure 3.4**.



Figure 3. 4: Water shaker bath

3.4.1 Effect of pH

This experiment was conducted to obtain the best suitable pH for Cr(VI) removal using FMO and Fe₃O₄/FMO adsorbents. In this experiment, initial Cr(VI) concentration and amount of adsorbents were fixed at 100 mg/L and 0.05 g, respectively while the pH solution was adjusted in the range from 2-10 using 0.1 M sodium hydroxide (NaOH) and 0.1 M hydrochloric acid (HCl). The solution mixture was taken into water shaker bath and agitated at a speed of 200 rpm for 2 hrs at room temperature.

3.4.2 Effect of dosage

For this experiment, the initial Cr(VI) concentration and optimum pH solution were fixed to between 100 mg/L and 2.0, respectively. In this experiment, the only parameter varied was the amount of the adsorbents (FMO and Fe₃O₄/FMO). The adsorbents dose were speckled from 0.02 to 0.4 g and the mixture was agitated at the same speed (200 rpm) using water shaker bath for 24 hrs at room temperature.

3.4.3 Effect of contact time

For the effect of time, the experiment were conducted using fixed Cr(VI) concentration, optimum pH and dosage. In the case of using FMO as adsorbent, the amount of dosage was fixed to be 0.25 g while for Fe₃O₄/FMO it was 0.15 g. For this study, the Cr(VI) initial concentration and pH was fixed at 100 mg/L and 2.0, respectively. In this experiment, Cr(VI) percentage was investigated at different time intervals until equilibrium was attained.

3.4.4 Effect of initial Cr(VI) concentration

In this study, optimum conditions such as pH, time, and dosage were maintained. In case of using FMO as adsorbent, the pH solution, amount of dose and time were kept as 2.0, 0.25 g and 85 min, respectively. For Fe₃O₄/FMO, the pH solution, maximum dosage and time were kept as 2.0, 0.15 g and 25 min, respectively. The

initial Cr(VI) concentration was tested in the range from 20 to 100 mg/L. The solution mixture was agitated using water shaker bath at speed of 200 rpm.

3.4.5 Effect of co-existing ions

This experimental study was conducted in order to investigate the selectivity performance of the adsorbents (FMO and Fe₃O₄/FMO) towards Cr(VI) in the presence of other co-existing ion such as Cu²⁺, Zn²⁺, Ni²⁺, SO₄²⁻, NO₃⁻ and Cl⁻. The above listed ions were individually introduced into solution containing Cr(VI), the solution mixture was agitated for 8 hrs using water shaker bath at speed of 200 rpm under room temperature before adsorption. The concentration of co-existing ions was varied from 20 to 100 mg/L while the Cr(VI) concentration was fixed to be 20 mg/L at all times.

3.4.6 Reusability studies

The purpose of this study was to investigate the reusability of adsorbents after several adsorption. In this experiment, the adsorbent were used for removal of Cr(VI) and after adsorption the adsorbent was washed with deionised water and dried using an oven at 50 °C for 1 hr. The dried adsorbent was then reused for Cr(VI) adsorption for several times (7 cycles).

3.5 Microbiological evaluation studies

3.5.1 Antibacterial activity of FMO against model pollutants using the plate count method

For the preparation of the nutrient agar, the manufacturer's method was followed where 28 g of nutrient agar was mixed with the 900 mL sterilized water in a 1L glass bottle. The solution was left to boil while stirring. Then the nutrient agar solution was sterilized in an autoclave (Sturdy SA-300VL) at 121 °C for 15 min. The agar was left to cool then transferred into 30 separate petri dishes and allowed to set. The nutrient

broth was also prepared following the manufacturers method and sterilized. Approximately, 100 mL of the prepared nutrient broth was transferred into 4 different 250 mL Erlenmeyer flask. The flasks were sterilized at the same conditions as above. A colony was then picked from each strain (*E.coli*, *S.aureas*, *P.aeruginosa* and *E.faecalis*) and placed in each flask. The strains were then placed in the incubator for 24 hrs at 37 °C to allow the strains to grow. Aliquots of 50 mL of each strain were transferred into 50 mL centrifuge tube and centrifuged at 4000 rpm for 15 min using the Rotanta 460R centrifuge. The pellets formed were cleaned by sterilised water and an aliquot of 100 ml of the same water was poured into 4 different Erlenmeyer flasks. These flasks were inoculated with four concentrations (0.05; 0.02; 0.01 and 0.005 mg/mL) of FMO per strain and were then incubated at 37 °C for 24 hrs while shaking. Then, 20 µl of each flask was diluted up to 1 000 dilution. From the dilution only 20 µl of the treated mixture was used for plating. The treated mixture was plated evenly on the agar and incubated again at 37 °C for 24 hrs. The following day the colonies were counted.

3.5.2 Antibacterial activity of FMO against natural pollutants using tempo reader

Four different water types (tap, river, pond and sewage) were used to test for the presence of bacterial strains (*E.coli* and *E.faecallis*) and a total population of microorganisms (*Aerobic count*). For the preparation, aliquots of 10 mL of each water type were diluted with peptone water (broth) and 100 mL of sterile distilled water. From the mixture, 1 mL of the mixture was added to the dehydrated media before treatment. Each water type was loaded on the tempo reader before treatment in order to collect the control. For the inoculation, treatment was performed using two concentrations, (0.005 mg/mL and 0.05 mg/mL) and incubated at 37 °C for 24 hrs (*E.coli* and *E.faecalis*) and 48 hrs for *Aerobic.count*. The sample information was loaded on to the tempo reader system whereas the mixtures were loaded onto the count cards and incubated for 24 hrs at 37 °C for (*E. coli* and *E. faecallis*) and *Aerobic.count* for 48 hrs, respectively. The results were then read using a tempo reader.

3.6 Conclusions

In summary, this chapter discussed all analytical techniques background such as XRD, FE-SEM & EDS, TGA, FTIR, BET and zeta potential used for characterization of prepared materials. This chapter also covered different methods used for sample preparation in order to analyse using the mentioned analytical techniques above. This chapter also discussed how the batch adsorption studies were conducted eg (Effect of pH, dosage, time and initial concentration). Microbiological evaluation methods were also summarized.



3.7 References

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CHAPTER 4

REMOVAL OF CHROMIUM(VI) FROM WATER USING FUNCTIONALISED *MORINGA OLEIFERA* AND DETECTION USING SPECTROPHOTOMETER

Abstract

The presence of heavy metals such as Cr(VI) in water tends to be a threat to animal and human life. Therefore, there's a need to remove or reduce the high concentration of Cr(VI) from aqueous solution as to provide clean water to the environment. In this work, the low cost adsorbent was prepared by reacting *Moringa oleifera* with epichlorohydrin and triethylamine using diethylamine (DEA) as modifying agent for removal of Cr(VI) from water. The prepared adsorbent was confirmed using XRD, FTIR, TGA, SEM, BET and Zeta potential. The FTIR results showed that amino groups were successfully grafted on the surface of *Moringa oleifera* (MO). It was also worth noticing that upon successful functionalisation, the zeta potential increased from -1.46 to 14.2 mv at pH solution of 2. Therefore, suggesting some positively amino groups were grafted into MO surface. Adsorption of Cr(VI) on the functionalised *Moringa oleifera* (FMO) was carried out by optimising parameters like pH, dosage, time and initial concentrations. The adsorption results showed that the removal Cr(VI) by FMO was pH dependent. The highest Cr(VI) removal was obtained at acidic media, at pH 2. Adsorption kinetics fitted very well with pseudo second order, suggesting chemisorption mechanism between FMO and Cr(VI). The FTIR results confirmed that there's chemical interaction between oxyanions of Cr(VI) and amine functional groups of FMO. Based on microbiological studies, it was found that FMO was active against real water sample for antibacterial activities. The correlation coefficient obtained from linear calibration curve of Cr(VI) was 0.9999, with a limit of detection (LOD) and limit of quantification (LOQ) of 0.446 and 1.486 mg/L, respectively. Lastly, FMO was also tested for its antibacterial activity using pond, river, tap and sewage water against several bacterial strains. It was found that the FMO was mostly potent against *E. coli*, *Staphylococcus aureus*

and total coliforms. Based on the data obtained this study has shown that environmentally safe adsorbents can be used as multifunctional materials for the treatment of water.

Keywords: Functionalised *Moringa oleifera*, Chromium(VI), Adsorption studies, Kinetics

4.1 Introduction

In recent years, there has been a high demand for fresh clean water due to rapid population growth and urbanization, therefore renders it as a scarce resource [1]. Due to rapid urbanization and industrialization different water pollutants like heavy metals, volatile organic compounds, chemicals and others are released into industrial wastewater [2]. Wastewater from several industries like mining's, manufacturing, electroplating, pharmaceutical and chrome plating contain heavy metals ions like copper, lead, cadmium, zinc, chromium, cobalt and arsenic [3]. All these metals ions are toxic to living organisms even at low concentrations (ppb levels) in aqueous solution [4]–[6]. Among these heavy metals, chromium was reported to be most toxic pollutant in the environment by US Environmental Protection Agency (USEPA) [7]. In aqueous solution, chromium tends to exist in two forms as Cr(VI) and Cr(III). Cr(VI) is known to be 500 times toxic compared to Cr(III) since it tends to spread out as HCrO_4^- and CrO_4^{2-} in the cell membranes [8]. The World Health Organization (WHO) and USEPA have set the limit of Cr(VI) concentration to be 0.10, 0.25 and 0.05 mg/L in surface water, industrial wastewater and drinking water, respectively [9], [10]. Drinking water with Cr(VI) concentration above the recommended limit can cause several health issues like lung cancer, stomach upsets, kidney and liver damages [11], [12]. Common wastewater technologies like ion exchange, membrane separation, precipitation, coagulation and adsorption have been applied for removing Cr(VI) present in wastewater [13]–[16]. However, a majority of these techniques have many drawbacks including high cost operations, incomplete removal, toxic sludge generation which requires additional treatment, low adsorption and selectivity [13]–[16]. Among all these common techniques, adsorption has been identified as the most highly effective

method for removing Cr(VI) from aqueous media due it being less expensive, easy to operate, highly efficient and can be regenerated [17], [18].

Agricultural waste products have gained a lot of attention as sustainable ways for removing toxic heavy metal ions from wastewater. The major advantages of agricultural waste products for sorption of heavy metals includes good adsorption capacity (even at low concentrations), easy accessibility in large amounts, being environmentally friendly, selectivity and accessible at low cost [19]. A few of these agricultural waste materials such as bagasse fly ash, pith carbon and rice husk have been used as dye decolorization agents. However, these raw materials as adsorbents have a poor adsorption capacity towards anion metals.

Several studies have shown that through chemical modification with quaternary ammonium and amine groups, their adsorption capacity can be enhanced [20]. Wartelle and Marshall prepared anion exchangers by quantizing various agricultural waste-materials including rice hulls, corn stoves and almond shell with *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride [21]. The prepared anion exchangers were used for removal of phosphate, arsenate, selenite and chromate from aqueous solution. Based on their results, the quaternized corn stover showed a good adsorption uptake for selenite, arsenate and chromate [21]. Another study by Orlando *et al.* [22]–[24] they have modified various agricultural waste materials (i.e. rice hull, rice bran, moringa oleifera, sawdust, sugarcane bagasse and coconut husk by grafting epichlorohydrin and dimethylamine on to them for nitrate remediation from aqueous solution [22]–[24]. The modified *Moringa oleifera* hull had 30.4 % of lignin content, which showed to have the highest nitrate adsorption capacity of 0.2 mmol/g, followed by coconut husk, sawdust and rice hull. The prepared anion exchangers from agricultural waste materials showed similar nitrate removal capacities as commercial anion exchanger (Amberlite IRA-900). Also, Chen *et al.* prepared an anion exchanger by reacting corn stalk raw material with epichlorohydrin and trimethylamine using diethylenetriamine (DETA) as a modifying agent [20]. The modified corn stalk (MCS) had a higher point zero charge value (pH_{pzc}) of 6.5 compared to the raw corn stalk, suggesting an increase of more positively charged groups on the surface of MCS. The MCS was more effective in

removing Cr(VI) ions even at neutral pH compared to RCS which was effective in acid medium (pH 2). In this study, a new less expensive anionic adsorbent was prepared by reacting *Moringa oleifera* powder with epichlorohydrin and triethylamine using diethylamine as a modifying agent for the removal of Cr(VI) from aqueous solution.

4.2 Experimental

4.2.1 Reagents

Potassium dichromate (97 % purity), Sodium hydroxide pellets (97% purity), Hydrochloric acid (37%), 1,5-Diphenylcarbazide (97 % purity), N,N-Dimethylformamide (99.8 %), Triethylamine (≥ 99.8 %), Epichlorohydrin (99 %), Diethylamine (≥ 99.5 %) were all purchased from Sigma-Aldrich, South Africa.

4.2.2 Preparation of functionalised *Moringa oleifera*

Moringa oleifera powdered leaves purchased at a local commercial store in Johannesburg, South Africa, was washed with deionised water and dried using an oven at 80 °C for 12 hrs. A pestle and mortar was used to crush the dried *Moringa oleifera* (MO) into fine powder. An amount of 2 g (*Moringa oleifera*) was mixed with epichlorohydrin (10 mL) and DMF (12 mL), the solution was stirred for 1 hr at 100 °C. Thereafter, diethylamine (4 mL) was added to the solution mixture and continued stirring for another 1 hr, then followed by adding trimethylamine (15 mL) and stirred for an additional 3 hrs. The resultant adsorbent was washed many times with deionised water and dried at 80 °C for 12 hrs [20].

4.2.3 Material characterization

The prepared adsorbent was characterized using the following analytical instruments; Field Emission-Scanning Electron Microscopy (FE-SEM, Zeiss Crossbeam 540, United Kingdom) coupled with Energy Dispersive X-ray

Spectroscopy (EDS) was used to investigate morphology and elemental composition of the adsorbents, X-ray diffraction (XRD, Ultima IV-Rigaku, Japan) for phase identification crystallinity and particle size. IR spectrum was obtained from Fourier transform infrared spectroscopy (FTIR, Bruker-Alpha, Germany) for identification of functional groups on the surface of functionalised *Moringa oleifera* (FMO) at scan range of 500-4500 cm^{-1}). The surface area was measured using Brunauer–Emmett–Teller (BET, Micromeritics TriStar II Plus, Germany). Thermal gravimetric analysis was conducted using (TGA, Hitachi-STA7200RV, Japan) for thermal stability determination. The chosen heat rate was 20 $^{\circ}\text{C}/\text{min}$ with a temperature range between 25 and 500 $^{\circ}\text{C}$ under nitrogen environment. Zeta potential (Zetasizer Nano ZS-Malvern, United Kingdom) was used to determine the surface charge after amination reaction.

4.3 Batch adsorption studies

Adsorption studies were conducted using batch method for the determination of optimum parameters like dosage, pH, contact time and concentration during adsorption process. The effect of pH was carried out at different pH values (2-10) to investigate whether Cr(VI) removal by FMO depends on the pH and also to determine optimum removal pH. In this experiment, a known amount of FMO was dispersed into 100 mL of reagent bottle with 50 mL of known Cr(VI) concentration. The reagent bottles were taken into a shaker water bath and agitated at a speed of 200 rpm for 24 hrs with fixed temperature of 25 $^{\circ}\text{C}$ in all experiments. To investigate the amount of FMO on Cr(VI) removal, different amounts of adsorbents were varied from 0.05-0.4 g with 100 mg/L Cr(VI) concentration fixed and optimum pH 2. The adsorption studies on the effect of time were conducted at different time intervals (5-140 min) until equilibrium was reached.

4.3.1 Adsorption kinetics

To determine Cr(VI) adsorption mechanism onto adsorbent, different kinetics models including pseudo-first order model, pseudo-second order model and intraparticle diffusion were investigated.

4.3.1.1 Pseudo-first-order

This model is mostly used for describing early stages of adsorption processes, it does not fit the whole contact time range. The linear **Equation 1** for pseudo first order model [26] is shown below as

$$\ln(q_e - q_t) = \ln(q_e - k_1 t) \quad (1)$$

Where q_e (mg/g) is the amount of Cr(VI) adsorbed on adsorbent at equilibrium, q_t (mg/g) is the adsorbed Cr(VI) amount on the adsorbent at a certain given time (t), and k_1 is known as pseudo first order constant. Pseudo first order parameters like k_1 , q_e and q_e were calculated from the linear plot obtained from **Equation (1)**.

4.3.1.2 Pseudo-second-order

This model assumes that the metal ion adsorption mechanism on the adsorbent surface may be chemisorption. Chemisorption involves the interaction of the metal ions and adsorbent via chemical bonding [27]. The linear **Equation 2** for pseudo second order model is represented below as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

Where k_2 (g/mg min) is pseudo second order rate constant. The adsorbed amount of Cr(VI) by adsorbent at equilibrium (q_e) and at certain time (q_t) are calculated from the linear plot graph.

4.3.1.3 Intra-particle diffusion model

Diffusion mechanism of adsorbate onto adsorbent can be determined using various models including Dumwald-Wagner model, homogenous solid diffusion and Weber-Morris model. In this study, Weber-Morris model was chosen since it provides insight mechanism steps involved during the adsorption process [28], [29]. The model assumes that the adsorption diffusion of adsorbate onto adsorbent occurs in different steps. This model in **Equation (3)** was used to determine Cr(VI) rate limiting step.

$$q_t = k_i t^{0.5} + C \quad (3)$$

Where k_i ($\text{mg/g}/\text{min}^{0.5}$) is the diffusion model constant and C (mg/g) is the thickness of boundary layer. According to this model, intraparticle diffusion is the rate-limiting step if the linear plot passes through zero.

4.3.2 Cr(VI) detection using UV-vis spectrophotometry

In this study UV-vis spectrophotometry (Agilent Technologies Cary 60 UV-Vis, Malaysia) was used for the detection of Cr(VI) at 540 nm wavelength using colorimetric method (1.5-Diphenylcarbazide) [25].

4.4 Results and discussions

4.4.1 Characterisation of the adsorbent

4.4.1.1 FESEM & EDS (Morphology and elemental analysis)

The FE-SEM microphotographs (**Figure 4.1**) were used to investigate the surface morphology of adsorbents (MO and FMO). **Figure 4.1(a)** shows that the surface of MO appeared to be smooth with some irregular shape and size. It can be well observed that the particles on the external surface had very sharp broken edges. The development of roughness on the surface of FMO as shown in **Figure 4.1(b)** could suggest the improvement of cellulose order during amination reaction [20].

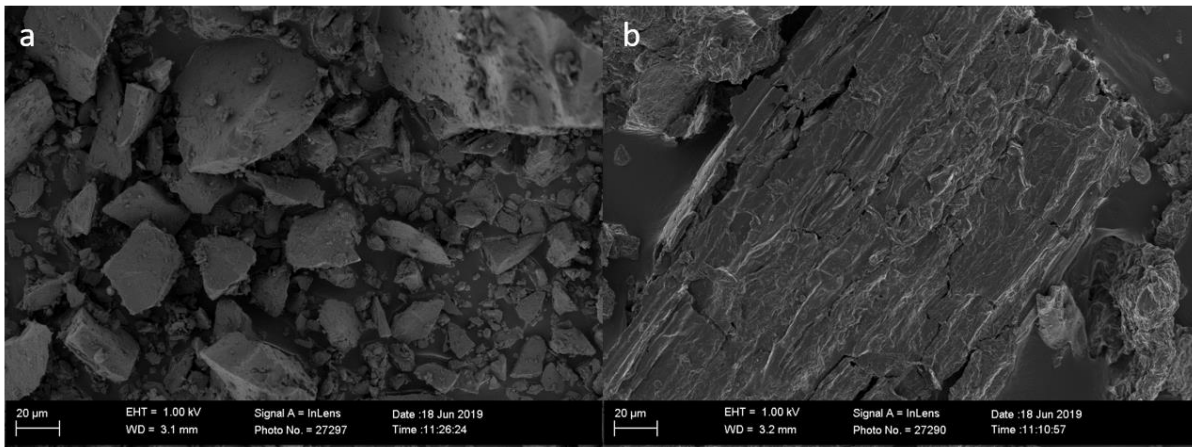


Figure 4. 1: FE-SEM images of (a) MO and (b) FMO

Figure 4.2 displayed the elemental composition of FMO before and after adsorption. There was no corresponding peak for chromium before adsorption. After adsorption, new peaks, which represented chromium were observed at approximately 0.5, 5.5 and 6.0 keV. Therefore, this served as conformation that Cr(VI) was adsorbed on the surface of FMO.

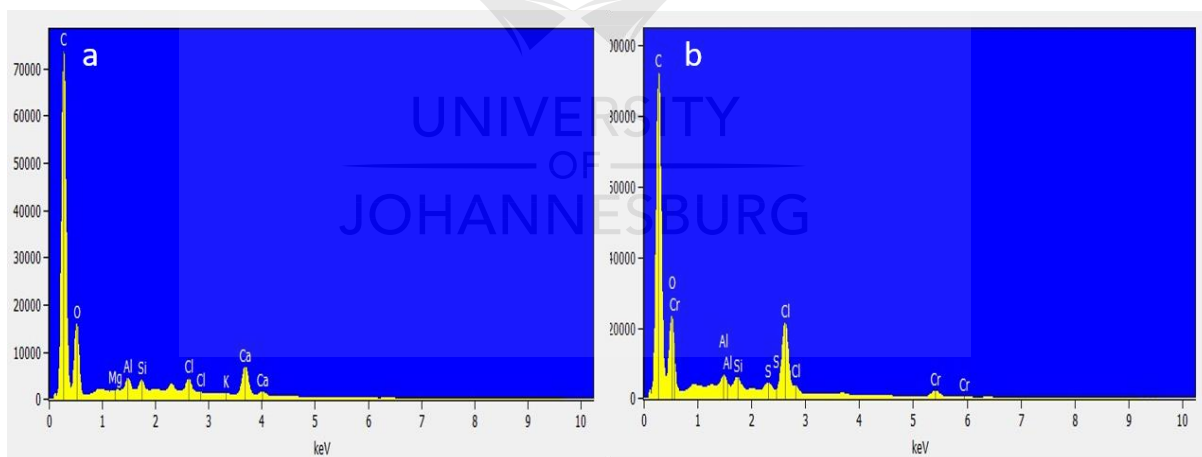


Figure 4. 2: EDS spectrum of (a) FMO (before adsorption) and (b) FMO (after adsorption)

4.4.1.2 BET surface analysis

To determine surface area of both modified MO and raw MO, BET surface area analyser was used for measurements (**Table 4.1**). The surface area of MO was measured to be 1.9198 m²/g. The modification of MO with amine groups slightly

reduced the surface area to 1.0942 m²/g. The decrease in surface area could be the result of successful grafting of amine groups onto the surface of MO. Similar results were reported by Chen *et al.*[20], where chemical modification of corn stalk with amine groups resulted in decrease of BET surface area of corn stalk. The pore volume of MO and FMO were 0.003425 and 0.003767 cm³/g, respectively, while the pore sizes were 7.1353 (MO) and 13.770 nm (FMO). **Figure 4.3** showed the adsorption/desorption isotherms of both adsorbents (MO and FMO). As shown in the figure, both adsorbents have no significant adsorption capacities since their quantity adsorbed is relatively low (< 2.5 cm³/g). These hysteresis loops are classified as type II according to International Union of Pure and Applied Chemistry (IUPAC), suggesting that both adsorbents (MO and FMO) exhibited different macroporous sizes [30].

Table 4. 1: Physical properties of the adsorbents.

Adsorbents	BET surface area (m ² /g)	Highest pore volume(cm ³ /g)	Highest pore sizes(nm)
MO	1.9198	0.003425	7.1353
FMO	1.0942	0.003767	13.770

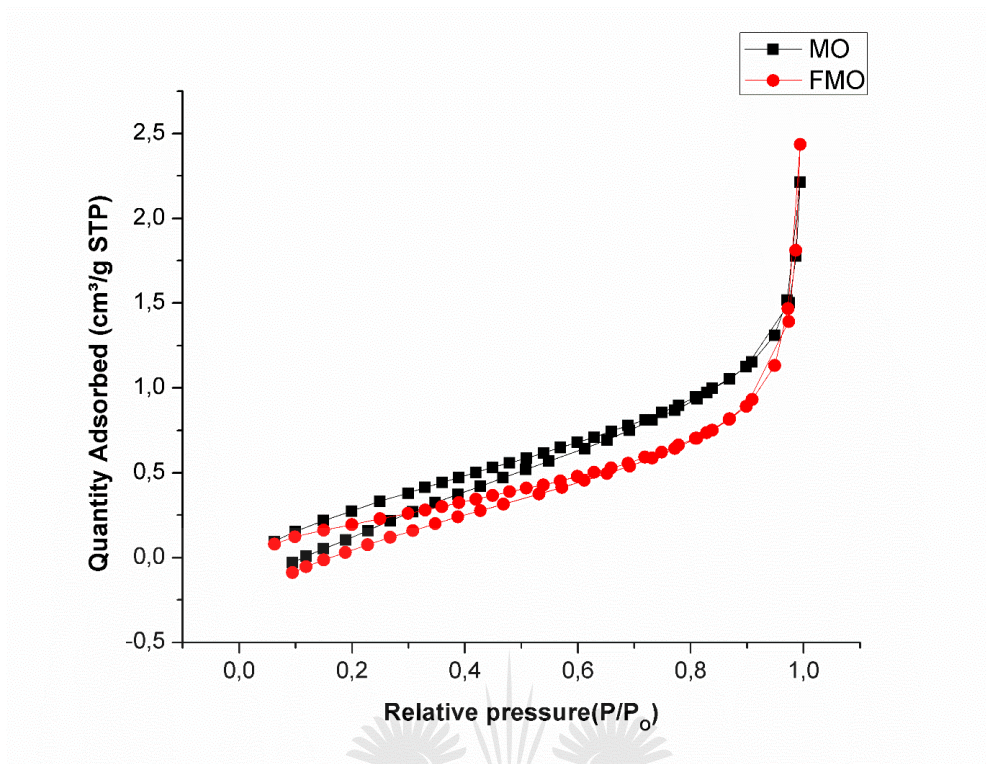


Figure 4. 3: Nitrogen adsorption/desorption isotherms of MO and FMO

4.4.1.3 XRD analysis

To determine the crystallinity of the prepared adsorbents (MO and FMO), XRD analysis were conducted. **Figure 4.4** displayed the XRD spectrum of MO and FMO. As shown in this figure, for both adsorbents (MO and FMO) there was a broad peak at $2\theta = 20^\circ$ which indicated that both MO and FMO are amorphous in nature.

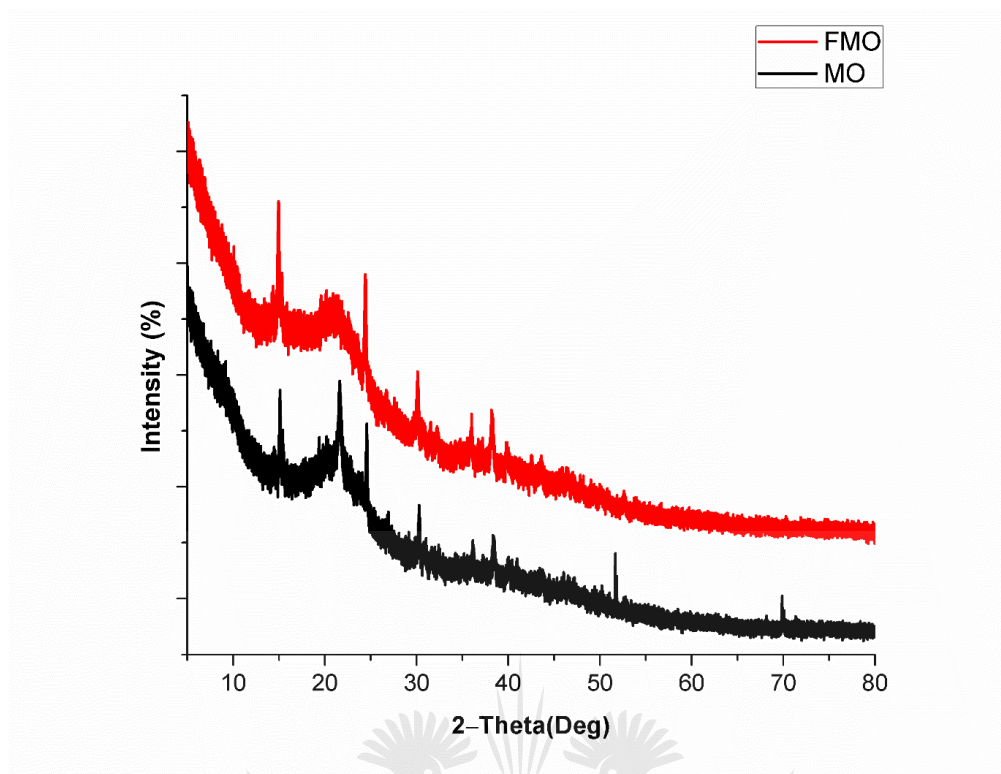


Figure 4. 4: XRD patterns for MO and FMO.

4.4.1.4 FTIR analysis

FTIR analysis was conducted for identification of functional groups present within the adsorbent. **Figure 4.5** showed the FTIR spectra of MO, FMO and FMO-Cr (after Cr adsorption onto FMO). IR spectra of MO displayed a broad peak at 3272 cm^{-1} which indicated hydroxyl group (O-H). The peaks appearing at $2916\text{-}2849\text{ cm}^{-1}$ were ascribed to aliphatic C-H group. The peak at 1621 cm^{-1} indicated the C=O stretch. The intense peak appearing at 1020 cm^{-1} could be attributed to alkoxy group (C-O). The IR bands of MO were maintained in the FMO, therefore showing that after the modification with amine groups, the MO structure was not disintegrated. The IR spectra of FMO showed a sharp peak at approximately 1351 cm^{-1} representing the C-N stretching of amino groups transferred on the surface of FMO. The bands appearing at 1647 and 1030 cm^{-1} were assigned to N-H stretching band of amino groups [20]. The broad band at $3369\text{-}3299\text{ cm}^{-1}$ could be assigned to the -OH and -NH group. As shown in **Figure 4.5**, after adsorption there was a slight reduction and shift of the adsorption

band indicating some possible functional groups which were responsible for uptake of Cr(VI). It can be observed that oxygen containing group played a minor role in Cr(VI) adsorption, whereas the amino groups played a major role [31].

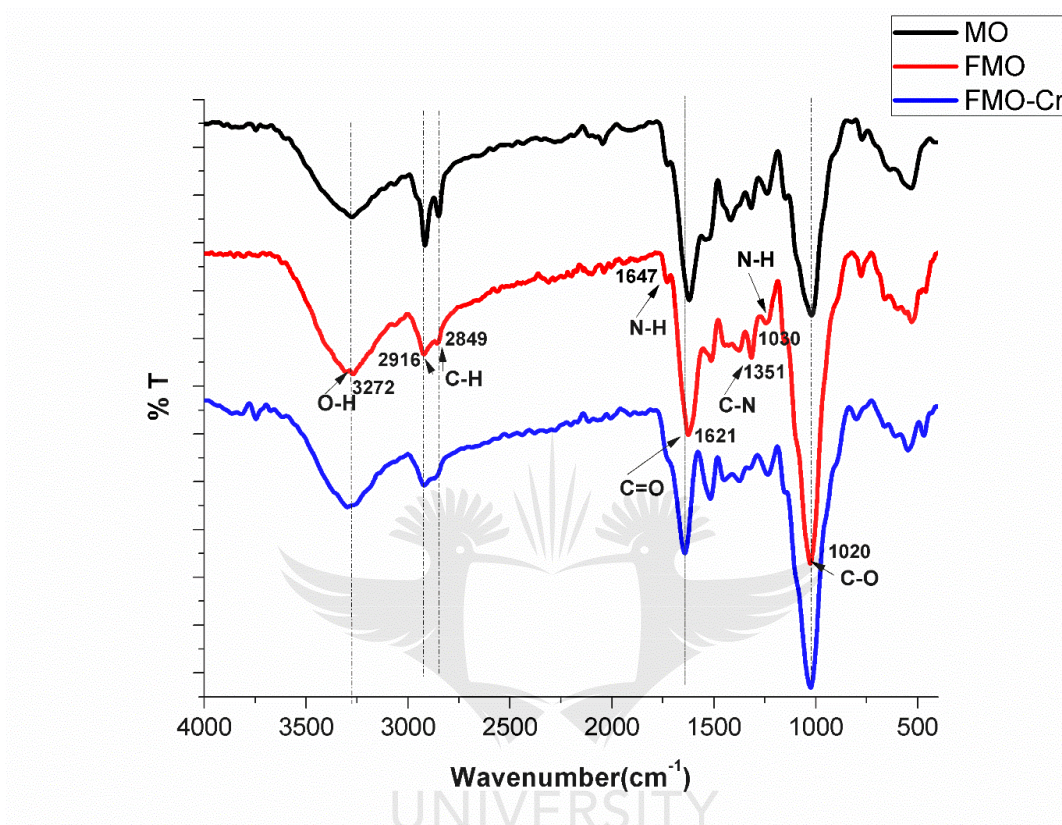


Figure 4. 5: IR spectra's of MO, FMO (before adsorption) and FMO-Cr (after adsorption)

4.4.1.5 Thermal analysis

Thermal gravimetric analysis was used for determination of weight loss ratio and thermal stability of MO and FMO. As shown in **Figure 4.6**, both MO and FMO started to lose their weight at approximately 100 °C due to loss of unbound water molecules or moisture on their surfaces [32]. The TGA curve's showed clearly that the modification of MO slightly increased thermal stability. Therefore, meaning the modification of MO with amine group's enhanced the thermal stability. The weight losses from 210 to 350 °C for both MO and FMO were due to dehydroxylation of MO and structural decomposition of FMO [20] [33] . The results were inconsistent with

other studies reported by Araújo *et al.*[32], whereby *Moringa oleifera* seeds started to lose its weight at approximately 200 °C.

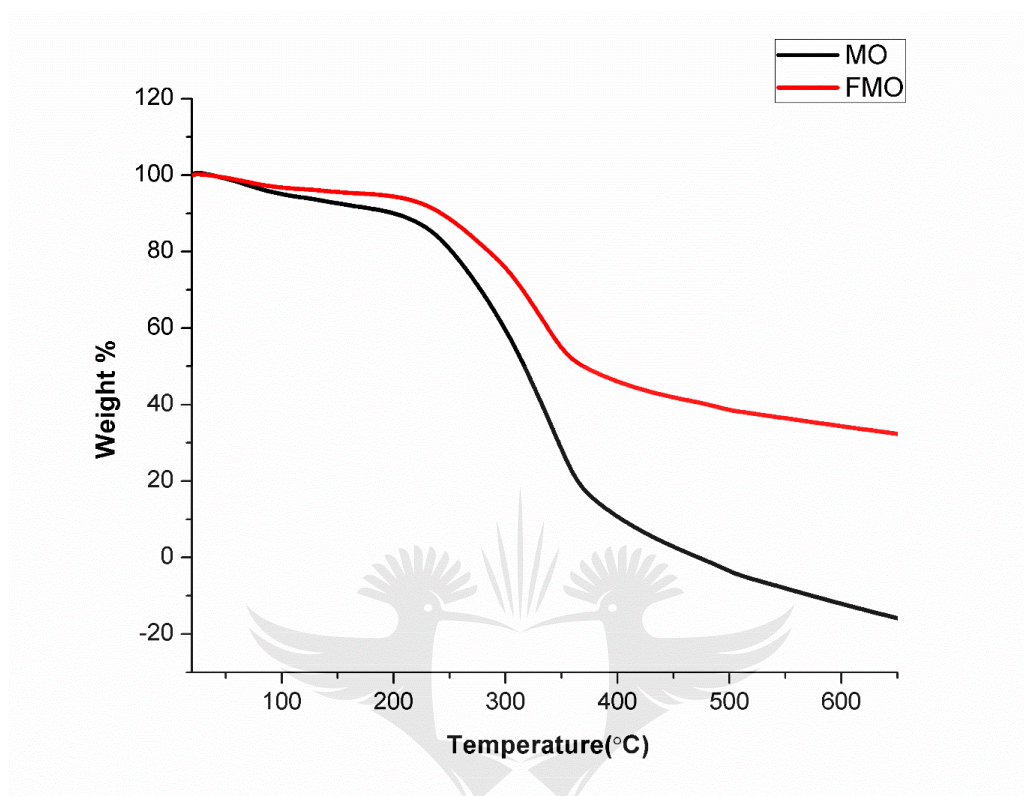


Figure 4. 6: TGA curves of MO and FMO

The DTG curves of both MO and FMO are shown in **Figure 4.7**. The DTGA results corresponded very well with the obtained TGA curves. As shown in **Figure 4.7**, there are huge endothermic peaks for both MO and FMO DTG curves at temperature approximately 350 °C which could be due to the decomposition of the materials.

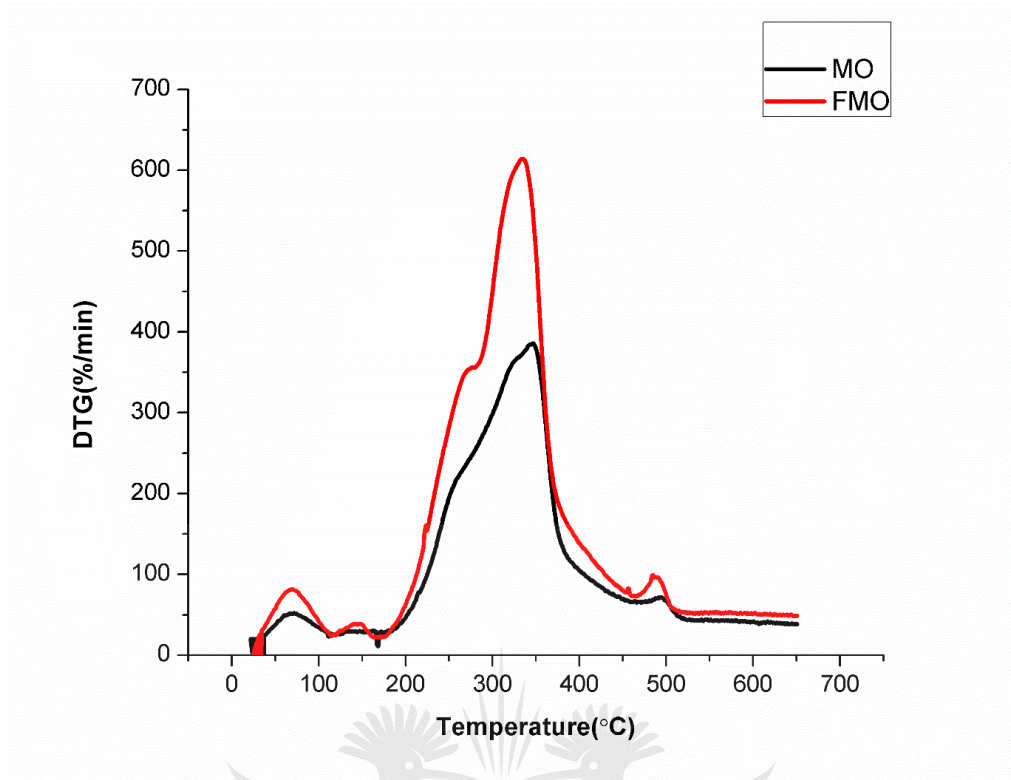


Figure 4. 7: DTG curves of MO and FMO

4.4.1.6 Zeta potential

Figure 4.8 showed the surface charge of both FMO and MO at different pH solution values. It can be observed that MO is negatively charged through the pH value ranges. The modification of *Moringa oleifera* (MO) with amine groups resulted in an increase in the zeta potential (increase in positively charged groups). After the modification, the surface charge of the *Moringa oleifera* was positively charged in acidic medium. The zero point charge (pH_{pzc}) for FMO was obtained at pH 4, suggesting that FMO is positively charged below this pH. It could be due to protonation of amine groups on the surface of FMO [34]. As depicted in the **Figure 4.9**, high Cr(VI) removal efficiency was observed below the zero point charge due to high electrostatic interaction between the positively charged adsorbent (FMO) and the anionic HCrO_4^- species (adsorbate) [35].

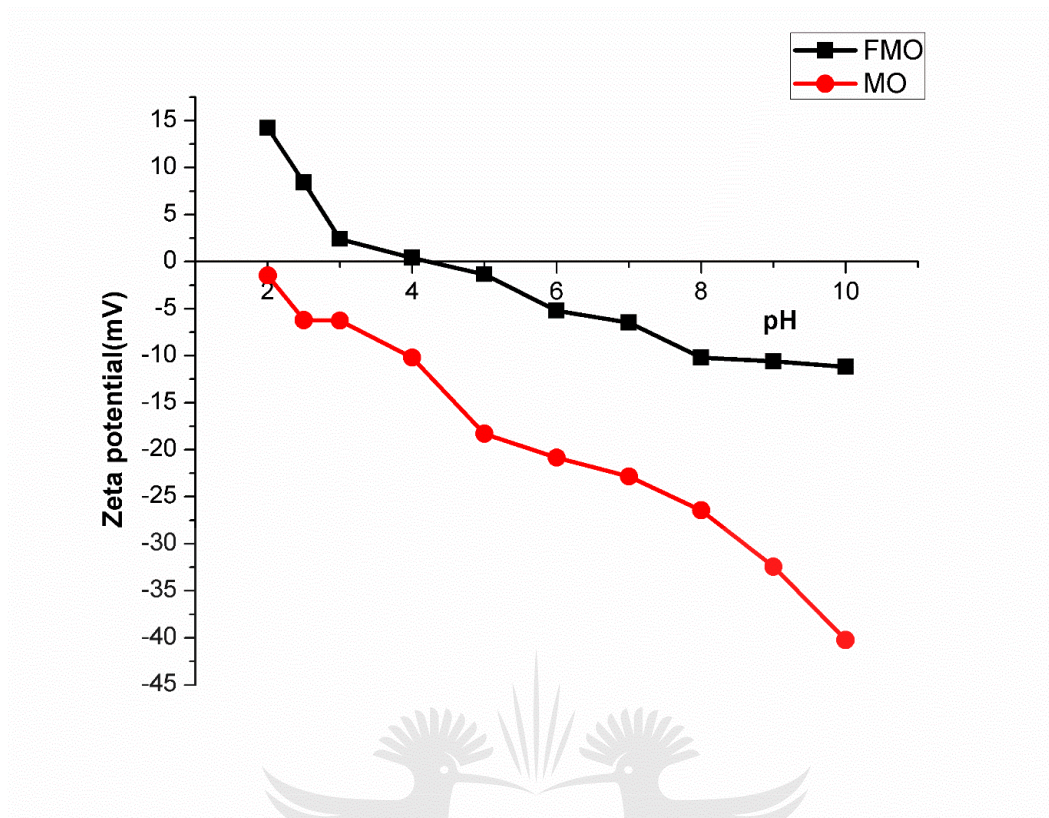


Figure 4. 8: Zeta potential of MO and FMO as a function of pH.

4.5 Batch adsorption studies

4.5.1 Influence of pH on Cr(VI) uptake

During Cr(VI) adsorption, pH is an important parameter which can control the electrical properties of both adsorbate and adsorbent. To investigate the influence of pH on Cr(VI) removal, pH of the Cr(VI) solution was adjusted between the ranges of 2-10. The Cr(VI) removal percentage increased with decrease in the pH solution (**Figure 4.9**). Cr(VI) removal percentage was very high in acidic medium (pH 2) than in alkaline region (pH >6). The high removal percentage of Cr(VI) at pH <3 could be due to protonation of adsorbent surface thus making the adsorbent surface to become more positively charged. In aqueous solution, Cr(VI) exist as oxyanions forms as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} . Therefore, the positively charged FMO (adsorbent) tend to interact with the Cr(VI) oxy-anions (adsorbate) through electrostatic interaction [36]. In an alkaline region the chromium removal decreased

because the Cr(VI) oxyanions $[\text{CrO}_4^{2-}]$ compete with OH^- for adsorption sites on the surface of the adsorbent. The optimum pH value was 2 with a maximum Cr(VI) removal percentage (80.15%).

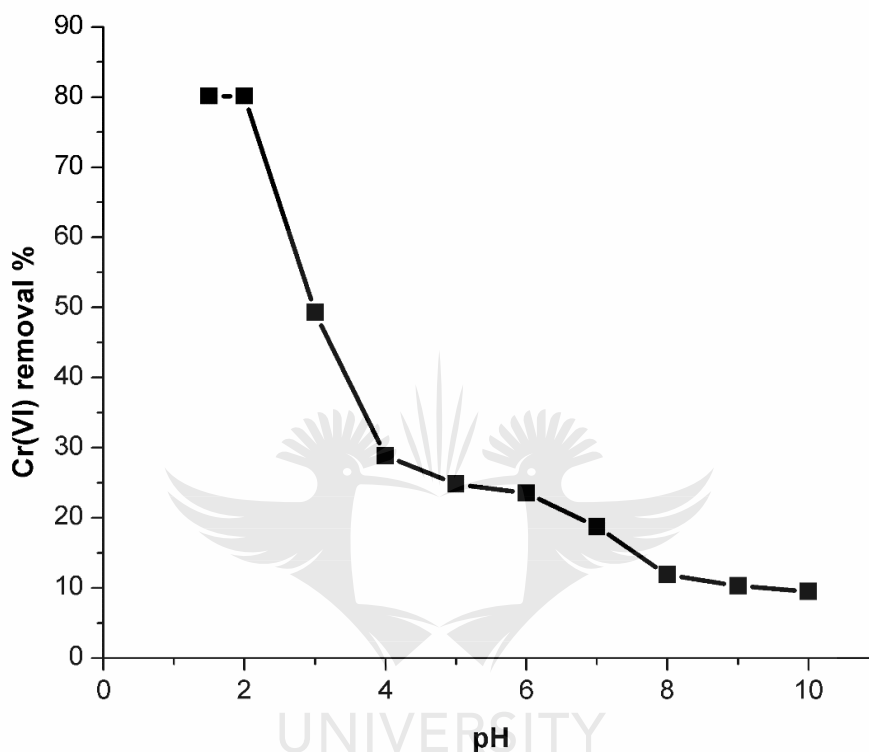


Figure 4. 9: Influence of pH on Cr(VI) removal using FMO

4.5.2 Effect of dosage

To study the amount of FMO on Cr(VI) removal, adsorption studies were conducted by varying different masses of FMO from 0.02 - 0.4 g. **Figure 4.10** displayed the percentage removal of Cr(VI) based on different dosages of FMO. The Cr(VI) removal percentage increased from 47.98 to 95.00 % with the increase of FMO dosage from 0.05 to 0.25 g. As the amount of FMO increased, the adsorption sites for Cr(VI) on the surface of FMO also increased. It can be noticed further that an increase in adsorbent (FMO) dose from 0.25 to 0.4 g did not have a significant impact on the Cr(VI) removal since the removal efficiency at this dose range

remained constant. The maximum adsorption (95.0%) was obtained with 0.25 g dosage (FMO), and this amount was used for later adsorption studies for Cr(VI) removal. According to the study conducted by Shiran *et al.*[37], the highest dose for Cr(VI) removal was reported to be 2.5 g using raw *Moringa oleifera* pods powder (MPP) as sorbent, which removed about 82 % of Cr(VI). Therefore, this could suggest that the modification of *Moringa oleifera* enhanced adsorption capacity towards the removal of Cr(VI). To understand the rate of adsorption of C(VI) by FMO, the effect of time studies on Cr(VI) removal were conducted.

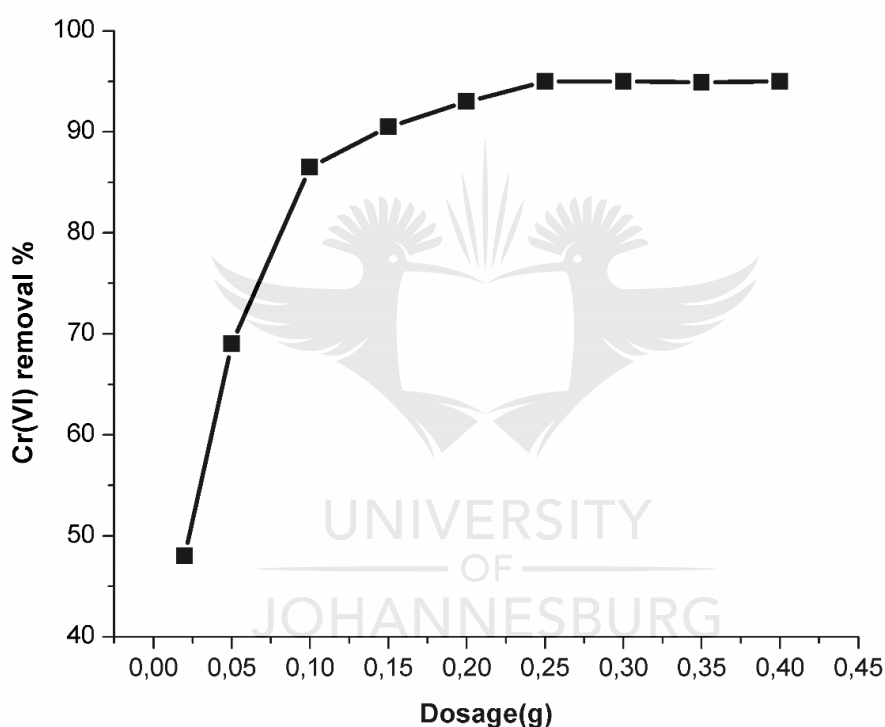


Figure 4. 10: Effect of dosage on the removal of Cr(VI) using FMO

4.5.3 Effect of contact time

To investigate the rate of Cr(VI) uptake from aqueous media by FMO, adsorption studies were conducted by varying time until the equilibrium was reached. **Figure 4.11** illustrated Cr(VI) removal percentage profile using FMO as an adsorbent with respect to time. It can be observed that sorption rate was very fast initially up to 85 min were equilibrium was attained (**Figure 4.11**). The plateau point

was reached since adsorption sites of the adsorbent were fully occupied by Cr(VI). The maximum adsorption (88.5%) was obtained at 85 min. According to the study conducted by Timbo *et al.*[38], the Cr(VI) adsorption equilibrium was attained after 60 min. The highest Cr(VI) removal percentage at that time was approximately 25.0 %. Similar results was reported by Sasikala *et al.*[39] were Cr(VI) adsorption equilibrium was reached within two hours.

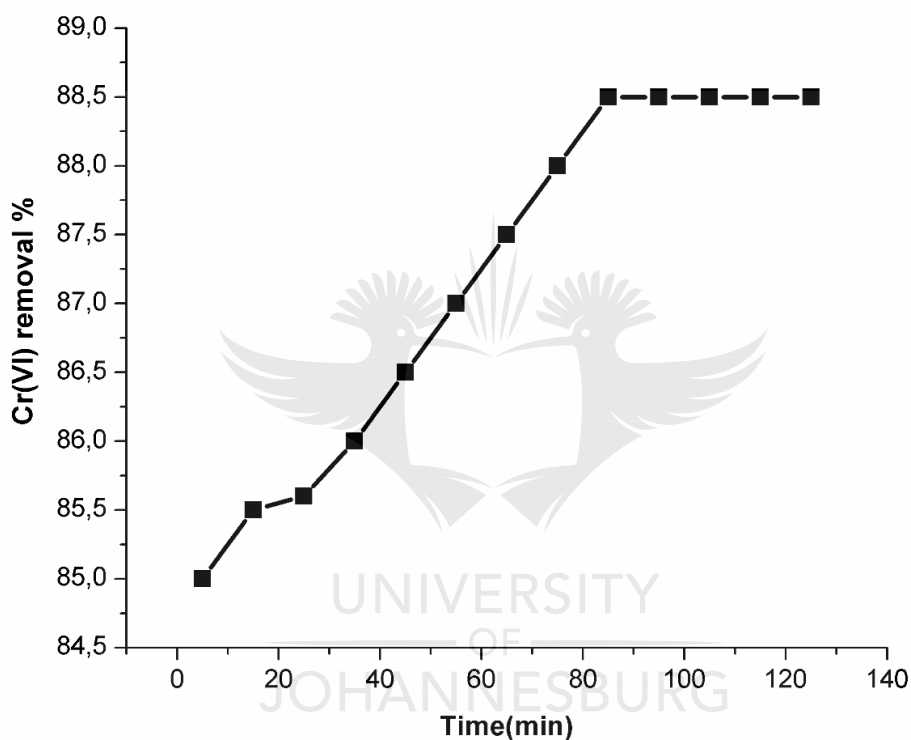


Figure 4. 11: Effect of contact time on Cr(VI) removal by FMO

4.5.4 Effect of Cr(VI) concentration

In this study, Cr(VI) concentration was varied in the range 20-100 mg/L at optimum pH (2), contact time (85 min) and dosage (0.25 g). It can be observed that the removal percentage of Cr(VI) decreased with an increase of Cr(VI) concentration, and this could be due to the saturation of available adsorption sites on the surface of the adsorbent by Cr(VI) (**Figure 4.12**). The FMO was able to remove 20 mg/L

Cr(VI) completely from aqueous solution. Therefore, 20 mg/L Cr(VI) was used for later studies as the optimum concentration.

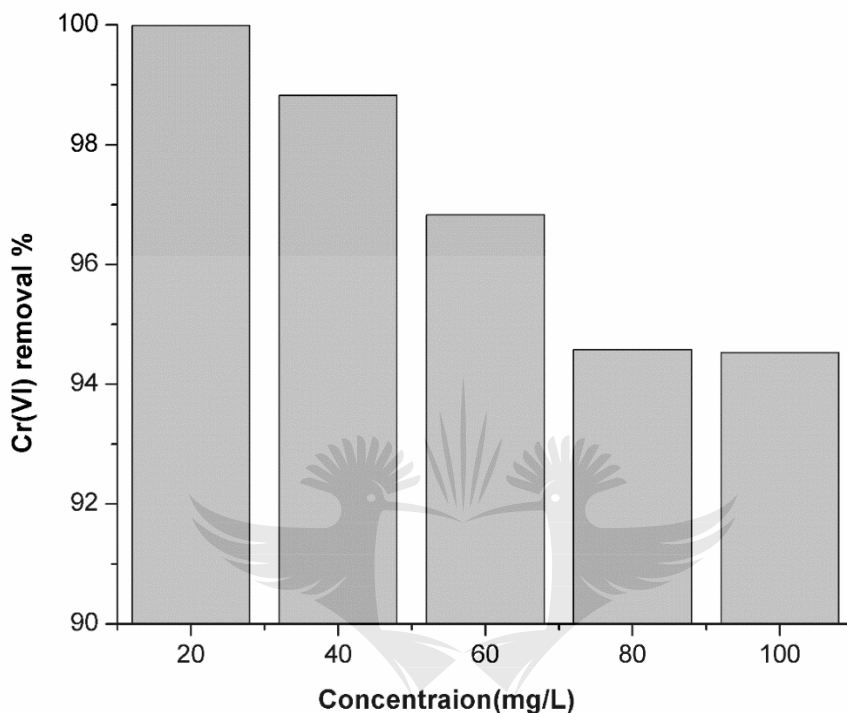


Figure 4. 12: Effect of concentration on Cr(VI) removal by FMO.

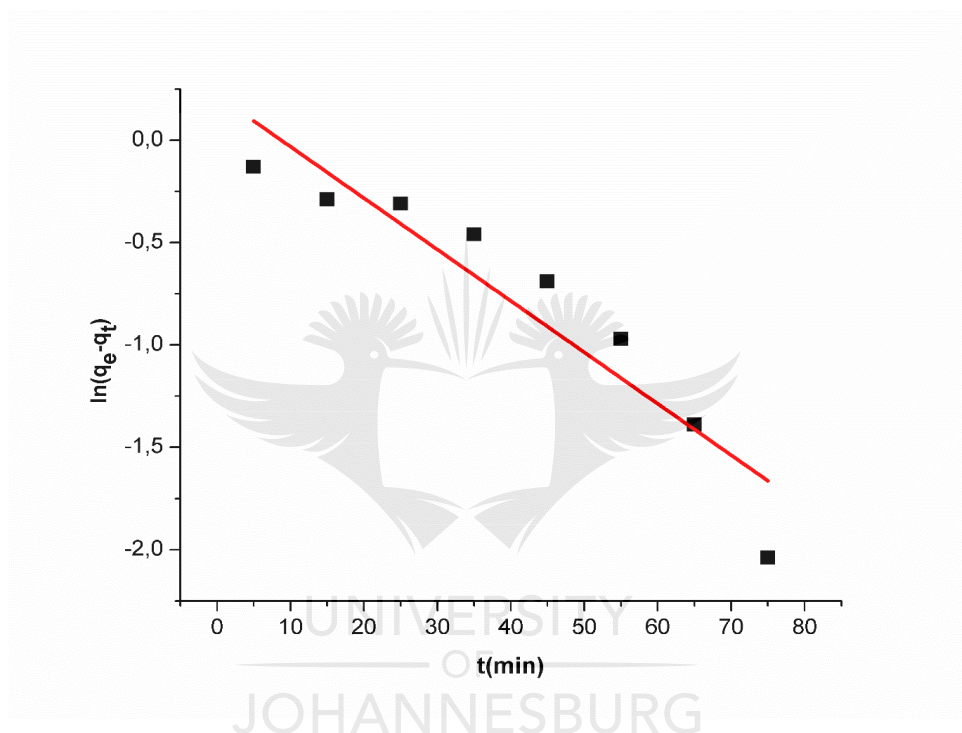
Further, adsorption kinetics were conducted to understand the rate of Cr(VI) onto FMO and also to investigate the adsorption mechanism between Cr(VI) and FMO.

4.5.5 Adsorption kinetics

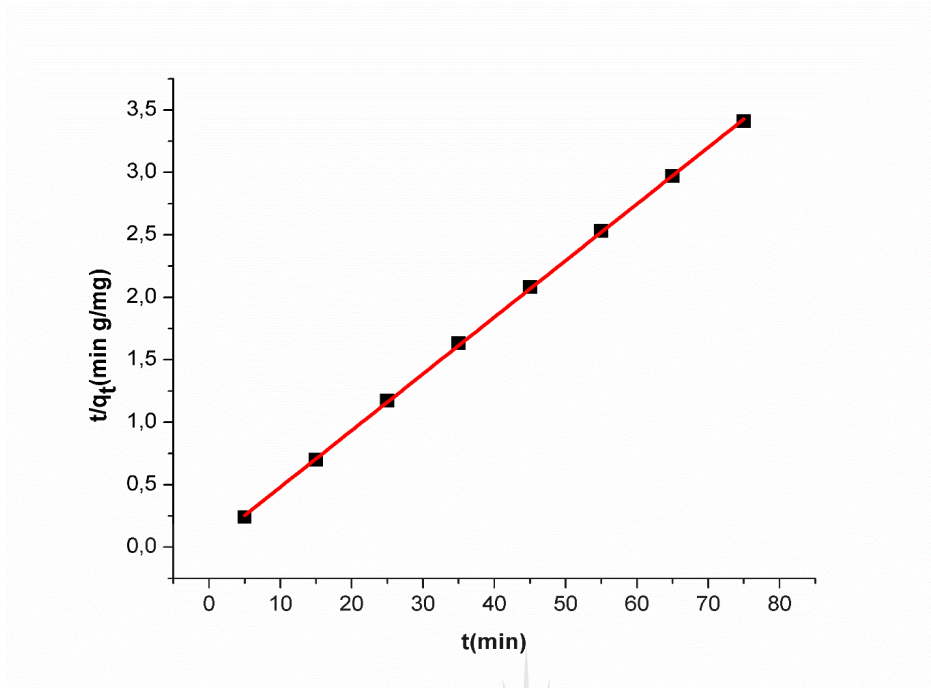
4.5.5.1 Pseudo-first order and second-order model

Table 4.2 shows the values of adsorption capacity (q_e), pseudo first order constant (k_1) and correlation coefficients (R^2) obtained from the linear plot shown in **Figure 4.13**. The correlation coefficient obtained from the pseudo second order ($R^2 = 0.99984$) was higher than that obtained from pseudo first order ($R^2 = 0.86554$)

as shown in **Figure 4.13(b)**. Therefore, this confirmed that experimental data followed pseudo second order model, which, suggested that adsorption process of Cr(VI) onto FMO was more of a chemical behavior than physical. As was depicted in the FTIR, the amino functional groups had significant role in Cr(VI) uptake. Similar observations were reported by Chen *at al.* [20] for chromium(VI) uptake using modified corn stalk. These uptake results confirms Cr(VI) adsorption behaviour by FMO could be due to electrostatic interaction.



(a)



(b)

Figure 4. 13: (a) Linear Pseudo-first-order and (b) Pseudo-second-order model for Cr(VI) adsorption by FMO.

Table 4. 2: Kinetics parameters obtained from linear plots.

Pseudo first order		Pseudo second order	
Linear		Linear	
Q_e	1.245	Q_e	22.07
K_1	0.0251	K_2	0.07235
R^2	0.86554	R^2	0.99984
Degree of freedom	6	Degree of freedom	6
Number of points analysed	8	Number of points analysed	8

4.5.5.2 Intra-particle diffusion

In **Figure 4.14**, the linear plot did not pass through origin, which indicates that intra-particle diffusion was not the rate determining step in the adsorption process of Cr(VI) onto FMO. Instead, the linear plot showed three distinct steps; (1) Cr(VI) ions

migration on the external surface of FMO (external diffusion), (2) migration of Cr(VI) ion from external surface into pore structures (pore diffusion), (3) Cr(VI) adsorption on the available binding sites within FMO pores (adsorption within the pores). The Intraparticle diffusion model parameters are listed in **Table 4.3**.

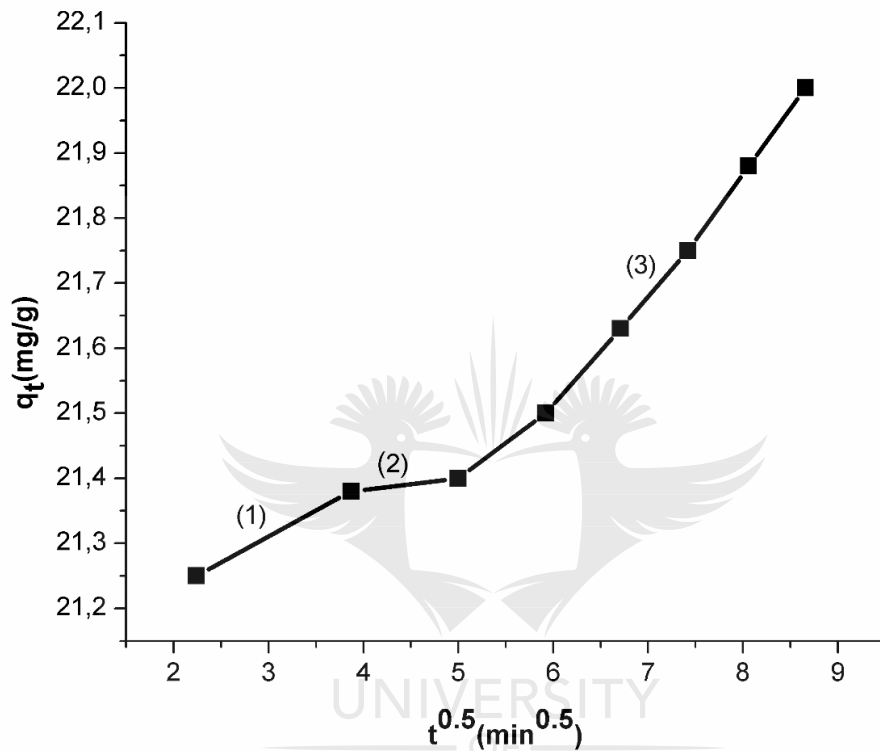


Figure 4. 14: Linear plot for intraparticle diffusion of Cr(VI) onto FMO.

Table 4. 3: Intraparticle diffusion model parameters.

k_1	C_1	$(R_1)^2$	k_2	C_2	$(R_2)^2$	k_3	C_3	$(R_3)^2$
0.9211	1.8067	1.00	0.9366	1.3753	1.00	0.1661	20.537	0.9887

4.5.6 Influence of co-existing ions on Cr(VI) removal

Industrial wastewater from chrome plating, mining's and leather tanning does not contain only Cr (VI), but consists of many other ions. In this experiment, the removal of Cr(VI) was studied in the presence of a few selected ions like Ni²⁺, Cu²⁺, Zn²⁺,

SO₄²⁻, Cl⁻ and NO₃⁻ at different concentrations (20-100 mg/L). The study was conducted to investigate the selectivity of FMO towards Cr(VI) in the presence of other ions. It can be observed that Ni²⁺, Cu²⁺ and Zn²⁺ had minor effect on Cr(VI) removal (**Figure 4.15**). At pH 2, the amine groups on the adsorbent (FMO) surface were positively charged therefore making electrostatic interaction between cations and adsorbent impossible. **Figure 4.15** showed that the three anions, SO₄²⁻, NO₃⁻ and Cl⁻ had some effect on Cr(VI) removal. NO₃⁻ and Cl⁻ had very small effect (1.68 %) on Cr(VI) removal, whereas in the presence of SO₄²⁻ the Cr(VI) removal was slightly affected especially at higher concentrations. At 100 mg/L SO₄²⁻, Cr(VI) removal percentage decreased from 100 to 95.02 %. This could be due to similar inner and outer sphere complexes for both Cr(VI) molecules and SO₄²⁻ which can lead to competition of unoccupied adsorption sites on FMO surface [40].

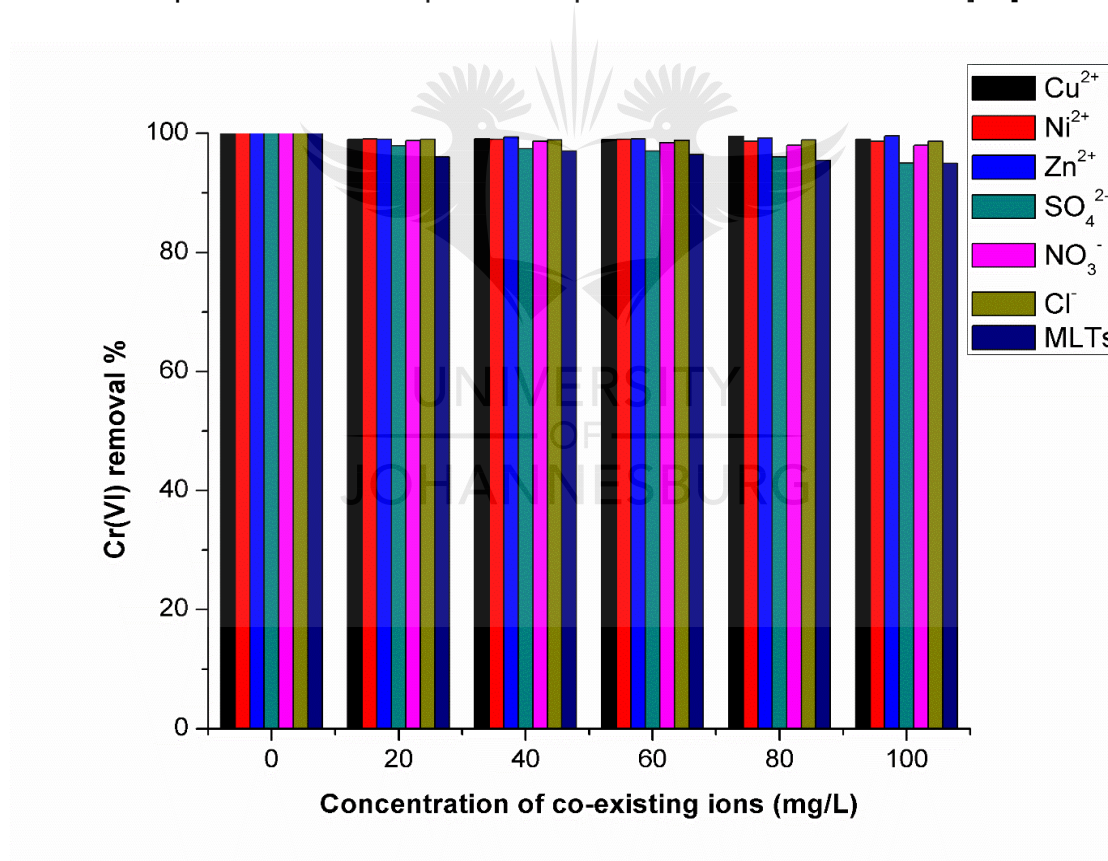


Figure 4. 15: Cr(VI) removal in the presence of co-existing ions.

4.5.7 Reusability studies

The reusability studies were based on the investigation of the effectiveness of the adsorbent (FMO) for Cr(VI) removal from aqueous solution after several cycles. In this study different adsorbents were used for comparison, the functionalised *Moringa oleifera* (FMO) and raw *Moringa oleifera* (MO). These studies were conducted at optimum conditions; dosage (0.25 g), pH (2), contact time (85 min) and concentration (20 mg/L). In **Figure 4.16**, Cr(VI) removal efficiency decreased with an increase in adsorption cycles. This could be due to the fact that as the adsorbent was regenerated after several adsorption cycles, its re-usability decreased. The removal efficiency of Cr(VI) displayed a slight decrease from 100 to 90 % from cycle 1 until cycle 7 using FMO as an adsorbent. The MO was not that effective, since the removal efficiency decreased dramatically with cycles. It can be observed that the removal efficiency decreased from 100 to 22 % after 7 cycles. The obtained results confirmed that in terms of longevity and effectiveness or stability, FMO is a better adsorbent as compared to MO. This was also depicted in **Figure 4.6**, where the FMO was more thermally stable as it decomposed slowly and at a higher temperature as compared to MO.

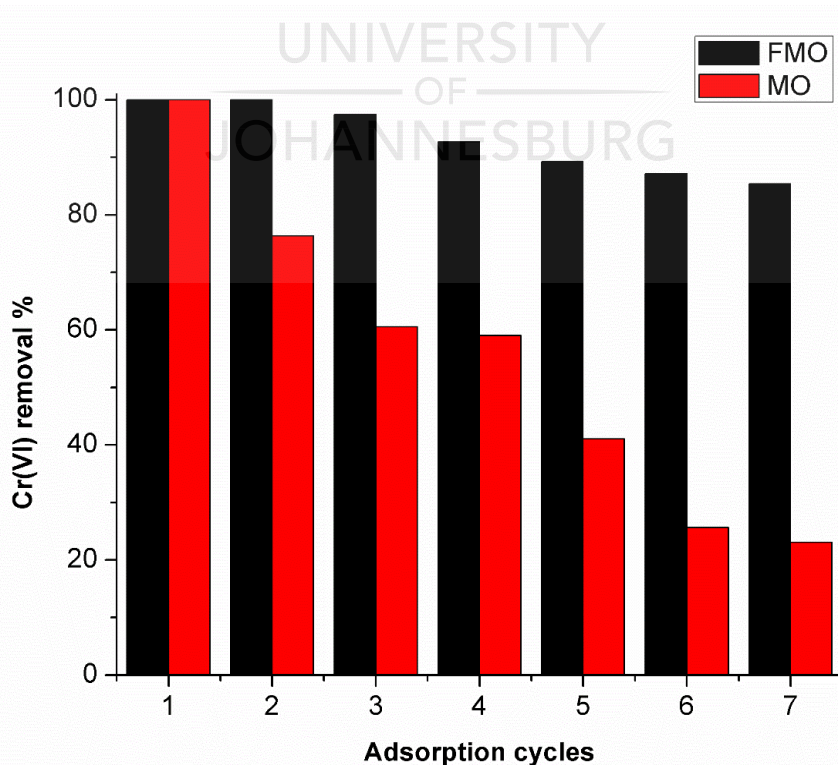


Figure 4. 16: Reusability of the adsorbents (MO and FMO).

4.6 Real water analysis

To investigate the ability of FMO for Cr(VI) removal in real water samples, adsorption studies were conducted under optimized conditions before and after spiking with known Cr(VI) concentration (20 mg/L). **Figure 4.17** displayed the adoption of Cr(VI) from spiked real water sample. As shown in the figure the real water contained 20 mg/L of Cr(VI) before adsorption and after the adsorption the concentration decreased to 5 mg/L. Therefore, FMO was able to remove 75 % of Cr(VI) from real water sample.

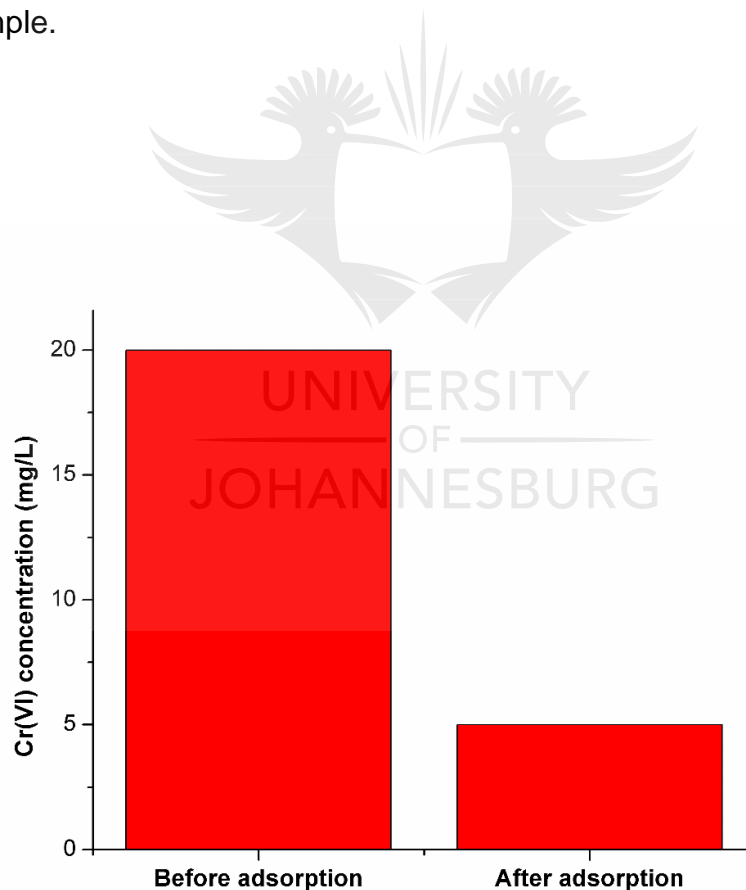


Figure 4. 17: Cr(VI) adsorption by FMO from real water sample.

4.7 Analytical figures of merit

The limit of detection and quantification were determined using the following equations, $LOD = \frac{3 \times SB}{m}$ and $LOQ = \frac{10 \times SB}{m}$, respectively. Where LOD represent the limit of detection, LOQ is the limit of quantification, SB is the relative standard deviation (RSD) of the blank and m is the slope obtained from the calibration curve. The correlation coefficient (R^2) obtained from the calibration curve was 0.9999. The relative standard deviation of the blank was measured in triplicates. **Table 4.4** below shows the summary of analytical figures of merit for Cr(VI) analysis using UV-vis spectroscopy.

Table 4. 4: UV-vis analytical figures of merit for Cr(VI) removal

Metal ions	Relative std.dev	Limit of quantification	Limit of detection
Cr(VI)	±0.097 mg/L	1.486 mg/L	0.446 mg/L

4.8 Microbiological evaluations of FMO

To test the effect of this material (FMO) in terms of removing other pollutants, antibacterial studies were also conducted.

Seeded water

The antibacterial studies were conducted to investigate the activity of FMO against four different strains namely *E.coli*, *P.aeurinosa*, *E.faecalis* and *S.aureus*. **Table 4.5** showed the activity of FMO against the above mentioned strains at various concentrations (0.005 - 0.05 mg/ml) on seeded water. As shown in **Table 4.5**, the obtained results confirmed that FMO was not active against these strains since the microbes were too numerous to count (TNTC).

Table 4. 5: The effect of FMO on different strains using different concentrations

Test organism	Control	0.005	0.01	0.02	0.05
<i>E. coli</i>	TNTC	TNTC	TNTC	TNTC	TNTC
<i>P. aeruginosa</i>	TNTC	TNTC	TNTC	TNTC	TNTC
<i>E. faecalis</i>	TNTC	TNTC	TNTC	TNTC	TNTC
<i>S aureus</i>	TNTC	TNTC	TNTC	TNTC	TNTC

Fouad *et al.*[41] reported antibacterial activity of ethanol (EEs), hot water and cold water extract (CWE) of *Moringa oleifera* against bacteria's isolated from camel abscesses. Hot water extract of *Moringa oleifera* was not active against the isolated bacteria's (*C. ulcerans*, *S. aureus*, *K. pneumoniae*, *C. pseudotuberculosis*, *P. aeruginosa* and *P. vulgaris*). However, both CWE and EEs of *Moringa oleifera* had highest antibacterial activity against those isolated bacteria's.

Real water samples

Another study was performed on real water samples (Tap water, University of Limpopo Pond water, sewage water and Letaba River). In this study, different strains including *aerobic count*, total coliform, *staphylococcus* and *E.coli* were tested against two concentrations (0.005 and 0.05 mg/ml) of FMO. From the tap water results in **Table 4.6**, it can be confirmed that FMO was more active against *staphylococcus* than other bacterial strains at concentration of 0.05 mg/ml. The FMO had no effect against *E.coli*, because there were no strains detected as shown from the control. In **Table 4.6**, the effect of FMO on total coliforms and aerobic count was minimal as there wasn't much change.

Table 4. 6: The effect of FMO on different strains from tap water.

Water type	Aerobic count	Total coliform	<i>Staphylococcus Aureus</i>	<i>E coli</i>
Tap water (control)	$>4.9 \times 10^5$	4.9×10^4	50	0
0.005	4.9×10^5	4.9×10^4	21	0
0.05	4.9×10^5	9.1×10^3	0	0

Table 4.7 showed that FMO was not effective in treating aerobic count but against total coliform the effect was minimal even at concentration of 0.05 mg/ml. The pond water did not contain any staphylococcus since it was not detected as shown from the control. Therefore, against this strain the treatment was not effective. Against *E. coli*, the FMO was effective as no strain was detected.

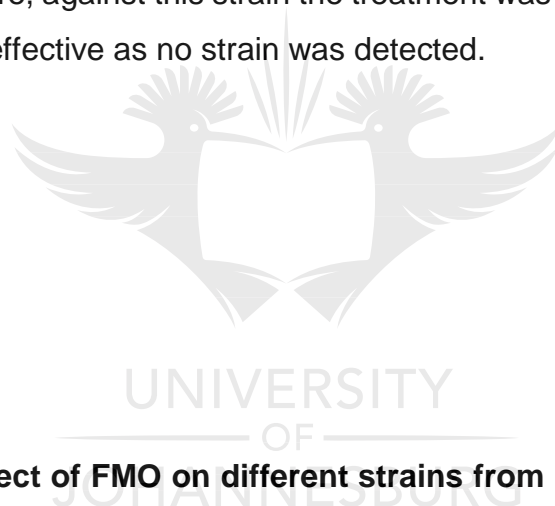


Table 4. 7: The effect of FMO on different strains from University of Limpopo (UL) Pond water

Water type	Aerobic count	Total coliform	<i>Staphylococcus aureus</i>	<i>E coli</i>
Pond (control)	$>4.9 \times 10^5$	4.9×10^4	0	10
0.005	4.9×10^5	4.9×10^4	0	0
0.05	4.9×10^5	1.7×10^4	0	0

Letaba river water did not contain any of *staphylococcus* and *E.coli* bacteria's as shown from control in **Table 4.8**. Therefore, there was no effect against both *staphylococcus* and *E.coli* as no strains were detected. Against the *aerobic count*

and *total coliform*, the effect was minimal using both concentrations (0.005 and 0.05 mg/ml).

Table 4. 8: The effect of FMO on different strains from Letaba river water

Water type	Aerobic count	Total coliform	<i>Staphylococcus aureus</i>	<i>E coli</i>
River (control)	$>4.9 \times 10^5$	4.9×10^4	0	0
0.005	4.9×10^5	4.9×10^3	0	0
0.05	4.9×10^5	3.9×10^3	0	0

From the results shown (**Table 4.9**), it can be observed that FMO was active against both *E.coli* and *staphylococcus* using both concentrations. Concentration of 0.005 mg/ml of FMO destroyed about 58.33 % strains of *E.coli*, it was noticed that as the concentration increased to 0.05 mg/ml the strains were completely destroyed. Similar results were observed against *staphylococcus*, since at higher concentrations the strains were also completely destroyed. Against *aerobic count* and *total coliforms*, the effect was minimal after treatment. For total coliforms at higher concentration, the number of strains increased which could be due to some of the phytochemicals within FMO serving as nutrients to this strains thus increasing their growth instead of destroying them.

Table 4. 9: The effect of FMO on different strains from UL sewage water.

Water type	Aerobic count	Total coliform	<i>Staphylococcus aureus</i>	<i>E coli</i>
Sewage (control)	$>4.9 \times 10^5$	7.1×10^2	40	1.2×10^2
0.005	4.9×10^5	5.1×10^2	10	50
0.05	3.7×10^5	9.1×10^3	0	0

The antimicrobial mechanism of amine functionalised *Moringa oleifera* is still unclear. However, it has been reported that the ammonium compounds of the quaternized dendrimers exert their antimicrobial action by disrupting and disintegrating cell membranes [42]. So, we also believe that amine functional groups on the surface of moringa oleifera interfered with cell membranes of bacterial strains. The FMO penetrated through cell membranes, and since *Moringa oleifera* consist of phytochemicals *Tannins*, *alkaloids* and *flavonoids*. These phytochemical substances present in *Moringa oleifera* tends to damage bacterial strains DNA leading to cell death.

4.9 Conclusions

In conclusion, we can report that amine functional groups were successfully grafted on the surface of *Moringa oleifera* (MO), and this was confirmed by FTIR. It was observed that the introduction of amine groups onto *Moringa oleifera* enhanced the adsorption capacity towards the removal of Cr(VI). Based on adsorption studies, it was found that functionalised *Moringa oleifera* (FMO) was more effective in removing Cr(VI) at low pH <2. Adsorption kinetics followed pseudo second order, suggesting that the adsorption mechanism between Cr(VI) and FMO was more of chemical behaviour than physical. It was noticed that the removal of Cr(VI) by FMO was selective towards Cr(VI) in the presence of cation metals. The FMO as an adsorbent was able to be reused for 3 cycles without losing its stability. Based on anti-bacterial studies, it was found that FMO was not active against the model pollutants. On real water samples, the FMO showed some activity.

4.10 References

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CHAPTER 5

REMOVAL OF CHROMIUM(VI) FROM WATER USING FUNCTIONALISED *MORINGA OLEIFERA* INCORPORATED WITH MAGNETITE NANOPARTICLES

Abstract

Chromium(VI) has been reported as one of the most toxic heavy metals in the environment. Drinking water containing high concentrations of Cr(VI) can result in a negative impact to human and animal health life's. Therefore, the present study is focused on removing this toxic metal from water. Herein, we investigate magnetic functionalised *Moringa oleifera* ($\text{Fe}_3\text{O}_4/\text{FMO}$) as an adsorbent for the removal of Cr(VI) from aqueous solution. The aim of incorporating the magnetite nanoparticles was for the recovery of the adsorbent ($\text{Fe}_3\text{O}_4/\text{FMO}$) after the adsorption of Cr(VI) from the solution by use of an external magnet. The $\text{Fe}_3\text{O}_4/\text{FMO}$ adsorbent was characterized using the following techniques, XRD, FTIR, SEM, BET, TGA and Zeta potential. FTIR results showed new developed intense peak at 685.6 cm^{-1} for Fe-O stretching, indicating successful incorporation of Fe_3O_4 nanoparticles onto FMO. The removal of chromium(VI) by $\text{Fe}_3\text{O}_4/\text{FMO}$ was carried out by varying different parameters such as pH, dosage, contact time and initial concentration. Based on the adsorption studies, it was found that pH had a crucial role in Cr(VI) removal. The adsorbent (0.15 g) removed more than 90 % of 100 mg/L Cr(VI) from the standard solution at pH (2). Adsorption kinetics studies obeyed pseudo second order model, suggesting electrostatic interaction mechanism between $\text{Fe}_3\text{O}_4/\text{FMO}$ and Cr(VI). Therefore, $\text{Fe}_3\text{O}_4/\text{FMO}$ is a promising magnetic adsorbent for removal of Cr(VI) from wastewater. The correlation coefficient (R^2) obtained from Cr(VI) calibration curve was 0.9999, with a limit of quantification (LOQ) and limit of detection (LOD) of 0.1486 and 0.446 mg/L, respectively.

Keywords: Magnetite (Fe_3O_4), Magnetic functionalised *Moringa oleifera* ($\text{Fe}_3\text{O}_4/\text{FMO}$), Chromium(VI), Adsorption studies, Kinetics.

5.1 Introduction

The release of heavy metals in the environment due to rapid industrialization and urbanization poses serious threats to human and animal life's. One of the heavy metals that is a serious health problem is chromium [1]. In aqueous solution, chromium exist in two oxidation states, as trivalent form [Cr(III)] or hexavalent form [Cr(VI)]. Cr(III) is an essential trace element which is required by our bodies for metabolic activities. On the other hand, Cr(VI) is considered as the most toxic element since it has a high mobility and solubility, as it enters through our cell membranes as CrO_4^{2-} or HCrO_4^- to oxidize biomolecules [2]–[4]. Therefore, World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have set the limit for Cr(VI) to be 0.10, 0.25 and 0.05 mg/L in surface water, industrial water and drinking water, respectively [5], [6]. In order to comply with the recommended limit, it is necessary that wastewater from industries are treated to reduce the high Cr(VI) concentration to the allowed permissible limit before being released into the environment. Several water treatment techniques including ion exchange, membrane separation, precipitation, coagulation and adsorption have been applied for Cr(VI) removal from water [7]–[10]. Unfortunately, a majority of these techniques suffer from several drawbacks such as incomplete Cr(VI) removal, high operational cost, low selectivity, not easy to operate and require trained personnel [7]–[10]. Adsorption technique on the other hand has been identified as a better alternative method for Cr(VI) removal because it is user friendly, less costly, highly efficient and the adsorbent can be generated [11]–[13].

In recent years, agricultural waste materials (i.e. rice barn, rice husk, corn stalk and sugarcane bagasse) have gained much attention as cheap and readily available adsorbents for the heavy metals remediation. However, these waste materials have been reported to have a poor adsorption capacity towards anion metals. Many researchers have shown that through chemical modification with amine groups their adsorption capacity tends to be enhanced [14]. For example, Chen *et al.* [14], have

reacted corn stalk with epichlorohydrin and triethylamine using diethylenetriamine as a modifier. Based on the results, the modified corn stalk (MCS) had a point zero charge (pH_{pzc} of 6.5) greater than of the raw corn stalk (RCS) (pH_{pzc} of 2.9), which suggested that the surface of the MCS contained more positively charged functional groups as compared to RC. The MCS was more effective for Cr(VI) removal even at approximately neutral pH, whereas RC was effective in acid media, at $\text{pH} < 2.9$. Another study reported by Marshall and Wartelle quaternized waste materials (i.e. rice hulls, corn stoves and almond shell) with *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride [15]. The quaternized waste materials were investigated for the removal of phosphate, arsenate, selenite and chromate from water. The results showed that quaternized corn stoves had a good adsorption capacity towards selenite, chromate and arsenate.

In this study, *Moringa oleifera* was functionalised with amine groups to enhance the adsorption capacity towards Cr(VI) removal. *Moringa oleifera* was reacted with epichlorohydrin and triethylamine in the presence of dimethylformamide (DMF) using diethylamine as a modifier. The functionalised *Moringa oleifera* (FMO) was incorporated with iron oxide nanoparticles (Fe_3O_4) to form a magnetic adsorbent ($\text{Fe}_3\text{O}_4/\text{FMO}$). The advantage of magnetic adsorbent $\text{Fe}_3\text{O}_4/\text{FMO}$ is that it can serve as an adsorbent for removal of contaminants from water and it can be removed from aqueous media after adsorption process using an external magnet.

5.2 Experimental

5.2.1 Reagents

All chemicals used for preparation of adsorbents and batch adsorption studies were of analytical grade. Potassium dichromate (97 % purity), Sodium hydroxide pellets (97 % purity), Ethanol (99.5 %), Methanol (99 %), Ammonia solution (35 %), Hydrochloric acid (37 %), 1,5-Diphenylcarbazide (99% purity), Sulphuric acid (99 %), Ferric chloride hexahydrate (≥ 98 % purity), *N,N*-Dimethylformamide (99.8 %), Epichlorohydrin (99 %), Diethylamine (≥ 99.5 %), and Triethylamine (≥ 99.5 %) were obtained from Sigma-Aldrich, South Africa.

5.2.2 Preparation of Fe₃O₄ nanoparticles, FMO and Fe₃O₄/FMO

Fe₃O₄ nanoparticles were prepared by dissolving 4.05 g FeCl₃.6H₂O in 50 mL of deionised water and mixed with 0.5 mL HCl (0.2M) and ultra-sonicated for 5 min at room temperature. Then 20 mL of 0.3 M NaSO₃ was added to the solution mixture, which resulted in red color. The solution mixture was left for a couple of minutes until the color returned to yellow. Thereafter, the yellow solution was added to 400 mL of deionised water containing 60 mL of 25 % ammonia solution and was followed by ultra-sonication for 30 min. The resultant Fe₃O₄ nanoparticles were washed with 50/50 % ethanol and deionised water [16].

FMO was prepared following the same method used in **chapter 4 (Section 4.2.2)**. For preparation of a magnetic adsorbent, magnetite was synthesized in the presence of FMO via co-precipitation method. Here, 4.05 g of FeCl₃.6H₂O was dissolved in 50 mL deionised water and mixed with 0.5 mL of 0.2 M HCl and ultra-sonicated for 5 min at room temperature. Then 20 mL of 0.3 M NaSO₃ was added to the solution mixture which resulted in a red color. The solution mixture was left for a couple of minutes until it returned to a yellow color, then 2 g of functionalised *Moringa oleifera* (FMO) was added to the yellow solution. Thereafter, the yellow solution was added to 400 mL deionised water containing 60 mL of 25 % ammonia solution and followed by ultra-sonication for 30 min. The resulted Fe₃O₄/FMO was then washed with 50/50 % ethanol and deionised water [16].

5.2.3 Material characterizations

The characterization techniques used for confirmation of magnetic functionalised *Moringa oleifera* in this section were described in **chapter 4 (Section 4.2.3)**.

5.3 Batch adsorption studies

The same batch adsorption conditions used in **chapter 4 (Section 4.3)** were also used in this study.

5.3.1 Adsorption kinetics

In this study the adsorption mechanism between Cr(VI) and Fe₃O₄/FMO were investigated using two kinetics models, pseudo first and pseudo second order model.

5.3.1.1 Pseudo-first-order

Eq (1) below shows the linear equation for pseudo first order model [18].

$$\ln(q_e - q_t) = \ln(q_e - k_1 t) \quad (1)$$

Where q_e (mg/g) is the equilibrium adsorption capacity, q_t (mg/g) is the adsorption capacity at interval time(t) and k_1 represent the pseudo first order constant

5.3.1.1 Pseudo-Second-order

The linear equation shown in Eq (2) is for pseudo second order model. This model is based on the assumption that the adsorption mechanism between adsorbate and adsorbent is via chemical bonding (chemisorption) [19].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

Where k_2 (g/mg min) is pseudo second order rate constant. The maximum adsorption capacity value at equilibrium (q_e) and at certain time (q_t)

5.3.2 Cr(VI) analysis using UV-vis spectrophotometry

Uv-vis spectrophotometer was used for determination of Cr(VI) concentration from aqueous solution using 1.5-Diphenylcarbazide [17].

5.4 Results and discussions

5.4.1 Characterisation of magnetic functionalised *Moringa oliefera*

5.4.1.1 FE-SEM

Figure 5.1 displayed surface morphology of prepared adsorbents (MO, FMO, Fe_3O_4 , and $\text{Fe}_3\text{O}_4/\text{FMO}$). As described in **chapter 4**, the surface morphology of MO had some irregular shape and sizes, while for FMO the external surface appeared to be rough after chemical modification. According to **Figure 5.1(d)**, the magnetite nanoparticles appeared to be spherical in shape covering the external surface of FMO. The spherical nanoparticles on the surface of FMO were not well dispersed but highly agglomerated.

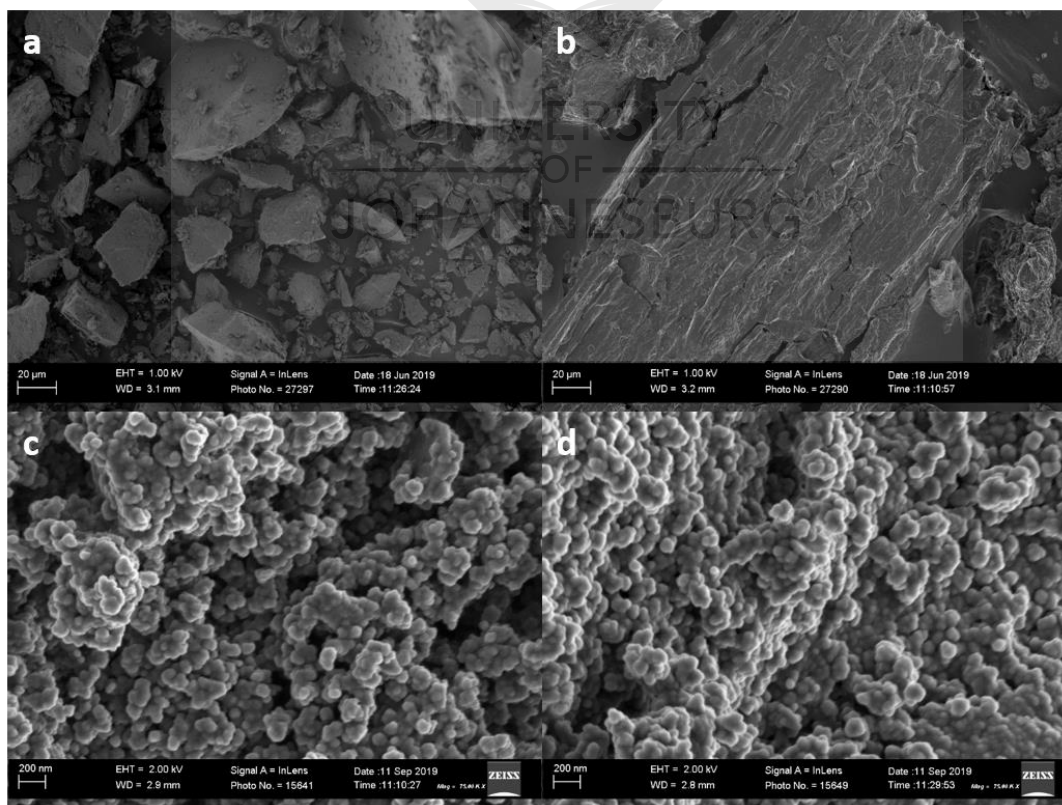


Figure 5. 1: FE-SEM images of (a) MO, (b) FMO, (c) Fe_3O_4 and (d) $\text{Fe}_3\text{O}_4/\text{FMO}$.

5.4.1.2 BET surface analysis

The surface area of the Fe_3O_4 , MO, FMO and $\text{Fe}_3\text{O}_4/\text{FMO}$ was measured using BET surface analyser. MO surface area was $1.9198 \text{ m}^2/\text{g}$. As described in **chapter 4**, the successful introduction of amine groups onto MO resulted in decrease surface area from 1.9198 to $1.0942 \text{ m}^2/\text{g}$. In **Table 5.1**, it is shown that successful incorporation of magnetite onto FMO surface resulted with a huge increase in surface area from 1.0942 to $30.6387 \text{ m}^2/\text{g}$. The average pore size of FMO also increased from 13.770 to 25.0386 nm upon successful incorporation of magnetite nanoparticles. **Figure 5.2** showed nitrogen adsorption-desorption isotherms of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{FMO}$ which exhibited different macroporous sizes. According to International Union of Pure and Applied Chemistry (IUPAC), these hysteresis loops of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{FMO}$ are classified as type II.

Table 5. 1: Physical properties of the adsorbents.

Adsorbents	BET surface area (m^2/g)	Highest pore volume (cm^3/g)	Average pore sizes (nm)
MO	1.9198	0.003425	7.1353
FMO	1.0942	0.003767	13.770
Fe_3O_4	52.2834	0.210120	16.0754
$\text{Fe}_3\text{O}_4/\text{FMO}$	30.6387	0.191788	25.0386

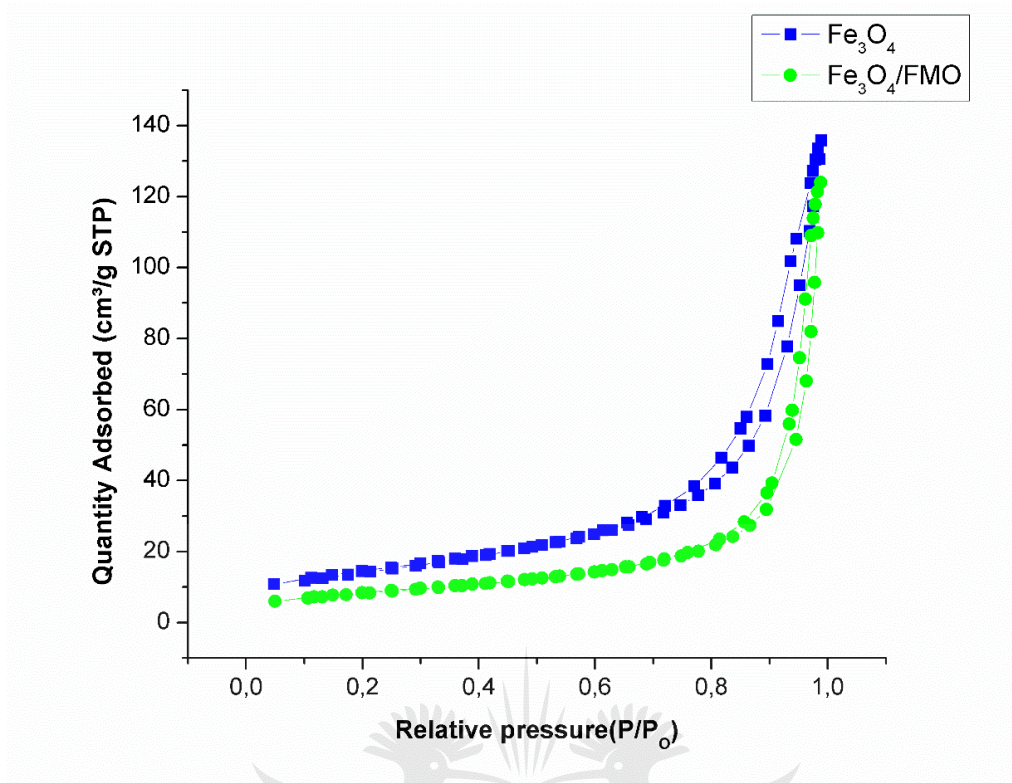


Figure 5. 2: Nitrogen adsorption/desorption isotherms for Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{FMO}$

5.4.1.3 XRD analysis

Figure 5.3 illustrated XRD spectrum of $\text{Fe}_3\text{O}_4/\text{FMO}$, which confirmed that the introduction of iron oxide (Fe_3O_4) onto FMO resulted in crystallinity of the composite. The XRD diffraction peaks at 2θ values of 30.21 , 35.53 , 43.31 , 54.50 , 57.30 , 62.90 and 74.3° were corresponding to miller index (220), (311), (400), (422), (511), (440) and (533), respectively which are representative of the iron oxide formation [20], [21]. It was observed that there was an obvious broad peak at 2θ value 20° with miller index (002) for FMO on the composite.

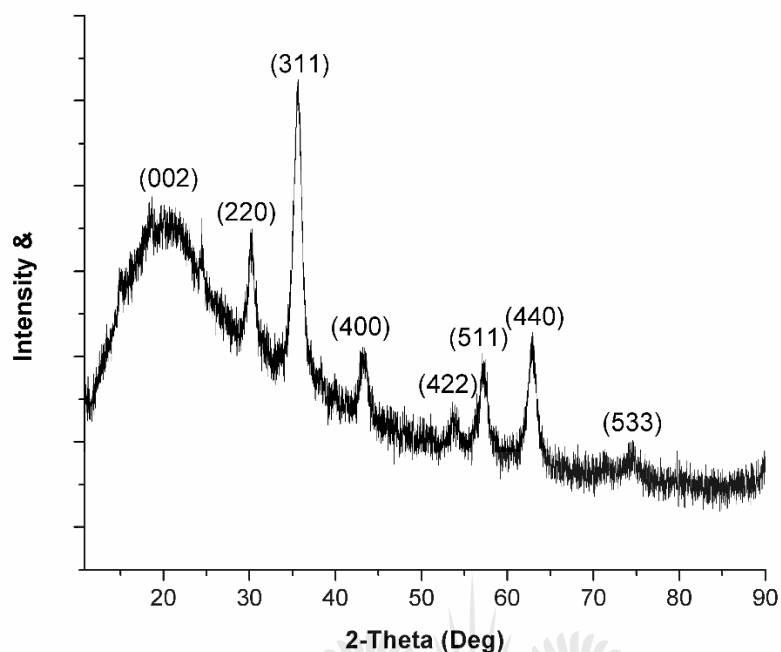


Figure 5. 3: XRD diffraction patterns for Fe₃O₄/FMO

To confirm the grafting of amine functional groups onto *Moringa oliefera* (MO) and the incorporation of magnetite nanoparticles, FTIR analysis were conducted.

5.4.1.4 FTIR analysis

Figure 5.4 presented the Infrared (IR) spectra's of MO, FMO, Fe₃O₄ and Fe₃O₄/FMO. As discussed in **chapter 4 (Section 4.1.4.4)**, the IR spectra for FMO displayed peaks at 1647 and 1030 cm⁻¹ which attributed to N-H stretching band of amino groups, while the peaks at 3369-3299, 1351, 1621 and 1020 were ascribed to -OH or -NH, C-N, C=O and C-O groups, respectively. The IR spectra of magnetite (Fe₃O₄) indicated a very sharp intense peak at the fingerprint region (685.6 cm⁻¹) which is attributed to Fe-O vibration [13]. It can be observed that the IR bands for FMO are preserved in the composites after successful incorporation of magnetite nanoparticles. Therefore, the incorporation of magnetite did not destroy FMO structure.

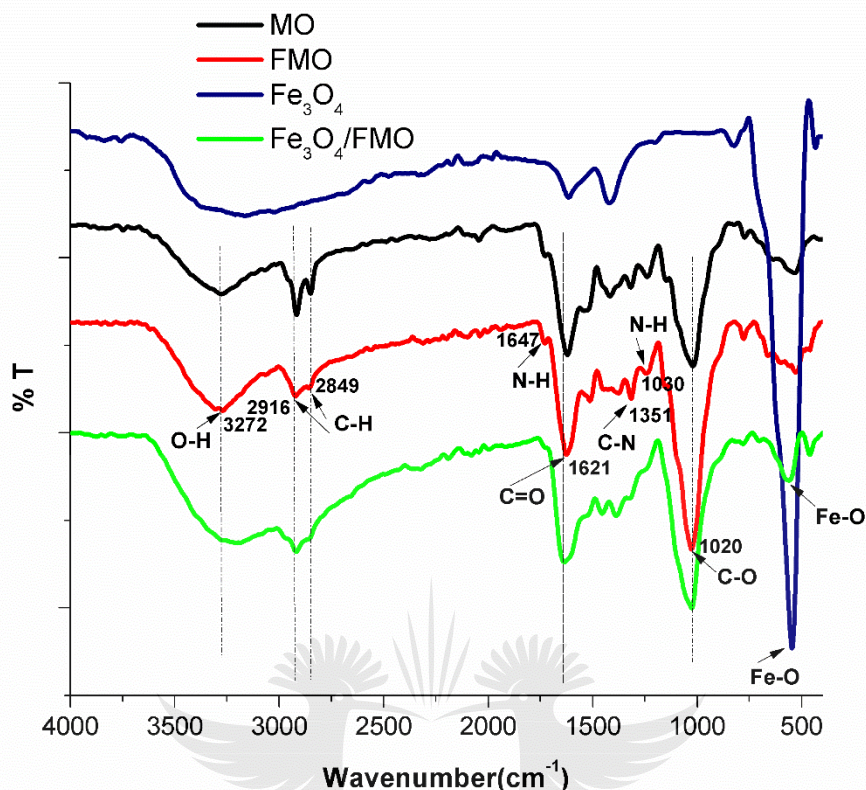


Figure 5. 4: IR spectra's of MO, FMO, Fe₃O₄ and Fe₃O₄/FMO

Upon confirming the formation of Fe₃O₄/FMO and identifying the functional groups present, thermal stability studies were conducted.

5.4.1.5 Thermal analysis

In this study, TGA was used to determine thermal stabilities of Fe₃O₄, MO, FMO and Fe₃O₄/FMO. The TGA analysis for MO and FMO were well described in **chapter 4** in details. As described in **chapter 4**, both adsorbents (MO and FMO) started to decompose at 210 until 350 °C. The TGA curve of magnetite (**Figure 5.5**) illustrated that it is the most thermal stable material compared to MO and FMO. The TGA curve of Fe₃O₄/FMO is more similar to the parent material (FMO). However, the incorporation of magnetite onto FMO enhanced the thermal stability of the composites since it was noticed that weight loss for Fe₃O₄/FMO was minimized. The

enhancement of the thermal stability also confirmed successful incorporation of magnetite nanoparticles onto FMO.

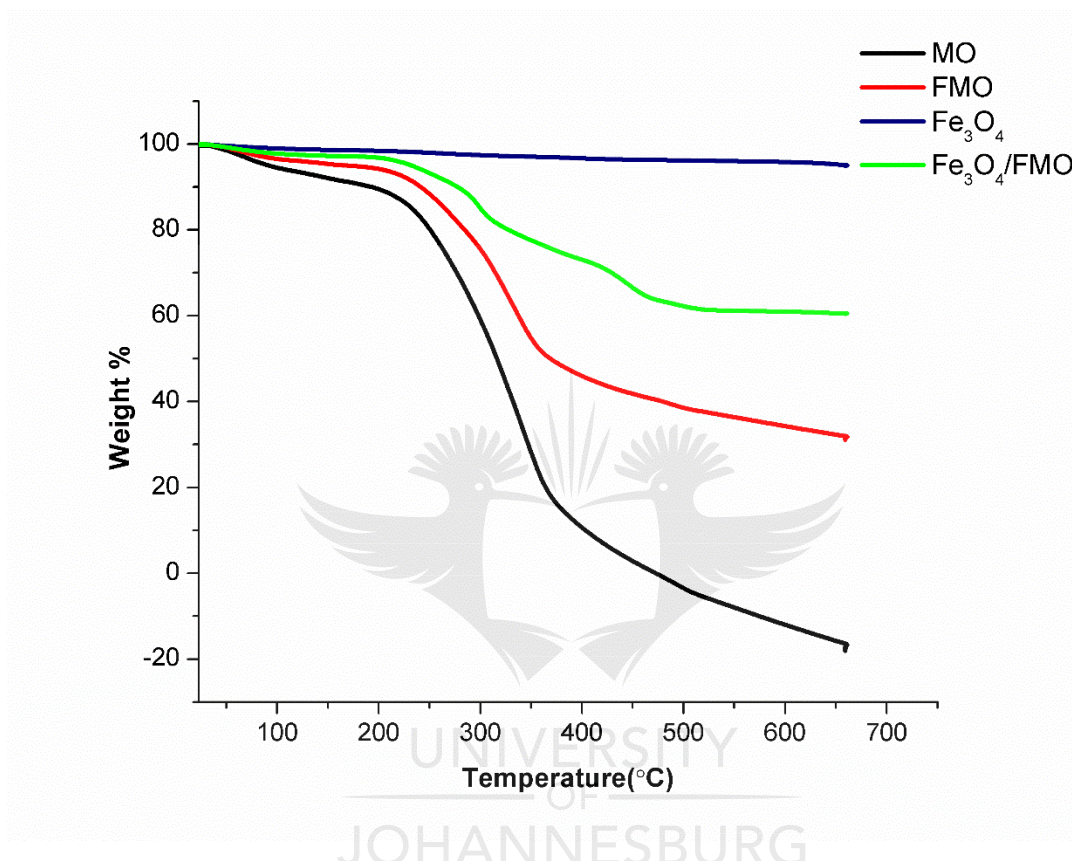


Figure 5. 5: TGA curves of MO, FMO, Fe₃O₄ and Fe₃O₄/FMO

Figure 5.6 displayed derivative thermalgravimetric (DTG) curves of MO, FMO, Fe₃O₄ and Fe₃O₄/FMO. The TGA derivatives corresponded well with TGA results. The DTG curve's for MO and FMO confirmed a huge endothermic peak at approximately 350 °C. These peaks indicated thermal decomposition of both adsorbents. The DTG curve of Fe₃O₄/FMO displays two distinctive endothermic peaks at approximately 300 and 450 °C, which confirmed the weight losses related to decomposition of the composites.

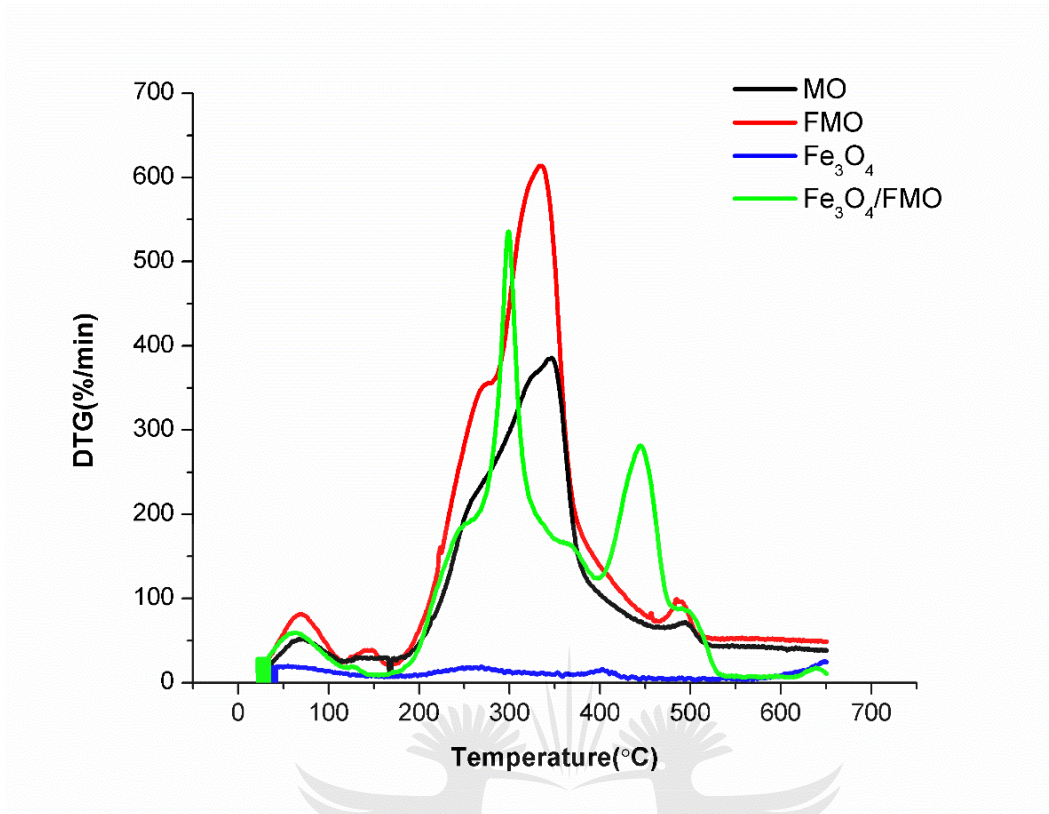


Figure 5. 6: DTG curves of Fe₃O₄, MO, FMO and Fe₃O₄/FMO.

5.4.1.6 Zeta potential

The surface charge of the prepared adsorbents (Fe₃O₄, MO, FMO, and Fe₃O₄/FMO) were measured using Zetasizer Nano ZS-Malvern. As shown in **Figure 5.7**, the point zero charges of the materials were measured at different pH values of the solutions (2-10). It can be observed that after chemical modification of MO with amine groups the pH zero point charge increased from 2.0 to 4.0, suggesting that FMO contains more positively charged functional groups compared to MO. This is an advantage because in aqueous solutions, Cr(VI) exist in the form of anions (Cr₂O₇²⁻, HCrO₄⁻ and Cr₂O₇²⁻). A similar behaviour was observed in this study when magnetite was successfully incorporated onto FMO, the pH zero point (pH_{zpc}) increased from 4.0 to 5.0. The obtained point zero charge (pH_{zpc}) was higher than that of modified activated carbon [22], coffee husk [23], oxidized corn hob [24] and thuja orientalis [25].

As depicted in **Figure 5.8**, the maximum Cr(VI) removal was observed at pH <5 due to attraction of positively charged adsorbent and negatively charged ions of Cr(VI) in the form of $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- .

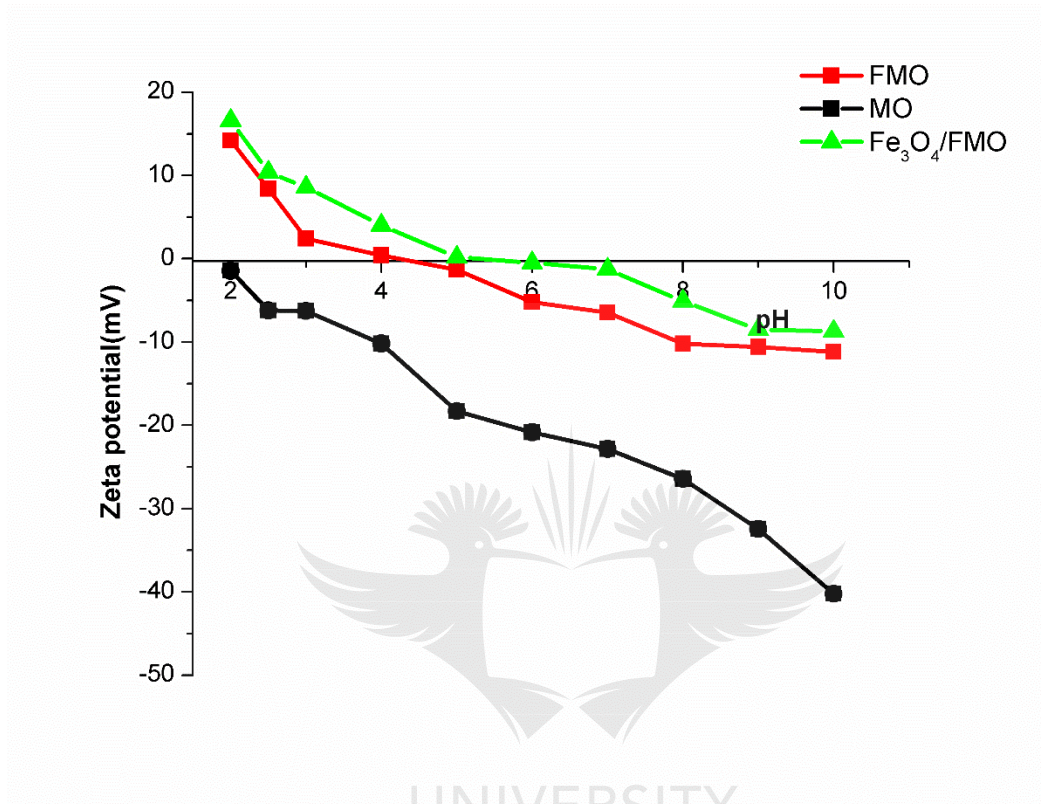


Figure 5. 7: Zeta potential of MO, FMO and Fe₃O₄/FMO as a function of pH.

5.5 Batch adsorption studies

5.5.1 Influence of pH on Cr(VI) uptake

This experiment was conducted to investigate whether Cr(VI) removal by Fe₃O₄/FMO was pH dependent. **Figure 5.8** shows the influence of pH on adsorption of Cr(VI) by magnetic functionalised *Moringa oleifera* (Fe₃O₄/FMO). It can be noticed that high removal efficiency was obtained at low pH (2). The same results were observed when using functionalised *Moringa oleifera* (FMO) as an adsorbent. The Fe₃O₄/FMO was able to remove about 90.1 % of Cr(VI) whereas FMO removed 80.1

% of Cr(VI) in the solution with the same pH. The reason for high Cr(VI) removal at low pH could be due to the fact that the surface of the adsorbent was protonated hence making the adsorbent surface positively charged. Therefore, the positively charged adsorbent tends to interact with Cr(VI) oxy anions ($\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^-) via electrostatic interaction [26].

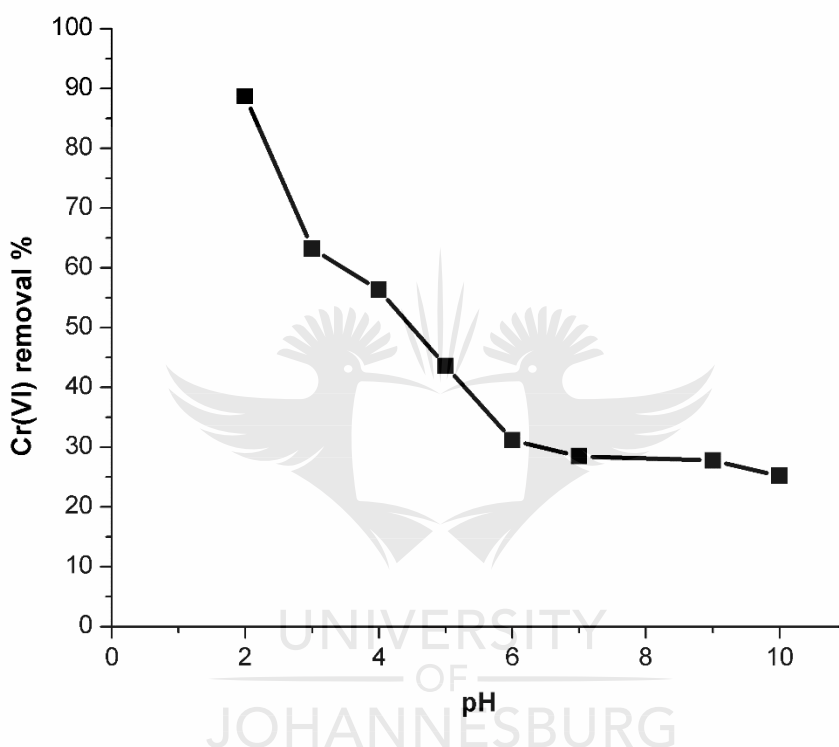


Figure 5. 8: Influence of pH on Cr(VI) removal using $\text{Fe}_3\text{O}_4/\text{FMO}$.

5.5.2 Effect of dosage

Figure 5.9 displayed Cr(VI) removal percentage with respect to different amount of magnetic functionalised *Moringa oleifera* ($\text{Fe}_3\text{O}_4/\text{FMO}$). It can be noticed that Cr(VI) removal percentage increased with an increase in $\text{Fe}_3\text{O}_4/\text{FMO}$ dosage. The same trend was observed when using FMO as the adsorbent in **chapter 4**. When using the functionalised *Moringa oleifera* (FMO) it was noticed that it required more than 0.15 g to remove more than 94 % of Cr(VI) from aqueous solution. In comparison to $\text{Fe}_3\text{O}_4/\text{FMO}$, only 0.15 g $\text{Fe}_3\text{O}_4/\text{FMO}$ was able to remove about 94 % of Cr(VI) from

aqueous solution. Therefore, it means that a very small amount of $\text{Fe}_3\text{O}_4/\text{FMO}$ is required to remove high amount $\text{Cr}(\text{VI})$ unlike FMO.

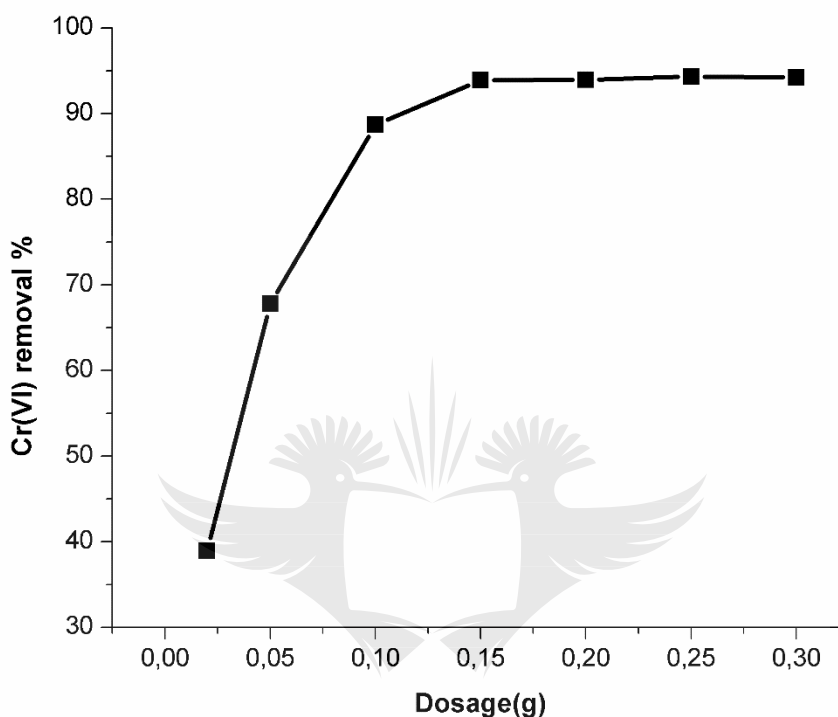


Figure 5. 9: Effect of dosage on the removal of $\text{Cr}(\text{VI})$ using $\text{Fe}_3\text{O}_4/\text{FMO}$.

5.5.3 Effect of contact time

To examine the effect of time for removal of $\text{Cr}(\text{VI})$, sorption studies of $\text{Cr}(\text{VI})$ on magnetic functionalised *Moringa oleifera* ($\text{Fe}_3\text{O}_4/\text{FMO}$) were conducted at different time intervals (from 5 until 90 min). **Figure 5.10** displayed the effect of time for removal of $\text{Cr}(\text{VI})$ using $\text{Fe}_3\text{O}_4/\text{FMO}$ as an adsorbent. It was noticed that adsorption equilibrium was attained at an earlier stage as compared to when FMO was used as an adsorbent. The equilibrium was reached at different times using FMO and $\text{Fe}_3\text{O}_4/\text{FMO}$. It was observed that FMO and $\text{Fe}_3\text{O}_4/\text{FMO}$ required about 85 and 25 min, respectively, to reach adsorption equilibrium. According to the study conducted by Sasikala *et al.* [27] for removal of $\text{Cr}(\text{VI})$ by raw *Moringa oleifera*, 120 min was

reported as the adsorption equilibrium. Noticeably, $\text{Fe}_3\text{O}_4/\text{FMO}$ required less contact time (25 min) as compared to FMO and MO. Therefore, in this study 25 min was the optimum contact time and used for later studies.

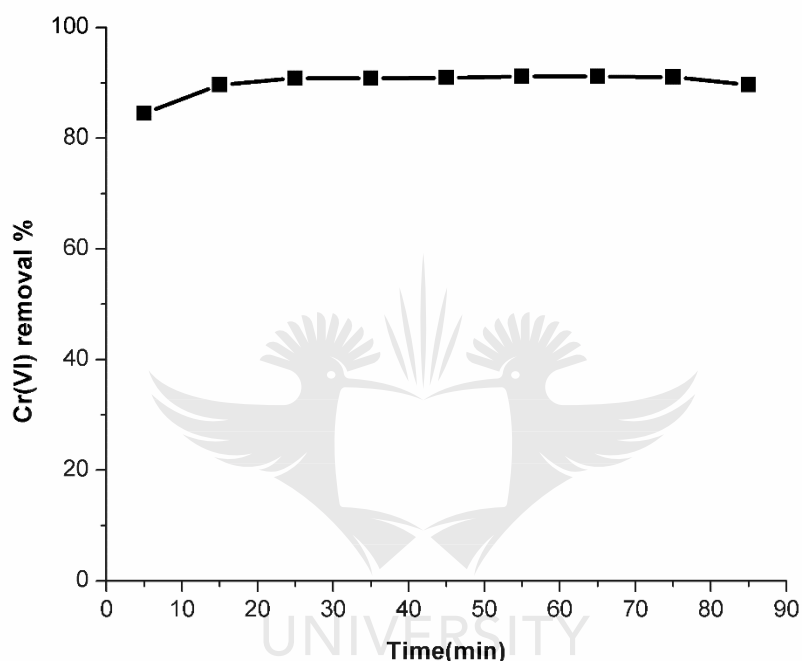


Figure 5. 10: Effect of contact time on Cr(VI) removal by $\text{Fe}_3\text{O}_4/\text{FMO}$.

5.5.4 Effect of Cr(VI) concentration

The experimental studies for the effect of initial concentration using magnetic adsorbent were conducted at different solutions containing 20-100 mg/L Cr(VI) with optimum conditions (pH 2, dose of 0.15 g $\text{Fe}_3\text{O}_4/\text{FMO}$ and contact time of 25 min).

Figure 5.11 indicated the effect of initial concentration for adsorption of Cr(VI) by magnetic adsorbent ($\text{Fe}_3\text{O}_4/\text{FMO}$). It can be observed that the removal percentage of Cr(VI) decreased with increase of Cr(VI) concentration, and this could be due to saturation of available adsorption sites on the surface of the adsorbent by Cr(VI). Similar behaviour was observed when using both *functionalised Moringa oleifera*

(FMO) and raw *Moringa oleifera* (MO) [26]. It was noticed that both FMO and Fe₃O₄/FMO were able to remove 20 mg/L Cr(VI) completely from aqueous solution. At higher concentration (100 mg/L), Fe₃O₄/FMO was more effective for Cr(VI) removal as compared to FMO since it was able to remove high amount of Cr(VI). This could be due to incorporation of magnetite onto FMO which enhanced the adsorption capacity towards the removal of Cr(VI). At 100 mg/L Cr(VI), Fe₃O₄/FMO was able to remove more than 95 % of Cr(VI) whereas FMO removed less than 95 % of Cr(VI).

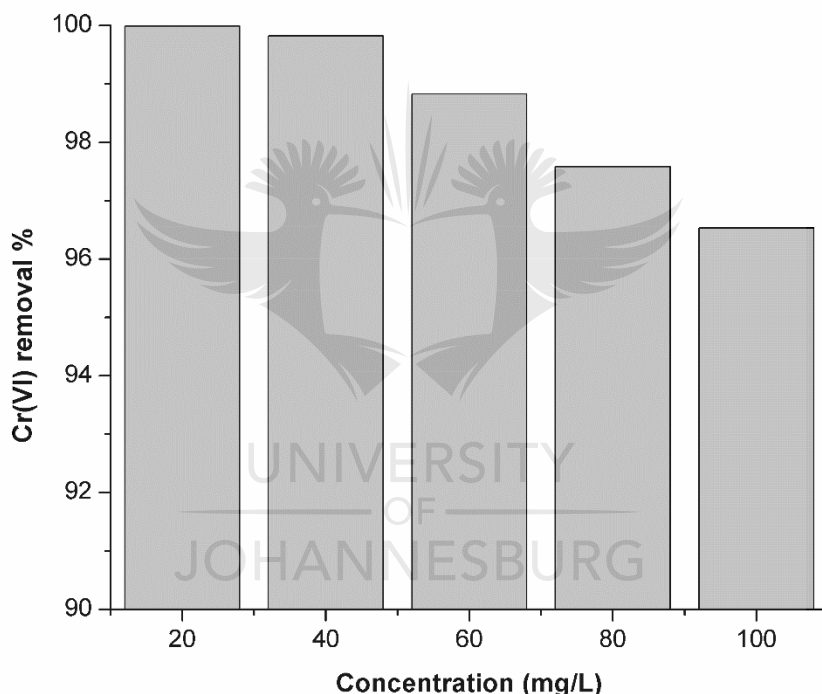
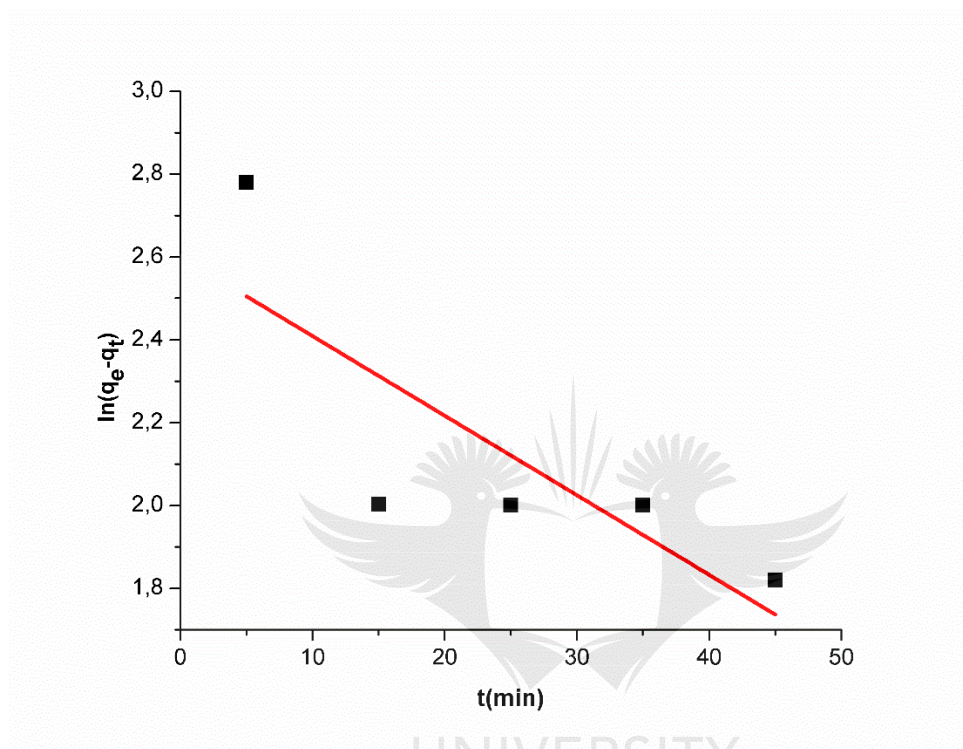


Figure 5. 11: Effect of concentration on Cr (VI) removal by Fe₃O₄/FMO.

5.5.5 Adsorption kinetics

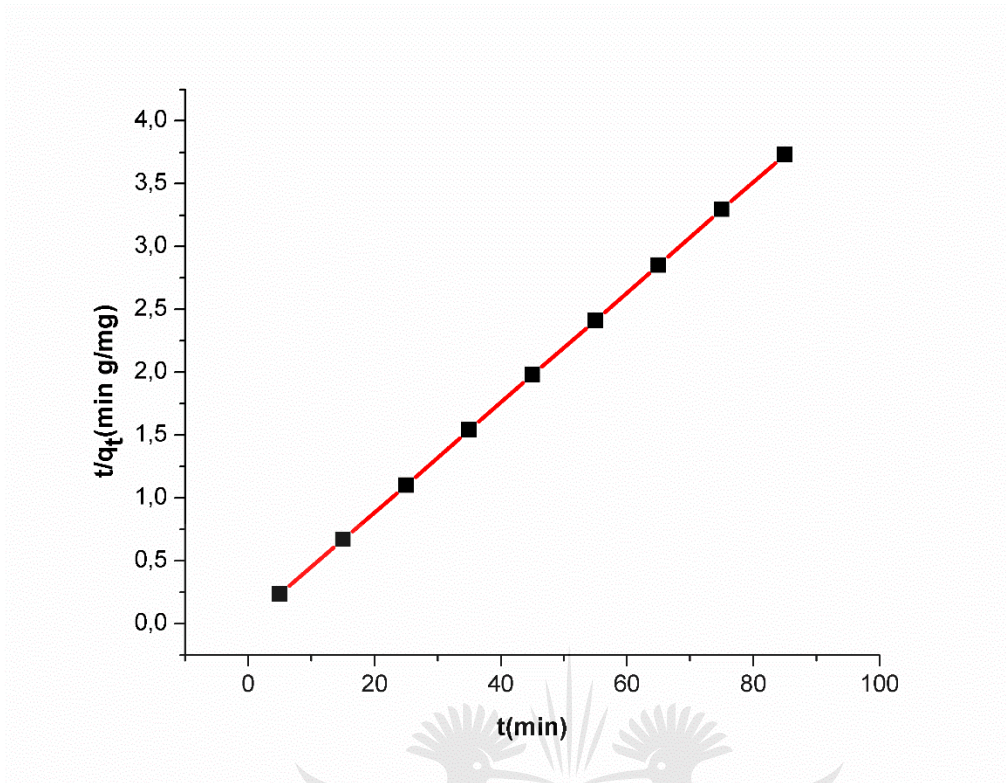
Table 5.2 showed all kinetic parameters values obtained from the linear plot in **Figure 5.12**. The correlation coefficient (R^2) determines which model fit with experimental data. The experimental data fitted well with pseudo second order since its correlation coefficient was greater ($R^2 = 0.99999$) as compared to pseudo first

order model ($R^2 = 0.53454$). This suggested that the adsorption mechanism between Cr(VI) and $\text{Fe}_3\text{O}_4/\text{FMO}$ was through chemical interaction (chemisorption).



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(b)

Figure 5. 12: (a) Linear Pseudo-first-order and (b) Pseudo-second-order model for Cr(VI) adsorption by Fe₃O₄/FMO.

Table 5. 2: Kinetics parameters obtained from linear plots.

Pseudo first order		Pseudo second order	
Linear		Linear	
Q_e	0.981	Q_e	1.013
K₁	0.0192	K₂	0.0437
R²	0.53454	R²	0.99999
Degree of freedom	3	Degree of freedom	7
Number of points analysed	5	Number of points analysed	9

5.5.6 Influence of co-existing ions on Cr(VI) removal

This experiment was conducted to investigate the selectivity of magnetic functionalised *Moringa oleifera* ($\text{Fe}_3\text{O}_4/\text{FMO}$) towards Cr(VI) removal in the presence of other competing ions. For this study, a few selected ions such as Zn^{2+} , Cu^{2+} , Ni^{2+} , NiO_3^- , SO_4^{2-} and Cl^- were investigated for their influence during Cr(VI) adsorption. The initial concentration for Cr(VI) was kept at 20 mg/L. **Figure 5.13** illustrated the removal of Cr(VI) in the presence of these other ions. Cr(VI) removal was not affected in the presence of each of the cations that were present in solution which therefore suggested that $\text{Fe}_3\text{O}_4/\text{FMO}$ was selective towards Cr(VI) in the presence of cations. Similar behaviour was observed when using functionalised *Moringa oleifera* (FMO) as an adsorbent. As depicted in **Figure 5.7**, the surface of $\text{Fe}_3\text{O}_4/\text{FMO}$ was positively charged which therefore made it impossible to attract positively charged ions (metal cations) via electrostatic interaction. The Cr(VI) removal in the presence anions was affected as indicated in **Figure 5.13**. In the presence of NiO_3^- and Cl^- , the Cr(VI) removal was slightly affected whereas in the case of SO_4^{2-} at higher concentration (100 mg/L), Cr(VI) removal was significantly affected since the percentage removal decreased from 100 to 93.02 %. The same behaviour was observed when FMO was used as adsorbent, the Cr(VI) removal percentage in the presence of SO_4^{2-} (100 mg/L) decreased from 100 to 95.02 %. This significant effect could be due to similar structure between Cr(VI) molecules and SO_4^{2-} which resulted in competing of adsorption sites on the surface of $\text{Fe}_3\text{O}_4/\text{FMO}$ [29].

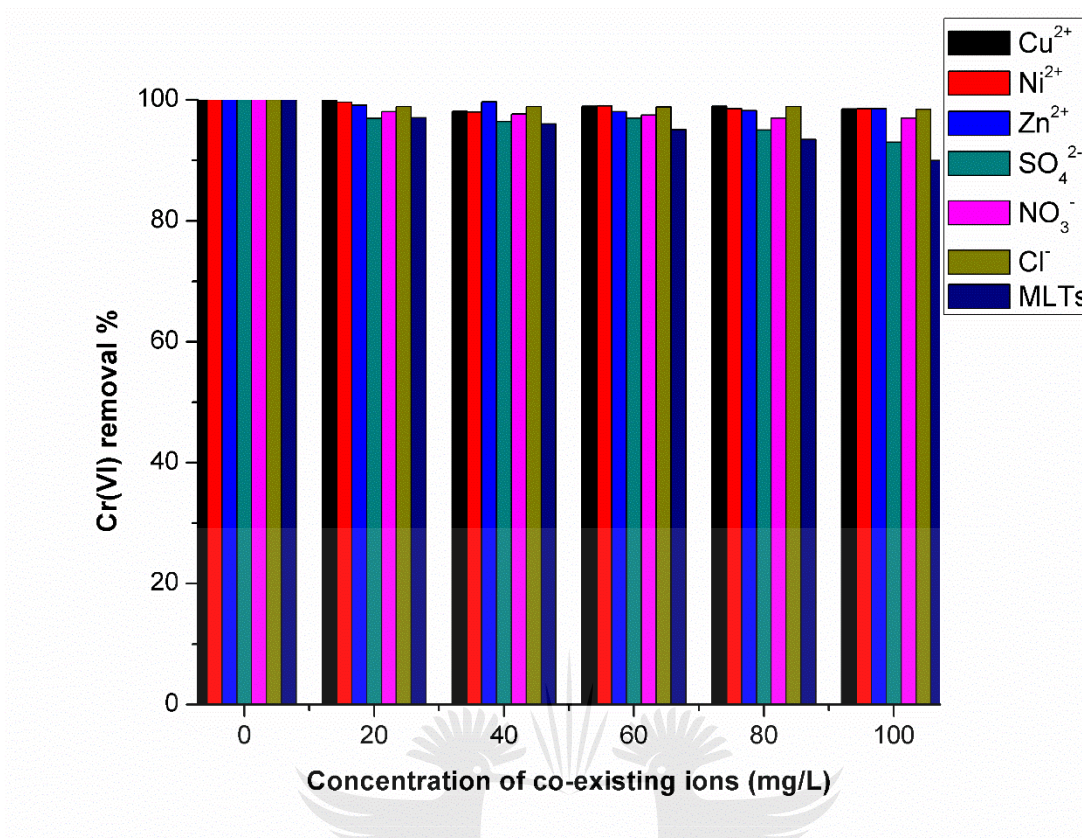


Figure 5. 13: Cr(VI) removal in the presence of co-existing ions.

5.5.7 Reusability studies

To investigate the stability of the adsorbent ($\text{Fe}_3\text{O}_4/\text{FMO}$) for Cr(VI) removal, adsorption studies were conducted for several number of cycles (7). In this study, the adsorbent was washed with deionised water after adsorption and reused. **Figure 5.14** illustrated the sorption efficiency of the regenerated adsorbent ($\text{Fe}_3\text{O}_4/\text{FMO}$) after 7 adsorption cycles. The Cr(VI) removal efficiency decreased with increase in adsorption cycles. The same trend was observed when FMO was used as adsorbent. This could be to the fact that as adsorbent was regenerated after several adsorption cycles, its re-usability decreased [28]. As it can be noticed from **Figure 5.14**, the Cr(VI) removal was slightly reduced after 3 adsorption cycles. From the 4th cycle onwards, the removal efficiency dramatically decreased from 87.64 to 68.2 %.

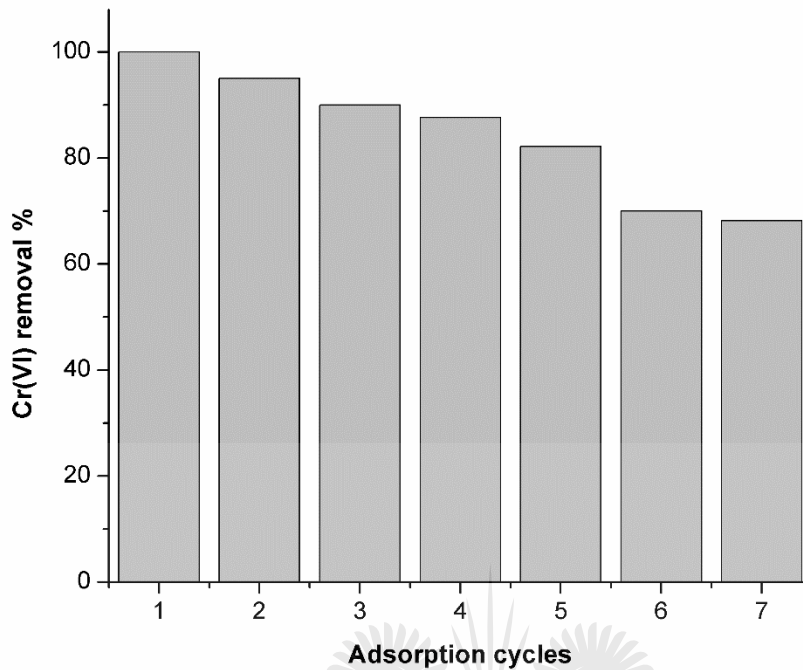


Figure 5. 14: Reusability of the adsorbent ($\text{Fe}_3\text{O}_4/\text{FMO}$).

5.6 Real water analysis

Figure 5.15 indicated the adsorption of spiked Cr(VI) from real water sample using magnetic functionalised *Moringa oleifera* ($\text{Fe}_3\text{O}_4/\text{FMO}$) under optimized conditions. It can be observed that the spiked initial concentration of Cr(VI) was 20 mg/L and after adsorption the Cr(VI) concentration reduced to 2 mg/L. Therefore, this meant that $\text{Fe}_3\text{O}_4/\text{FMO}$ removed 90% of Cr(VI) from real water sample. In comparison to FMO, only 70 % of Cr(VI) was removed from spiked water sample.

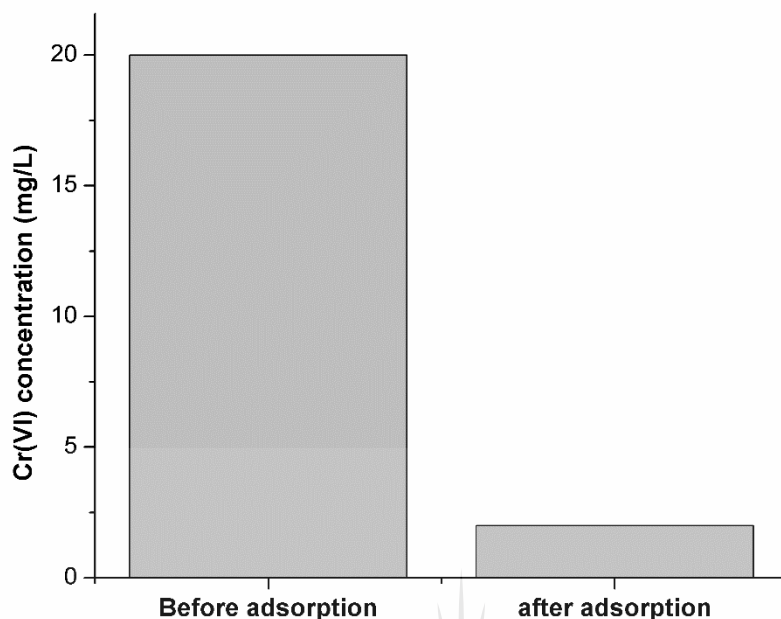


Figure 5. 15 : Cr(VI) adsorption by Fe₃O₄/FMO from real water sample.

5.7 Analytical figures of merit

The limit of detection (LOD) and limit of quantification (LOQ) obtained from linear calibration curve of Cr(VI) with correlation coefficient (R^2) 0.9999 were 0.1486 and 0.446 mg/L, respectively. The same LOQ and LOQ were obtained from **chapter 4 (Section 4.7)**

5.8 Conclusions

In this study, Fe₃O₄/FMO was prepared and served as an adsorbent for Cr(VI) removal from aqueous solution. The successful existence of Fe₃O₄/FMO was confirmed by XRD, FTIR, and SEM analysis. The highest Cr(VI) removal by Fe₃O₄/FMO was obtained at low pH (2). The adsorption process fitted very well with pseudo second order model with a correlation coefficient (R^2) of 0.9999. Adsorption mechanism was based on electrostatic interaction between the positively functional

groups of $\text{Fe}_3\text{O}_4/\text{FMO}$ and negatively charged Cr(VI) ions ($\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^-). The applied adsorbent ($\text{Fe}_3\text{O}_4/\text{FMO}$) was easily separated from aqueous solution and had a high removal percentage (90.1 %) towards Cr(VI) removal as compared to FMO (80.1 %) at pH 2. Therefore, this adsorbent has a potential of being applied in industrial wastewater treatment to remove various negatively charged inorganic contaminants from wastewater.



5.9 References

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this study both functionalised *Moringa oleifera* (FMO) and magnetic functionalised *Moringa oleifera* were successfully prepared for removal of Cr(VI) from aqueous solution. The prepared adsorbents were confirmed using XRD, FTIR, and SEM. The FTIR results revealed that amino groups and iron oxide were grafted on the surface of *Moringa oleifera*. From FTIR results, it was worth noting that the incorporation Fe₃O₄ nanoparticles did not destroy the FMO structure since IR bands of FMO were still maintained in the composite. Based on adsorption studies, it was observed that the introduction of iron oxide nanoparticles (Fe₃O₄) onto FMO enhanced adsorption capacity towards Cr(VI) removal. Both adsorbents, FMO and Fe₃O₄/FMO were effective in removing Cr(VI) from aqueous solution at a low pH. The maximum Cr(VI) removal using both adsorbent was obtained at pH 2. From FTIR results of FMO, it was noticed that amino functional groups had a major role in Cr(VI) uptake. Based on co-existing ions studies, we noticed that both adsorbents (FMO and Fe₃O₄) were selective towards Cr(VI) in the presence of cation metals. This was due to the fact that at low pH (2), both adsorbents surface were positively charged which therefore make it impossible for electrostatic interaction with positively charged ions (cation metals).

Anti-bacterial activities of FMO were investigated on four different strains (*E.coli*, *P.aeruginosa*, *E.faecalis* and *Staphylococcus*). It was found that FMO was not active against these bacterial strains since microbes were numerous to count (TNTC) based on simulated water, however based on real water samples FMO was active against these strains.

6.2 Recommendations for future work

- The biological activity on magnetic functionalised *Moringa oleifera* was not done in this study, therefore for future work the biological activity will be tested using Fe₃O₄/FMO
- Since FMO was not active against *E.coli*, *P.aeruginosa*, *E.faecalis* and *Staphylococcus* based on simulated water, we therefore hope that magnetic functionalised *Moringa oleifera* (Fe₃O₄/FMO) could be active.
- We noticed that FMO has a poor regeneration ability, therefore since *Moringa oleifera* is a widely available plant tree, it can still be feasible even when reused after one adsorption cycle.
- Vibrating sample magnetometer (VSM) will be applied in future work to investigate the magnetic properties of Magnetic functionalised *Moringa oleifera* (Fe₃O₄/FMO)

