Performance Evaluation of Magnetic Polymer-Zeolite Nanocomposite for Adsorptive Removal of Contaminants from Water

by

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DECLARATION BY CANDIDATE

“I hereby declare that the dissertation submitted for the degree D Tech: Engineering: Chemical at Tshwane University of Technology is my own original work and has not previously been submitted to any other institution of higher education. I further declare that all sources cited or quoted are indicated and acknowledged by means of a comprehensive list of references”.

NOMCEBO HAPPINESS MTHOMBENI
DEDICATION

This work is dedicated to

My late parents Emma Mamochini and Ezekial Themba Hadebe. You will forever be in my heart.

My husband Zwelethu Mthombeni for all the support and love you have given me over the years during this journey. Thank you my love.

Our amazing children Bongani, Nkateko and Xihlamariso and Rixongile Mthombeni. You are mommy rock stars.

My grandmother Beauty Motaung, my mother and father Berth and Nelson Mthombeni. Mawe and Papa I can’t express enough the amount of gratitude I have for to the support you have given me.

My brother Percy Mthombeni you are a blessing.

My amazing and fabulous sisters: Nombuso, Thandazo, Zandile Hadebe and Duduzile Mthombeni.

My aunt Khosi Matlala

My brothers Sibusiso Hadebe and Mbusi Mthombeni

To all my friends thank you and everyone who has been there for me

God bless
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MOST IMPORTANTLY OUR HEAVENLY FATHER ABOVE AND HIS SON JESUS CHRIST
Abstract
Polymer network can be easily incorporated inside the structure of zeolite due to the presence of highly ordered pores, channels and cages in different forms and sizes in the structure of zeolite. Polymer–zeolite nanocomposite has the potential to overcome the limitations of both materials while combining the advantages of polymers and zeolites. Consequently, this work reports on the preparation of zeolite-clay and zeolite-polymer based nanocomposites and their application in the remediation of water contaminated with metals. In particular, zeolite-bentonite (B/Z) and zeolite- polypyrrole (MZPPY) nanocomposites were examined to evaluate their performance for the removal of Cr(VI), V(V) and Mn(II) in both batch and column experiments. Polypyrrole and natural zeolite was prepared by chemical polymerization of pyrrole in the presence of magnetized zeolite dispersed in aqueous solution. Bentonite/zeolite adsorbent was prepared by physically mixing calcium bentonite and natural zeolite. The structure and morphology of the prepared adsorbents were analyzed with the Fourier transform infrared (FTIR), field-emission microscope (FE-SEM), energy dispersive X-ray (EDX), high resolution transmission electron microscope (HR-TEM) and X-ray diffraction (XRD). The effects of magnetic zeolite loading within the composite, initial pH, sorbent dosage, temperature and initial solution concentration on metal ions removal efficiency were investigated. Batch sorption isotherms data at solution pH 2 and pH 4-5 for Cr(VI) and V(V), respectively, were satisfactorily described by the Langmuir isotherm model with a maximum sorption capacity of 344 mg/g and 65 mg/g for Cr(VI) and V(V), respectively, at 25 °C. Equilibrium data for sorption of Mn(II) using bentonite /zeolite adsorbent fitted well to the Freundlich isotherm model. Meanwhile, the kinetic data for all ions fitted to the pseudo-second order kinetic model. From thermodynamic studies, it was revealed that the adsorption process is spontaneous and endothermic in nature. The presence of co-existing
ions affected the Mn(II) removal efficiency when using the B/Z adsorbent while in the presence of SO$_4^{2-}$ ions the performance of MZPPY was significantly affected during Cr(VI) removal. In a continuous fixed-bed operation undertaken to evaluate the efficiency of bentonite/zeolite and magnetic zeolite polypyrrole as adsorbents for the removal of Cr(VI), V(V) and Mn(II) from aqueous solution under the effect of various process parameters like bed mass, flow rate and initial metal ion concentrations, results indicated that the column performed well at low flow rate. Also, breakthrough time increased with increasing bed mass. The Yoon–Nelson, Thomas and Bohart–Adams models were applied to experimental data to predict the breakthrough curves and to determine the characteristic parameters of the column that are useful for process design. The Yoon–Nelson and Thomas models predictions were in very good agreement with the experimental results at all the process variables studied. The adsorption-desorption studies indicated that MZPPY retained its original adsorption capacity up to two consecutive cycles. Based on performance data, it can be concluded that the MZPPY composite is a competitive sorption media for Cr(VI) and V(V) removal from aqueous environments. High values of AER in column studies and low adsorption capacity in batch studies indicate that B/Z is not effective in treating water contaminated with Mn(II) and hence not recommended.

Keywords: natural zeolite, bentonite, polypyrrole, chromium, manganese, vanadium, adsorption
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Publications


• MTHOMBENI N. H., ONYANGO, M. S. & AOYI, O. Fixed-bed Column Operation for Chromium (VI) Removal from Aqueous Solution using Magnetic Zeolite-Polypyrrole Composite (To be submitted)

Conferences

• MTHOMBENI, N. H., MBAKOP AND, S. & ONYANGO, M. S. Adsorptive Removal of Manganese from Industrial and Mining Wastewater. 2016 Sustainable Research and Innovation (SRI) Conference May 4-6; 2016, Nairobi, Kenya

CHAPTER 1

1. Introduction

Water is acknowledged as the most important and indispensable of all the natural resources and it is critical in all aspects of life (Kamika and Momba, 2012). One of the world's greatest challenges in recent years is water shortages which are due to climate change, (Masese et al., 2013, Dudgeon, 2010) as well as population growth, increased levels of urbanization, mounting demand from user sectors, a lack of investment in infrastructure, deteriorating water quality due to pollution and the effects of climate change, the significance of water in economic and social development is increasingly being recognized (Zhuwakinyu, 2012).

South Africa is a water stressed country and water availability is not consistent across the South African landscape and varies greatly between different catchments (SAEO, 2012). The effects of variable rainfall patterns and different climatic regimes are compounded by high evaporation rates across the country. It is estimated that the effect of climate change on water resources suggests that South Africa may experience a reduction of 10% in average rainfall reducing surface water runoff up to 50-75% by 2025 (UNEP-FI, 2009).

Mining has played a central role in the development and growth of the South African economy but impacts water resources negatively (UNEP-FI, 2012). Mining and metallurgical industries are associated with heavy metals wastewaters that are directly or indirectly discharged into the environment increasingly. There has been an increasing ecological and global public health concern associated with environmental contamination by heavy metals (Tchounwou et al., 2012). Heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy
metal ions are known to be toxic or carcinogenic (Hu et al., 2005). There a lot of metals which are have been found to be toxic to human beings and ecological environments, such as Cr, Cu, Pb, V, Hg, Zn, Mn, Ni and other metals (Ojedokun and Bello, 2016, Meena et al., 2008). Several treatment methods to remove heavy metals from mining wastewaters have been reported. Heavy metal ions in wastewater are commonly removed by chemical treatment, oxidation and hydrolysis, ion-exchange, bio-sorption and adsorption (Patterson, 1985). Most recently, many efforts have been addressed on the developing of new technologies in which technological, environmental and economic constraints are taken into consideration. The purification methods have to avoid generation of secondary waste and to involve materials that can be recycled and easily used on an industrial scale.

Adsorption compared with other methods appears to be an attractive process in view of its efficiency and capacity of removing heavy metal ions over wide range of pH and to a much lower level, ability to remove complex form of metals that is generally not possibly by other methods. It is also environmentally friendly, cost effective and its ease of operation compared to other processes with which it can be applied in the treatment of acid mine and heavy metal containing wastewater (Rao et al., 2010). In the past several investigations have been undertaken for the removal of heavy metals from wastewater using different low-cost materials. These include amongst many others activated carbon made from agricultural wastes, alumina and natural zeolite (Ngomsik et al., 2006). Adsorption technique though robust in nature suffers from massive mass transfer resistance due to inherently large surface areas and large diffusion lengths of the adsorbents. To overcome limiting factors in adsorption, nanomaterial adsorption media could be designed to maximize mass transport kinetics by providing contaminants with rapid
access to high surface area and by promoting internal mass transport (Hristovski et al., 2007).

Because of their size, nanomaterials exhibit novel properties as large surface area, potential for self-assembly, high specificity, high reactivity, and catalytic potential make nanoparticles excellent candidates for wastewater treatment applications (Zhang et al., 2006).

Clays have been considered to be excellent adsorbent materials due to large surface area, chemical and mechanical stability, layered structure, and high cation exchange capacity (Bhattacharyya and Gupta, 2008). Natural zeolites are widely available and have been studied extensively due to their properties such as non-toxicity, their robustness, high selectivity and easy removal, which are crucial factors for a successful water management (Margeta et al., 2015). However, natural zeolite has poor capacity for most contaminants. To improve performance of natural zeolites, the surface needs to be modified. Conducting polymers such as polypyrrole offer good prospects for functionalization due to their nontoxicity, environmentally stability, ease of preparation and high efficiency for removal of toxic metals in water (Bhaumik et al., 2011a, Bhaumik et al., 2011b, Bhaumik et al., 2012, Bhaumik et al., 2013a, Bhaumik et al., 2013b, Setshedhi et al., 2014, Setshedhi et al., 2015) [26-32]. Polymers have very low density and therefore in real industrial applications, large volume of fixed beds would be required thus limiting their use.

The incorporation of a conducting polymer into an inorganic host such as zeolite has been considered as an important method to generate a new type of hybrid materials that have unique properties. Zeolites are considered the most suitable host materials due to their well-ordered pore systems that can serve as substrate for growing of conducting polymers (Yu et al., 2014). Polypyrrole carries charges in the polymer matrix, and has some positively charged nitrogen
atoms which provide a good prospect for its applications in adsorption or filtration (Bhaumik et al., 2011b, Zhang and Bai, 2003).

Both natural zeolite and polymers are bulk adsorption materials which have inherent limitations as they suffer from massive mass transfer resistance due to large surface areas and large diffusion lengths. These limitations could be overcome by developing nanocomposites in which nanoparticles are imbedded in bulk materials (Hristovski et al., 2007). Separation of these nanomaterials from water is still a challenge though. Magnetic adsorbents have gained much attention recently in this respect because upon use they can easily be retrieved from solution with applied magnetic field (Bhaumik et al., 2011a, O’Handley, 2000). Magnetic separation has been combined with adsorption for heavy metal removal from contaminated water at laboratory scales (Hu et al., 2005, Mayo et al., 2007, Yavuz et al., 2006, Cheng et al., 2012, Bhaumik et al., 2011b). Magnetic separation is especially desirable in industry because it overcomes many of the issues present in filtration, centrifugation or gravitational separation, and requires much less energy to achieve a given level of separation (Wang et al., 2009, Wang and Lo, 2009).

Adsorption process can be configured in batch and continuous fixed bed mode. Batch adsorption studies provide fundamental information about effectiveness of adsorption process using specific adsorbent and to determine the maximum adsorption capacity. For industrial wastewater treatment systems the continuous fixed-bed column adsorption is often more applicable (Karimi et al., 2012).
Therefore, this study focuses on the adsorption of Cr(VI) and V(V) using magnetic zeolite polypyrrole (MZPPY) and removal of Mn(II) using zeolite bentonite (B/Z) adsorbent. Batch adsorption studies will be used to evaluate process parameters such as pH, sorbent dosage, initial metal ion concentration, time and temperature. Furthermore, fixed-bed column studies will be utilized to simulate the industrial continuous adsorption processes while varying the influent metal ion concentration, bed mass and influent flow rate.

1.1. **Problem statement and motivation**
South Africa is blessed with the occurrence of many minerals, often in large quantities and of strategic importance to it and to other nations. Mining and metallurgical industries, forming the backbone of the South African economy, has resulted in extensive environmental pollution problems. One such problem is heavy metal pollution, which is one of the most destructive forms of pollution in the world, and is widely accepted as responsible for costly environmental and socio-economic impacts.

High concentrations of heavy metals and other toxic elements can severely contaminate surface and groundwater, as well as soils. Most rural communities depend solely on these surface and groundwater wells, which contain high levels of water contaminants such as heavy metals that have harmful effects on the environment and humans. As such industrial and mining discharge streams must be treated using appropriate techniques. Industrial effluent treatment processes are designed to ensure that when wastewaters are discharged into natural water sources, any adverse effect are reduced or prevented, and where permitted treated water recycled.
Various treatment methods such as mineral precipitation and co-precipitation, reverse osmosis, insoluble hydroxide formation, ion exchange, solvent extraction, coagulation and adsorption are utilized to treat wastewaters. Of all these methods, an adsorption technique is the most versatile and cost-effective method for the removal of pollutants in wastewater. However, most traditional adsorbents suffer from diffusion limitation within the particles which leads to a decrease in the adsorption rate and available capacity. Recently, nanostructured materials have proven advantageous over traditional adsorbents due to very large surface area, accessible active sites and a short diffusion length, which result in high adsorption capacity, rapid extraction dynamics and high adsorption efficiencies. The application of magnetic nanoadsorbents has attracted attention to solve environmental problems because they have large surface area, are highly dispersible in water and are easily separable from aqueous solution by the application of external magnetic field. Natural zeolite and clays which are widely available, cheap and non-toxic are commonly used as adsorbents for water treatment.

Consequently, this study explores the application of magnetic zeolite and clay nanostructured adsorbent for treatment of mining wastewater with intent to recycle the treated water to be reused in the process. The effect of several process variables will be explored.

1.2. Hypothesis

- It is hypothesized that zeolite-clay and zeolite-polymer nanostructured materials are robust and stable in aqueous environments
- It is then hypothesized that zeolite-clay and zeolite-polymer based nanomaterials are capable of remedying mining wastewater to acceptable standard for various applications
- It is also hypothesized that the performance of zeolite-clay and zeolite-polymer based nanomaterials are influenced by the water quality parameters and process conditions
• It is further hypothesized that the interaction between nanostructured adsorbents and water contaminants is chemical in nature and hence the adsorption data can be modeled using chemical adsorption based models

• It is finally hypothesized that the nanostructured adsorbents can be regenerated and reused

1.3. Research Aims
The goal of the research is to explore the application of nanostructured materials in mining wastewater with intent to recycle the treated water to be reused in the process. The goal of the research is to protect the environment and human health by minimizing exposure of toxic metals found in mining wastewater by treatment with these clay nanomaterials. It is expected that the results will improve the quality of water and reduce the impact of mine wastewater in the environment.

Consequently, the specific objectives of this project are to:

• Develop and characterize zeolite based nanomaterials for mining wastewater treatment.

• To establish selectivity, robustness and stability of the nanomaterials in treatment of mining wastewater contaminants using batch tests and generate equilibrium and kinetic data for various pollutants in mining wastewater

• Evaluate the performance of the nanomaterials for various pollutants sorption in a fixed-bed column

• Model batch and column data using chemical reaction mechanism as the dominating step in order to extract preliminary adsorption design data

• Test reusability of the developed media as a means of establishing cost implications of the new material
CHAPTER 2

2. Introduction

Global water demand for freshwater resources is largely influenced by population growth, urbanization, food and energy security policies, and macro-economic processes such as trade globalization, industrialization, changing diets and increasing production and consumption (Connor, 2015). These also contribute to the polluting of water resources, further reducing their immediate accessibility and thus compromising the capacity of ecosystems and the natural water cycle to satisfy the world’s growing demand for water (MEA, 2005). It is projected that the water demand will increase by 55% by 2050, mainly due to growing demands from manufacturing, thermal electricity generation and domestic use (Connor, 2015, MEA, 2005).

South Africa is classified as a water-stressed country with an annual fresh water availability of less than 1,700 m$^3$ per capita (the index for water stress) (Otieno and Ochieng, 2004). There is uneven distribution of rainfall across South Africa with the eastern part of the country being much wetter than the western part due to the nature of the weather conditions (Turpie and Visser, 2013). There are also alternating periods of droughts and floods which affect the amount of water across South Africa (Water, 2011). Climate change is expected to alter the water cycle and will subsequently impact water availability and demand (Haddeland et al., 2014).

Also mining, mineral processing and extractive-metallurgical operations generate toxic liquid effluents and large volumes of solid waste that results in serious environmental consequences (Azapagic, 2004, Ahluwalia and Goyal, 2007). Industrial and mining activities such as electroplating, metal smelting and chemical industries, and manufacturing processes are few sources of anthropogenic heavy metals in water (Chowdhury et al., 2016, He et al., 2008).
Mining minerals are associated with acid drainage problems that have a long-term impact to waterways and biodiversity (Akcil and Koldas, 2006). Domestic, industrial, and agricultural wastewater containing high concentrations of metals are often discharged into the environment in many developing countries due to poor treatment of this water (Gupta, 2008).

2.1. Heavy metals in water and health impacts

The sources of drinking water such as surface water, groundwater, and seawater are likely to be polluted by heavy metals (Bryan and Langston, 1992, Chowdhury et al., 2016). Wastewater streams discharged from mining, paint manufacture, petroleum refining, battery manufacture, chemical, plating and smelting industries contain heavy metals contaminants. Mn and other metals such as Fe, V, Al, Zn and Cu are often present in high concentrations in mine drainage waters than in unpolluted streams and groundwater (Banks et al., 1997, Hallberg and Johnson, 2005, Luptakova et al., 2012).

Concentrations of heavy metals and other solutes in acid mine drainage are commonly elevated due to aggressive dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water along paths down flow from oxidizing pyrite (Blowes and Ptacek, 1994, Cravotta III, 1994). The study conducted by Hansen (Hansen, 2015) indicated that seepage from the tailings impoundments in the Witwatersrand basin in South Africa are acidic and contain elevated concentrations of trace metal concentrations, specifically Mn, Al, Cr, Co, Cu, Ni, Zn and U, as well as SO₄. The AMD from the gold mines in West Rand have been also found to contain high concentrations of these metals (Durand, 2012). This chapter gives an overview of the occurrence and speciation of vanadium, chromium and manganese in the environment, whereby various
conventional treatment techniques commonly used for treatment of these heavy metals are discussed. Moreover, insight about adsorption technology and various adsorbents previous used for adsorption are presented.

2.1.1. **Vanadium**

Vanadium is a trace metal that is found naturally both in soil and water (Cran and Tracey, 1998) and does not occur in nature as metallic vanadium. It is a corrosion-resistant, steel-grey metal; existing in oxidation states ranging from −1 to +5. Its most common valence states are +3, +4, and +5 (Barceloux and Barceloux, 1999). Vanadium pentoxide (V$_2$O$_5$) is the most common existing and used form of vanadium. Ammonium metavanadate (NH$_4$VO$_3$), sodium metavanadate (Na$_2$VO$_3$) and sodium orthovanadate (Na$_3$VO$_4$) are also common forms of vanadium (Imtiaz et al., 2015, Cran and Tracey, 1998).

Vanadium is very widely distributed and is mined in South Africa, Russia, and China. Vanadium is used as a steel additive and most of the vanadium consumption is as a ferrovanadium (a mixture of iron and vanadium). Vanadium is also used in titanium alloys, batteries, catalyst in chemical and polymer industries (Navarro et al., 2007, Imtiaz et al., 2015, Moskalyk and Alfantazi, 2003). Vanadium pentoxide is formed during the smelting of iron ore, from uranium ores and by a salt roast process from boiler residues or residues from elemental phosphate plants. During the burning of fuel oils in boilers and furnaces, vanadium pentoxide is present in the solid residues, soot, boiler scale, and fly ash (Costigan et al., 2001).
Vanadium is a heavy metal pollutant for ground waters as well as surface water impacted by mostly mining and can also be observed in water resources such rivers, lakes and seas (Imtiaz et al., 2015).

There are three main exposure routes to vanadium: air, drinking water and the food chain. The concentration of vanadium in fresh water highly depends on the geographical location (WHO, 2000). Vanadium is a heavy metal pollutant for ground waters as well as surface water impacted by mostly mining can also observed in water resources such rivers, lakes and seas (Imtiaz et al., 2015). At oxic water conditions and about neutral to slightly alkine pH soluble vanadate is the most dominant species. Under non-oxic conditions sparingly available oxidovadium (IV) hydroxide is generated and transported in water in the form of colloids. A decrease in pH and addition of phosphate based corrosion inhibitors to drinking water can re-mobilize vanadate thus eventually increasing vanadate concentrations beyond tolerable levels (Sigel et al., 2014).

The toxicity of vanadium compounds generally increases as valence increase. Pentavalent compounds are the most toxic. The pH of the aqueous medium has a great impact on vanadium toxicity (Crans, 2005). Adverse respiratory effects have been reported in humans and animals exposed to vanadium compounds at concentrations much higher than those typically found in the environment. The gastrointestinal system is becomes sensitive to toxicity following oral exposure and hematological system following inhalation or oral exposure (Barceloux and Barceloux, 1999).
Figure 2-1. Eh-pH diagram for the system V-O₂-H₂O, for dissolved EV<10⁻⁴ mol/kg (11.5 mg/L as VO₄) (Langmuir et al., 2004).

The Eh-pH diagram in Figure 2-1 depicts speciation of V (III)-V(V) at different pH, most aqueous V(V)solutions are dilute and only mononuclear (monomeric) species are expected: VO₂⁺, VO (OH)₃ (aq.), VO₂(OH)₂⁻, VO₃(OH)⁻₂, and VO₄³⁻, depending on pH. At pH 2 to 6 decavanadates may be present, from pH 6 to 9, metavanadates, (VO₃)ₓ⁻, and form slowly at 25 °C from depolymerization of decavanadates. At pH 9-12 the pyrovanadate is formed. The orthovanadate species, VO₄³⁻, exists in aqueous solution above pH (Baes and Mesmer, 1977)
2.1.2. Chromium

Chromium is the 21st most abundant element in the Earth’s crust. It is a hard, brittle metal that with difficulty can be forged, rolled and drawn unless in a pure form. It is easier to work with and it is an excellent alloying metal with iron. The bright silvery property makes it an appropriate metal to provide reflective, non-corrosive attractive finish to electroplating (Krebs, 2006). The principal chromium ore is ferric chromite, $\text{FeCr}_2\text{O}_4$, found mainly in South Africa (with 96% of the world’s reserves), Russia and the Philippines (Mohan and Pittman Jr, 2006).

The oxidation states of chromium are $+6$ in chromates ($\text{CrO}_4^{2-}$) and dichromates ($\text{Cr}_2\text{O}_7^{2-}$), $+3$ which is most stable and $+2$ (Daintith, 2014). The hydrolysis of Cr(III) is complex. It produces mononuclear species $\text{CrOH}^{2+}$, $\text{Cr(OH)}_2^+$, $\text{Cr(OH)}_4^-$, neutral species $\text{Cr(OH)}_3^0$ and polynuclear species $\text{Cr}_2(\text{OH})_2$ and $\text{Cr}_3(\text{OH})_4^{5+}$. The hydrolysis of Cr$^{6+}$ produces only neutral and anionic species, predominately $\text{CrO}_4^{2-}$, $\text{HCrO}_4^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$ (Mohan et al., 2005a, Mohan et al., 2006, Mohan and Pittman Jr, 2006). At low pH and high concentrations $\text{Cr}_2\text{O}_7^{2-}$ predominates while at pH greater than 6.5 Cr(VI) exist as $\text{CrO}_4^{2-}$ (Mohan et al., 2005a).

On a worldwide basis, about 80% of the chromium mined goes into metallurgical applications mainly in manufacturing of stainless steel, 15% is used in chromium chemicals manufacture and the remainder refractory applications (Barnhart, 1997). Chromium is considered an essential nutrient and also has detrimental health hazard properties. Cr(VI), is considered harmful even in small intake quantities, however Cr(III), is considered essential for good health in moderate intake (Guertin, 2005).
Figure 2-2: The Redox potential (Eh)-pH diagram for Cr-O-H systems (Palmer and Wittbrodt, 1991, Lukman et al., 2014)

Industries like paint and pigment manufacturing, stainless steel production, corrosion control, textile, leather tanning, chrome electroplating, metal finishing industries, wood preservation, and photography discharge effluent containing hexavalent chromium, Cr(VI) to surface water (El Nemr et al., 2015). i, 1982). However, due to the dynamic interconversion of chromium (III) and (VI) in aqueous environments, the availability of chromium (III) may lead to a health risk if this conversion to chromium (VI) occurs. The impacts of chromium (VI) to human health are lung cancer, respiratory irritation, dermatosis, dermatitis, and kidney and liver damage and gastrointestinal tract. Dermatosis, nephritis, and liver damage are the results of absorption of very large quantities of chromium due to exposure over a long period and a relatively small risk
of stomach cancer is associated with chromium (VI), due to dynamic interconversion of chromium (III) and (VI) in aqueous environments (Kimbrough et al., 1999).

2.1.3. Manganese

Manganese is a brittle, gray-pink metal with an atomic weight of 54.938. It is too brittle to be used unless alloyed. Manganese has only one stable natural isotope, 55Mn. Manganese occurs naturally and is the third most abundant transition metal on the earth crust \(9.5 \times 10^2\) ppm (Tavlieva et al., 2015, Cox, 1995). It can exist in 11 oxidation states with manganese compounds Mn(II), Mn(IV) and Mn(VII) being the most environmentally and biologically important (Mahmoud et al., 2012, USEPA, 1994). Manganese most common minerals are oxides [pyrolusite \((\text{MnO}_2)\)] and hydro-oxides [psilomelane \(\text{BaMn}^{2+}\text{Mn}^{4+}_{8}\text{O}_{16}(\text{OH})_4\)] and braunite \((\text{Mn}^{2+}\text{Mn}^{3+}_{6})(\text{SiO}_{12})\), and to a lesser extent as rhodochrosite \((\text{MnCO}_3)\).

![Eh–pH diagram for the Mn–O₂–H₂–H₂O system at 25 °C (Lu et al., 2013)](image)

Figure 2-3. Eh–pH diagram for the Mn–O₂–H₂–H₂O system at 25 °C (Lu et al., 2013)
Mn(II) compounds are stable in acid solution but are readily oxidized in alkaline medium. The Eh-pH diagram of Mn in Figure 3 shows Mn$^{2+}$ is formed at low pH, which progressively react with OH$^-$ as pH increases to produce metal hydroxides (Mn(OH)$_2$) or oxides (Huang, 2016).

South Africa has the world’s largest resources of manganese which is estimated to be around 80%. Manganese is used in the manufacture of iron and steel alloys, batteries, glass and fireworks, a significant fertilizer for plants, food additive for stocks and catalyst for organic synthesis (Li et al., 2010). Manganese is also found in the effluents of mine waters, either neutral or acid (AMD) (Silva et al., 2012). Mn is one of the most widely used metals in the world and one of the important indexes of water pollutants (Ma et al., 2013). Exposure to excess manganese may lead to Mn intoxication that may result in the onset of a neurological phenotype known as manganism which presents with motor symptoms resembling Parkinson’s disease (Erikson et al., 2007, Martinez-Finley et al., 2013, Roels et al., 2012).

Manganese occurs naturally in many surface water and groundwater sources and in soils that may erode manganese into waters. Improper disposal of dry-cell batteries or other toxic wastes from industries can yield higher manganese concentrations well above those normally found in environmental water (WHO, 2011) and cause significant harm to public health (Frisbie et al., 2012). Manganese at lower doses is an essential nutrient for humans and animals. Mn at elevated concentrations is a powerful neurotoxin which affects the nervous system and causes learning disabilities and intellectual impairment in children (Bouchard et al., 2007, Bouchard et al., 2011). Studies have shown that children exposed to 240–350 μg manganese/L in water had elevated manganese concentration in their hair and exhibited impaired manual dexterity and
speed, short-term memory, and visual identification when compared with children from areas which manganese was controlled (He et al., 1994). Children exposed to manganese intoxication from water containing above 1.0 µg manganese/L, had attention and memory impairments conditions (Woolf et al., 2002) and others presented neurologic symptoms including a repetitive stuttered speech, poor balance, coordination, and fine motor skills (Sahni et al., 2007). Manganese intoxication is also linked to Mn induced Parkinsonism (Lucchini et al., 2009, Aschner et al., 2009), low fetal weight (Grazuleviciene et al., 2009, Zota et al., 2009), infant mortality (Hafeman et al., 2007, Spangler and Spangler, 2009) and increased cancer rates (Spangler and Reid, 2010).

2.2. Conventional methods of heavy removal from water

Several treatment methods to remove Mn, Cr(VI) and V(V) from wastewaters have been reported. Heavy metals such as manganese, chromium and vanadium and in wastewater is commonly removed by precipitation (Silva et al., 2012, Pakarinen and Paatero, 2011, Silva et al., 2010, Zhang et al., 2010b, Nishimura and Umetsu, 2001, Golbaz et al., 2014, Golder et al., 2011, Kongsricharoern and Polprasert, 1995, Kongsricharoern and Polprasert, 1996, Geldenhuys et al., 2003), ion-exchange (Haghsheno et al., 2009, White and Asfar-Siddique, 1997, Alvarado et al., 2013, Cavaco et al., 2007, Fan et al., 2013), oxidation and filtration (Roccaro et al., 2007, Piispanen and Sallanko, 2010), coagulation and flocculation (Fu-Wang et al., 2009), biosorption (Mohan et al., 2005b, Hou et al., 2012, Dittert et al., 2014, Febrianto et al., 2009, Khambhaty et al., 2009, Li et al., 2008, Vijayaraghavan et al., 2011), reverse osmosis (Afonso et al., 2004, Benito and Ruíz, 2002, Bhattacharya et al., 2013, Bódalo et al., 2005, Richard, 2004, Li et al., 2014), ultrafiltration (Aroua et al., 2007, Chakraborty et al., 2014), electrochemical (Almaguer-
Busso et al., 2009, Lakshmipathiraj et al., 2008, Liu et al., 2011, Ouejhani et al., 2008), and adsorption (Chen and Liu, 2014, Al-Rashdi et al., 2011, Anirudhan et al., 2013, Anupam et al., 2011, Baccar et al., 2009, Baral et al., 2006, Behnajady and Bimeghdar, 2014, Chen et al., 2014).

Precipitation is widely used in process industries because it is cheap and relatively easy to operate (Fu and Wang, 2011). Hydroxide precipitation technique is the most widely used chemical precipitation technique due to its relative simplicity, low cost and ease of pH control. Although most metals are precipitated as hydroxides other methods such as sulfide and carbonate precipitation are also used (Wang et al., 2005). Lime and limestone are the most commonly employed precipitant agents due to their availability and are inexpensive in most countries and have been employed to remove manganese and other heavy metals in water (Aziz and Smith, 1996, Aziz and Smith, 1992, Aziz et al., 2008, Barakat, 2011). The major expense associated with precipitation is the treatment cost of the chemicals and the precipitated sludge that is produced (Wang et al., 2005). Excessive sludge production requires further treatment, and the problems associated with precipitation are slow metal precipitation, poor settling, and the aggregation of metal precipitates have long term environmental effects for sludge disposal (Aziz et al., 2008).

Ion exchange in wastewater treatment is used for demineralization. Ion-exchange processes have been widely used to remove manganese and other heavy metals from wastewater because it is very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation (Lee et al., 2007). Ion exchange is the exchange of ions between the substrate and surrounding medium. Ion exchange resins are suitable to use at wide range of
different pH values and at high temperatures and are insoluble in most organic and aqueous solutions (Goher et al., 2015). They contain a covalent bonding between the charged functional groups and the cross linked polymer matrix (Sherrington, 1998). The disadvantage of using this technology is that ion exchange media is easily fouled by organics and other solids in the wastewater.

The electrochemical method is one of the technologies that are used as alternative option for the remediation of water and wastewaters mainly due to its advantages such as environmental compatibility, versatility, high energy efficiency, amenability of automation and safety. Electrochemical methods include electrocoagulation, electro-oxidation and electro-reduction (Pulkka et al., 2014). This process uses an electric field as the driving force for the separation of ions using ion exchange membranes or plates to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Metallic ions that are positively charged cling to cathodes that is negatively charged and the metal deposit can be stripped and recovered. Corrosion of the electrodes is the main disadvantage of using this method because electrodes would frequently have to be replaced (Barakat, 2011). Electrochemical water or wastewater technologies have not been widely used because they involve relatively large capital investment and expensive electricity supply (Chen and Hung, 2007).

Coagulation and flocculation are important pretreatment processes. The coagulants that are used often in water treatment are aluminum and ferric salts. The purposes of coagulation are to destabilize particles present in the raw water and to convert dissolved natural organic matter into particles (Edzwald, 2007). The main objects of coagulation are the hydrophobic colloid and
suspended particle which consist of insoluble particles (Chang and Wang, 2007). Flocculation utilizes polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps that can be removed by filtration, straining or floatation (Wang et al., 2005). Heavy metals that are soluble in water after coagulation cannot be effectively removed and coagulation units must be followed by other treatment techniques (Chang and Wang, 2007).

Membrane filtration technologies that are used for removal of heavy metals include microfiltration, ultrafiltration, nanofiltration and reverse osmosis depending on the size of the particle that can be retained. Nanofiltration is the intermediate process between ultrafiltration and reverse osmosis and the advantages of this process include ease of operation, reliability and comparatively low energy consumption (Eriksson, 1988). It also helps to minimize scale formation on the equipment involved in both reverse osmosis and thermal desalination processes (Izadpanah and Javidnia, 2012). Membrane filtration technology can remove heavy metal ions with high efficiency but high costs, process complexities, membrane fouling, and low permeate flux have limited its use for heavy metal removal (Fu and Wang, 2011).

2.3. Adsorption of heavy metals from wastewater

Adsorption is a common method of heavy metal removal from water. Several physicochemical properties such as specific surface area, pore structure, and surface chemistry of adsorbents regulate the adsorption efficiency, selectivity, equilibrium time of adsorption, regeneration capacity, and their stability in aqueous solutions (Islam et al., 2015, Yang et al., 2008, Xue and Li, 2008, Faust and Aly, 1987). The adsorptive capacity of the adsorbent is also influenced by the adsorbate properties of group functionality, branching or geometry, polarity, hydrophobicity,
dipole moment, molecular weight and size, and aqueous solubility. The solution conditions such as pH, temperature, adsorbate concentration, ionic strength, and competitive solutes also have an effect on the adsorption capacity (Faust and Aly, 1987).

Physico-chemical treatment methods have important role to play in today’s wastewater treatment contaminated with Mn, Cr, V and other heavy metal ions and will continue to have increased use because of established practice and continued improvisation. Adsorption, ion exchange, and coagulation, continue to dominate the wastewater treatment mainly through improved materials, devices, and practices (Bhandari and Ranade, 2014). They offer various advantages such as their rapid process, ease of operation and control, flexibility to change of temperature. Unlike in biological system, physico-chemical treatment can accommodate variable input loads and flow such as seasonal flows and complex discharge. Chemical plants can be modified if required and the treatment system generally requires a lower space and installation cost (Selvam et al., 2015, Barakat, 2011).

Adsorption technique is one of the wastewater treatment technologies that is recognized as an effective, economically favorable, and easy to operate method for heavy metal wastewater treatment and has a wide range of applications (Gupta and Ali, 2013, Le Cloirec and Faur-Brasquet, 2008). It offers flexibility in design and operation and mostly it will produce treated effluent that is odorless, free of color and is suitable for reuse. Adsorption process is usually reversible and the regeneration of the adsorbent will result in economical desorption processes (Gautam et al., 2013, Dinu and Dragan, 2014).
2.4. Models for adsorption

Sorption is used to describe every type of capture of a substance from the external surface of solids, liquids, or mesomorphs as well as from the internal surface of porous solids or liquids (Pouloupolos and Inglezakis, 2006). The molecule that accumulates or adsorbs at the interface is called an adsorbate, and the solid on which the adsorption occurs is called the adsorbent. Adsorption is basically an attraction of adsorbate molecules, a gaseous or liquid component, to an adsorbent surface, a porous solid. Interaction between adsorbate and adsorbent is comprised of molecular forces including permanent dipole, induced dipole, and quadrupole electrostatic effects, also called Van der Waals forces (Thomas and Crittenden, 1998).

2.4.1. Kinetics

Adsorption equilibrium is not established instantaneously particular for porous adsorbents. The mass transfer from the solution to the adsorption sites within the adsorbent particles is constrained by mass transfer resistances that determine the time required to reach the state of equilibrium. The rate of adsorption is usually limited by diffusion processes toward the external adsorbent surface and, in particular, within the porous adsorbent particles. The mass transfer parameters and equilibrium data are important input data for the determination of the required contact times in slurry reactors as well as for fixed-bed design. The adsorption process can be characterized by the following four consecutive steps:

- Transport of the adsorbate from the bulk liquid phase to the hydrodynamic boundary layer localized around the adsorbent particle
- Transport through the boundary layer to the external surface of the adsorbent, termed film diffusion or external diffusion
- Transport into the interior of the adsorbent particle (termed intraparticle diffusion or internal diffusion) by diffusion in the pore liquid (pore diffusion) and/or by diffusion in the adsorbed state along the internal surface (surface diffusion)

- Energetic interaction between the adsorbate molecules and the final adsorption sites (Worch, 2000)

It is commonly assumed that the first and the fourth step are very fast and the total rate of the adsorption process is determined by film and/or intraparticle diffusion. Since film diffusion and intraparticle diffusion act in series, the slower process determines the total adsorption rate (Worch, 2000). Several mathematical models have been applied to describe adsorption kinetic process, which can generally be classified as adsorption reaction models and adsorption diffusion models (Qiu et al., 2009).

2.4.1.1. Pseudo-first-order rate equation

The pseudo-first-order model is well known model to correlate data for various solutes. The Lagergren pseudo-first-order model is the earliest known equation to describe the adsorption rate in the liquid phase. It is expressed as:

\[ \frac{dq}{dt} = k_1(q_e - q) \]  \hspace{1cm} (2-1)

Integration of the above equation with following boundary condition: \( t = 0 \rightarrow q_t = 0, \text{and} \ t = t \rightarrow q_t = q_t \) results to the following expression:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  \hspace{1cm} (2-2)
\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t 
\]  
(2-3)

where \( q_e \) and \( q_t \) refer to the amount of ion adsorbed (mg/g) at equilibrium and at any time, \( t \) (min), respectively, and \( k_1 \) is the equilibrium rate constant of pseudo first-order adsorption (l/min) (Ismadji et al., 2015).

2.4.1.2. Pseudo Second-Order Equation

(Ho and McKay, 2000) made the assumption that the process may be pseudo-second order and the rate limiting step may be chemical sorption or chemisorption involving valence forces through sharing or the exchange of electrons in order to develop mathematical model to describe sorption process during agitation. It must also be assumed that the sorption follows Langmuir model. The kinetic rate equation is expressed as:

\[
\frac{dq_t}{dt} = k(q_e - q_t)
\]  
(2-4)

Integrating this for the boundary conditions \( t = 0 to t = t \) and \( q_t = 0 to q_t = q_t \), gives:

\[
\frac{1}{(q_e-q_t)} = \frac{1}{q_e} + kt
\]  
(2-5)

With the linear form given as:

\[
\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t
\]  
(2-6)

If the initial sorption rate is

\[
h_0 = kq_e^2
\]  
(2-7)

Then

\[
q_t = \frac{t}{\frac{1}{h_0} + \frac{1}{q_e}}
\]  
(2-8)
This can be rearranged to this expression

\[
\frac{t}{q_t} = \frac{1}{h_0} + \frac{1}{q_e} t
\]  \hspace{1cm} (2-9)

\(h_0\) can be determined experimentally by plotting of \(t/q_t\) against \(t\).

### 2.4.1.3. Elovich model

Elovich’s equation is another rate equation based on the adsorption capacity

\[
\frac{dq}{dt} = a e^{-\alpha q}
\]  \hspace{1cm} (2-10)

where \(q\) is the quantity adsorbed during the time \(t\), \(\alpha\) the initial adsorption rate, and \(a\) is the desorption constant during any one experiment (Ho, 2006).

The integrated form can be rewritten as:

\[
q = \left(\frac{2.3}{\alpha}\right) \ln(t + t_0) - \left(\frac{2.3}{\alpha}\right) \ln t_0
\]  \hspace{1cm} (2-11)

if

\[
t_0 = \frac{1}{aa}
\]  \hspace{1cm} (2-12)

the plot of \(q\) as a function of \(\ln(t + t_0)\) should yield a straight line with a slope of \(2.3/\alpha\). Elovich equation is commonly applied to determine the kinetics of chemisorption of gases onto heterogeneous solids, and it is restricted, as it only describes a limiting property ultimately reached by the kinetic curve (Ho, 2006).

(Chien and Clayton, 1980) assumed that \(a\alpha t \gg 1\) and by integrating and applying the boundary conditions of \(q = 0\) at \(t = 0\) and \(q = q\) at \(t = t\), then the equation becomes

\[
q = \alpha \ln(aa) + \alpha \ln(t)
\]  \hspace{1cm} (2-13)
the constants can be obtained from the slope and the intercept of a straight line plot of \( q \) against \( \ln(t) \) (Ho, 2006).

### 2.4.1.4. Ritchie’s equation

(Ritchie, 1977) made assumptions that \( \theta \) is the fraction of surface sites which are occupied by an adsorbed gas, and that \( n \) the number of surface sites occupied by each molecule of the adsorbed gas, and \( \alpha \) is the rate constant. Also assuming that the rate of adsorption depends solely on the fraction of sites which are unoccupied at time \( t \), and then the equation can be expressed as

\[
\frac{d\theta}{dt} = \alpha (1 - \theta)^n
\]  

Integrating equation

\[
\frac{1}{(1-\theta)^{n-1}} = (n - 1)at + 1 \quad \text{for } n \neq 1
\]  

or

\[
\theta = 1 - e^{-\alpha t} \quad \text{for } n = 1.
\]

It is assumed that no site is occupied at \( t = 0 \) when introducing the amount of adsorption, \( q \), at time \( t \), then equation 2-15 becomes

\[
\frac{q - q_n^{n-1}}{(q - q_n)^n - 1} = (n - 1)at + 1
\]

Equation 16 becomes

\[
q = q_n (1 - e^{-\alpha t})
\]

where \( q_n \) is the amount of adsorption after an infinite time (Ho, 2006)

### 2.4.2. Diffusion models
2.4.2.1. Intraparticle diffusion model

The fractional approach to equilibrium change is done according to a function of \( (Dt/r^2)^{1/2} \), where \( r \) is the radius of adsorbent particle and \( D \) is the effective diffusivity of solute within the particle. The initial rate of Intraparticle diffusion is obtained by curve linearization of

\[ qt = f(t^{1/2}) \]

which is expressed as

\[ qt = k_p t^{1/2} + C \]  \hspace{1cm} (2-19)

where \( k_p \) is the IPD rate constant (mg/ (g min\(^{1/2}\))) and \( C \) is a constant for any experiment (mg/g).

To obtain the intercept it has been indicated that extrapolation of the linear portion of the plot back to the axis provides intercepts which are proportional to the extent of the boundary layer thickness, that is, the larger the intercept the greater the boundary layer effect (McKay et al., 1980, Wu et al., 2009).

The initial adsorption behavior is determined by the following equations:

\[ q_i = k_p t_i^{1/2} + C \]  \hspace{1cm} (2-20)

where \( t_i \) is the longest time in adsorption process and \( q \) is the solid phase concentration at time \( t = t_i \) for an adsorption system. Therefore subtracting the equations

\[ q_i - q_t = k_p(t_i^{1/2} - t^{1/2}) \]  \hspace{1cm} (2-21)

Rearrangement yields

\[ \left( \frac{q_i}{q_t} \right) = 1 - R_t \left[ 1 - \left( \frac{t}{t_i} \right)^{1/2} \right] \]  \hspace{1cm} (2-22)
where \( Ri = \frac{k_p t_i^{1/2}}{q_i} \), which is defined as the initial adsorption factor of the intraparticle diffusion model. The characteristic curve based on intraparticle diffusion model can be obtained from the following equation

\[
R_i = \frac{q_i - C}{q_i} = 1 - \left( \frac{C}{q_i} \right)
\]  

\( R_i \) can be represented in terms of the ratio of the initial adsorption amount \( (C) \) to the final adsorption amount \( (q_i) \). When there is no initial adsorption behavior in an adsorption system \( R_i = 1 \) then equation 2-20 passes through the origin. When \( C = q_i \) when adsorption occurs right at the beginning of the process \( R_i = 0 \) (Wu et al., 2009).

2.4.2.2 Film Diffusion

The film diffusion mass transfer rate equation can be described as follows;

\[
ln \left( \frac{C_t}{C_0} \right) = -k_{ed} \left( \frac{A}{V} \right) t
\]  

(2-24)

where, \( k_{ed} \) is external diffusion rate constant (cm/min), \( C_t \) is the concentration at time \( t = t \), \( C_0 \) is the concentration at time \( t = 0 \), \( A/V \) is external sorption area to the total solution volume and \( t \) is time. The plots of \( ln \left( C_t/C_0 \right) \) versus time can be used to describe whether the sorption proceeds sequentially through the sorbent particle and in the bulk of the solution by diffusion (Shah et al., 2014, Gao et al., 2008, Gupta et al., 2009).

2.4.3 Adsorption Isotherms

The equilibrium in adsorption systems is commonly represented by the equilibrium isotherm. The equilibrium isotherm represents the distribution of the adsorbed material between the
adsorbed phase and the solution phase at equilibrium, and is characteristic for a specific system at a particular temperature (Poulopoulos and Inglezakis, 2006).

2.4.3.1. Langmuir isotherm

The Langmuir equation introduced a clear concept of the monomolecular adsorption on the energetically homogeneous surfaces. This isotherm describes adsorbate-adsorbent systems in which the adsorbents that exhibit the Langmuir isotherm behavior are supposed to contain fixed individual sites, each of which equally adsorbs only one molecular, forming thus forming a monolayer, namely, a layer with the thickness of the molecule (Cecen and Aktas, 2011). Langmuir further supposed that the rate of desorption from the surface is directly proportional to the fractional surface coverage and that the rates of adsorption and desorption are equal at equilibrium (Thomas and Crittenden, 1998). Langmuir adsorption isotherm normally is expressed as follows:

\[
q = \frac{q_{\text{max}} b C_e}{(1 + b C_e)}
\]  

(2-25)

where \( C_e \) (mg/L) is the equilibrium adsorbate concentration in solution, \( q_{\text{max}} \) (mg/g) is the solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface, \( b \) is the Langmuir constant related to energy of adsorption and \( q \) (mg/g) is the adsorption capacity (mg adsorbate adsorbed per g of adsorbent).

The linearized equation form of the Langmuir equation is given as:

\[
\frac{1}{q} = \frac{1}{q_{\text{max}}} + \left( \frac{1}{b q_{\text{max}}} \right) \left( \frac{1}{C_e} \right)
\]  

(2-26)

The constants in the Langmuir isotherm can be determined by plotting 1/q versus 1/C\(_e\) which gives a linear plot whereby Langmuir parameters can be extracted. The essential features of
Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter $R_L$:

$$R_L = \frac{1}{(1 + (b \times C_o))}$$

where $C_o$ is the initial solute concentration of in mg/L. The value of $R_L$ indicates the shape of the isotherm whether the adsorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

2.4.3.2. Freundlich isotherm

The Freundlich equation is usually applied in a case of heterogeneous surface energies consisting of sites with different adsorption potentials, and each type of site is assumed to adsorb molecules (Poulopoulos and Inglezakis, 2006, Cecen and Aktas, 2011). The model has the following form (Freundlich, 1906):

$$q = K_F C_e^{1/n}$$ (2-27)

The linearized form of the equation is expressed as:

$$\log q = \log K_F + \frac{1}{n} \log C_e$$ (2-28)

$K_F$ (mol$^{1-n}$L$^n$g$^{-1}$) and $n$ are Freundlich constant which represent the adsorption capacity and the adsorption intensity respectively (Saini, 2015). A plot of $\log C_e$ vs. $\log q_e$ gives a linear curve with the intercept value of $K_F$ and the slope of $1/n$.

2.4.3.3. Dubinin–Radushkevich isotherm model

This is an empirical model initially developed to describe isotherms for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism (Dubinin et al.,
1947, Nguyen and Do, 2001, Foo and Hameed, 2010). The approach was usually applied to distinguish the physical and chemical adsorption of metal ions (Foo and Hameed, 2010).

It is more generally applicable than the Freundlich isotherm since it is not limited by the homogenous surface and constant adsorption potential assumption (Saini, 2015). The D-R equation is expressed as:

\[ q = (q_m) \exp(-K_{DR} \varepsilon^2) \]  

(2-29)

and the linear form is shown as:

\[ \ln q = \ln q_m - K_{DR} \varepsilon^2 \]  

(2-30)

\( K_{DR} \) is the activity constant related to average adsorption energy (mol\(^2\)/kJ\(^2\)) and \( \varepsilon \) is the Polanyi potential (kJ/mol) which can be calculated from this equation:

\[ \varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \]  

(2-31)

E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be calculated by the following relationship:

\[ E = (2K_{DR})^{-1/2} \]  

(2-32)

2.1.1. Temkin isotherm model

This isotherm describes the adsorbent –adsorbate interactions assuming that the adsorption heat decreases linearly rather than logarithmic as the coverage proceeds (Saini, 2015). The derivation of the isotherm equation is characterized by a uniform distribution of binding energies (Foo and Hameed, 2010, Saini, 2015). The equation for the isotherm expressed in the following form:

\[ q = \frac{RT}{b_T} \ln A_T C_e \]  

(2-33)

The linear equation is expressed as:
\[ q = \frac{RT}{b_T} \ln A_T + \left( \frac{RT}{b_T} \right) \ln C_e \]  \hspace{1cm} (2-34)

2.1.2. Modified Langmuir isotherm

Langmuir isotherm can be modified in several ways to improve its fit with experiments. The Langmuir-Freundlich equations combine Langmuir and Freundlich equations:

\[ q = \frac{K_{LF} C_e^{1/n}}{1 + a_{LF} C_e^{1/n}} \]  \hspace{1cm} (2-35)

where \( K_{LF} \) is the Langmuir–Freundlich constant and \( a_{LF} \) is the affinity coefficient (Bhaumik et al., 2011a).

2.4.3.4. Redlich-Peterson isotherm

Redlich–Peterson isotherm amends inaccuracies of two parameter Langmuir and Freundlich isotherm equations in some adsorption systems (Wu et al., 2010). It is a hybrid isotherm which incorporates three parameters into an empirical equation. It has a linear dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria over a wide concentration range, that can be applied either in homogeneous or heterogeneous systems due to its versatility (Foo and Hameed, 2010).

The equation is represented as:

\[ q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{b_{RP}}} \]  \hspace{1cm} (2-36)

where \( K_{RP} \) and \( a_{RP} \) are Redlich–Peterson constants and \( b_{RP} \) is the Redlich–Peterson model exponent.
2.4.3.5. BET isotherm

Brunauer–Emmett–Teller developed an equation capable of correlating multilayer adsorption systems and is a theoretical model most widely applied in the gas–solid equilibrium systems (Foo and Hameed, 2010, Brenner, 2013). The derivation of the equation follows Langmuir approach except that the adsorption takes place in the multilayers even before monolayer coverage is complete. The model assumes that for each adsorption site an arbitrary number of adsorbate molecules may be accommodated. The rate of adsorption in the first layer is different from those other layers (Brenner, 2013). The liquid–solid interface equation is exhibited as:

\[
q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)(1 + (C_{BET} - 1)(C_e/C_s))}
\]

where \(C_{BET}\), \(C_s\), \(q_s\) and \(q_e\) are the BET adsorption isotherm (L/mg), adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively (Foo and Hameed, 2010).

2.4.3.6. Thermodynamic parameters

Activation energy in adsorption process, is defined as the energy that must be overcome by the adsorbate ion to interact with the functional groups on the surface of the adsorbent. It is the minimum energy needed for a specific adsorbate-adsorbent interaction to take place, even though the process may already be thermodynamically possible. The activation energy (Ea) can be determined from experimental measurements of the adsorption rate constant at different temperatures according to the Arrhenius equation as follows (Saha and Chowdhury, 2011):

\[
\ln k = \ln A - \frac{E_a}{RT}
\]
where \( k \) is the adsorption rate constant, \( A \) is the frequency factor constant, \( E_a \) is the activation energy (kJ.mol\(^{-1}\)), \( R \) is the gas constant (8.314 J/mol/K) and \( T \) is the temperature (K). Values of \( E_a \) and \( A \) can be determined from the slope and the intercept by plotting \( \ln k \) versus \( 1/T \).

Thermodynamic considerations of an adsorption process are necessary to ascertain whether the process is spontaneous or not. The Gibb’s free energy change, \( \Delta G^0 \), is a fundamental indication of spontaneity of a chemical reaction. Enthalpy (\( \Delta H^0 \)) and entropy (\( \Delta S^0 \)) parameters must be considered in order to determine the Gibb’s free energy of the process. The free energy of an adsorption process is related to the equilibrium constant by the classical Van’t Hoff equation (Saha and Chowdhury, 2011):

\[
\Delta G^0 = -RT \ln k_d
\]

(2-39)

\[
\ln k_d = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]

(2-40)

where \( \Delta G^0 \) is the Gibb’s free energy change (kJ/mol), \( R \) is the ideal gas constant (8.314J/mol/K), and \( T \) is temperature (K) and \( k_d \) is the single point or linear sorption distribution coefficient which is defined as:

\[
k_d = \frac{C_a}{C_e}
\]

(2-41)

where \( C_a \) is the equilibrium adsorbate concentration on the adsorbent (mg /L) and \( C_e \) is the equilibrium adsorbate concentration in solution (mg/L).

A decrease in the negative value of \( \Delta G^0 \) with an increase in temperature indicates that the adsorption process is more favorable at higher temperatures. This could be possible because the mobility of adsorbate in the solution increase with increase in temperature and that the affinity of adsorbate on the adsorbent is higher at high temperatures. On the contrary, an increase in the negative value of \( \Delta G^0 \) with an increase in temperature implies that lower temperature makes the
adsorption easier. Also reactions occur spontaneously at a given temperature if $\Delta G^0$ is a negative quantity (Saha and Chowdhury, 2011).

2.4.4. Fixed bed column

Adsorption in a fixed-bed adsorber is a time and distance dependent process. Each adsorbent particle in the bed accumulates adsorbate from the percolating solution as long as the state of equilibrium is reached, during the adsorption process. This equilibration process proceeds successively, layer by layer, from the column inlet to the column outlet (Worch, 2012). Batch adsorption test are unable provide adequate scaled up data that can be used to design flow columns. They are inadequate to estimate the breakthrough behavior of adsorbents, an indispensable parameter for appropriate design of an adsorption column. Batch adsorption is economically infeasible in contrast to contaminant adsorption using dynamic columns. Dynamic column experiments aids in resolving the limitations of laboratory and field pilot testing, and in compiling relevant data for scale-up design (Rahaman et al., 2015).

The performance of continuous packed beds is described through the concept of the breakthrough curve. The breakthrough point and the breakthrough curve depend on the nature of the adsorbate and the adsorbent, the operating conditions and the geometry of the column (Hung et al., 2012). The breakthrough curve is usually expressed by $C_t/C_0$ as a function of time or volume of the effluent for a given bed depth. $C_t$ is the effluent concentration from the column and $C_0$ the influent concentration. Effluent volume ($V_{eff}$) can be calculated as follows:

$$V_{eff} = F \times t_e$$  \hspace{1cm} (2-42)
where $t_e$ is the bed exhaustion time at which concentration in the effluent reached 99.5% of initial concentration and $F$ is the volumetric flow rate (Tamez Uddin et al., 2009). The total quantity of contaminant adsorbed in the column ($m_{ad}$) is calculated from the area above the breakthrough curve multiplied by the flow rate (Chen et al., 2012).

$$M_{ad} = \frac{F}{1000} \int_{t=0}^{t=\text{total}} C_{ad} \, dt$$

(2-43)

where $C_{ad}$ is the concentration of metal removal (mg/L)

Total amount of contaminant passed through the column is calculated by the following expression

$$m_{total} = \frac{c_0 \times F \times t_e}{1000}$$

(2-44)

Then the total removal percent with respect to flow volume can be calculated from this equation

$$\text{Total removal} \, (\%) = \frac{m_{ad}}{m_{total}} \times 100$$

(2-45)

Equilibrium metal uptake or maximum capacity of the column, $q_{eq}$ (mg/g), in the column is calculated as the following (Chen et al., 2012):

$$q_e = \frac{M_{ad}}{m}$$

(2-46)

The capacity of the bed at breakthrough point is determined from the following equation:

$$q_b = \frac{c_0}{m} \int_{v=0}^{V_b} \left(1 - \frac{C_t}{C_0}\right) \, dV$$

(2-47)

where $q_b$ is the bed capacity at breakthrough point (mg/g), $m$ is the bed mass (g), $C_0$ is the initial adsorbate concentration (mg/L), $C_t$ is the concentration of treated water of the outlet solution (mg/L) at any time $t$ and $V_b$ is the volume processed at breakthrough point (L).
The performance of a fixed bed column is directly related to the number of bed volumes (BV) processed before the breakthrough point is reached (Onyango et al., 2009, Mthombeni et al., 2012). The number of bed volumes at breakthrough point is given by the following equation:

\[ BV = \frac{\text{Volume of water at breakthrough point (L)}}{\text{Volume of adsorbent bed (L)}} \]  

(2-48)

The adsorbent exhaustion rate (AER) per volume of water treated at breakthrough point and is expressed as:

\[ AER = \frac{\text{Mass of adsorbent material (g) in column}}{\text{Volume of water treated (L)}} \]  

(2-49)

The empty bed contact time (EBCT), is used to determine the optimum adsorbent usage in a fixed-bed column. It is expressed as follows (Ma et al., 2014).

\[ EBCT = \frac{\text{adsorbent bed volume (mL)}}{\text{flowrate (mL/min)}} \]  

(2-50)

2.4.5. Breakthrough curves modelling

2.4.5.1. Thomas model
Thomas model is developed on the assumption that (1) the adsorption is not limited by chemical interactions but by mass transfer at the interface and (2) the experimental data follows Langmuir isotherms and second-order kinetics (Foo et al., 2013, Wang et al., 2015, Nguyen et al., 2015a).

The model can be described by the following expression:

\[ \frac{C_t}{C_0} = \frac{1}{1 + \exp \left( \frac{k_{Th}q_0 m}{F} - k_{Th}C_0 t \right)} \]  

(2-51)

where \( k_{Th} \) is the Thomas rate constant (mL/min mg), \( q_0 \) is the adsorption capacity (mg/g), \( C_0 \) is the inlet concentration (mg/L), \( C_t \) is the outlet concentration at time \( t \) (mg/L), \( m \) is the mass of adsorbent (g), \( F \) is the feed flow rate (mL/min), and \( t \) is time (min).
2.4.5.2. **Bohart–Adams model**

The model assumes that equilibrium is not instant and the adsorption rate is controlled by external mass transfer (Quintelas et al., 2013, Nguyen et al., 2015a). The model can be expressed as:

\[
\frac{C_t}{C_0} = \exp \left( k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{U_0} \right)
\]  

(2-52)

where \( k_{BA} \) is the kinetic constant (L/mg min), \( N_0 \) is the saturation concentration (mg/L), \( z \) is the bed depth of the fixed bed column (cm) and \( U_0 \) is the superficial velocity (cm/min) defined as the ratio of the volumetric flow rate \( F \) (cm\(^3\)/min) to the cross-sectional area of the bed (cm\(^2\)).

2.4.5.3. **Yoon–Nelson model**

This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent (Bhaumik et al., 2013b, Chen et al., 2012, Setshedi et al., 2014). Yoon–Nelson model for a single component system can be expressed as:

\[
\frac{C_t}{C_0 - C_t} = \exp(k_{YN} t - \tau k_{YN})
\]  

(2-53)

where \( k_{YN} \) is the rate constant in (min\(^{-1}\)), \( \tau \) is the time required for 50% adsorbate breakthrough (min) and \( t \) is the processing time (min).

2.5. **Removal of heavy metals from water by adsorption**

2.5.1. **Activated carbon and low cost activated carbon adsorbents**

Activated carbon has been found to be a good adsorbent due to its high capacity of adsorption because of small particle sizes and active free valences. However activated carbon as an
adsorbent for water treatment is restricted due to its high production cost and the regeneration process that involves costly chemicals (Gupta and Ali, 2013). To decrease the high cost of activated carbon several studies on using waste materials have been conducted to find a low-cost adsorbent (Dias et al., 2007). A variety of low-cost activated carbons from agricultural waste materials such as coconut shell fibers and coconut shell developed and used for the removal of heavy metals from synthetic wastewater (Mohan et al., 2005a, Mohan et al., 2006). The use of biomass waste-derived activated carbon to remove heavy metals has also been explored (Budinova et al., 2009). Several studies have reported that process parameters such as pH, heavy metal ion concentration, temperature and sorbent particles size significantly influence the adsorption process. Since the choice of the sorbent material for any adsorption process is important and depends on its cost, availability and suitability to remove the given pollutant; scattered studies have been conducted for the past years to develop adsorbents mainly from several agricultural and industrial waste materials with the dual aim of low cost as well as effectiveness for adsorption process optimization (Mthombeni et al., 2015a).

2.5.1.1. Removal of chromium using activated carbon and low cost waste adsorbents

A variety of low-cost activated carbons from agricultural waste materials such as coconut shell fibers and coconut shell have been developed and used for the removal of heavy metals from synthetic wastewater (Mohan et al., 2005a, Mohan et al., 2006). Activated carbon obtained from Pterocladia capillacea, a red marine macroalga, was tested for its ability to remove toxic Cr(VI) from aqueous solution (El Nemr et al., 2015). Batch equilibrium tests at different pH conditions showed that at pH 1.0, a maximum chromium uptake was observed for both inactivated dried red alga P. capillacea and its activated carbon. The Langmuir maximum sorption capacities for dried red alga and its activated carbon were 12 and 66 mg/g, respectively.
Sugashini and Begum (2015) prepared activated carbon (AC) from carbonized rice husks using ozone as an activating agent and used for the adsorption of Cr(VI) ions. The Brunauer-Emmett-Teller surface area of the carbons was increased from 20 to 380 m²/g by the activation. The authors observed that the silica attached to the carbonaceous material is loosened, leading to a release of carbon during the ozone activation which exists as both molecular and atomic oxygen on the surface of carbon. Atomic oxygen oxidizes the carbon surface into acidic functional groups such as carboxylic, ketonic and phenolic. A maximum removal percentage (94%) of Cr(VI) ions was obtained for a 100 mg/L aqueous solution at the optimized conditions of pH value of 2.0, adsorbent dosage of 0.2g, time of 2.5 h and stirring speed of 300 r/min. They found that the adsorption isotherms fitted well to the Freundlich equation and the adsorption rate followed pseudo second order kinetics which indicated that the adsorption was spontaneous and exothermic.

Batch adsorption removal of Cr(VI) ions from aqueous solutions onto black rice husk ash was investigated by Georgieva et al. (2015) under different conditions. The most favorable conditions for removing Cr(VI) from aqueous solutions via adsorption onto black rice husk ash were found to be pH 2, adsorbent dosage level of 15 g/L in the concentration range 25–200 mg L⁻¹, temperature interval 10–30 °C and contact time 30–120 min. The percent of removal of Cr(VI) ions at initial concentration 50 mg/L at 30 °C was 98.46%. The value of activation energy (41.57 kJ mol⁻¹) is on limit between physical and chemical adsorption, but the physisorption was the predominant adsorption mechanism for Cr(VI) removal by the adsorbent. Sulfuric acid modified avocado seed as a low-cost carbonized adsorbent, was investigated by Bhaumik et al. (2014b) for the removal of toxic Cr(VI) from water/wastewater in batch
experiments. A low temperature of 100 °C chemical carbonization treatment was used for the production of the adsorbent. It was revealed that there was formation of agglomerated and rodlike structured particles after carbonization of avocado seed and there was the presence of oxo-functional groups on the surface of sulfuric acid modified avocado seed. Adsorption of

Table 2-1. Comparison of activated carbons and low cost adsorbents sorption capacities of Cr(VI) ions

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Mode of operation</th>
<th>Adsorbent dosage (g/L)</th>
<th>pH</th>
<th>Removal %</th>
<th>Adsorption capacity (mg/g)</th>
<th>Model used to calculate adsorption capacity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk activated carbon</td>
<td>Batch : 100</td>
<td>4</td>
<td>2</td>
<td>94</td>
<td>62.9 mg/g</td>
<td>Langmuir</td>
<td>(Sugashini and Begum, 2015)</td>
</tr>
<tr>
<td>Black rice husk ash</td>
<td>Batch : 50</td>
<td>15</td>
<td>2</td>
<td>99</td>
<td>n/a</td>
<td>n/a</td>
<td>(Georgieva et al., 2015)</td>
</tr>
<tr>
<td>Activated rice husk</td>
<td>Batch : 10</td>
<td>14</td>
<td>2</td>
<td>93</td>
<td>n/a</td>
<td>Freudlich</td>
<td>(Bishnoi et al., 2004)</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>Batch : 10</td>
<td>14</td>
<td>4</td>
<td>99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red marine macroalgae</td>
<td>Batch : 100</td>
<td>2</td>
<td>12</td>
<td>mg/g</td>
<td>12 mg/g</td>
<td>Langmuir</td>
<td>(El Nemr et al., 2015)</td>
</tr>
<tr>
<td>(Pterocladia capillacea)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-based activated carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green honey myrtle</td>
<td>Batch : 250</td>
<td>5</td>
<td>2-10</td>
<td>97-99</td>
<td>62.5 mg/g</td>
<td>Langmuir</td>
<td>(Kuppusamy et al., 2016)</td>
</tr>
<tr>
<td>(Melaleuca diosmifolia)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material Description</td>
<td>Batch:</td>
<td>C1</td>
<td>C2</td>
<td>C3</td>
<td>C4</td>
<td>Langmuir</td>
<td>Reference</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>--------</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Acid–base modified activated carbon</td>
<td>5-50</td>
<td>2</td>
<td>n/a</td>
<td>n/a</td>
<td>13.9 mg/g</td>
<td>Langmuir</td>
<td>(Liu et al., 2007)</td>
</tr>
<tr>
<td>Activated carbon from lagoon seeds</td>
<td>100</td>
<td>2</td>
<td>3</td>
<td>n/a</td>
<td>35.2 mg/g</td>
<td>Langmuir</td>
<td>(Yang et al., 2015)</td>
</tr>
<tr>
<td>Fe-modified <em>Trapa natans</em> husk activated carbon</td>
<td>20</td>
<td>1.5</td>
<td>2-3</td>
<td>95</td>
<td>11.83 mg/g</td>
<td>Langmuir</td>
<td>(Liu et al., 2010)</td>
</tr>
<tr>
<td>Quaternary amine-anchored activated carbons</td>
<td>10-150</td>
<td>1</td>
<td>5.5</td>
<td></td>
<td>10.57 mg/g</td>
<td>Langmuir</td>
<td>(Wang et al., 2016)</td>
</tr>
<tr>
<td><em>AC</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.247 mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>AC-T</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99% mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>AC-E</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>112.36 mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated carbon-Fe</td>
<td>5.7–63.3</td>
<td>1</td>
<td>5.38</td>
<td>n/a</td>
<td>34.39 mg/g</td>
<td>Langmuir</td>
<td>(Sun et al., 2014b)</td>
</tr>
<tr>
<td>Activated carbon-Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33.74 mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated carbon-Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33.67 mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15.07 mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powdered activated carbon</td>
<td>0.05-0.25</td>
<td>0.1</td>
<td>4</td>
<td>99.4</td>
<td>46.9 mg/g</td>
<td>Langmuir</td>
<td>(Jung et al., 2013)</td>
</tr>
<tr>
<td>Activated carbons derived from peanut shells</td>
<td>10-100</td>
<td>n/a</td>
<td>4</td>
<td>46.3</td>
<td>16.26 mg/g</td>
<td>Langmuir</td>
<td>(Al-Othman et al., 2012)</td>
</tr>
<tr>
<td>Algae bloom</td>
<td>200</td>
<td>1</td>
<td>1</td>
<td>99</td>
<td>155.52</td>
<td>Langmuir</td>
<td>(Zhang et al.,</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Batch: 10-100</td>
<td>0.6</td>
<td>2</td>
<td>97</td>
<td>140 mg/g</td>
<td>Langmuir</td>
<td>2010a)</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>---------------</td>
<td>-----</td>
<td>---</td>
<td>----</td>
<td>-----------</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>Jatropha wood (JKV2T700)</td>
<td></td>
<td></td>
<td></td>
<td>68</td>
<td>106 mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peanut shells (CHV100T400)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylonitrile - divinylbenzene activated carbon</td>
<td>Batch: 1.2</td>
<td>2</td>
<td>n/a</td>
<td>101.2 mg/g</td>
<td>Langmuir</td>
<td>(Duranoğlu et al., 2012)</td>
<td></td>
</tr>
<tr>
<td>Prawn shell activated carbon</td>
<td>Batch: 25-125</td>
<td>1.6</td>
<td>n/a</td>
<td>99</td>
<td>100 mg/g</td>
<td>Langmuir</td>
<td>(Arulkumar et al., 2012)</td>
</tr>
<tr>
<td>Activated carbon derived from E. crassipes root biomass</td>
<td>Batch: 10-100</td>
<td>4.5</td>
<td>77-92</td>
<td>36.34 mg/g</td>
<td>Langmuir</td>
<td>(Giri et al., 2012)</td>
<td></td>
</tr>
</tbody>
</table>

n/a= not available

Cr(VI) onto surface of sulfuric acid modified avocado seed was highly pH dependent and found to be an optimum at pH 2.0. Adsorption isotherm results suggested that the capacity increases with an increase in temperature. Nonlinear regression analysis revealed that the Freundlich isotherm model provided a better correlation than the Langmuir isotherm model for Cr(VI)
adsorption onto sulfuric acid modified avocado seed. The maximum Cr(VI) adsorption capacity of 333.33 mg/g was obtained at 25 °C.

Adsorption kinetics was best described by the pseudo-second-order model. The presences of coexisting ions were found to slightly affect the Cr(VI) removal efficiency of sulfuric acid modified avocado seed. Experiment with real wastewater sample containing 47.34 mg/L of Cr(VI) demonstrated that by the use of only 0.03 g/25 mL of sulfuric acid modified avocado seed, almost 100% removal at pH 2.0 was achieved. Studies on the adsorption of Cr(VI) on activated carbon and low cost waste derived activated carbon is summaries in Table 2-1.

2.5.1.2. Activated carbon as an adsorbent for manganese

The removal of manganese and other metal ions from industrial wastes using granular activated carbon which recorded an adsorption capacity of 2 mg/g for manganese ion removal has been investigated Goher et al. (2015). Modification and impregnation of the activated carbon has also been used to increase the surface adsorption and removal capacity and to add selectivity to activated carbon. Granulated activated carbon modified with tannic acid (Üçer et al., 2006), Fe$^{3+}$ impregnated activated carbon (Mondal et al., 2008) were used for the removal of manganese and other heavy metals ions.

Budinova et al. (2009) explored the use of biomass waste-derived activated carbon to remove arsenic and manganese. The maximum sorption capacity for Mn(II) ions was 23.4 mg/g. The removal of manganese ionic species was observed to increase sharply between pH 2 and 4, and the maximum uptake was attained and remained constant at pH values above 4. This was attributed to partial hydrolysis of Mn (II) ions with increasing pH, resulting in the formation of
complexes with OH⁻ such as Mn(OH)⁺, Mn(OH)₂, Mn₂(OH)₃⁺, Mn₂OH³⁻, Mn(OH)₄²⁻ species in solution.

Adsorption of manganese (II) ions from aqueous solution using activated carbon derived Ziziphus a spina-christi seed was investigated by Omri and Benzina (2012). It was suggested that the adsorption mechanism involved chemical bonding and cation exchange on the surface of the prepared activated carbon which contains functional groups of oxygen and aromatic compounds.

Table 2-2. Mn adsorption studies using activated carbon

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Experimental conditions</th>
<th>Initial concentration (mg/L)</th>
<th>Adsorbent dosage (g/L)</th>
<th>pH</th>
<th>Removal efficiency (%)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant modified carbon</td>
<td>Batch experiments</td>
<td>50</td>
<td>1</td>
<td>7</td>
<td>56.8</td>
<td>40</td>
<td>(Anbia and Amirmahmoodi, 2011)</td>
</tr>
<tr>
<td>unmodified mesoporous carbon</td>
<td>Temp: 70±C</td>
<td>50</td>
<td>1</td>
<td>7</td>
<td>82.2</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>*cetyltrimethyl ammonium bromide</td>
<td>Time: 420 min</td>
<td>50</td>
<td>1</td>
<td>7</td>
<td>70.5</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>*sodium dodecyl sulfate</td>
<td>Batch experiments</td>
<td>n/a</td>
<td>0.1-6</td>
<td>n/a</td>
<td>2.5</td>
<td>25</td>
<td>(bin Jusoh et al., 2005)</td>
</tr>
<tr>
<td>Activated carbon-granular</td>
<td>Temp: Room</td>
<td>n/a</td>
<td>0.2-0.9</td>
<td>n/a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time: 6hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n/a : not available
The possible mechanisms of ion exchange considered was that a manganese ion (Mn$^{2+}$) attaches itself to two adjacent hydroxyl groups and two-oxyl groups which donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution. The Langmuir adsorption capacity was found to be 172.41 mg/g.

Akl et al. (2013) demonstrated the potential use of activated carbons derived from olive stones for the removal of Fe (III) and Mn (II) from aqueous solutions. Further results obtained in some other studies on use of activated carbon are summarized in Table 2-2.

2.5.1.3. Removal of vanadium using activated carbon and other agricultural water and byproducts

It has been reported that activation of carbon with ZnCl$_2$ in coir pith generated more interspaces between carbon layers leading to more microporosity and more surface area compared to the carbon prepared in the absence of ZnCl$_2$ (Namasivayam and Sangeetha, 2006). The study reported ZnCl$_2$ activated carbon to be an effective adsorbent for the removal of vanadium (V) from aqueous solution with successful regeneration of the adsorbent. The Langmuir adsorption capacity was found to be 24.9 mg/g. Maximum removal of V(V) occurred in the pH range 4.0 to 9.0. Desorption of V(V) was observed to increase with increase in pH due to the increased concentration of OH$^-$. The authors suggested that the effect of pH and desorption studies show that ion exchange mechanism is operative in the adsorption process.

Bhatnagar et al. (2008) investigated the potential of metal sludge which as a waste product of electroplating industry in removing vanadium from water. The adsorption capacity of metal sludge for vanadium was found 24.8 mg/g at 25 $^\circ$C. The adsorption process was found to be endothermic and experimental data conform to Langmuir model. The analysis of kinetic data...
indicated that adsorption system was a pseudo-first-order process and it was controlled by intraparticle diffusion.

A novel adsorbent grafted tamarind fruit shell bearing $-\text{NH}_3^+\text{Cl}^-$ bearing functional moiety was prepared by Anirudhan and Radhakrishnan (2010). It was synthesized from tamarind fruit shell (TFS) through graft copolymerization of hydroxyethylmethacrylate onto tamarind fruit shell in the presence of N,N′-methylenebisacrylamide as a cross linking agent using K$_2$S$_2$O$_8$/Na$_2$S$_2$O$_3$ initiator system, followed by transmidation and hydrochloric acid treatment. The maximum adsorption was observed in the pH range 3.0–6.0. The adsorption was found to be dependent on the initial concentration and exothermic. The adsorption followed the reversible second-order kinetics and the low Ea (~4.06 kJ/mol) indicated that the process was controlled by diffusion. Equilibrium adsorption studies demonstrated that the adsorption process obeys Langmuir isotherm model and the maximum adsorption capacity of V(V) was 45.86 mg/g at 30°C. The values of change in entropy ($\Delta S^\circ$) and heat of adsorption ($\Delta H^\circ$) for V(V) adsorption on functionalized grafted tamarind fruit shell were estimated as $-47.20 \text{ J/mol K}$ and $-15.64 \text{ kJ/mol}$, respectively. The values of isosteric heat of adsorption ($\Delta H_i$) were found to be constant (~26.0 kJ/mol) which indicated that adsorbent used possessed nearly homogeneous surface sites. The spent adsorbent regenerated with 0.2 M NaOH, achieved up to 96% recovery and can be reused in four adsorption–desorption cycles without any substantial loss in adsorption capacity.

Hu et al., (2014) evaluated the potential of dried orange juice residue was as an economical and environmentally benign sorbent through chemical loading with zirconium (IV). The adsorption properties for vanadium (V) and chromium (VI) from synthetic and actual waste water onto the Zr(IV)-loaded orange juice residue were investigated. The results indicated that the adsorption of
V(V) is strongly dependent on solution pH, and the maximum separation coefficient ($\beta_{V/Cr} = 45$) between V(V) and Cr(VI) takes place at pH 2.85. It was proposed that the anion exchange or nucleophilic substitution reaction between OH$^-$ and metal oxo-anions was the main adsorption mechanism. The authors indicated that adsorption of V(V) onto the gel can be described well by Langmuir adsorption and pseudo-second-order rate equations. The maximum adsorption capacities for V(V) and Cr(VI) were estimated as 51.0943245 and 14.9748768 mg/g, respectively.

The adsorbed vanadium was effectively desorbed using a diluted NaOH solution. It was reported that there is a negligible interference of coexisting anions, such as nitrates and chlorides. It was also demonstrated that the bed was not completely saturated until 320 bed volumes for V(V) were treated, while for Cr(VI), $C_i$ became equal to $C_0$ only at 30 bed volumes, suggesting that there was a larger adsorption capacity of Zr(IV)-SOW toward V(V) over Cr(VI).

2.5.2. *Low cost byproducts adsorbents and biosorbents for manganese removal*

2.5.2.1. *Agricultural waste*

Industrial byproducts and agricultural wastes locally available in certain regions have been utilized as low-cost adsorbents. Of the different biological methods, bioaccumulation and biosorption have been demonstrated to possess good potential to be an alternative replace most of conventional physicochemical treatment methods for the removal of metals (Khoo and Ting, 2001, Vijayaraghavan and Yun, 2008). Biosorption is the binding of metals to organic mater; it is a passive metabolic independent process (Acheampong et al., 2010). Biomaterials of microbial and plant origin interact effectively with heavy metals (Vijayaraghavan and Yun, 2008) and the sorption on these biomaterials is attributed to their constituents, which are mainly proteins, carbohydrates and phenolic compounds, since they contain functional groups such as
carboxylates, hydroxyls and amines, which are able to attach to the metal ions (Lesmana et al., 2009). Biosorbent materials that are easily available include three groups: algae, fungi, and bacteria (Wang and Chen, 2009, Volesky and Holan, 1995).

Adsorption of Mn(II) from water was investigated using a thermally decomposed leaf (Li et al., 2010). The adsorbent dosage used was 10g/L for a concentration of 100 mg/L. According to their results the removal percentage of manganese increased from 0-99% for pH values between 1.8 - 3.84, with the adsorption capacity determined at 61–66 mg/g. The adsorption on the thermally decomposed leaf involved the chemisorption relevant to phosphate, ferrous oxide and carbonate while physisorption was attributed to carbon black containing abundant microspheres. Maize husk, which is an abundant agricultural waste was used to prepare a biosorbent (Adeogun et al., 2013) for Mn(II) ions. In another study green tomato husk modified and unmodified with formaldehyde was evaluated for simultaneous removal of iron and manganese (García-Mendieta et al., 2012).

Rice husk is the by-product of the rice milling industry produced in large quantities as a waste. It consists of crude protein, ash (including silica), lignin, hemicellulose, and cellulose. It is insoluble in water, has good chemical stability, high mechanical strength and possesses a granular structure, making it a good adsorbent material suitable for removing heavy metals from wastewater (Peng and Sun, 2010). It has been suggested that the removal of Mn(II) ions by rice husk from aqueous solutions using is a chemisorption process, where there is a chemical reaction between surface OH-groups of SiO₂ and Mn (II), releasing H⁺ ions in the solution (Tavlieva et al., 2015). Another study using rusk husk in which Langmuir maximum adsorption
capacity 8.3 mg/g was reported by Krishnani et al. (2008). The results of rice husks and other agricultural by-products are shown in Table 2-3.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Mode of operation</th>
<th>Initial concentration (mg/L)</th>
<th>Adsorbent dosage (g/L)</th>
<th>pH</th>
<th>Removal efficiency (%)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermally decomposed leaf</td>
<td>Batch experiments</td>
<td>100</td>
<td>10</td>
<td>3.8</td>
<td>99</td>
<td>61-66</td>
<td>(Li et al., 2010)</td>
</tr>
<tr>
<td>Maize husk</td>
<td>Batch experiments</td>
<td>100</td>
<td>0.8</td>
<td>2</td>
<td>93.4</td>
<td>9</td>
<td>(Adeogun et al., 2013)</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Batch experiments</td>
<td>100</td>
<td>2.5</td>
<td>7</td>
<td>26.62</td>
<td>12-18</td>
<td>(Tavljeva et al., 2015)</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Batch and column experiments</td>
<td>200</td>
<td>3</td>
<td>6</td>
<td>Not available</td>
<td>7.7</td>
<td>(Krishnani et al., 2008)</td>
</tr>
<tr>
<td>Banana peel</td>
<td>Batch experiments</td>
<td>10</td>
<td>4</td>
<td>4</td>
<td>90</td>
<td>3.6</td>
<td>(Ali and Saeed, 2015)</td>
</tr>
<tr>
<td>Green tomato husk</td>
<td>Batch experiments</td>
<td>10</td>
<td>0.1</td>
<td>6</td>
<td>84.8</td>
<td>15.2</td>
<td>(García-Mendieta et al., 2012)</td>
</tr>
</tbody>
</table>

n/a : not available

*Saccharomyces cerevisiae* has received increasing attention due to its unique nature and its metal sorption capacity (Wang and Chen, 2006, Das et al., 2008, Chen and Wang, 2008, Fadel et al.). Eleven *S. cerevisiae* yeast strains in alive and dead forms were screened and studied by (Fadel et al.) for biosorption and bioaccumulation of manganese from synthetic aqueous solution. It was found that *S. cerevisiae* F-25 in alive form was the most effective biosorbent for Mn(II) and biosorbed 22.5 mg/g yeast biomass. The results revealed that environmental conditions that
favored maximum Mn(II) concentrations biosorption by *S. cerevisiae* F-25 in alive form were 4.8 mg/l after 30 min at pH 7, agitation 150 rpm and yeast biomass concentration 0.1 gm/l at 30°C.

Hasan et al. (2012) studied the biosorption isotherms of *Bacillus sp.* and sewage activated sludge in laboratory-scale experiments using the isotherm models developed by Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, and Redlich-Peterson (R-P). It was revealed that *Bacillus sp.* is a more effective biosorbent than sewerage activated sludge. Biosorption of manganese by *Bacillus sp.* was found to be significantly better fitted to the Langmuir-1 isotherm than the other isotherms, while the Dubinin-Radushkevich isotherm was the best fit for sewage activated sludge. The Langmuir maximum biosorption capacities of manganese onto *Bacillus sp.* and sewage activated sludge were 43.5 mg Mn$^{2+}$/g biomass and 12.7 mg Mn$^{2+}$/g biomass, respectively. The D-R isotherm showed that the biosorption processes by both *Bacillus sp.* and sewage activated sludge occurred via the chemical ion-exchange mechanism between the functional groups and Mn$^{2+}$ ion.

Mn(II) ions biosorption was studied by Kamarudzaman et al. (2015) using *Pleurotus* spent mushroom compost performed in a fixed-bed column. Mn(II) ions biosorption in fixed-bed column achieved better performance at a flow rate of 1 mL/min, bed height of 30 cm and initial Mn(II) concentration of 10 mg/L. The breakthrough time and exhaustion time were obtained at 16.5 hours and 26.7 hours, respectively.

The ability of in vitro roots cultures of *Typha latifolia* and *Scirpus americanus* to remove Mn and other metal ions was studied by Santos-Díaz and Barrón-Cruz (2011). *T. latifolia* roots were able to uptake 1.680 mg /g, while the *S. americanus* roots removed 4.037 mg/g. The potential of
macrophyte *Spirodea polyrhiza* (L.) Schleiden from the phoomdi biomass of *Loktak* lake, India as an adsorbent to remove Mn(II) and other metal ions from metal solution system was investigated by Meitei and Prasad (2014). Metal adsorption was fast and equilibrium was attained within 120 min. Langmuir isotherm best described the equilibrium with maximum adsorption capacities of 35.7 mg/g for Mn (II) ions. Adsorption of the specific metal ions from binary and ternary metal solution system showed antagonistic nature due to screening effect and competition between the metal ions for active sites on the biomass.

Hexavalent chromium biosorption by raw and acid-treated *Oedogonium hatei* from aqueous solutions has been studied by Gupta and Rastogi (2009). The nature of biomass–metal ions interactions showed that the participation of −COOH, −OH and −NH₂ groups in the biosorption process. Biosorbents could be regenerated using 0.1 M NaOH solution, with up to 75% recovery. A novel biosorbent *Caryota urens* inflorescence waste biomass (CUIWB) was used for the removal of hexavalent chromium from aqueous solutions. Investigations carried out proved that CUIWB is a good potential biosorbent for the treatment of hexavalent chromium in aqueous media with a Langmuir capacity of 100 mg/g (Rangabhashiyam and Selvaraju, 2015).

The use of dried and re-hydrated biomass of the seagrass *Posidonia oceanica* was investigated by (Pennesi et al., 2013) as an alternative and low cost biomaterial for removal of vanadium(III) from wastewaters. For the single-metal solutions, the optimum was at pH 3, where a significant proportion of vanadium was removed (ca. 70%)

Kaczala et al. (2009) investigated batch sorption with untreated Pinus sylvestris sawdust after settling/sedimentation phase to remove vanadium and lead from a real industrial wastewater. It
was found that when the initial pH was reduced from 7.4 to 4.0, the sorption efficiency increased from 43% to 95% for V.

2.5.2.2. Removal of heavy metals using chitosan

Chitosan occurs naturally and as a polysaccharide which is found in insects, arthropods and crustaceans, fungal biomass and algae by deacetylation of chitin, and has an ability to effectively remove heavy metal ability due to its amino groups and hydroxy groups (Lu et al., 2001, Padilla-Rodríguez et al., 2015). It is inexpensive, abundant, biodegradable, and widely available from sea food-processing wastes (Bailey et al., 1999, de Castro Dantas et al., 2001, Pal and Banat, 2014, Jung et al., 2013).

Abdeen et al. (2015) in their study explored the ability of polyvinyl alcohol/chitosan binary dry blend as an adsorbent for removal of Mn(II) ion from aqueous solution. The chitosan material was made from shell from shrimps collected from sea food shops. It was found that the biosorption capacity of the polyvinyl alcohol/chitosan adsorbent increases from 0.596 to 9.22 mg/g with increasing metal ion concentrations from 5 to 100 mg/L. They also concluded from their study that the optimum pH for biosorption of Mn (II) ion on polyvinyl alcohol/chitosan was 5.0. In a study done by Al-Wakeel et al. (2015) the adsorption capacity of glycine onto modified chitosan resin was found to be 71.4mg/g at pH 6. Reiad et al. (2012) investigated the adsorption of manganese using microporous chitosan/polyethylene glycol blend membrane which showed adsorption capacity of up to 18 mg/g for manganese ions at pH 5.9.

(Robinson-Lora and Brennan, 2010) evaluated the role of chitin derived from processed crab shells and its associated proteins in the removal of manganese from mine impacted waters under abiotic and anoxic conditions using sorption processes. According to their results the maximum
sorption capacity was found to depend greatly on the pH of the solution, with very minimal or no adsorption observed at pH less than 5. At pH 5.4 value the adsorption capacity was 0.165 mg/g and 0.981 mg/g at pH 8.7.

Crab shells were found to possess better uptake capacities of 69.9 mg/g for Mn(II). The removal of Mn(II) by crab shell was found to be pH dependent, with optimum sorption occurring at pH 6. The mechanism of metal removal by crab shell was identified as micro-precipitation of metal carbonates followed by adsorption onto chitin at the surface of crab shell (Vijayaraghavan et al., 2011).

Masukume et al. (2014) found that the adsorption of Mn sea shells as adsorbents from acid mine water is very low. The removal efficiencies of manganese ranged from 12.1% (sorbent mass, 0.1 g/50mL) to 54.4% (sorbent mass, 1 g/50 mL).

Ananpattarachai and Kajitvichyanukul (2016) prepared a novel bio-catalyst by addition of titanium dioxide in the mixture solution of chitosan and xylan in acetic acid and evaluated photocatalytic reduction of Cr(VI)in aqueous solution under ultraviolet irradiation. From the rough surface modification from xylan addition and the chelating ability of chitosan, the enhancement of Cr(VI) removal by adsorption and photocatalysis of this bio-catalyst was pronounced. The photocatalytic reduction rate of Cr(VI) was $0.56 \times 10^{-3}$ and $0.03 \times 10^{-3}$ ppm-min for the titania bio-catalyst and titania nanopowder, respectively. Significant dependence of Cr(VI) removal on the titania and chitosan loading could be explained in terms of the relationship between kinetics of Cr(VI) photocatalytic reactions and the loading amount of each chemical. The authors suggested that according to the Langmuir–Hinshelwood model, the
photocatalytic rate constant of surface reaction of Cr(VI) was increased with an increasing of chemical loading in bio-catalyst.

A carbonaceous chitosan adsorbent with good stability in acid solution the amine groups were retained completely after simple and green hydrothermal carbonization treatment and was used effectively to remove Cr(VI) (Shen et al., 2016). Under optimal conditions, the adsorption capacity of the chitosan for Cr(VI) reached as high as 388.60 mg/g and the prepared chitosan adsorbent could be reused at least five times with adsorption efficiency more than 92%.

Zhang et al. (2014) prepared and investigated an inorganic-biopolymer composite based on chitosan-zirconium (IV) as a biosorbent for the removal of vanadium (V) ions from aqueous solution. Batch experiments were performed to evaluate various relevant parameters affecting the adsorption capacity such as pH, initial concentration, and contact time, temperature and co-existing ions. The authors reported that the optimum pH was 4.0 and the equilibrium was achieved after 4 h for V(V) adsorption. The Langmuir isotherm model described well the adsorption of V(V), with the maximum adsorption capacity of 208 mg/g at 30°C. The kinetics data fitted well to pseudo-second-order equation, indicating that chemical sorption as the rate-limiting step of adsorption mechanism. Co-existing ions such as nitrate, chloride and sulfate had a certain effect on the uptake of V(V). It was reported that the V(V) loaded chitosan-zirconium (IV) composite could be regenerated by 0.01 mol/L sodium hydroxide, with efficiency greater than 95%.

Liu and Zhang (2015) prepared a new chitosan bead modified with titanium ions was prepared and studied the adsorption of vanadium ions from aqueous solutions using the prepared chitosan bead. Batch adsorption experiments revealed a maximum of adsorption capacity of 124.5 mg/g at
pH 4. It was suggested that at pH < 4, there were more H⁺ ions enough to restrict the free movement of V(V) ions toward the adsorption sites. At > pH 4, there was some competition in the adsorption process of V(V) ions with the adsorbent. The batch experiments also revealed that the adsorption capacity of V(V) immobilized on the adsorbent was enhanced with the increase of initial vanadium concentration and reached a maximum value (207 mg/g). The adsorption of vanadium followed the pseudo second-order kinetic and the Langmuir isotherm model, with a maximum adsorption capacity of 210 mg/g. The thermodynamic parameters revealed that the nature of adsorption was feasible, spontaneous (ΔG° < 0) and endothermic process (ΔH° > 0). It suggested that the mechanisms of adsorption were possibly attributed to electrostatic attraction.

Padilla-Rodríguez et al. (2015) synthesized protonated chitosan flakes (PCF) and evaluated them for the effective removal of vanadium (III, IV, and V) oxyanions from aqueous solutions. The authors showed that the adsorption capacity of vanadium increased when using protonated chitosan flakes instead of chitosan beads. 99-100% vanadium oxyanions removal was achieved during the first 2 hrs. of contact when using 5 g/L protonated chitosan flakes adsorbent and the initial vanadium concentration of 0.500 mg/L, while chitosan beads only removed 4-18%. Vanadium (III, IV and V) adsorption described the Langmuir's model. Even when common anions were added, such as chloride, carbonate, sulfate and phosphate vanadium ions were still removed effectively. (Nakajima, 2002) studied the aspects and the mechanism of vanadium adsorption by the persimmon tannin gel using the ESR spectroscopy. The persimmon tannin gel can adsorb vanadium effectively from aqueous solutions containing VOCl₂ and NH₄VO₃, respectively. The adsorption of vanadium from the VOCl₂ solution was at maximum at around pH 5–6, while that from the NH₄VO₃ solution, and was maximum at pH 3.75.
Biosorbents have a shorter life span compared with conventional sorbents and have low adsorption capacities (Gadd, 2008, Alfarra et al., 2014) Furthermore the separation of biosorbents would be difficult after adsorption (Fu and Wang, 2011).

2.5.3. *Clay and zeolite based adsorbents*

2.5.3.1. *Chromium removal using clays and zeolite based adsorbents*

Clays are hydrous aluminosilicates and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both. Thus, clays invariably contain exchangeable cations and anions held to the surface (Bhattacharyya and Gupta, 2008). Bentonite aluminium phyllosilicate (clay) mainly consists of montmorillonite (smectite group) and is chosen because of its favorable swelling capacities, its high cation adsorption capacities and its strong mechanical stability (Norrfors et al., 2016, Malamis and Katsou, 2013). The crystal structure of montmorillonite is composed of units made up of two layers of silica tetrahedral with a central layer of alumina octahedron sheet between them. The tetrahedral and octahedral sheets combine in such a way that the tips of the tetrahedral of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms in this layer, which are common to both sheets, become oxygen instead of hydroxyl. It is thus referred to as a three-layered clay mineral with T–O–T layers making up the structural unit (Bhattacharyya and Gupta, 2008). The structure of montmorillonite is presented in Figure 2-4.
Montmorillonite, due to its large surface area and high cation exchange capacity, has been studied for potential applications as an environmental remediation agent to remove Cr(VI) (Hu and Luo, 2010).

Montmorillonite modified with aluminum hydroxypolyacation and cetyltrimethylammonium bromide was studied by (Hu and Luo, 2010). The authors found that aluminum hydroxypolyacation and cetyltrimethylammonium bromide had either entered the interlayer or sorbed on the external surface of the clay. Different intercalation orders resulted in different structures. The experimental data revealed that if aluminum hydroxypolyacation was intercalated before cetyltrimethylammonium bromide, the adsorption capacity was better than that of intercalated simultaneously or cetyltrimethylammonium bromide pre-intercalated. The pH of the solution and environmental temperature had significant influences on the adsorption of Cr(VI). The optimal pH for the removal was about 4, and the temperature of 25°C was best suitable. They found that all adsorption processes were rapid during the first 5 min and reached
equilibrium in 20 min. The adsorption kinetics could be described quite well by pseudo-second-order model. The adsorption rates of 3.814 mg/g/min and the adsorption capacities 11.97 mg/g was achieved. The adsorption of modified montmorillonite was suggested to be mainly induced by the surface charge and the complexation reaction between cetyltrimethylammonium bromide and hexavalent chromium species at the edge of the clay particle.

Yuan et al. (2009) prepared montmorillonite-supported magnetite nanoparticles by co-precipitation and hydrosol method and to investigate the removal mechanism of hexavalent chromium by synthesized magnetite nanoparticles. The montmorillonite supported magnetite nanoparticles were found to exist on the surface or inside the antiparticle pores of clays, with better dispersing and less coaggregation than the ones without montmorillonite support. It was revealed that the Cr(VI) uptake was mainly governed by a physico-chemical process, which included an electrostatic attraction followed by a redox process in which Cr(VI) was reduced into trivalent chromium. The adsorption of Cr(VI) was found to be highly pH-dependent and the kinetics of the adsorption followed the pseudo-second-order model. The adsorption data of unsupported and clay-supported magnetite nanoparticles fitted well with the Langmuir and Freundlich isotherm equations. The montmorillonite-supported magnetite nanoparticles showed a much better adsorption capacity per unit mass of magnetite (15.3 mg/g) than unsupported magnetite (10.6 mg/g), and were more thermally stable than their unsupported counterparts.

Santhana Krishna Kumar et al. (2012) reported the detailed study on the adsorption of hexavalent chromium using dodecylamine intercalated sodium montmorillonite as a potential adsorbent. The adsorption involved primarily the electrostatic interaction of hydrogen(tetraoxochromate (VI)
anion with the protonated dodecylamine and the surface hydroxyl groups of the clay material. The pseudo second order kinetic model fitted the experimental data and an adsorption capacity of 23.69 mg/g was obtained from the Langmuir isotherm model. Adsorption process was found to be exothermic and favorably spontaneous.

Attapulgite clay-carbon nanocomposite is an exceptionally promising candidate as a low-cost, sustainable, and effective adsorbent for the removal of toxic ions from water. Attapulgite clay, which is a magnesium aluminum silicate that is abundant in nature, and glucose, which is a green chemical obtained from biomass are cheap and ecofriendly materials. Compared to carbon-based materials, the nanocomposite exhibited high adsorption ability for Cr(VI) ions with maximum adsorption capacities of 177.74 mg/g. (Chen et al., 2011a).

Zeolites are defined as hydrated aluminosilicate minerals with crystalline microporous structure. The structure consists of three-dimensional frameworks of SiO$_4$ and AlO$_4$ tetrahedral that are linked to each other through oxygen atoms (Figure 2-5) (Broach et al., 2000). Their intricate structural arrangement is also responsible for the high specific surface area (>700 m$^2$/g). The isomorphic framework substitution of tetravalent silicon by trivalent aluminum in the mineral’s structure creates a net negative charge that is counterbalanced by the presence of cations (usually Ca$^{2+}$, Na$^+$ and K$^+$) which are situated in cavities. These cations species promotes the ion exchange capabilities with other cations including heavy metals. The cavities are occupied by large ions and water molecules which are able to move, allowing ion exchange necessary to balance the negative charge in the framework (Malamis and Katsou, 2013, Broach et al., 2000, Figueiredo and Quintelas, 2014).
Natural zeolites have advantages over other cation exchange materials such as commonly used organic resins, because they are cheap, they exhibit excellent selectivity for different cations at low temperatures, which is accompanied with a release of non-toxic exchangeable cations (K⁺, Na⁺, Ca²⁺ and Mg²⁺) to the environment, they are compact in size and they allow simple and cheap maintenance in the full-scale applications. Clinoptilolite is one of the most investigated zeolite in basic and applied research. In the structure of clinoptilolite, there are three types of channels, of which two are parallel, and made of ten and eight-membered rings of Si/AlO₄, while one, defined by eight-membered rings, is vertical Figure 2-6 (Margeta et al., 2013).

Leyva-Ramos et al. (2008) prepared a surface modified zeolite by adsorbing the cationic surfactant hexadecyltrimethylammonium (HDTMA) bromide on the external surface of the zeolite. It was found that the surface area and pore volume were reduced due to pore blocking caused by the surfactant molecules adsorbed on the zeolite. The Cr(VI) was adsorbed considerably on surface modified zeolite but not on the natural zeolite. The Cr(VI) adsorption capacity of surface modified zeolite showed a maximum at pH 6 and diminished 18 and 2.7 times with an increase in pH from 6 to 10 and decreasing pH from 6 to 4, respectively. The
adsorption capacity reduced when temperature from was increased 15 to 25 °C since the adsorption of Cr(VI) on surface modified zeolite was due to an exothermic reaction. Desorption studies showed that Cr(VI) was irreversibly adsorbed on surface modified corroborating that Cr(VI) was chemisorbed on the surface modified zeolite.

Figure 2-6. Binding of building units (PBU and SBU) in three-dimensional zeolite- clinoptilolite structure (Margeta et al., 2013).

Salgado-Gómez et al. (2014) investigated the zeolite-rich tuff from the state of Chihuahua, which was conditioned sodium chloride solution and modified with a hexadecyltrimethylammonium bromide solution. Then was used to evaluate the removal of Cr(VI) from aqueous solution. The removal efficiency of chromium ions from aqueous solution was found to be influenced by pH and the specific chromium species involved plays involved in the adsorption process. A number of important parameters can influence the sorption process of Cr(VI)ions on natural zeolite such as: conductivity, pH, temperature of treated water, ionic strength, initial concentration of chromium in solution, zeolite mass, and zeolite particle size. Table 2-4 presents the achievements of clinoptilolite in the adsorption of Cr(VI).
Table 2-4. Clinoptilolite as an adsorbent for removal of Cr(VI) ions

<table>
<thead>
<tr>
<th>Modification</th>
<th>Initial concentration (mg/L)</th>
<th>Adsorbent dosage (g/L)</th>
<th>pH</th>
<th>Adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface modification by Fe(II)</td>
<td>2.5-350</td>
<td>200</td>
<td>4-</td>
<td>0.3 mg/g</td>
<td>(Lv et al., 2014a)</td>
</tr>
<tr>
<td>Bacteria loaded clinoptilolite</td>
<td>10-300</td>
<td>10</td>
<td>5-6</td>
<td>n/a</td>
<td>(Erdoğan and Ülkü, 2012)</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium bromide</td>
<td>32-225</td>
<td>25</td>
<td>5</td>
<td>3.55 mg/g</td>
<td>(Zeng et al., 2010)</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium bromide</td>
<td>1-740</td>
<td>12.5</td>
<td>3</td>
<td>13.622 mg/g</td>
<td>(Bajda and Kłapyta, 2013)</td>
</tr>
<tr>
<td>Fe₃O₄-polypyrrole</td>
<td>300-1100</td>
<td>2</td>
<td>2</td>
<td>344.83 mg/g</td>
<td>(Mthombeni et al., 2015b)</td>
</tr>
</tbody>
</table>

n/a = not available

2.5.3.2. Manganese removal by clays and zeolite based adsorbents

Natural materials clays and zeolites have been explored for treating wastewater contaminated with metals due to their metal-binding capacity (Acheampong et al., 2010), low cost and abundance. Dimirkou and Doula (2008) studied the removal of Mn²⁺ in drinking water using clinoptilolite (natural zeolite).
<table>
<thead>
<tr>
<th>Clay Sorbent</th>
<th>Initial concentration (mg/L)</th>
<th>Adsorbent dosage (g/L)</th>
<th>pH</th>
<th>Adsorption capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greece Clinoptilolite</td>
<td>0.2 – 1000</td>
<td>1</td>
<td>7.53</td>
<td>7.69</td>
<td>(Doula, 2006, Dimirkou and Doula, 2008)</td>
</tr>
<tr>
<td>Fe-Clinoptilolite</td>
<td></td>
<td>1</td>
<td>8.14</td>
<td>27.1 mg/g</td>
<td>(Inglezakis et al., 2010)</td>
</tr>
<tr>
<td>Vermiculite</td>
<td></td>
<td>0.5</td>
<td>7.1±</td>
<td>N/a (70 % Mn removal)</td>
<td></td>
</tr>
<tr>
<td>Serbian natural zeolite</td>
<td>400</td>
<td>10</td>
<td>5.5</td>
<td>10 mg/g</td>
<td>(Rajic et al., 2009)</td>
</tr>
<tr>
<td>Brazilian vermiculite</td>
<td>550</td>
<td>2.5</td>
<td>6.4</td>
<td>31.53 mg/g</td>
<td>(da Fonseca et al., 2006)</td>
</tr>
<tr>
<td>Kaolite</td>
<td>N/a</td>
<td>10</td>
<td>N/a</td>
<td>0.446 mg/g</td>
<td>(Yavuz et al., 2003)</td>
</tr>
<tr>
<td>Synthetic zeolite made from fly ash</td>
<td>10</td>
<td>100</td>
<td>2-12</td>
<td>N/a</td>
<td>(Belviso et al., 2014)</td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>25-250</td>
<td>N/a</td>
<td>6</td>
<td>7.69 mg/g</td>
<td>(Ates, 2014)</td>
</tr>
<tr>
<td>Al-Natural zeolite</td>
<td>6</td>
<td>6</td>
<td></td>
<td>25.12 mg/g</td>
<td></td>
</tr>
<tr>
<td>NH4-Natural zeolite</td>
<td>6</td>
<td>6</td>
<td></td>
<td>24.33 mg/g</td>
<td></td>
</tr>
<tr>
<td>Turkey natural zeolite</td>
<td>20</td>
<td>37</td>
<td>2.5</td>
<td>0.37 mg/g</td>
<td>(Motsi et al., 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5 4.5</td>
<td></td>
<td>0.52 mg/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.52 mg/g</td>
<td></td>
</tr>
<tr>
<td>Natural zeolite – Slovakia</td>
<td>14.4</td>
<td>40</td>
<td>7</td>
<td>0.076 mg/g</td>
<td>(Shavandi et al., 2012)</td>
</tr>
<tr>
<td>Brazilian natural scolecite</td>
<td>50</td>
<td>16.7</td>
<td>6</td>
<td>2.1 mg/g</td>
<td>(Dal Bosco et al., 2005)</td>
</tr>
</tbody>
</table>
According to them clinoptilolite modified with Fe adsorbs more manganese (27.1 mg/g) than unmodified clinoptilolite (7.69 mg/g.). Doula (2006) noted that high manganese adsorption
capacity of clinoptilolite modified with Fe was due to Fe-clusters located on the surface and to high surface negative charge. The removal of metals by zeolite is known to be a complex process which involves ion exchange and adsorption (Perić et al., 2004). (Yavuz et al., 2003), explored the removal of manganese from aqueous solution by adsorption on natural kaolinite. The Langmuir adsorption capacity for Mn was found to be 0.446 mg/g. Several studies have been conducted on metal uptake including manganese using clays and minerals and the results are shown in Table 2-5.

2.5.3.3. Vanadium removal by clay based absorbents

Layered double hydroxides have recently attracted significant attention for their potential applications such as ion exchangers and adsorbents (Li and Duan, 2006, Song et al., 2013). The adsorption of vanadium ions onto Mg/Al layered double hydroxides has been reported (Song et al., 2013, Wang et al., 2012). Mg/Al layered double hydroxides were prepared by co-precipitation and the calcination of the substance and transforms into mixed oxides. Song et al., 2013 suggested that the small particle size which was reported to range from nano to microns provide good adsoprtion capacity for vanadate. The study results proved that vanadate can be removed at optimum experimental conditions with a removal rate of 99.9% for 100 mg/L. Wang et al. 2014 reported that the maximum adsorption was achieved at pH 2.5. They suggested that because vanadium (V) in aqueous solution exists predominately as $\text{H}_3\text{V}_2\text{O}_7^-\text{in the pH range of 2.5–7.0. At pH 2.0, vanadium in the (+5) oxidation state occurs as the VO}^{2+}\text{cation, and lower adsorption capacity is due to anion preferable of calcined hydrotalcite for anion vacancy in the layer after calcination. They also noted that the decrease in adsorption capacity at higher pH values was due to competition between OH}^-\text{and vanadium anions for available surface sites of adsorbents.}$
Manohar et al. (2005) investigated the possibility of using natural bentonite clay as a precursor to produce aluminum-pillared clay for the removal of vanadium (IV) from aqueous solutions. They performed batch experiments as a function of solution pH, contact time, vanadium (IV) concentration, adsorbent dose, ionic strength, and temperature. The authors reported that the maximum adsorption capacity was observed in the pH range 4.5-6.0. The maximum vanadium removal of 99.8 and 88.5% was reported to occur at pH 5.0 from an initial concentration of 5 and 10 mg/L, respectively. It was concluded that the intraparticle diffusion of metal that occurs through pores in the clay is the main rate-limiting step. The temperature dependence indicated that the nature of adsorption was endothermic. It was found that the percentage removal of vanadium (IV) decreased with increasing ionic strength. The desorption data showed that the spent PILC can be regenerated for further use by 0.1 M HCl.

2.6. Nanotechnology

Recent advances in nanotechnology offer opportunities to develop next-generation water supply systems. The unique properties of nanomaterials such as high surface area, photosensitivity, catalytic and antimicrobial activity, electrochemical, optical, and magnetic properties, and tunable pore size and surface chemistry, provide useful features for many applications. Nanomaterials can be applied as sensors for water quality monitoring, specialty adsorbents, solar disinfection/decontamination, and high performance membranes. The modular, multifunctional and high-efficient processes enabled by nanotechnology also provide a high performance to aging infrastructure and to develop high performance, low maintenance decentralized treatment systems including point-of-use devices (Qu et al., 2013b).

Nanomaterials are typically defined as materials smaller than 100 nm in at least one dimension. At this scale the physical and chemical properties of nanomaterials can become very different
from those of the same material in larger bulk form, many of which have been explored for applications in water and wastewater treatment. Some of these applications utilize the smoothly scalable size-dependent properties of nanomaterials which relate to the high specific surface area, such as fast dissolution, high reactivity, and strong sorption and other discontinuous properties, such as superparamagnetism, localized surface plasmon resonance, and quantum confinement effect (Qu et al., 2013a).

2.6.1. Polymer based nanoadsorbents

2.6.1.1. Removal of chromium with polymer based nanoadsorbents

Various polymers have been used as adsorbents in the removal of Cr(VI) from wastewaters. Conducting polymers such as polythiophene (PTh), polypyrrole (PPy), polyaniline (PANI), and their derivatives stand out as the most promising members of the conjugated polymer family because of their unique electrical behavior, excellent environmental and thermal stability, low-cost synthesis, and mechanical strength (Jaymand, 2014, Wang et al., 2010, Hatamzadeh et al., 2014, Wu and Lin, 2006). Polypyrrole find applications in various fields such as microelectronics, composite materials, optics and biosensors as adsorbent (Karthikeyan et al., 2009). Polypyrrole and its derivatives have attracted a great deal of attention in its application for water treatment. The ion-exchange capacities depend on the polymerization conditions, the type and size of the counter ions incorporated during the polymerization process as well as on the ions present in the electrolyte solution, the polymer thickness and the ageing of the polymer (Weidlich et al., 2001). Polymer matrix based nanocomposites has emerged initially with interesting observations which involves exfoliated clay and more recently studies with carbon nanotubes, carbon nanofibers, exfoliated graphite (graphene), nanocrystalline metals, nanoscale inorganic fillers or fiber modifications have also emerged (Paul and Robeson, 2008).
(Bhaumik et al., 2011d) prepared a Fe$_3$O$_4$ coated polypyrrole (PPy) magnetic nanocomposite via \textit{in situ} polymerization of pyrrole monomer for the removal of highly toxic Cr(VI). Up to 100% adsorption removal was found with 200 mg/L Cr(VI) aqueous solution at pH 2. They suggested that ion exchange and reduction on the surface of the nanocomposite may be the possible mechanism for Cr(VI) removal by the PPy/Fe$_3$O$_4$ nanocomposite according to the XPS studies. Adsorption results showed that Cr(VI) removal efficiency by the nanocomposite decreased with an increase in pH. Adsorption kinetics data was found to be best described by the pseudo-second-order rate model while isotherm data fitted well to the Langmuir isotherm model. The authors concluded that thermodynamic study revealed that the adsorption process is endothermic and spontaneous in nature. They also indicated that in spite of the very poor recovery of the adsorbed Cr(VI); the regenerated adsorbent can be reused successfully for only two successive adsorption–desorption cycles without appreciable loss of its original capacity. The authors’ also demonstrated the effectiveness of the nanocomposite in a fixed bed column using environmental water. They processing 5.04 L water with initial 76.59 mg/L Cr(VI) concentration using only 2 g of adsorbent mass to below acceptable level (Bhaumik et al., 2013b). Removals of Cr(VI) by polymer based adsorbents are summarized in the Table 2-6 below.
Table 2-6. Adsorption capacities of Cr(VI) ions on polymer based nanoadsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Synthesis: oxidant</th>
<th>C_i Cr(VI) (mg/L)</th>
<th>Adsorbent dosage (g/L)</th>
<th>pH</th>
<th>Temperature: Adsorption capacity or removal percentage</th>
<th>Temperature: Adsorption capacity</th>
<th>Model used to calculate adsorption capacity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy/Fe_3O_4 nanocomposite</td>
<td>FeCl_3</td>
<td>200</td>
<td>2</td>
<td>2</td>
<td>25°C: 169.49 mg/g</td>
<td>Langmuir</td>
<td>(Bhaumik et al., 2011d)</td>
<td></td>
</tr>
<tr>
<td>Glycine doped polypyrrole</td>
<td>Ammonium peroxysulfate</td>
<td>200-500</td>
<td>2</td>
<td>2</td>
<td>25°C: 217.39 mg/g</td>
<td>Langmuir</td>
<td>(Ballav et al., 2012)</td>
<td></td>
</tr>
<tr>
<td>Polypyrrole-coated halloysite nanotube clay nanocomposite:</td>
<td>FeCl_3</td>
<td>100-500</td>
<td>1.5</td>
<td>2</td>
<td>25°C: 149.25 mg/g</td>
<td>Langmuir</td>
<td>(Ballav et al., 2014a)</td>
<td></td>
</tr>
<tr>
<td>Fe_3O_4 coated glycine doped polypyrrole magnetic nanocomposites</td>
<td>Ammonium peroxysulfate</td>
<td>200-650</td>
<td>2</td>
<td>2</td>
<td>25°C: 238 mg/g</td>
<td>Langmuir</td>
<td>(Ballav et al., 2014b)</td>
<td></td>
</tr>
<tr>
<td>Polyacrylonitrile/polypyrrole core/shell nanofiber mat</td>
<td>FeCl_3</td>
<td>100-200</td>
<td>3.33</td>
<td>2</td>
<td>25°C: 61.8 mg/g</td>
<td>Langmuir</td>
<td>(Wang et al., 2013)</td>
<td></td>
</tr>
<tr>
<td>Polypyrrole-polyaniline. nanofibers</td>
<td>FeCl_3</td>
<td>100-400</td>
<td>1</td>
<td>2</td>
<td>25°C: 227.27 mg/g</td>
<td>Langmuir</td>
<td>(Bhaumik et al., 2012)</td>
<td></td>
</tr>
<tr>
<td>Graphene oxide-alpha cyclodextrin-polypyrrole nanocomposites</td>
<td>FeCl_3</td>
<td>100-700</td>
<td>0.5</td>
<td>2</td>
<td>25°C: 606.06 mg/g</td>
<td>Langmuir</td>
<td>(Chauke et al., 2015)</td>
<td></td>
</tr>
</tbody>
</table>
n/a = not available

2.6.1.2. Removal of manganese using polymer based nano adsorbents

Other adsorbents such as poly(sodium acrylate)–graphene oxide double network hydrogel adsorbent have been prepared and studied for the removal of Mn$^{2+}$. The maximum Langmuir adsorption capacity for Mn$^{2+}$ was found to be 165.5 mg/g at pH 6 and a temperature of 303 K. The adsorbent indicated good reusability performance (Xu et al., 2015).

Idris, (2015) studied functionalized mesoporous silica employed as adsorbent for Mn(II) from aqueous solutions. The surface area of functionalized mesoporous silica and diethylenetriamine
functionalized were found to 760 and 318 m$^2$/g (N$_2$ adsorption). Mn(II) adsorption was found to be pH dependent and best results were obtained at pH 6.5–7. The adsorption onto the diethylenetriamine functionalized- mesoporous silica followed the pseudo-second-order kinetic model. The equilibrium data fitted well to the Langmuir isotherm model and the maximum adsorption capacity of Mn(II) was found to be 88.9 mg/g. The authors concluded that the adsorption occurred on a homogeneous surface by monolayer sorption without interaction between the adsorbed ions.

The adsorption of manganese ions from aqueous solution by polyaniline/sawdust nanocomposite was experimentally investigated by Qomi et al. (2014). The experiments evaluated the effect of various experimental parameters i.e., pH, adsorbent dosage and contact time on the removal efficiency. The results showed that optimum conditions for manganese removal are at pH 10, adsorbent dosage of 10 g/L and equilibrium contact time of 30 min. The adsorption capacity for manganese ions was obtained to be 58.824 mg/g.

Moawed et al. (2013) modified the polyurethane foam with polyhydroxyl and used it as a new sorbent for separation of manganese and iron ions in natural samples. The maximum sorption of Mn(II) was found in the pH range of 6–8. The kinetics of sorption of the Mn(II) was found to be fast with an average value of half-life of 11.7 min. The sorption capacity of polyhydroxyl polyurethane foam was 8.7 µmol/g.

Khan et al. (2014) performed comparative sorption study of dissolved manganese and cobalt ions onto alginate beads and thermally activated nano-carbon beads. Optimum metal uptake was observed at pH 8 with about 80–92% metal ions adsorbed within 4 h, followed by a slower
adsorption stage. It was revealed that increases in initial Mn(II) concentration from 52.28 to 891.5 mg/L increased sorption on alginate beads and activated nano-carbon beads from 18.07 to 63.7 mg/g and 23 to 78 mg/g, respectively.

Islam et al. (2015) prepared porous phosphine-functionalized electrospun poly(vinyl alcohol)/silica composite nanofiber using a facile electrospinning technique. The composite nanofibers with 0.5 g/L fiber loading was found to be able to remove almost completely 96% the Mn$^{2+}$ ions from aqueous solutions with an initial concentration of 120 mg/L, at pH 6 within 15 min of contact time. A reasonably simple acid treatment with a 1 M HCl solution was found to be extremely effective in regenerating the nanofiber adsorbent, and 92.5% of the metal ions were removed from the adsorbent even in the fifth regeneration/reuse cycle. The adsorption equilibrium studies revealed the excellent adsorption capacity of the nanofiber for Mn$^{2+}$ ions to be 234.7 mg/g.

2.6.2. Magnetic nanoadsorbents

After adsorption, it can be difficult to separate powder adsorbents from the aqueous solution using conventional separation methods such as filtration and sedimentation, because adsorbents may block filters or be lost. Separation technologies utilizing magnetic adsorbents as an alternative method for water treatment has received considerable attention in recent years (Sun et al., 2014a). For ease of separation and regeneration of adsorbents, recently research has been focused on magnetic separation technology (Reddy and Lee, 2013). Magnetic particles can be used to adsorb and remove contaminants from aqueous effluents, and after adsorption process, can be separated from the medium by a simple magnetic process (Yao et al., 2014).
Sun et al., (2014a) prepared novel amino-functionalized magnetic cellulose composite and tested for its ability to remove Cr (VI). This was prepared a by a 4 step process involving synthesis of magnetic silica nanoparticles using co-precipitation method followed by the hydrolysis of sodium silicate, then coating with cellulose through the regeneration of cellulose dissolved in 7 wt.% NaOH/12 wt.% urea aqueous solvent, grafting of glycidyl methacrylate using cerium initiated polymerization and ring-opening reaction of epoxy groups with ethylenediamine to yield amino groups. The results demonstrated that Cr(VI) adsorption was highly pH dependent and the optimized pH value was 2.0. The adsorption isotherms of the adsorbent fitted well the Langmuir model, with the maximum adsorption capacity of 171.5 mg/g at 25°C. The adsorption rate was considerably fast, and the adsorption reached equilibrium within 10 min. The thermodynamic parameters obtained showed that the adsorption of Cr(VI) onto the adsorbent was an exothermic and spontaneous process. The Cr(VI) ions could be effectively desorbed using a 0.1 mol/L NaOH solution. They concluded that composite material could be promising adsorbent for Cr(VI) removal, with the advantages of high adsorption capacity, rapid adsorption rate and convenient recovery under magnetic field.

Mesoporous magnetic Fe₃O₄@C nanoparticles was synthesized by a one-pot approach and used as adsorbents for removal of Cr (IV) from aqueous solution by Zhang et al. (2013). Their results revealed that the mesoporous magnetic Fe₃O₄@C nanospheres have excellent adsorption efficiency and be easily isolated by an external magnetic field. In comparison with magnetic Fe₃O₄ nanospheres, the mesoporous magnetic Fe₃O₄@C exhibited 1.8 times higher removal rate of Cr (VI). They suggested that the mesoporous structure and an abundance of hydroxy groups on the carbon surface may have been responsible for high absorbent capability.
Li et al. (2013c) prepared N-doped porous carbon with magnetic nanoparticles formed in situ (RHC-mag-CN) fabricated through simple impregnation then polymerization and calcination (Figure 2-7). The doped nitrogen in RHC-mag-CN was in the form of graphite-type layers with the composition of CN. The resultant nanocomposite maintained a high surface area of 1136 m²/g with 18.5 wt. % magnetic nanoparticles (Fe₃O₄ and Fe) inside, which showed a saturation magnetization of 22 emu/g. It was reported that 92% of Cr(VI) could be removed within 10 min for dilute solutions at 2 g/L adsorbent dose. They suggested that the high adsorption was related to the synergetic effects of physical adsorption from the surface area and chemical adsorption from complexation reactions between Cr(VI) and Fe₃O₄. They also noted that the basic CNs in RHC-mag-CN increase the negative charge density and simultaneously increase the adsorption of metallic cations, such as Cr(III) formed in the acid solution from the reduction of Cr(VI). They concluded that the formation of magnetic nanoparticles inside not only supplied complexing sites for the adsorption of Cr(VI), but also showed perfect magnetic separation performance from aqueous solution.

![Figure 2-7. Schematic fabricating of RHC-mag-CN nanocomposite.](image-url)
Thinh et al. (2013) prepared magnetic chitosan nanoparticles by co-precipitation via epichlorohydrin cross-linking reaction. The average size of magnetic chitosan nanoparticles was estimated at ca. 30 nm. They found that the adsorption of Cr(VI) was highly pH-dependent and the kinetics follows the pseudo-second-order model. Langmuir maximum adsorption capacity at pH 3 and room temperature was calculated as 55.80 mg/g. The authors suggested that magnetic chitosan nanoparticles could serve as a promising adsorbent for the removal of Cr(VI) nanoscale zero-valent iron assembled on magnetic Fe$_3$O$_4$/graphene nanocomposite was synthesized by (Lv et al., 2014b) for Cr(VI) removal from aqueous solution. Nanoscale zero valent iron particles were found to be perfectly dispersed either among Fe$_3$O$_4$ nanoparticles or above the basal plane of graphene. The composite material showed Cr(VI) removal efficiency of 83.8%, which was much higher than those of individual materials (18.0% for nanoscale zero valent iron, 21.6% for Fe$_3$O$_4$ nanoparticles and 23.7% for graphene). Maximum Cr(VI) adsorption capacity varied from 66.2 to 101.0 mg/g with decreasing pH from 8.0 to 3.0 at 30°C. Thermodynamic studies indicated spontaneous tendency and exothermic nature of the adsorption process. The authors suggested that the robust performance of nanoscale zero-valent iron assembled on magnetic Fe$_3$O$_4$/graphene nanocomposites arises from the formation of micro- nanoscale zero-valent iron - graphene/ nanoscale zero-valent iron Fe$_3$O$_4$ batteries and strong adsorption capability of broad graphene sheet/Fe$_3$O$_4$ surfaces. They also suggested that the electrons released by nanoscale zero-valent iron spread all over the surfaces of graphene and Fe$_3$O$_4$, and the adsorbed Cr(VI) ions on them capture these floating electrons and reduce to Cr(III). Fe$_3$O$_4$ NPs also served as protection shell to prevent Nanoscale Zero Valent Iron from agglomeration and passivation.
Pang et al. (2011) developed a stable magnetic nanoparticle with a shell core structure of $\gamma$-Fe$_2$O$_3$@Fe$_3$O$_4$. According to their results, the adsorbent was able to effectively remove anionic Cr(VI) in the pH range of 2–3, which was attributed to the large amount of protonated imine groups on its surface, and the adsorbent could be magnetically separated from liquid quickly. Adsorption equilibrium was reached within 30 min and independent of initial Cr(VI) concentration. The calculated thermodynamic parameters indicated that adsorption of Cr(VI) was spontaneous and exothermic in nature. Competition from coexisting ions (K$^+$, Na$^+$, Ca$^{2+}$, Cu$^{2+}$, Cl$^-$, and NO$_3^-$) was found to be insignificant. The adsorbent had satisfying acid–alkali stability and could be regenerated by 0.02 mol/L NaOH solution.

Chen et al. (2013) prepared a magnetically separable adsorbent, named chitosan/montmorillonite–Fe$_3$O$_4$ (CTS/MMT–Fe$_3$O$_4$) microsphere by microemulsion process. The microspheres were applied as adsorbents for the removal of Cr(VI) from aqueous solution. They investigated the effects of montmorillonite content (wt %), the initial concentration of Cr(VI) solution, initial pH value of Cr(VI) solution and the adsorption dose on the adsorption capacity of the microspheres. Experiments showed that the adsorption capacity of CTS/xMMT–Fe$_3$O$_4$ microspheres for Cr(VI) is higher than the mean value of those of chitosan and montmorillonite. The optimum pH value for Cr(VI) adsorption was found at pH 2, and the adsorption capacity increased with an increase in adsorption temperature. The adsorption kinetics was described by the pseudo-second order equation, while the isotherm was described by Langmuir equation. Furthermore, the material could be reused in a number of cycles. Meanwhile, Tang et al. (2014), synthesized a magnetic mesoporous silica composite with high uniformity and polyaniline (PANI) grafting and successfully applied to removed Cr(VI). They indicated
that with the assistance of high adsorption capacity of protonated PANI and the magnetic mesoporous composite at low pH, Cr(VI) was adsorbed and then reduced to less toxic Cr(III) by PANI. The data obtained from the kinetic study fitted well to the pseudo-second-order model and Langmuir model well described the sorption isotherms with the maximum adsorption capacity of 193.85 mg/g. Competition from coexisting ions (K\(^+\), Na\(^+\), Ca\(^{2+}\), Cl\(^-\), SO\(_4^{2-}\), NO\(_3^-\)) was proved to be insignificant. Moreover, the exhausted adsorbent could be well regenerated and kept above 83% removal efficiency in the first three cycles, which demonstrated that it was cost-effective. The authors concluded that this novel magnetic adsorbent may offer a simple adsorption and synergistic reduction treatment option to remove Cr(VI) contaminant from industrial wastewater and natural water bodies. The use of magnetic adsorbents in removing Cr(VI) from aqueous offers a significant advantage over other adsorbents which is the ability to separate them from an aqueous solution on application of a magnetic field.

2.6.3. Polymer clay based nanoadsorbents

Clay minerals have low surface area and poor affinity to pollutants due to some of the inaccessible sites of the stacked lamellar sheets and hydration of the clay mineral surface tends to reduce accessibility of the interlayer spaces (Setshedi et al., 2013, Unuabonah and Taubert, 2014). Polymer clay based nanocomposites include the use of smectite-type clays, such as hectorite, montmorillonite, and synthetic mica, as fillers to enhance the properties of polymers. The principle used in polymer clay based nanocomposites is to separate not only clay aggregates but also individual silicate layers in a polymer which then enables the excellent mechanical properties of the individual clay layers to function effectively, while the number of reinforcing components also increases dramatically because each clay particle contains hundreds or thousands of layers (Gao, 2004). The modification of the two-dimensional clays using
conductive polymer attracted increasingly attention in the field of water treatment owing to the high cation exchange capacity, abundant active adsorption sites and organic functional groups (Mu et al. 2016). Setshedi et al. (2013) prepared the exfoliated polypyrrole-organically modified montmorillonite clay nanocomposite as a potential adsorbent, via in situ polymerization of pyrrole monomer for adsorption of toxic Cr(VI) from aqueous solution. According to their results the WAXD and SAXS studies indicated that the clay sheets were exfoliated in the prepared nanocomposite. HR-TEM results showed good dispersion of the clay into the polymer matrix. An improved surface area was observed by authors for the nanocomposite compared to the montmorillonite clay. Batch adsorption experimental studies revealed that Cr(VI) adsorption process was rapid, spontaneous in nature and favored an increased temperature at pH 2. The kinetic experimental data fitted well to the pseudo second order kinetic model while the equilibrium data was described well by the Langmuir isotherm. The Langmuir maximum adsorption capacity of Cr(VI) at pH 2 were found to be 112.3, 119.34, 176.2 and 209.6 mg/g at 19°C, 25°C, 35°C and 45°C, respectively. The selective adsorption of Cr(VI) was demonstrated in binary adsorption systems with co-existing ions. Desorption experiments revealed that the nanocomposite can be reused effectively for two consecutive adsorption–desorption cycles without any loss of its original capacity.

Shyaa et al., (2015) observed that the capacity of chromium adsorption on polyaniline/zeolite increases with initial metal concentration, the metal ion adsorption on surfactant is well represented by the Freundlich isotherm. The maximum adsorption of Cr(VI) occurred at pH 2–6, and decreased at higher pH values.
Pan et al. (2016) prepared alkaline clay which was immobilized with cationic star polymer to yield amino groups, and the cationic star polymer-immobilized alkaline clay was applied to remove Cr(VI) from the aqueous solution in batch experiments. Various influencing factors, including pH, contact time and immobilization amount of cationic star polymer on adsorption capacity of cationic star polymer-immobilized alkaline clay for Cr(VI) were also investigated. The results obtained demonstrated that Cr(VI) adsorption was highly pH dependent. The optimized pH value was 4.0. The adsorption isotherms of the adsorbent fit the Langmuir model well, with the maximum adsorption capacity of 137.9 mg/g at 30 °C.

A polypyrrole-coated halloysite nanotube nanocomposite was prepared via in situ polymerization of pyrrole in the dispersion of HNTs and assessed for the removal of toxic Cr(VI) from aqueous solutions (Ballav et al., 2014a). The maximum adsorption capacity was found to be 149.25 mg/g at pH 2.0 at 25 °C and the adsorption process was spontaneous and endothermic in nature. XPS stud confirmed the adsorption of Cr(VI) onto the nanocomposite where some part of Cr(VI) reduced to Cr (III) by electron-rich polypyrrole moiety. The desorption study suggested that the nanocomposite can be reused three times without loss of its original removal efficiency.

2.7. Conclusion

All heavy metals treatment methods have their advantages and limitations. Adsorption can be considered as the most effective and economic method for the treatment of wastewaters containing heavy metals because it is low cost, and locally and naturally available material can be utilized efficiently for the removal of heavy metals ions from environmental water. Whereas commercial activated carbon is as an effective adsorbent for the removal of heavy metals its high cost restricts its use. The review showed that agricultural waste, waste based chitosan and clay
minerals are low-cost alternative adsorbents in which surface modification of these material surfaces provides increased capacity for adsorption and selectivity of Cr, V and Mn ions. Although various adsorbents and nano adsorbents can be applied, selection of the most suitable adsorbent and nano adsorbent in removing target heavy metal pollutants depends on the characteristics of effluents to be treated, technical applicability, discharge standards, cost-effectiveness, regulatory requirements, and long-term environmental impacts. Due to their ability to minimize the generation of secondary waste using less resources and capability of removing any types of pollutants from contaminated water effectively, the use of nanomaterials could offer alternative solution to heavy metals problem in environmental water and protecting the aquatic environment in the future (Kurniawan et al., 2012).

Clay polymers nanocomposite adsorbents for water treatment combine the advantageous properties of their respective components, such as mechanical stability, a particular high surface structure, surface charge, chemical stability, significantly improved adsorption capacities for micropollutants. What makes the magnetic clay polymer nanocomposites more favorable as adsorbents is the fact that they can be easily removed from the solution by a simple magnetic process after use.
CHAPTER 3

Adsorption of Hexavalent Chromium Onto Magnetic Natural Zeolite-Polymer Composite

Abstract
Magnetic natural zeolite-polypyrrole (MZ-PPY) composite was prepared for enhanced removal of hexavalent chromium [Cr(VI)] from aqueous solution. The structure and morphology of the prepared adsorbent was analyzed with the Fourier transform infrared (FTIR), field-emission microscope (FE-SEM), energy dispersive X-ray (EDX), high resolution transmission electron microscope (HR-TEM) and X-ray diffraction (XRD). The effects of magnetic zeolite loading within the composite, initial pH, sorbent dosage, temperature and Cr(VI) concentration on Cr(VI) removal efficiency were investigated. Up to 99% removal efficiency was obtained when the pH was 2 and the initial Cr(VI) concentration was 300 mg/L. The sorption kinetic data fitted well to the pseudo-second order model and isotherm data fitted well to the Langmuir isotherm model. The maximum adsorption capacity determined from the Langmuir isotherm increased from 344.83 to 434.78 mg/g as the temperature was increased from 25 °C to 45 °C. Thermodynamic parameters revealed that the adsorption process is spontaneous and endothermic in nature. The results further indicated that the adsorption capacity is decreased in the presence of SO$_4^{2-}$ ions. The adsorption–desorption studies indicated that MZ-PPY retained its original Cr(VI) sorption capacity up to two consecutive cycles.

3. Introduction
Mining and metallurgical industries are associated with heavy metals containing wastewaters that are directly or indirectly discharged into the environment. Heavy metals are known to be toxic or carcinogenic (Hu et al., 2005). Hexavalent chromium as an example of heavy metal
often exists in the effluents of the electroplating, tanning, mining, and fertilizer industries and acts as carcinogen, mutagen, and teratogen in biological systems (Huang et al., 2013, Li et al., 2013a, Bhaumik et al., 2014b). Consequently effluents containing hexavalent chromium must be treated using appropriate techniques. Several treatment methods to remove Cr(VI) from wastewaters have been reported (Mohan et al., 2006). These include chemical precipitation (Golbaz et al., 2014, Golder et al., 2011, Kongsricharoern and Polprasert, 1995, Kongsricharoern and Polprasert, 1996), ion exchange (Alvarado et al., 2013, Cavaco et al., 2007, Fan et al., 2013), reverse osmosis (Afonso et al., 2004, Benito and Ruíz, 2002, Bhattacharya et al., 2013, Bódalo et al., 2005), ultrafiltration (Aroua et al., 2007, Chakraborty et al., 2014), electrochemical (Almaguer-Busso et al., 2009, Lakshmipathiraj et al., 2008, Liu et al., 2011, Ouejhani et al., 2008), bio-sorption (Hou et al., 2012, Dittert et al., 2014, Febrianto et al., 2009, Khambhaty et al., 2009, Li et al., 2008) and adsorption (Anirudhan et al., 2013, Anupam et al., 2011, Baccar et al., 2009, Baral et al., 2006, Behnajady and Bimeghdar, 2014, Chen et al., 2014). Many efforts have been devised to develop new technologies in which technological, environmental and economic constraints are taken into consideration.

The purification methods have to avoid generation of secondary waste and to involve materials that can be recycled and easily used on an industrial scale. Adsorption compared with other methods appears to be an attractive process in view of its efficiency and capacity of removing heavy metal ions over wide range of pH and to a much lower level, and an ability to remove complex form of metals that is generally not possibly by other methods. It is also environmentally friendly, cost effective and easy to operate compared to other processes (Rao et al., 2010). In the past, several investigations have been undertaken for the removal of heavy
metals from wastewater using different adsorption media. These include amongst many others activated carbon made from other materials (Baccar et al., 2009, Bishnoi et al., 2004, Demirbas et al., 2008, Duranoğlu et al., 2012), treated saw dust (Baral et al., 2006), agricultural wastes (Gao et al., 2008), alumina and natural zeolite (Ngomsik et al., 2006).

Natural zeolite is stable over wide environmental conditions and is low cost adsorption media that is suited for fixed bed operations. However, it has poor capacity for most contaminants. Thus to render it effective for water treatment, surface modification is required. In recent studies polypyrrole and polyaniline have been reported as excellent adsorbent for the removal of Cr(VI) (Bhaumik et al., 2011d, Bhaumik et al., 2012, Bhaumik et al., 2014a). However these polymers have very low density and therefore in real industrial applications, large volume of fix beds would be required thus limiting their use. Both natural zeolite and polymers are bulk adsorption materials. In adsorption, bulk materials have inherent limitations as they suffer from massive mass transfer resistance due to large surface areas and large diffusion lengths. To overcome these limiting factors in adsorption, adsorption media could be designed to have some nano-features in order to maximize mass transport kinetics by providing contaminants with rapid access to high surface area and by promoting internal mass transport (Hristovski et al., 2007). One way of achieving this is by developing nanocomposites in which nanoparticles are imbedded in bulk materials.

Consequently this study explores the use of magnetic natural zeolite-polypyrrole composite as a robust adsorption media for hexavalent chromium removal from water. The effects of several variables are considered including the composition of zeolite in the composite, solution pH, adsorbent dose, temperature and contact time. Appropriate kinetic and equilibrium models are
used to interpret experimental results. It is shown that the material exhibit enhanced capacity for hexavalent chromium.

3.1. Materials and Methods

3.1.1. Materials

Zeolite (natural clinoptilolite) was supplied by Ajax Industries CC in Cape Town, South Africa. All the chemical reagents used in this study were of analytical reagent grade [AR Grade] and were obtained from Sigma-Aldrich. FeCl$_3$·6H$_2$O, FeCl$_2$·4H$_2$O and NaOH were used for magnetic zeolite preparation. Anhydrous FeCl$_3$ was used as an oxidant for polymerization of pyrrole (Py). A stock solution of Cr(VI) was prepared by dissolving a known amount of potassium dichromate ($K_2Cr_2O_7$) with deionised water. Hydrochloric acid (HCl), ethanol and 1,5 diphenylcarbazide were also used in the study to adjust the pH of the solution and for analysis of Cr(VI), respectively.

3.2. Methods

3.2.1. Synthesis of magnetic zeolite

Zeolite was first conditioned with 1 M NaCl for 36 h at room temperature. Thereafter, the solids were vacuum filtered and washed thoroughly with deionized water. Afterwards the solids were air dried for 48 h. Magnetic zeolite was prepared through co-precipitation of Fe$^{3+}$ and Fe$^{2+}$. First, 250 mL of sodium hydroxide solution (1 M) and a known amount of conditioned zeolite powder were placed in a three-neck round bottom flask and heated to 90$^\circ$C in an oil bath. The mixture was homogenously mixed by vigorously stirring and deoxygenating by bubbling of N$_2$ gas. Molar ratio 2:1 of ferrous chloride and ferric chloride was prepared by adding 25 mL of 0.25 M HCl. Then Fe$^{3+}$/Fe$^{2+}$ solution was added drop wise to the vigorously stirred mixture of zeolite
and NaOH under N₂ atmosphere. The reaction temperature was maintained at 95 °C for an additional hour under the nitrogen environment. The solution was continuously stirred and cooled down to room temperature. The obtained magnetic zeolite powder was washed repeatedly with deionized water until neutral pH was obtained. Finally, obtained magnetic powder was dried under vacuum for 12 h.

3.2.2. Synthesis of the magnetic zeolite-polypyrrole composite (MZPPY)

A known amount of magnetic zeolite (0.5 - 4g) was dispersed in 80 mL deionised water and ultrasonicated for 20 min. Then 0.8 mL of pyrrole was syringed into the mixture and then shaken for 5 min. Pyrrole was polymerized by 6 g FeCl₃ oxidant. After 3 h of stirring, the mixture was filtered and the residue was washed with water and acetone. The composite was then dried at 80°C for 6 h. The prepared composite is hereafter referred to as MZPPY.

3.2.3. Characterization

The structure of magnetic zeolite-polypyrrole composite was characterized by using Fourier transformed infrared (FTIR) spectrometer (Perkin–Elmer Spectrum100 spectrometer), equipped with an FTIR microscopy accessory, on the attenuated total reflection (ATR) diamond crystal. To characterize the morphology of the magnetic zeolite and the composite, field-emission scanning electron microscopy (FE-SEM) images with energy dispersive X-ray analysis (EDX) were obtained on a LEO, Zeiss SEM. A JEOL JEM 2100F microscopy with a LAB6 filament operating at 200 kV was used to obtain high resolution transmission electron microscope (HR-TEM) images. The TEM samples were dispersed on a copper grid coated with a carbon film to reduce charging. X-ray diffraction (XRD) patterns measurements were performed on a PANalytical X’Pert PRO-diffractometer using Cu Kα radiation (wavelength, λ = 1.5406Å) with variable slits at 45 kV/40mA.
3.2.4. Batch adsorption experiments

3.2.4.1. Effect of magnetic zeolite loading within the composite, pH and sorbent dosage

A stock solution containing 1000 mg/L Cr(VI) was diluted to prepare appropriate concentrations to perform batch adsorption experiments. The adsorption process was studied by contacting MZPPY adsorbent with 50 mL solution containing 300 mg/L Cr(IV) in 100 mL plastic bottles. The samples were placed in a thermostatic shaker and agitated for 24 h at 150 rpm. The effect of the magnetic zeolite composition of the composite was tested at pH 2 while effect of pH was studied by varying the solution pH in the range of 2-12 by using 0.1 M of NaOH or HCl. The mass of MZPPY used for both studies was 0.1 g. Magnetic zeolite was also tested for comparison under the same experimental conditions. The effect of MZPPY dosage on the removal of Cr(VI) was studied by varying the mass of the adsorbent from 0.025 to 0.15 g using 50 mL of solution (300 mg/L) at pH 2.0. At the end of all experiments, the adsorbent was separated from solution by filtration and the filtrate was analysed for residual Cr(VI) using the UV–Vis spectrometer at 540 nm. For analysis 1,5 diphenylcarbazide reagent used. The removal efficiency of Cr(IV) was determined by the following equation.

\[
\% \text{Removal} = \left( \frac{C_o - C_e}{C_o} \right) \times 100
\]

where \(C_o\) and \(C_e\) are the initial and the equilibrium concentration (mg/L) of Cr(VI), respectively.

3.2.4.2. Effect of co-existing ions

To investigate the effect of competitiveness of various co-existing ions such as Cu\(^{2+}\), Ni\(^{2+}\), Al\(^{3+}\), Cl\(^-\), NO\(_3\)^- and SO\(_4\)^{2-} on Cr(VI) adsorption, 50 mL of 200 mg/L Cr(VI) solutions containing 200 mg/L each of various components with 0.1 g of adsorbent were shaken at pH 2.0. After
equilibrium was established, the adsorbent was separated from the solution and the filtrate was analysed for Cr(VI) concentration.

3.2.4.3. Regeneration studies

Regeneration of an adsorbent is very important therefore adsorption-desorption studies were conducted to investigate the reusability of the MZPPY composite. First 0.1 g of MZPPY was contacted with 50 mL solution containing 200 mg/L of Cr(VI) at pH 2. Then desorption of Cr(VI) loaded adsorbent was performed by contacting 50 mL aqueous solution of 0.1-1 M NaOH and placed in a thermostatic shaker for 24 h. The best desorbing NaOH concentration was used for further desorption experiments. The amount of Cr(VI) desorbed was measured. Regeneration of the spent adsorbent was done by treating MZPPY with 2 M HCl for 3 h and then reused. Three adsorption–desorption cycles were performed, using the same adsorbent to test the reusability of the adsorbent.

3.2.4.4. Kinetics and equilibrium isotherm studies.

The kinetic experiments for adsorption of Cr(VI) were carried out at pH 2 in a 1 L batch reactor. A 1 g of MZPPY was added to the 1000 mL of solutions with initial concentrations of 100, 175 and 300 mg/L. The reactor was stirred at a constant agitation speed of 150 rpm with an overhead stirrer. 5 mL sample solution was withdrawn at predetermined time intervals from the reaction mixture and filtered through a syringe filter and analysed for residual Cr(VI) concentrations. Amount of chromium adsorbed was calculated using the following equation

$$q_t = \left( \frac{C_0 - C_t}{m} \right) \times V$$

(3-2)
where $q_t$ is the adsorbed amount of chromium per unit mass of the adsorbent (mg/g) at any time ($t$), $C_t$ is the residual concentration (mg/L) of chromium at any time $t$, $m$ is the mass of the adsorbent added (g) and $V$ is the sample volume (L).

Sorption isotherm were generated by contacting 0.1 g of adsorbent with 50 mL of Cr(IV) containing solution ranging from 300 to 1100 mg/L in 100 mL plastic sample bottles. The pH of the solution was fixed at 2. The samples were shaken for 24 h at varying temperatures (25° C, 35° C and 45° C) at 150 rpm. The equilibrium sorption capacity was calculated by following equation

$$q_e = \left( \frac{C_o - C_e}{m} \right) \times V$$  \hspace{1cm} (3-3)

where $q_e$ is the equilibrium amount of Cr(VI) adsorbed per unit mass ($m$) of adsorbent (mg/g).

3.3. Results and discussion

3.3.1. Characterization of the adsorbent.

The FTIR spectrum of MZPPY before and after adsorption process is shown in Figure 3-1. The bands at 1423 cm$^{-1}$ and 1513 cm$^{-1}$ are related to C-N stretching and PPy ring stretching vibration. While the C-H stretching vibration, the C-H deformation are observed at 1080 and 958-824 cm$^{-1}$, respectively (Setshedhi et al., 2013, Bhaumik et al., 2011d). The adsorption of Cr(VI) on the adsorbent is indicated by a shift of the peaks to increasing wavelength. New vibrations peaks of 783 and 906 cm$^{-1}$ are observed on the adsorbent spectra after adsorption. These are attributed to intrinsic vibrations of Cr-O and Cr=O bonds. This indicates that Cr(VI)
ions is adsorbed on the surface of the MZPPY by replacing the doping Cl⁻ ions. The diffraction patterns of the crystalline structure of the (a) magnetic zeolite (MZ) (b) MZPPY adsorbent before and (c) MZPPY after adsorption are shown in Figure 3-2. The peaks at 35.83°, 43.14°, 57.24° and 63.01° can be assigned to (311), (400), (511) and (440) which are associated with Fe₃O₄ crystal planes.

Figure 3-1. FTIR spectra of the MZPPY (a) before and (b) after adsorption with Cr(VI).
Figure 3-2. XRD pattern of magnetic zeolite (a) and MZPPY before (b) after (c) Cr(VI) adsorption and (d) after regeneration process
It is observed that there is no change in the crystalline structure of MZPPY before and after adsorption. The surface morphology of the adsorption material was evaluated using field-emission scanning electron microscopy (FE-SEM). Figure 3-3 shows the SEM images of (a) magnetic natural zeolite, (b) MZPPY before adsorption and (c) MZPPY after adsorption. Figure 3-3(a) shows a smooth layered surface of natural zeolite (clinoptilolite) particles. It can be seen that the zeolite has completely been covered by PPy and has a cauliflower-like structure in Figure 3-3 (b). Natural zeolite particles have been reported to act as growth centres for polypyrrole chains and consequently aid in making of a dense and compact structure for zeolite-polypyrrole composite (Rashidzadeh et al., 2013).
Figure 3-3. Scanning electron microscopic images of (a) magnetic zeolite and (b) MZPPY before and (c) after adsorption of Cr(VI).

Figure 3-4 shows the TEM images of (a) magnetic zeolite, and (b)-(d) MZ-PPy composites before adsorption at different magnifications. From the images, irregular layers of zeolite are observed in the magnetic zeolite (MZ) image. Almost spherical Fe$_3$O$_4$ nanoparticles are observed within the structure of MZ and MZPPY images and exist as agglomerates due to high surface area and magneto dipole–dipole interactions between the particles (Bhaumik et al., 2011a).

Figure 3-4. Transmission electron microscopic images of (a) magnetic zeolite and MZPPY ((b)–(d)).
Figure 3-5. Energy dispersive X-rays (EDX) spectra of MZPPY (a) before and (b) after Cr(VI).
Energy dispersive X-rays (EDX) was used to analyse the elemental constituents of the MZPPY before and after Cr(VI) adsorption. The EDS spectra in Figure 3-5 show the presence of major elements found in zeolite (Na, Mg, Al, Si, Ca, K), and Fe and Cl peaks are due to the presence of magnetite and oxidant. After Cr(VI) adsorption process, additional peaks of Cr are observed in Figure 4-5b which provides a direct evidence for Cr(VI) adsorption on the surface of the MZPPY composite.

The pH of point-of-zero (pH_{pzc}) charge of the MZPPY was determined by measuring the zeta potential of the composite as a function of pH. The point of zero charge of the MZPPY is at about 7.5 (Figure 3-6), thus indicating that when pH is less than pH_{pzc}, the MZPPY has positive surface charge and can attract anions, while at pH greater than (pH_{pzc}), the surface charge of MZPPY is negative which will attract cations.

![Zeta potential of the MZPPY at different pH values.](image)

Figure 3-6. Zeta potential of the MZPPY at different pH values.
3.3.2. Effect of magnetic zeolite loading within the composite, pH and sorbent dosage on Cr(VI) removal

The amount of MZ loaded onto the polymer was investigated to establish the optimum mass that can be loaded onto the polymer. The higher the mass of MZ in the composite the higher is the density of MZPPY for better fixed bed operation. The results in Figure 3-7 indicate that polymer improved the performance of magnetic zeolite which only achieved the highest chromium removal of 35.63 %. Upon the addition of pyrrole to different masses of MZ, the Cr(VI) removal efficiency improved from 65.64 % at 0 g of MZ and to 99.99% at a MZ loading of 1.5 g to 3 g. An increase in performance as the loading was increased is probably due to an increase in the number of active sites provided by the magnetite nanoparticles in the zeolite which have a high affinity for Cr(VI) (Shen et al., 2009b, Shen et al., 2009a). Interestingly, a decrease in performance (chromium removal of 88.2 %) is observed when the MZ mass was increased to 4g. Thus 3 g was chosen for subsequent studies. The bulk density of the polypyrrole, zeolite and magnetic zeolite/polyprrole was found to be 0.034; 0.876 and 0.195 g/mL. This indicates that the density of polypyrrole was improved by the incorporation of magnetic zeolite, a feature so desired for fixed bed operation.

The pH of the solution is an important parameter for metal ion sorption since it not only affects the surface charge of adsorbent but also the degree of ionization and speciation of adsorbate during reaction (Demiral et al., 2008). To investigate the effect of pH on the adsorption efficiency of Cr(VI) onto MZPPY, the pH of the solution was varied from 2.0 to 12 at a temperature of 25 C ± 1° C.
Figure 3-7. Effect of magnetic zeolite loading onto PPY. Initial concentration: 300 mg/L; Temperature: 25°C; dose: 2 g/L; contact time: 24 hrs

Results in Figure 3-8 shows that Cr(IV) removal is pH-dependent and that maximum removal occurs at pH 2. Hexavalent chromium exists in aqueous solution in the form of oxyanions such as HCrO$_4^-$, Cr$_2$O$_7^{2-}$ and CrO$_4^{2-}$. The dominant form of Cr(VI) between pH 1.0 and 4.0 is monovalent HCrO$_4^-$, which is then gradually converted to the divalent form CrO$_4^{2-}$ as pH increases (Bhaumik et al., 2011d, Gupta et al., 2010, Yang et al., 2014). The higher uptake at lower pH is due to the strong attraction between predominant oxyanions HCrO$_4^-$ and the positively charged surface of the adsorbent. The increased removal can be further attributed to the anion exchange property of the polypyrrole through replacement of the doped Cl$^-$ with either HCrO$_4^-$ or Cr$_2$O$_7^{2-}$ (Bhaumik et al., 2011d). As the pH is increased more hydroxyl ions are
present in the solution and compete with chromate ions resulting in the reduction of Cr(VI) removal.

Figure 3-8. Effect of pH on the adsorption of Cr(VI) by MZPPY and magnetic zeolite. 300 mg/L; Temperature : 25°C; dose: 2 g/L; contact time : 24 hrs

The effect of adsorbent dosage is an important parameter as it determines the capacity of an adsorbent for a given initial concentration, which contributes to the overall cost of water treatment. The results in Figure 3-9 show that the removal efficiency of Cr(VI) was increased from 68.16% at 0.025 g to 99.99% at 0.1 g to 0.15 g. An increase in the sorbent dosage increases the number of active sites available for the chromium ions to interact with. As a consequence, performance improves with mass of adsorption media. The results therefore suggest that MZPPY is highly efficient in Cr(VI) removal as only a small quantity (2g/L) is required to achieve excellent performance.
Figure 3-9. Effect of dosage of adsorbent on the adsorption of Cr(VI). 300 mg/L; Temperature: 25°C; contact time: 24 hrs

3.3.3. Effect of co-existing ions

In most cases industrial wastewaters contain various kinds of ions including chloride, sulphate, nitrate, copper, zinc, and nickel. The adsorption of Cr(VI) onto the MZPPY was investigated in the presence of co-existing ions. Results (see Figure 3-10) indicate that there is no decrease in Cr(VI) removal in the presence of ions such as Cl⁻, NO₃⁻, Ni²⁺, Cu²⁺, and Zn²⁺. However, the presence of SO₄²⁻ in the aqueous solution inhibited the adsorption of Cr(VI) whose capacity reduced from 99 mg/g to 87 mg/g. This indicates that there was competition between the SO₄²⁻ and HCrO₄⁻ ions for the adsorption sites on the adsorbent surface, and this resulted in less Cr(VI) adsorption. SO₄²⁻ and HCrO₄⁻ ions are both negatively charged and during adsorption, both anions are electrostatically attracted to the positively charged sites of the adsorbent (Bhaumik et al., 2016).
3.3.4. Regeneration studies

For economic and environmental reasons, an adsorption media should be regenerable and reused. Figure 3-11 shows cycles used to test reusability of MZPPY. In the first two cycles, the adsorption capacity of MZPPY was maintained at 99 mg/g. However, there was a remarkable decrease in capacity in the subsequent cycles. In particular, the adsorption capacity was reduced to 60 mg/g in the third cycle and further to 36 mg/g. These results therefore indicate that MZPPY can be reused twice successfully in adsorption-desorption cycles without the loss of adsorption capacity. There were no structural changes observed in XRD pattern in Figure 3-6 (d) after regeneration process. The decrease in adsorption capacity may be due to the rupture of polymer
chain by repeated oxidation reaction with highly oxidizing Cr(VI) species, thereby reducing the mass (sorption sites) of the used adsorbent (Bhaumik et al., 2012).

Figure 3-11. Adsorption–desorption cycles

3.3.5. Kinetic studies

The adsorption kinetic studies at three different initial concentrations are shown in Figure 3-12. It is observed that when the initial Cr(VI) concentration increases from 100–300 mg/L, the adsorption capacity of the MZPPY increases too. It is also observed that a rapid uptake was experienced in the first 10 minutes but slowed down considerably as reaction approached equilibrium. The rapid uptake in the initial time period is due the high driving force exerted by the large concentration gradient. For the same reason, the higher uptake at higher initial
concentration is a consequence of larger concentration gradient between the bulk solution and sorbent phase.

Figure 3-12. Adsorption kinetics for adsorption of Cr(VI) adsorption onto MZPPY.

The kinetic data were further interpreted using the Lagergren pseudo–first order and the Ho pseudo-second order kinetic models (Ho and McKay, 2000). The linearized models of pseudo-first and pseudo-second order kinetic models are given in Eq. (3-4) and Eq. (3-5), respectively.

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

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]
where \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/mg/min) are the rate constants of the pseudo-first order and pseudo-second order adsorption models, respectively. The pseudo-first order and pseudo second order rate parameters for chromium sorption were, respectively, calculated from the linear plots of log \((q_e-q_t)\) versus \(t\) and \(t/q_t\) versus \(t\) (Figure 3-13), and are listed in Table 3-1.

Figure 3-13. The pseudo-second order kinetic plot for adsorption of Cr(VI) adsorption onto MZPPY.

From the values of correlation coefficients \((R^2)\) and calculated equilibrium capacity values which are consistent with experimental values, the interaction between MZPPY and chromium ions can be said to follow the pseudo-second order mechanism.
Table 3-1. Kinetics parameters for Cr(VI) adsorption onto MZPPY-

<table>
<thead>
<tr>
<th>$C_o$ (mg/L)</th>
<th>Experi-metal model</th>
<th>Pseudo-first –order model</th>
<th>Pseudo-second –order model</th>
<th>Intraparticle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (L/min)</td>
<td>$k_1$ (mg/g)</td>
<td>$q_e$ (mg/g)</td>
<td>$k_2$ (g-ml)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>$R^2$</td>
<td>$K_p$</td>
</tr>
<tr>
<td>100</td>
<td>89.2</td>
<td>0.080</td>
<td>56.45</td>
<td>0.987</td>
</tr>
<tr>
<td>175</td>
<td>124.3</td>
<td>0.068</td>
<td>82.32</td>
<td>0.977</td>
</tr>
<tr>
<td>300</td>
<td>155.3</td>
<td>0.030</td>
<td>73.14</td>
<td>0.980</td>
</tr>
</tbody>
</table>

The intra-particle diffusion model was used to analyse the nature of the rate controlling step in adsorption. The model gives a relationship between the time dependant adsorption capacity $q_t$ and $t^{0.5}$ and is express in equation (3-6):

$$q_t = K_p t^{0.5} + C$$

where $K_p$ is the intraparticle diffusion rate constant (mg/g/min^{0.5}) and $C$ is a parameter related to the thickness of boundary layer. If the value of $C$ is large then the boundary layer is large too.
The results show that the adsorption of Cr(VI) by the adsorbent is not linear on the entire adsorption process time indicating that more than one process is involved in the sorption of Cr(VI) by MZPPY. The slope of linear plots of the initial portion of the curve is presented in Table 3-1. This indicates that the initial rapid adsorption of Cr(VI) may be due to the external boundary layer diffusion and the subsequent slower uptake is attributed to intraparticle diffusion (Bhaumik et al., 2012).

3.3.6. *Equilibrium isotherm and thermodynamic studies*

To determine the capacity and thermodynamics parameters of Cr(VI) adsorption by MZPPY, adsorption isotherms were obtained at three different temperatures and are presented in
Figure 3-15. Results indicate that Cr(VI) adsorption onto MZPPY is enhanced with an increase in temperature.

Figure 3-15. Nonlinear isotherm plots: (-) Langmuir model, (—) Freundlich model at different temperatures of Cr(VI) sorption onto MZPPY.

Meanwhile the adsorption equilibrium data were fitted with linearized Langmuir (3-7) and Freundlich (3-8) isotherm models. The Langmuir adsorption isotherm model assumes monolayer adsorption onto a surface with a finite number of sites that are identical and equivalent, and that no lateral interaction and steric hindrance between the adsorbed molecules exists even on adjacent sites (Foo and Hameed, 2010). Freundlich isotherm is the earliest known relationship describing the non-ideal, reversible adsorption that is not restricted to the formation of monolayer.
\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad \text{(3-7)}
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{(3-8)}
\]

where \(q_m\) is the monolayer adsorption capacity (mg/g), \(C_e\) is the equilibrium solute concentration (mg/L), \(b\) is the free energy of adsorption, \(K_F\) and \(1/n\) are Freundlich constants related to the adsorption capacity (mg/g) and intensity of adsorption, respectively. The plots of linearized Langmuir and Freundlich isotherms are shown on Figure 3-16 and Figure 3-17, respectively.

Figure 3-16. Equilibrium data fit to linear Langmuir isotherm of Cr(VI) sorption onto MZPPY.
Figure 3-17. Equilibrium data fit to linear Freundlich isotherm (c) of Cr(VI) sorption onto MZPPY.

The related isotherm parameters with regression coefficients $R^2$ are given in Table 3-2. From the regression coefficients, the equilibrium data are better described by the Langmuir isotherm. The maximum adsorption capacity determined from the Langmuir isotherm increased from 344.83 to 434.78 mg/g as the temperature increased from 25°C to 45°C, which confirms that the adsorption process is endothermic in nature. The capacity values obtained in this study is quite competitive compared to those reported in literature (Setshedii et al., 2013, Salgado-Gómez et al., 2014, Hu and Luo, 2010, Sarkar et al., 2010, Santhana Krishna Kumar et al., 2012, Leyva-Ramos et al., 2008, Yuan et al., 2009, Kalhori et al., 2013). (See Table 3-3)
### Table 3-2. Langmuir and Freundlich isotherms parameters for Cr(VI) adsorption onto MZPPY

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_o$ (mg/g)</td>
<td>$b$ (L/mg)</td>
</tr>
<tr>
<td>25 °C</td>
<td>344.83</td>
<td>0.386</td>
</tr>
<tr>
<td>35 °C</td>
<td>370.37</td>
<td>0.730</td>
</tr>
<tr>
<td>45 °C</td>
<td>434.78</td>
<td>1.35</td>
</tr>
</tbody>
</table>

### Table 3-3. Comparison of maximum sorption capacity of other adsorbents for hexavalent chromium adsorption at room temperature.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_o$ (mg/g)</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exfoliated polypyrrole-organically modified montmorillonite clay</td>
<td>119.3</td>
<td>2</td>
<td>(Setshed et al., 2013)</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium-modified zeolite-rich tuff</td>
<td>1.0585</td>
<td>3</td>
<td>(Salgado-Gómez et al., 2014)</td>
</tr>
<tr>
<td>Montmorillonite modified with hydroxyaluminum and cetyltrimethylammonium bromide</td>
<td>11.970</td>
<td>4</td>
<td>(Hu and Luo, 2010)</td>
</tr>
<tr>
<td>Bentonite based Arquad® 2HT-75 organoclay</td>
<td>14.64</td>
<td>4.7</td>
<td>(Sarkar et al., 2010)</td>
</tr>
<tr>
<td>Dodecylamine modified sodium montmorillonite</td>
<td>23.69</td>
<td>2.5</td>
<td>(Santhana Krishna Kumar et al., 2012)</td>
</tr>
<tr>
<td>Surfactant-modified zeolite</td>
<td>5.07</td>
<td>6</td>
<td>(Leyva-Ramos et al., 2008)</td>
</tr>
</tbody>
</table>
Meanwhile, the dimensionless separation factor, $R_L$, which is an essential characteristic of the Langmuir model for defining the favourability of an adsorption process, was determined from equation (4-9):

$$R_L = \frac{1}{1 + bC_o} \quad (3-9)$$

An adsorption process is favourable if $0 < R_L < 1$ but unfavourable when $R_L > 1$. The average $R_L$ values summarised in Table 3.2 at different temperatures suggest that the adsorption was favourable.

The standard enthalpy change ($\Delta H^\circ$) and the standard entropy ($\Delta S^\circ$) for Cr(VI) sorption on MZPPY were obtained using Van’t Hoff equation.

$$\ln b = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3-10)$$
where $b$ is the adsorption coefficient from the Langmuir adsorption isotherm, $\Delta H^\circ$ is the enthalpy change (J/mol), $\Delta S^\circ$ is the entropy change (J/mol/K), $R$ is the gas constant (8.314 J/mol/K) and $T$ is temperature in K. The values of $\ln b$ versus $1/T$ are plotted according to equation (10) and shown in Figure 3-18. The adsorption enthalpy change, entropy change and Gibbs free energy change were calculated and are reported in Table 3-4. The Gibbs free energy change ($\Delta G^\circ$) of adsorption was calculated from Equation (3-11)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$  

(3-11)

Figure 3-18. Plot to determine thermodynamic parameters of Cr(VI) adsorption onto MZPPY.
Table 3-4. Thermodynamics parameters for the adsorption of Cr(VI) on MZPPY composite.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (J/mol/K)</th>
<th>ΔG (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25° C</td>
<td>-14.1894</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35° C</td>
<td>46.58</td>
<td>206</td>
<td>-16.9584</td>
</tr>
<tr>
<td>45° C</td>
<td></td>
<td></td>
<td>-19.0921</td>
</tr>
</tbody>
</table>

The positive value of ΔH° indicates that the adsorption is endothermic nature, which is also supported by the increase in the value of uptake capacity of the sorbent with the rise in temperature. The positive value of ΔS° suggests an increase in disorder at the solid–liquid interface during the sorption of Cr(VI) on MZPPY. The magnitude of G° decreases with an increase in temperature and the negative values indicates the spontaneous nature of sorption process.

It has been previously reported that the mechanisms of adsorption of Cr (VI) onto polypyrrole based materials involves ion exchange mechanism via the replacement of doped Cl− by HCrO4− ions. The XPS studies conducted suggested that some fraction of adsorbed Cr(VI) was reduced to Cr(III) by a reduction process which is due to the presence of electron rich polypyrrole moieties (Bhaumik et al., 2011d).

Conclusion

MZPPY with improved density was successfully synthesized, characterized and used as an adsorbent for the removal of Cr(VI) from aqueous solution. The results indicate that removal efficiency is dependent on pH, initial concentration, adsorbent mass, contact time and temperature. The removal efficiency of 99.99% was obtained when the pH was 2 and the initial Cr(VI) concentration was 300 mg/L. The sorption kinetic data fitted to the pseudo-second order model while the equilibrium data fitted well to the Langmuir isotherm model. The Langmuir
adsorption capacity increased from 344.83 to 434.78 mg/g with an increase in temperature from 25°C to 45°C. Thermodynamic parameters confirmed that the adsorption process is spontaneous, endothermic in nature and marked with an increased randomness at solid–liquid interface. In the presence of SO₄²⁻ as a co-existing ion, Cr(VI) adsorption onto MZPPY was slightly decreased. Regeneration studies indicated that MZPPY can be used in two cycles without loss of capacity. This work confirms that the MZPPY is an effective adsorbent for the removal of Cr(VI) in aqueous solution. However, further studies need to be conducted against industrial wastewater to obtain real performance data.


CHAPTER 4

Vanadium (V) adsorption isotherms and kinetics using polypyrrole coated magnetized natural zeolite

Abstract

Magnetized natural zeolite-polypyrrole (MZPPY) composite as a potential adsorbent for vanadium was prepared via polymerization of pyrrole monomer using FeCl₃ oxidant in aqueous medium in which magnetized natural zeolite particles were suspended. The MZPPY composite was characterized by attenuated total reflectance Fourier transform infrared spectroscope (ATR-FTIR), field emission scanning electron microscope (FE-SEM) and high resolution transmission electron microscope (HR-TEM). Batch adsorption studies were performed to test the ability of the adsorbent to remove V(V) ions from aqueous solution. From sorption equilibrium modelling, the equilibrium data is well described by Langmuir, Sips and Redlich–Peterson isotherms while the adsorption kinetics is described by the pseudo-second order model. The Langmuir adsorption capacity is 65.0 mg/g at 298K. Thermodynamic parameters confirm the spontaneous and endothermic nature of the vanadium adsorption process. Meanwhile V(V) removal process is found not to be affected by co-existing ions. Furthermore, the material can be used in 2 adsorption cycles without compromising its capacity.

4. Introduction

Industries such as glass, textile, ceramic, photography, metallurgy, rubber and plants producing industrial inorganic chemicals and pigments discharge vanadium and vanadium compounds into water bodies (Anirudhan and Radhakrishnan, 2010, Wang et al., 2012). Vanadium is a toxic

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metal and exists in environment both as tetravalent [V(IV)] and pentavalent [V(V)] ion (Aureli et al., 2008). The pentavalent form is more toxic than the tetravalent one and is the most stable species under oxidation conditions (Filik and Yanaz, 2009, Patel et al., 1990). Vanadium ions enter the human body through food chain and contaminated water consumption and cause breathing disorders, paralysis and negative effects on the liver and kidney (Zhang et al., 2014). It is therefore essential to treat vanadium-polluted streams prior to their discharge to the environment. Vanadium in wastewater streams are commonly treated by techniques which include but not limited to microbial fuel cell technology (Zhang et al., 2012), photocatalytic reduction (Sturini et al., 2013), ion exchange and solvent extraction (Li et al., 2013b), adsorption (Hu et al., 2014, Kaczala et al., 2009) and biological methods (Pennesi et al., 2013).

Amongst the aforementioned vanadium removal techniques, adsorption has been widely studied due to its inherent robust features that makes it the preferred choice. The technique requires the use of adsorbing materials (adsorbents). A wide variety of adsorbents have been studied and used for the removal of V(V) ions from aqueous solutions (Namasivayam and Sangeetha, 2006, Peacock and Sherman, 2004, Jansson-Charrier et al., 1996, Nakajima, 2002). For optimum adsorption the choice of the adsorbent material is important and depends on its cost, availability and suitability to remove the given pollutant.

Because of its sorption ability for numerous pollutants, its abundance, high ion exchange capacity, relatively high surface area and relatively low cost; natural zeolite has been recognized as an efficient adsorbent for a large number of water treatment applications including removal of organics and heavy metals from industrial wastewaters (Shahbazi et al., 2014, Moussavi et al.,
To improve adsorption performance of natural zeolites, the surface needs to be modified. Our studies have shown that conducting polymers such as polypyrrole and polyaniline offer good prospects for functionalization due to their nontoxicity, environmentally stability, ease of preparation and high efficiency for removal of toxic metals in water (Bhaumik et al., 2011a, Bhaumik et al., 2011b, Bhaumik et al., 2012, Bhaumik et al., 2013a, Bhaumik et al., 2013b, Setshedie et al., 2014, Setshedie et al., 2015).

After adsorption it can be difficult to separate polymerized powdered adsorbents from water using conventional separation methods such as filtration and sedimentation. In an effort for easy separation pellet adsorbents are also used. However, they are associated with decreased adsorption capacity depending on the binder used which increases the bulk density of the extrudate (Shams and Mirmohammadi, 2007, Sun et al., 2008). A method combining magnetic separation as an alternative for treatment of wastewaters has for this reason received attention in recent years (Chen et al., 2013, Chen et al., 2011b, Faghihian et al., 2013, Li et al., 2013a, Lv et al., 2014b). Because of size and magnetic property, magnetic adsorbents have large surface area, are highly dispersible in water and exhibit superparamagnetic properties which make them easily separable from aqueous solution by the application of external magnetic field (O’Handley, 2000). The main advantage of this technology is that it can dispose a mass of wastewater in a very short period of time (Feng et al., 2010) and reduces production of large quantity of sludge associated with sedimentation and filtration.
This study investigates the sorption properties of magnetized natural zeolite-polypyrrole composite in the removal of vanadium from aqueous solution. The prepared adsorption material is characterized and its adsorption ability explored in a batch set up. Appropriate kinetic and equilibrium models are applied to obtained data in order to get insight into vanadium adsorption characteristics.

4.1. Experimental

4.1.1. Chemicals and methods

Natural zeolite (clinoptilolite) was provided by Ajax Industries CC in Cape Town, South Africa. Pyrrole (Py, 99%) Anhydrous iron (III) chloride (FeCl$_3$), hydrochloric acid (HCl), sodium hydroxide (NaOH), iron (II) chloride tetrahydrate (FeCl$_3$·6H$_2$O), iron (III) chloride hexahydrate (FeCl$_2$·4H$_2$O) were purchased from Sigma-Aldrich. Synthetic vanadium stock solution was prepared by dissolving 2.39 g of sodium metavanadate (anhydrous, 99.9% metals basis-Sigma Aldrich) powder in 1000 mL deionized water. The mixture was placed on a hot plate where it was magnetically stirred and heated at a temperature of 50°C for 10 min.

4.1.2. Methods

Magnetic zeolite-polypyrrole composite (MZPPY) was prepared by the method reported in our previous study (Mthombeni et al., 2015b). Accordingly, zeolite was magnetized by chemical co-precipitation of Fe$^{3+}$ and Fe$^{2+}$ ions at a ratio of 1:1 in the presence of zeolite under N$_2$ environment. During magnetization, the solution was continuously stirred and cooled down to room temperature. The obtained magnetic zeolite powder was washed repeatedly with deionized
water until a neutral pH was attained. The resulting magnetic zeolite was dried under vacuum for 12 h. 3 g of the obtained dry magnetic zeolite powder was dispersed into 80 mL of deionized water and ultrasonicated for 20 min. 0.8 mL of pyrrole was added drop-wise and 6 g of oxidant (FeCl$_3$) was also added. The mixture was shaken for 3 h at room temperature to allow polymerization to go into completion. Finally, acetone (10 mL) was added to stop the reaction. Afterwards, the precipitated magnetic zeolite-polypyrrole composite was vacuum filtered, thoroughly rinsed with distilled and dried at 80°C for 6 h.

4.1.2.1. Characterization

The functional groups on the surface of MZPPY were characterized using Fourier transform infrared spectroscopy (FTIR performed on a Perkin–Elmer Spectrum100 spectrometer), equipped with an FTIR microscopy accessory and a diamond crystal. The field emission scanning electron microscopy (FE-SEM) was used to characterize the morphology of the adsorbents. FE-SEM images with energy dispersive X-ray analysis (EDX) were obtained on a LEO, Zeiss SEM. High resolution transmission electron microscope (HR-TEM) images were obtained from a JEOL JEM 2100F microscopy with a LAB6 filament operating at 200 kV. X-ray diffractometer with a CuKα ($\lambda = 1.5406\text{Å}$) monochromated radiation source operated at 45.0 kV and 40.0 mA.

4.1.2.2. Batch adsorption, isotherms and kinetics studies

The effect of pH was studied by varying the initial pH of the V(V) solution within the range of 2–8, and contacting 0.15 g of raw zeolite, magnetite, polypyrrole and MZPPY with 50 mL of 100 mg/L V(V) solution. Sorption isotherm studies were carried out in a temperature controlled thermostatic shaker. 50 mL of V(V) solutions of concentration ranging from 25 to 250 mg/L were contacted with 0.15 g of magnetic zeolite-polypyrrole composite in 100 mL plastic
bottles. The samples were shaken for 24 h at varying temperatures of 298, 308 and 318 K at 160 rpm. The experiments were performed at pH 4.5. At the end of the experiment, samples were filtered using syringe filters and the residual vanadium concentration was measured by Inductively Couple Plasma- Emission Spectroscopy (ICP-OES). The V(V) removal percentage was determined by using the following equation:

\[
\% \text{Removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

Meanwhile the equilibrium sorption capacity was determined using the following equation:

\[
q_e = \left( \frac{C_0 - C_e}{m} \right) \times V
\]

where \(q_e\) is the equilibrium amount of V(V) adsorbed per unit mass of adsorbent (mg/g), \(m\) is the sorbent mass (g), \(V\) is the sample volume (L), \(C_e\) is the equilibrium concentration (mg/L) and \(C_0\) is the initial concentration (mg/L). The adsorption kinetics experiments were carried out in a batch reactor with initial V(V) concentrations of 50, 80 and 110 mg/L. A mass of 3 g of the sorbent was used. The reactor was continuously stirred at a speed of 250 rpm. At predetermined time intervals a 5 mL sample was withdrawn from the reactor. Each sample was immediately filtered using syringe filters and the resulting filtrates were analysed using Inductively Couple Plasma- Emission Spectroscopy (ICP-OES) at a wavelength of 292.4 nm to determine the vanadium residual concentration. The amount of vanadium removed at any given time was calculated using Eq. (5-3).

\[
q_t = \frac{C_0 - C_t}{m} \times V
\]
where \( C_t \) (mg/L) is the vanadium residual concentration at time \( t \) and \( q_t \) (mg/g) is the time dependent amount of vanadium adsorbed per unit mass of adsorbent.

### 4.2. Effect of co-existing ions and desorption studies

Usually industrial wastewater discharges may contain vanadium along with other ions which may have competitive effect on V(V) adsorption. Therefore, it is important to investigate the competitive effect of coexisting ions on V(V) removal using MZPPY. 50 mL of 100 mg/L V(V) solutions containing 100 mg/L of various components (Ni^{2+}, Cu^{2+}, Cl\(^-\), NO\(_3\)\(^-\) or SO\(_4\)\(^{2-}\)) were contacted with 0.15 g at pH 4.5 for 24 hrs. At the end of the experiment, the residual concentration of V(V) was determined.

Meanwhile the reusability of the adsorbent is an important economic factor; therefore, adsorption-desorption studies were conducted to investigate the potential of reusing the MZPPY composite. Initially, equilibrium experiments were carried out at 25 °C using 0.15 g of MZPPY which was contacted with 50 mL of 100 mg/L solution containing V(V) at pH 4.5. Thereafter desorption experiments were performed by contacting 0.15 g of V(V) loaded adsorbent with varying concentration (0.1 M – 1 M) and volumes (10 – 40 mL) of NaOH solution for 24 h. For regeneration, the spent MZPPY composite was treated with 2 M HCl for 3 h and then reused. To evaluate the reusability of the adsorbent, three adsorption-desorption cycles were performed.

### 4. Results and Discussion

#### 4.2.1. Characterization of the adsorbent

Fe\(_3\)O\(_4\) precipitates on the external surface and internal surface of pores of zeolite and coats the surface when the mixture of Fe\(^{2+}\)/Fe\(^{3+}\) is added to the alkaline reaction mixture. Figure 4.1a
shows the FTIR of magnetized zeolite spectrum which shows the characteristics bands related to zeolites. A band at 3620 cm$^{-1}$ is assigned to acidic hydroxyls Si–O(H)–Al, while a band at 3430 cm$^{-1}$ is due to the vibration of the bonds O–H–O. A band at 1630 cm$^{-1}$ is connected to deformation vibration of absorbed water (Korkuna et al., 2006). A band at 1020 cm$^{-1}$ is due to the asymmetric valence vibrations in tetrahedra SiO$_4$ (Faghihian et al., 2013). Another band near 645 cm$^{-1}$ is considered to arise from Si–O–Na bond (Korkuna et al., 2006). The characteristic band of iron oxide which is Fe–O stretching vibration bond of is observed at 578 cm$^{-1}$ (Maity and Agrawal, 2007).
Figure 4-1. FTIR spectra of the magnetized zeolite (a) and MZPPY (b) before and (c) after adsorption with V(V).
The FTIR spectrum of the MZPPY before adsorption (Figure 4.1b) demonstrates peaks at 958 - 824 cm\(^{-1}\), 1080 cm\(^{-1}\), 1423 cm\(^{-1}\) and 1513 cm\(^{-1}\) that are considered to arise from C–H deformation, C–H stretching, conjugated C–N stretching and pyrrole ring stretching, respectively (Setshedi et al., 2013, Rezaul Karim et al., 2007). New peaks at wavelengths of 813 cm\(^{-1}\) and 980 cm\(^{-1}\) are observed on the adsorbent spectra after adsorption (Figure 4.1c). These are considered to arise from V–O stretching bands that are reported to appear in the region between 800 and 1000 cm\(^{-1}\) (Frost et al., 2003, Frost et al., 2006, Palmer et al., 2007). A peak at 1643 cm\(^{-1}\) is also observed which is attributed to the stretching vibration of V=O (Hu et al., 2014), and therefore confirms the adsorption of V(V).

The morphology of the adsorption media was evaluated by scanning electron microscope and images are shown in Figure 4.2 for natural zeolite (Figure 4.2a), magnetized zeolite (Figure 4.2b), magnetic zeolite-polypyrrole media before (Figure 4.2c) and after adsorption (Figure 4.2d). It can be seen that polypyrrole completely covered the surface of magnetized zeolite and has cauliflower-like structure which is a characteristic morphology of polypyrrole deposits (Boukerma et al., 2006) and that no change is observed in the morphology of the adsorbent after adsorption. Natural zeolite particles act as growth centres for polypyrrole chains and consequently aid in making the MZPPY dense and compact structure (Rashidzadeh et al., 2013). Figure 4.3 shows the TEM images of MZPPY composites before adsorption at two different magnifications. The TEM images of the composites indicate that the magnetic zeolite particles are embedded in the polypyrrole matrix. The darker shaded core is magnetic Fe\(_3\)O\(_4\) nanoparticles which are within the structure of zeolite and light shaded area is polypyrrole in the composite, due to the different electron penetrability. Energy dispersive X-rays (EDX) was used to analyse
the elemental constituents of the sorption media before and after V(V) adsorption. It is observed that additional peaks of V at 4.94 and 5.41 keV appear upon V(V) adsorption (Figure 4.5). The EDX data therefore provide a direct evidence for V(V) adsorption on the surface of the MZPPY.

Figure 4-2. Scanning electron microscopic images of natural zeolite (a), magnetized zeolite (b), magnetic zeolite–polypyrrole media before (c) and after adsorption (d).

The magnetic property of MZPPY is as shown in Scheme 5.1 in which the MZPPY after V(V) adsorption are attracted by magnet. This further confirms that the composites are magnetic in nature and provide a good prospect for an effective application in magnetic adsorption for industrial wastewater treatment. Figure 4-6 shows the XRD patterns for natural zeolite and magnetized natural zeolite, respectively. The x-ray diffraction pattern of the natural zeolite show
peaks of major intensity corresponding to clinoptilolite. The x-ray diffraction pattern of modified natural zeolite shows peaks corresponding to clinoptilolite and Fe$_3$O$_4$ crystal plane.

![Figure 4-3](image1.png)

Figure 4-3. Transmission electron microscopic images of MZPPY.

![Figure 4-4](image2.png)

Figure 4-4. Energy dispersive X-rays (EDX) spectra of MZPPY before V(V) adsorption
Figure 4-5. Energy dispersive X-rays (EDX) spectra of MZPPY after V(V) adsorption
Figure 4-6. XRD pattern of natural zeolite and magnetized zeolite
4.2.2. *Effect of pH*

The effect of initial solution pH on V(V) percentage removal by the MZPPY composite and its constituents zeolite, polypyrrole and magnetite is shown in Figure 5. It is evident that the highest (58%) V(V) removal efficiency was found for the MZPPY composite, whereas for polypyrrole, magnetite and zeolite removal efficiencies recorded were 49%, 26% and 18%, respectively, at pH 4-5.

![Figure 4-7. Effect of pH on the adsorption of V(V) by MZPPY, polypyrrole, magnetite and zeolite.](image)

The results indicate that V(V) removal is dependent on solution pH and that maximum removal occurs at pH 4-5. The effectiveness of sorption at different initial solution pH of V(V) is greatly
related to the speciation of V(V) in aqueous solution as well as the surface characteristics of the adsorbent. The decrease in removal percentages at below pH 3.0 might be attributed to the existence of VO$_2^{+}$ ion, which experiences electrostatic repulsion from the protonated amino groups of the adsorbent (Anirudhan and Radhakrishnan, 2010, Zhang et al., 2014). By increasing the initial solution pH, the surface of MZPPY is deprotonated and its exchange capacity therefore increased. A decrease in vanadium removal at pH range of 6-9 could be explained by the polymerization ability of vanadium ions at various pH levels. This polymeric species could limit the removal efficiency of vanadium ions even at optimum pH especially when high concentration of vanadium is involved (Crans, 2005, Cran and Tracey, 1998). In general, the study on the effect of pH reveals that combining different materials into a composite provides improved performance in adsorption.

4.2.3. Adsorption kinetics of V(V) onto MZPPY

Figure 5. 8 presents the sorption kinetics data of vanadium for three different initial concentrations (50 ppm - 110 ppm) as a function of contact time. The adsorption rate of V(V) onto MZPPY was very rapid at the initial stage of adsorption and then progressed at a slower rate to reach the final equilibrium stage. Such rapid uptake is indicative of readily available and accessible sorption sites in the composite. The time dependent kinetics sorption data was analysed using non-linear method on Origin 9.1 software by pseudo-first (Tseng et al., 2010), pseudo-second order (Ho and McKay, 2000) and Elovich (Chien and Clayton, 1980) kinetic models given in Eqs. (4-4)–(4-6):

\[
q_t = qe(1 - e^{-k_1t})
\]  
(4-4)

\[
q_t = \frac{qe^{k_2t}}{1+qe^{k_2t}}
\]  
(4-5)

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)
\]  
(4-6)
where $k_1$ and $k_2$ are the pseudo first-order and pseudo-second-order rate constants, $\alpha$ and $\beta$ are the Elovich equation constants.

Figure 4-8. Adsorption kinetics plot of V(V) onto MZPPY at three different concentrations and with experimental data fitted to kinetic models.

The kinetic parameters are summarised in Table 4.1. The kinetic model that best describes the kinetic sorption data was assessed by considering the correlation coefficient ($R^2$) and sum of squared errors (SSE). Based on the $R^2$ and the SSE values, it is suggested that the adsorption kinetic data is best described by the pseudo-second-order equation (Eq. (4-5)). This may suggest
that chemisorption was part of the mechanism for the removal of V(V) by the MZPPY which further corroborates results of EDX.

Table 4-1. Kinetics parameters for V(V) adsorption onto MZPPY

<table>
<thead>
<tr>
<th>$C_o$ (ppm)</th>
<th>Pseudo-first –order model</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (L/min)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
<td>$SSE$</td>
</tr>
<tr>
<td>110</td>
<td>0.248</td>
<td>25.2820</td>
<td>0.87</td>
<td>10.020</td>
</tr>
<tr>
<td>80</td>
<td>0.615</td>
<td>19.3832</td>
<td>0.70</td>
<td>38.427</td>
</tr>
<tr>
<td>50</td>
<td>0.193</td>
<td>10.2070</td>
<td>0.75</td>
<td>103.777</td>
</tr>
<tr>
<td>Pseudo-second –order model</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_2$ (g-mg/min)</td>
<td>$q_e$</td>
<td>$R^2$</td>
<td>$SSE$</td>
</tr>
<tr>
<td>110</td>
<td>0.012</td>
<td>27.285</td>
<td>0.99</td>
<td>2.099</td>
</tr>
<tr>
<td>80</td>
<td>0.042</td>
<td>20.524</td>
<td>0.97</td>
<td>9.28</td>
</tr>
<tr>
<td>50</td>
<td>0.029</td>
<td>10.805</td>
<td>0.98</td>
<td>18.32</td>
</tr>
<tr>
<td>Elovich model</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$R^2$</td>
<td>$SSE$</td>
</tr>
<tr>
<td>110</td>
<td>33.834</td>
<td>0.7434</td>
<td>0.89</td>
<td>8.163</td>
</tr>
<tr>
<td>80</td>
<td>1978.80</td>
<td>0.5707</td>
<td>0.90</td>
<td>12.502</td>
</tr>
<tr>
<td>50</td>
<td>120.260</td>
<td>0.3111</td>
<td>0.93</td>
<td>29.171</td>
</tr>
</tbody>
</table>

4.2.4. Adsorption isotherm

The adsorption isotherm of V(V) onto the MZPPY sorbent was investigated to evaluate the material adsorption capacity at temperatures 298, 308 and 318 K. The results are given in Figure
4.9. It is observed that the adsorption capacity increased with an increase in metal concentration and temperature. The equilibrium adsorption results were modelled using Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906), Sips (Langmuir-Freundlich), Redlich–Peterson (Redlich and Peterson, 1959) and Dubinin–Radushkevich (Dubinin et al., 1947) adsorption isotherms (Eq 4-7 – 4-11):

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]  
(4-7)

\[ q_e = K_F C_e^{1/n} \]  
(4-8)

\[ q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \]  
(4-9)

\[ q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{b_{RP}}} \]  
(4-10)

\[ q_e = (q_m) \exp(-K_{DR} \varepsilon^2) \]  
(4-11)

\[ \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \]  
(4-12)

where \( q_m \) the monolayer maximum adsorption capacity (mg/g); \( K_F, K_S, K_{RP} \), are Freundlich, Sips, and Redlich–Peterson constants (L/g); \( b, a_s, a_{RP} \) are affinity coefficients (L/mg); \( 1/n \) is a heterogeneity coefficient; \( K_{DR} \) is the adsorption energy related constant (mol\(^2\)/kJ\(^2\)) and \( \varepsilon \) is the Polanyi potential (kJ/mol) given by Eq. (4-12). Matches between experimental and model results are shown in Figures 4.10-4.12. From these figures isotherm parameters were extracted and are summarized in Table 4.2. The Langmuir maximum adsorption capacity (\( q_m \)) and \( b \) values increase with an increase in temperature from 65.1 to 75.0 mg/g and 0.10 to 0.17 (L/mg), respectively. The Freundlich isotherm parameters also increase with an increase in temperature while the Redlich-Peterson, Sips and Dubinin-Radushkevich isotherm parameters do not show any specific trend.
To determine which isotherms fitted the experimental data, both the regression coefficient ($R^2$) and the sum of squared errors (SSE) values were considered. It can be concluded from the $R^2$ and SSE values summarised in Table 4-2 that the Langmuir, Redlich-Peterson and Sips isotherms describe the experimental data fairly well.

Figure 4-9. Effect of temperature of V(V) sorption onto MZPPY
Figure 4-10. Equilibrium isotherms of V(V) sorption onto MZPPY and nonlinear isotherm plots:
(-) Langmuir model, (---) Freundlich model at 298 K, (⋯) Langmuir Freundlich, (·-·-·) RedlichPeterson, (-'-'-) Dubinin–Radushkevich

Figure 4-11. Equilibrium isotherms of V(V) sorption onto MZPPY and nonlinear isotherm plots:
(-) Langmuir model, (---) Freundlich model at 308 K, (⋯) Langmuir Freundlich, (·-·-·) RedlichPeterson, (-'-'-) Dubinin–Radushkevich
Figure 4-12. Equilibrium isotherms of V(V) sorption onto MZPPY and nonlinear isotherm plots: (-) Langmuir model, (---) Freundlich model at 318 K , (···) Langmuir Freundlich, (····) RedlichPeterson, (---) Dubinin–Radushkevich

Further, favorability of interaction between V(V) and MZPPY was explored by considering the dimensionless constant called equilibrium parameter $R_L$ (Eq. 5-13).

$$RL = \frac{1}{\left(1 + bC_0\right)}$$  \hspace{1cm} (4-13)

The $R_L$ values between 0 and 1 indicate favourable adsorption. The $R_L$ values were found to be between 0.050 and 0.031 for all the concentrations of V(V) studied and temperatures indicating that the process was favourable.
Table 4-2. Isotherms parameters for vanadium adsorption onto MZPPY

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>Redlich-Peterson isotherm</th>
<th>Dubinin–Radushkevich isotherm</th>
<th>Sips isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_m$ (mg/g)</td>
<td>$b$ (L/mg)</td>
<td>$R^2$</td>
<td>$R_L$</td>
<td>$SSEs$</td>
</tr>
<tr>
<td>298 K</td>
<td>65.056</td>
<td>0.101</td>
<td>0.99</td>
<td>0.050</td>
<td>2.782</td>
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<tr>
<td>308 K</td>
<td>70.013</td>
<td>0.119</td>
<td>0.99</td>
<td>0.043</td>
<td>3.696</td>
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<tr>
<td>318 K</td>
<td>74.967</td>
<td>0.166</td>
<td>0.99</td>
<td>0.031</td>
<td>3.613</td>
</tr>
<tr>
<td></td>
<td>$K_F$ (L/g)</td>
<td>$1/n$</td>
<td>$R^2$</td>
<td>$SSEs$</td>
<td></td>
</tr>
<tr>
<td>298 K</td>
<td>18.269</td>
<td>0.279</td>
<td>0.96</td>
<td>13.377</td>
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<tr>
<td>308 K</td>
<td>20.001</td>
<td>0.288</td>
<td>0.94</td>
<td>27.911</td>
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<tr>
<td>318 K</td>
<td>21.774</td>
<td>0.319</td>
<td>0.96</td>
<td>7.998</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$K_r$ (L/g)</td>
<td>$ar$ (L/mg)</td>
<td>$n$</td>
<td>$R^2$</td>
<td>$SSEs$</td>
</tr>
<tr>
<td>298 K</td>
<td>6.225</td>
<td>0.086</td>
<td>1.024</td>
<td>0.99</td>
<td>2.719</td>
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<tr>
<td>308 K</td>
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<tr>
<td>318 K</td>
<td>17.440</td>
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<td></td>
<td>$Q_m$ (mg/g)</td>
<td>$K_{ad}$ (mol$^2$/kJ$^2$)</td>
<td>$E$</td>
<td>$R^2$</td>
<td>$SSEs$</td>
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<td>5.200</td>
<td>0.96</td>
<td>18.038</td>
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<tr>
<td>318 K</td>
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<td>0.007</td>
<td>8.170</td>
<td>0.88</td>
<td>68.428</td>
</tr>
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<td></td>
<td>$K_s$ (L/g)</td>
<td>$\beta_s$ (L/mg)</td>
<td>$a_s$</td>
<td>$R^2$</td>
<td>$SSEs$</td>
</tr>
<tr>
<td>298 K</td>
<td>5.109</td>
<td>1.118</td>
<td>0.0816</td>
<td>0.99</td>
<td>2.581</td>
</tr>
<tr>
<td>308 K</td>
<td>4.121</td>
<td>1.350</td>
<td>0.065</td>
<td>0.99</td>
<td>0.849</td>
</tr>
<tr>
<td>318 K</td>
<td>17.329</td>
<td>0.745</td>
<td>0.195</td>
<td>0.99</td>
<td>1.269</td>
</tr>
</tbody>
</table>

Meanwhile Table 4-3 presents a comparison of Langmuir adsorption capacity with other earlier reported adsorbents in literature. A direct comparison with other adsorbents is difficult because of the different experimental conditions applied. However, the V(V) uptake value obtained in this study is highly competitive.
### Table 4-3. Comparison of maximum sorption capacity of other adsorbents for vanadium removal

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$Q_m$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGTFS-$\text{NH}_3^+\text{Cl}^-$</td>
<td>45.86</td>
<td>(Anirudhan and Radhakrishnan, 2010)</td>
</tr>
<tr>
<td>Chitosan-Zr(IV) composite</td>
<td>208</td>
<td>(Zhang et al., 2014)</td>
</tr>
<tr>
<td>Zr(IV)-SOW</td>
<td>56.75</td>
<td>(Hu et al., 2014)</td>
</tr>
<tr>
<td>ZnCl$_2$ activated carbon</td>
<td>24.9</td>
<td>(Namasivayam and Sangeetha, 2006)</td>
</tr>
<tr>
<td>Metal hydroxide adsorbents:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>25.06</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_3$ and $\beta$-FeOOH</td>
<td>111.11</td>
<td></td>
</tr>
<tr>
<td>FeOOH</td>
<td>45.66</td>
<td></td>
</tr>
<tr>
<td>MZPPY</td>
<td>74.97</td>
<td>Current study</td>
</tr>
</tbody>
</table>

The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy were also determined. The Gibb’s free energy change is obtained using following relationship:

\[
\Delta G^o = -RT \ln b
\]  \hspace{1cm} (4-14)

where $R$ is the gas constant (8.314 J/mol/K), $T$ is temperature in K and $b$ is the Langmuir constant. Enthalpy and entropy changes were determined from Eq. (4-15).

\[
\ln b = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}
\]  \hspace{1cm} (4-15)

The values of $\Delta G^o$ are negative for all temperatures (Table 4.4), and decreases from -42.8 to -58.8 kJ/mol when the temperature is increased from 298 to 318 K indicating that the sorption of vanadium on MZPPY was thermodynamically spontaneous and favourable at high temperature.
Table 4-4. Thermodynamics parameters for the adsorption of V(V) on MZPPY composite.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (J/mol/K)</th>
<th>ΔG (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-42.761</td>
<td></td>
<td>-42.761</td>
</tr>
<tr>
<td>308</td>
<td>19.468</td>
<td>46.029</td>
<td>-48.311</td>
</tr>
<tr>
<td>318</td>
<td></td>
<td></td>
<td>-58.751</td>
</tr>
</tbody>
</table>

The positive value of $\Delta H$ indicates that the adsorption process is endothermic in nature while the positive value of $\Delta S$ indicates an increased randomness state at the solid-solution interface during the fixation of vanadium on the active sites of the adsorbent (Hu et al., 2014).

4.2.5. Effect of co-existing ions and desorption studies

The effects of competitive common ions, such as chloride, sulfate, nitrate, copper and nickel ($\text{Cl}^-$; $\text{SO}_4^{2-}; \text{NO}_3^{-}; \text{Cu}^{2+}; \text{Ni}^{2+}$) that are normally present in mining and industrial waters were studied. The results in Figure 4.13 indicate that the presence of these commons ions do not affect adsorption of V(V) onto MZPPY. These results suggest that the MZPPY can be used to remove vanadium in effluents even in the presence of common competing ions, which are frequent in the environment. The economics of an adsorption process is determined by how many times an adsorbent can be used in adsorption-desorption cycle. For this reason 0.1-1.0 M NaOH was used to desorb V(V) bound on MZPPY. 0.3 M NaOH was found to be the best performing concentration for desorption of vanadium from MZPPY. Thus, different volumes of 0.3 M NaOH were used (10–40 mL) in order to investigate the possibility of regenerating the MZPPY adsorbent at minimum volumes of NaOH. It was observed that there was no significant difference between the volumes used for regeneration.
Figure 4.13. Effect of coexisting ions on the adsorption of V(V) onto MZPPY

Figure 4.14 shows that the adsorbent could be successfully used for two consecutive cycles but the adsorption capacity dropped to 53% in the third cycle. These results correspond to our previous results that showed that the adsorbent can be successfully used in two cycles (Mthombeni et al., 2015b).
4.3. Conclusions

The removal of V(V) ion from aqueous solution was carried out in a batch adsorption mode using MZPPY. The MZPPY adsorbent exhibited effectiveness in the removal of vanadium from aqueous solution. The vanadium uptake was depended on the initial concentration and temperature. Adsorption of V(V) ions increased with an increase in temperature and initial concentration. The sorption kinetics of V(V) was described by the pseudo-second-order kinetic model. The adsorption process was found to be spontaneous and endothermic in nature. The equilibrium sorption data fitted well to the two-parameter Langmuir and the three-parameter isotherms; Langmuir-Freudlich and Redlich–Peterson models. The Langmuir maximum
adsorption capacity increased with an increase in temperature from 65.1 to 75.0 mg/g when temperature was increased from 298 K to 318 K. Adsorption of V(V) in the presence of other competitive ions was not affected. The adsorbent retained the original adsorption capacity after two adsorption–desorption cycles, which confirms the reusability of the adsorbent.
CHAPTER 5

Fixed bed Column studies for Chromium (VI) and Vanadium (V) removal from aqueous using of Magnetic Zeolite Polypyrrole

Abstract

The removal of Cr(VI) and V(V) using magnetic zeolite polypyrrole (MZPPY) composite was investigated in a fixed bed adsorption column. The effects of adsorbent mass, influent Cr(VI) and V(V) concentration and flowrate on the adsorption bed performance characteristics of adsorbent was explored. Experimental results confirmed that the breakthrough curves were dependent on bed mass, initial Cr(VI) and V(V) concentration and flowrate. Three kinetic models; Yoon–Nelson, Thomas, Bohart–Adams were applied to the experimental data to predict the breakthrough curves to determine the characteristic parameters of the column that are useful for process design. The Yoon–Nelson and Thomas models were found appropriate for description of the breakthrough curves. Based on performance data, it can be concluded that the MZPPY composite is a competitive sorption media for Cr(VI) and V(V) removal from aqueous environments. The performance of the column was better at lower flow rate and initial metal ion concentration and higher bed mass.

5. Introduction

Mining and metallurgical industries are associated with heavy metals wastewaters that are directly or indirectly discharged into the environment increasingly, especially in developing countries. Heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic (Hu et al., 2005b). Heavy metals such chromium and vanadium are often discharge to the environment from industrial activities. Chromium exists in two forms as non-toxic trivalent Cr(III) ions play an essential role in the
metabolism of plant and animals, and hexavalent toxic Cr(VI) ions which is known to be carcinogenic (Sugashini and Begum, 2015). The toxicity of vanadium is also dependent on its oxidation state, the pentavalent form V(V) is more toxic than the tetravalent V(IV) one (Filik and Yanaz, 2009, Patel et al., 1990). Several treatment methods to remove heavy metals from mining and industrial wastewater have been reported. Adsorption compared with other methods appears to be an attractive process in view of its efficiency and capacity of removing heavy metal ions over wide range of pH and to a much lower level, ability to remove complex form of metals that is generally not possibly by other methods. It is also environmentally friendly, cost effective and its ease of operation compared to other processes with which it can be applied in the treatment of heavy metal containing wastewater (Rao et al., 2010).

Liquid-phase adsorption separation and purification process can be configured in a number of ways such as batch, fixed-bed, and fluidized bed. Fixed bed adsorption columns have become the most widely used due to advantages of such as: inherent production of high quality drinking water, its simplicity, ease of operation and handling as well as the possibility of in situ regeneration. The fixed bed mode is suitable for use as a point-of-use (POU) system and ideal for individual household and small communities (Onyango et al., 2009, Setshedhi et al., 2014). Batch and continuous column operation are the main modes used in water treatment. Batch operations are only limited to treatment of small quantity of water and easy to apply on laboratory studies but difficult to apply for field studies (Bharathi and Ramesh, 2013, Kumar and Bandyopadhyay, 2006, Hasan et al., 2010). The adsorption capacity obtained from batch equilibrium experiments is useful in providing fundamental information about the effectiveness of material in removing metal ions. Batch experimental data are generally not applicable to most treatment system such
as column operations where contact time is not sufficiently long for the attainment of equilibrium (Bharathi and Ramesh, 2013, Bhaumik et al., 2013b, Low and Lee, 1991). The continuous adsorption systems have significant process engineering advantages, such as treating large volume of wastewater, easy to scale-up from laboratory scale processes to industrial scale and simple operation (Kumar and Bandyopadhyay, 2006, Long et al., 2014, Nguyen et al., 2015a).

Therefore, it is important to evaluate the performance of magnetic zeolite polypyrrole (MZPPY) in a fixed-bed column condition for the removal of Cr(VI) and V(V). The aim of this study is to perform continuous column study for the removal of Cr(VI) and V(V) and to investigate the performance of MZPPY composite under various process variables such as flow rate, bed mass and influent metal ion concentration. Thomas, Bohart –Adams and Yoon-Nelson models were used to analyze the experimental data.

5.1. Materials and methods

Magnetic zeolite polypyrrole composite (MZPPY), Cr(VI) and V(V) solutions were prepared by the methods reported in sections 3.2. and 4.2.

5.2. Column studies

Column experiments were performed using a polyvinyl chloride (PVC) column of 20 mm diameter and 30 cm length. Each column was packed with MZPPY sorbent with glass beads and glass wool placed in the upper and bottom ends of each column to hold the adsorbent media. Water contaminated with metal ions (Cr(VI) and V(V)) was pumped vertically upwards continuously through the column using a peristaltic pump (Figure 5.1.). The effect of several process variables was studied and is described in section 5.2.1. to 5.2.4.
5.2.1. *Effect of bed mass of magnetic zeolite polypyrrole*

Contaminated water containing Cr(VI) and V(V) at initial concentration of 20 mg/L and 47 mg/L respectively was pumped through the column using 1, 2.5, and 5 g of MZPPY for each run, at a flow rate of 1.5 mL/min. The treated water samples were collected at 60 min time intervals and analyzed for residual metal ion. Residual Cr(VI) concentration was analyzed using the UV–Vis spectrometer at 540 nm using 1,5 diphenylcarbazide reagent. Meanwhile the residual V(V) concentration was analyzed using inductively couple plasma-emission spectroscopy (ICP-OES) at a wavelength of 292.4 nm.

5.2.2. *Effect of flow rate*

Cr(VI) and V(V) contaminated waters at initial concentrations of 20 mg/L and 47 mg/L respectively were pumped vertically at a flow rate of 1.5, 2.5, and 4.5 mL/min through columns packed with 2.5 g MZPPY sorbent.
5.2.3. *Effect of initial metal concentration*

The bed mass was kept constant at 2.5 g while water contaminated with Cr(VI) and V(V) was pumped upwards at a constant flow rate of 1.5 mL/min through the column. The initial concentrations of Cr(VI) were 20, 35 and 74 mg/L. The initial concentrations of V(V) were 47, 63 and 84 mg/L. Treated water sample collection and metal ion analysis was done described in Section 5.2.1.

5.2.4. *Environmental sample*

An environmental water sample with a Cr(VI) concentration of 5 mg/L was collected from Lanxess Chrome Mine in Rustenburg. The physical composition of the water is given in summarized Table 5-1. The water was pumped vertically upward at a flow rate of 1.5 mL/min through columns packed with 2.5 g MZPPY media.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
<th>SANS 241</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>mg/L</td>
<td>5.0</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>6.98</td>
<td>5–9.5</td>
</tr>
<tr>
<td>Iron</td>
<td>mg/L</td>
<td>1.43</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Sulphate</td>
<td>mg/L</td>
<td>364</td>
<td>&lt; 400</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg/L</td>
<td>1.28</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Aluminium</td>
<td>mg/L</td>
<td>0.06</td>
<td>&lt; 0.3</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/L</td>
<td>84.0</td>
<td>&lt; 200</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/L</td>
<td>4.37</td>
<td>&lt; 70</td>
</tr>
</tbody>
</table>
5.2.5. Breakthrough analysis

The objective of operating a fixed bed column is to reduce the concentration of a given contaminant to a value below the maximum allowable concentration. The performance of the bed is directly related to the number of bed volumes processed before the breakthrough point (Bhaumik et al., 2013b, Setshedhi et al., 2014, Mthombeni et al., 2012). In the study the breakthrough point was when Cr(VI) and V(V) concentration in the treated water sample reached 0.05 mg/L and 0.1 mg/L, respectively (allowable limit for domestic use). The capacity of the bed at breakthrough point is determined from the following equation:

\[ q_b = \frac{C_0}{m} \int_0^{V_b} \left(1 - \frac{C_t}{C_0}\right) dV \]  

(5-1)

where \( q_b \) is the bed capacity at breakthrough point (mg/g), \( m \) is the bed mass (g), \( C_0 \) is the initial adsorbate concentration (mg/L), \( C_t \) is the concentration of treated water of the outlet solution (mg/L) at any time \( t \) and \( V_b \) is the volume processed at breakthrough point (L).

The total cost of the fixed bed is determined by the volume of the bed and size of the column (Onyango et al., 2009). The performance of a fixed bed column is directly related to the number of bed volumes (BV) processed before the breakthrough point is reached (Onyango et al., 2009, Mthombeni et al., 2012). The number of bed volumes at breakthrough point is given by the following equation:

\[ BV = \frac{\text{Volume of water at breakthrough point (L)}}{\text{Volume of adsorbent bed (L)}} \]  

(5-2)

The adsorbent exhaustion rate (AER) is defined as the mass of adsorbent material exhausted per volume of water treated at breakthrough point and is expressed as:
\[ AER = \frac{\text{Mass of adsorbent material (g) in column}}{\text{Volume of water treated (L)}} \]  

(5-3)

The rate at which the adsorbent becomes exhausted is an indication on how often the adsorbent will be replaced and the operating costs involved. Low values of AER imply good performance of the bed (Onyango et al., 2009). The empty bed contact time (EBCT), is used to determine the optimum adsorbent usage in a fixed-bed column. The capital and operating costs for a fixed-bed adsorption system are dependent on the EBCT and the adsorbent exhaustion rate (Ko et al., 2000, Ma et al., 2014, McKay and Bino, 1990). The EBCT is defined as the time required for the influent to fill the volume of the adsorbent bed and is a direct function of the influent flow rate and volume of the adsorbent bed. It enables system designers to determine the adsorption column size required (Ma et al., 2014).

\[ EBCT = \frac{\text{adsorbent bed volume (mL)}}{\text{flowrate (mL/min)}} \]  

(5-4)

5.3. Results

5.3.1. Effect of bed mass

By varying the bed mass of the adsorbent the amount of active sites available and the contact time between metal ions and the adsorbent are increased. The effect of varying bed mass is shown in Figure 5-2 and 5-3 as breakthrough curves for Cr(VI) and V(V) adsorptions respectively.
Figure 5-2. Breakthrough curves for adsorption of Cr(VI) from water using MZPPY at different bed masses. Flow rate of 1.5 mL/min and initial concentration of 20 mg/L at pH 2.

It is observed that the breakthrough time increases with an increase in bed mass. The experimental breakthrough time for removal of Cr(VI) and V(V) increased from 900 to 4440 min and from 60 to 840 min, respectively when the bed mass was increased from 1 to 5 g. The adsorbent is saturated faster at lower bed mass due to lesser active site, which results in an early breakthrough point. Furthermore, the lower bed mass which have shorter bed heights may lead to axial dispersion as the predominant mass transfer phenomenon and thus automatically reducing the radial diffusion of metal ions.
Figure 5-3. Breakthrough curves for adsorption of V(V) from water using MZPPY at different bed masses. Flow rate of 1.5 mL/min and initial concentration of 47 mg/L at pH 4.5.

In comparison with the higher bed mass which has longer bed height, the mass transfer zone gets broadened and more sorption sites are available for adsorption (Singha et al., 2012). Treated water volumes processed at breakthrough point for Cr(VI) removal were 1.35; 2.52 and 6.66 L for 1; 2.5 and 5 g, respectively. The volumes processed for V(V) were 0.09; 0.63 and 1.26 L for 1, 2.5; and 5 g, respectively. The empty bed contact time (EBCT) also increases from 2.51 to 10.47 min with an increase in bed mass from 1 to 5 g. (See Table 5-2 and 5-3)
Table 5-2. Summary of results at breakthrough point for Cr(VI) removal using MZPPY

<table>
<thead>
<tr>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Time at breakthrough point (min)</th>
<th>Capacity mg/g</th>
<th>Volumes processed at breakthrough point (L)</th>
<th>Bed volume processed (g/L)</th>
<th>AER (min)</th>
<th>EBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900</td>
<td>28.99</td>
<td>1.35</td>
<td>287</td>
<td>0.74</td>
<td>2.51</td>
</tr>
<tr>
<td>2.5</td>
<td>1680</td>
<td>21.6</td>
<td>2.52</td>
<td>308</td>
<td>0.99</td>
<td>5.44</td>
</tr>
<tr>
<td>5</td>
<td>4440</td>
<td>28.63</td>
<td>6.66</td>
<td>424</td>
<td>0.75</td>
<td>10.47</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Time at breakthrough point (min)</th>
<th>Capacity mg/g</th>
<th>Volumes processed at breakthrough point (L)</th>
<th>Bed volume processed (g/L)</th>
<th>AER (min)</th>
<th>EBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>1680</td>
<td>28.99</td>
<td>2.52</td>
<td>308</td>
<td>0.99</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>960</td>
<td>24.77</td>
<td>2.88</td>
<td>353</td>
<td>0.87</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>660</td>
<td>25.66</td>
<td>2.97</td>
<td>364</td>
<td>0.84</td>
<td>1.81</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial Cr (VI) concentration (mg/L)</th>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Time at breakthrough point (min)</th>
<th>Capacity mg/g</th>
<th>Volumes processed at breakthrough point (L)</th>
<th>Bed volume processed (g/L)</th>
<th>AER (min)</th>
<th>EBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1680</td>
<td>28.99</td>
<td>2.52</td>
<td>308</td>
<td>0.99</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>1500</td>
<td>31.55</td>
<td>2.25</td>
<td>275</td>
<td>1.11</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>1200</td>
<td>53.2</td>
<td>1.8</td>
<td>220</td>
<td>1.39</td>
<td>5.44</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Environmental sample</th>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Time at breakthrough point (min)</th>
<th>Capacity mg/g</th>
<th>Volumes processed at breakthrough point (L)</th>
<th>Bed volume processed (g/L)</th>
<th>AER (min)</th>
<th>EBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mg/L</td>
<td>6600</td>
<td>19.3</td>
<td>9.9</td>
<td>1212</td>
<td>0.25</td>
<td>5.44</td>
<td></td>
</tr>
</tbody>
</table>
### Table 5-3. Summary of results at breakthrough point for V(V) removal using MZPPY

<table>
<thead>
<tr>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Time at breakthrough point $t_b$ (min)</th>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Capacity at breakthrough point mg/g</th>
<th>Volumes processed at breakthrough point L</th>
<th>Bed volume processed at breakthrough point g/L</th>
<th>AER g/L</th>
<th>EBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>6.37</td>
<td>0.09</td>
<td>24</td>
<td>11</td>
<td>24</td>
<td>2.51</td>
</tr>
<tr>
<td>2.5</td>
<td>420</td>
<td>11.85</td>
<td>0.63</td>
<td>77</td>
<td>4</td>
<td>44</td>
<td>5.44</td>
</tr>
<tr>
<td>5</td>
<td>840</td>
<td>12.01</td>
<td>1.26</td>
<td>80</td>
<td>4</td>
<td>44</td>
<td>10.47</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Time at breakthrough point $t_b$ (min)</th>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Capacity at breakthrough point mg/g</th>
<th>Volumes processed at breakthrough point L</th>
<th>Bed volume processed at breakthrough point g/L</th>
<th>AER g/L</th>
<th>EBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>420</td>
<td>11.89</td>
<td>0.63</td>
<td>77</td>
<td>4</td>
<td>4</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>6.7</td>
<td>0.36</td>
<td>44</td>
<td>7</td>
<td>7</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>60</td>
<td>5.08</td>
<td>0.27</td>
<td>33</td>
<td>9</td>
<td>9</td>
<td>1.81</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial V(V)concentration (mg/L)</th>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Time at breakthrough point $t_b$ (min)</th>
<th>Mass of MZPPY adsorbent (g)</th>
<th>Capacity at breakthrough point mg/g</th>
<th>Volumes processed at breakthrough point L</th>
<th>Bed volume processed at breakthrough point g/L</th>
<th>AER g/L</th>
<th>EBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>420</td>
<td>11.89</td>
<td>0.63</td>
<td>77</td>
<td>4</td>
<td>4</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>360</td>
<td>13.57</td>
<td>0.54</td>
<td>66</td>
<td>5</td>
<td>5</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>60</td>
<td>3.02</td>
<td>0.09</td>
<td>11</td>
<td>28</td>
<td>28</td>
<td>5.44</td>
<td></td>
</tr>
</tbody>
</table>

#### 5.3.2. Effect of flowrate

The adsorption process is depended on the contact time between the adsorbent and the adsorbate (Setshedi et al., 2014). The results in Figure 5-4 and 5-5 indicate that at a lower flow rate more processing time was required for breakthrough point to be reached. The volume of treated water at breakthrough point was found to be 2.52; 2.88 and 2.97 L for Cr (VI), and 0.63; 0.36 and 0.27 L for V(V) with corresponding bed volumes of 308; 353 and 364 for Cr(VI) removal and 77; 44
and 33 for V(V) removal at 1.5; 3 and 4.5 mL/min, respectively. The AER values obtained for Cr(VI) removal are 0.99, 0.87 and 0.84 g/L, while the AER values for V(V) removal are 3.97, 6.94 and 9.26 at the flow of 1.5, 3, 4.5 mL/min, respectively. The decrease in performance of the bed with an increase in flow rate may be due to the increase in the movement of mass transfer zone, which results in a decrease adsorbent–adsorbate contact time.

Figure 5-4. Breakthrough curves for the removal Cr(VI) from water using MZPPY at different flow rates. Initial concentration of 20 mg/L, bed mass of 2.5 g.
5.3.3. Effect of initial concentration

The effect of initial concentration on breakthrough performance of the MZPPY adsorbent was studied by varying the initial Cr(VI) and V(V) concentrations from 20 to 74 mg/L and 47 to 84 mg/L, respectively. The breakthrough curves obtained from the tests are shown in Figure 5-6 and 5-7. It is observed from the graphs that the breakthrough point decreases with an increase in initial concentration Cr(VI) and V(V).
Figure 5-6. Effect of initial concentration of Cr(VI) on breakthrough performance MZPPY at pH 2.

Volume of treated water at breakthrough point decreased when the initial concentration of metal ions was increased, and are 2.52; 2.25 and 1.8 L for 20; 35 and 74 mg/L Cr(VI) concentration, respectively. And the volumes processed for 47; 63 and 84 mg/L V(V) concentration were recorded at 0.63; 0.54 and 0.09 L; respectively. Also at higher initial concentration binding sites are saturated faster which results in an earlier breakthrough point. At high metal ion concentrations, there is an increase in driving force for mass transfer which leads to faster saturation of the adsorbent's active sites, resulting in an increase in the adsorbent exhaustion rate.
(Chen et al., 2012). The bed volumes at breakthrough point are 308; 275 and 220 for Cr(VI) while the bed volumes for V(V) are 77; 66 and 11; respectively. The AER values obtained for Cr(VI) removal was 0.99; 1.11 and 1.39 and for V(V) removal was 3.97; 4.63 and 27.78; respectively. High values of AER at higher initial metal ion concentration indicates that in operation the adsorbent will need to be replaced at a higher frequency when processing water containing higher initial metal ion concentration.

Figure 5-7. Effect of initial concentration of V(V) on breakthrough performance of MZPPY at pH 4.5.
5.3.4. Removal of Cr(VI) from environmental water sample

The water sample at pH value 6.98 and 5 mg/L of Cr(VI) was also tested. The water sample also contained 1.43 mg Fe/L; 364 mg SO\textsubscript{4}\textsuperscript{2-}/L; 1.28 NO\textsubscript{3}\textsuperscript{-}/L; 0.06 mg Al/L; 84 mg Cl\textsuperscript{-}/L and 4.37 mg Mg/L as coexisting ions. As a result the breakthrough point was observed at 6600 min (Figure 5.8) with the volume of water treated recorded as 9.9 L. The bed volume processed was 1212 and AER value of at 0.25 g/L was achieved. The good performance of the column was due to the low initial concentration of Cr(VI) in the sample. High bed volume processed indicates that effects of most coexisting ions are negligible but it was indicated earlier in section 3.2.3 that SO\textsubscript{4}\textsuperscript{2-} ions reduced the adsorption capacity of MZPPY.

![Breakthrough curves for the removal of Cr(VI) from environmental water sample with initial concentration of 5 mg/L; at flow rate 1.5 mL/min; bed mass 2.5 g and pH 2.](image)

Figure 5-8. Breakthrough curves for the removal of Cr(VI) from environmental water sample with initial concentration of 5 mg/L; at flow rate 1.5 mL/min; bed mass 2.5 g and pH 2.
5.3.5. **Breakthrough curves modelling**

To model the breakthrough behaviors of Cr(VI) and V(V) sorption using MZPPY composite three mathematical models, namely; Yoon–Nelson, Thomas and Bohart–Adams were used to match and model fixed bed column experimental data.

5.3.5.1. **Thomas model**

Thomas equation is one of the most widely used models often used to interpret fixed bed column adsorption data. This model assumes that adsorption process data follows Langmuir isotherm and also obeys second-order reversible reaction kinetics. It also assumes that there is absence of internal and external diffusion limitation (Karimi et al., 2012). The model can be expressed as:

\[
\frac{C_t}{C_0} = \frac{1}{1 + \exp \left( \frac{k_{Th}q_0^m}{v} - k_{Th}C_0t \right)}
\]

where \( k_{Th} \) is the Thomas rate constant (mL/min mg), \( q_0 \) is the adsorption capacity (mg/g), \( C_0 \) is the initial metal ions concentration (mg/L), \( C_t \) is the effluent metal ions concentration at time \( t \) (mg/L), \( m \) is the mass of adsorbent (g), \( v \) is the feed flow rate (mL/min), and \( t \) is time (min). The parameters of fitted models are listed in Table 5-4. The high correlation coefficients of which was \( \geq 0.98 \), for all the experimental data conditions suggests that the experimental data are well described by the Thomas model. However, adsorption capacities determined by the model did not match the experimental adsorption capacities. Meanwhile the \( k_{Th} \) values increased with an increase in both the adsorbent bed mass and flow rate and decreased as the initial Cr(VI) ion concentration was increased. The \( q_0 \) values increased for all experimental Cr(VI) sorption conditions.
The values of $k_{Th}$ and $q_0$ calculated for V(V) sorption process listed in Table 5-5 indicate that the values decrease as the bed mass increased. It is also observed that $k_{Th}$ and $q_0$ values increased as the influent flow rate is increased. The $k_{Th}$ values did not show any specific trend while the $q_0$ values decrease with increase in initial concentration. In addition, an increase in $k_{Th}$ values is also noted as the flow rate increases.

### 5.3.5.2. Bohart-Adams model

The Bohart-Adams model is based on assumption that equilibrium is not instant and the adsorption rate is controlled by external mass transfer (Wang et al., 2015). The model can be expressed as follows:

$$
\frac{C_t}{C_0} = \exp \left( k_{AB} C_0 t - k_{AB} N_0 \frac{z}{U_0} \right)
$$

where $k_{BA}$ is the kinetic constant (L/mg·min), $N_o$ is the saturation concentration (mg/L), $z$ is the bed depth of the fixed bed column (cm) and $U_0$ is the superficial velocity (cm/min) defined as the ratio of the volumetric flow rate $v$ (cm$^3$/min) to the cross-sectional area of the bed (cm$^2$). The values of $k_{BA}$ and $N_o$ are listed in Table 5-4 and 5-5. It is observed that the experimental breakthrough curves are not described well by the Bohart–Adams model based on low regression values. The poor simulation by Bohart-Adams model can be explained by the fact that the isotherms exhibited Langmuir equilibrium characteristics and cannot be approximated sufficiently by a rectangular isotherm (Chu, 2010).
Table 5-4. Thomas, Adams–Bohart and Yoon–Nelson models constants for the Cr(VI) sorption

<table>
<thead>
<tr>
<th>Mass of adsorbent (g)</th>
<th>Thomas Model Parameters</th>
<th>Bohart-Adams Model Parameters</th>
<th>Yoon-Nelson Model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{Th}$ (mL/min mg)</td>
<td>$q_0$ (mg/g) $R^2$</td>
<td>$k_{BA}$ (L/mg min) $N_0$ $R^2$</td>
</tr>
<tr>
<td>1</td>
<td>2.03×10$^{-4}$ 22705</td>
<td>0.99 9.45×10$^{-5}$ 20409 0.96 0.00439 1626.72 0.99</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>4.44×10$^{-4}$ 32744</td>
<td>0.99 1.48×10$^{-4}$ 13211 0.96 0.00958 2526.54 0.99</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.73×10$^{-4}$ 35111</td>
<td>0.99 1.58×10$^{-4}$ 14036 0.99 0.00892 5419.11 0.99</td>
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</table>

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>4.44×10$^{-4}$ 32744</td>
<td>0.99 1.48×10$^{-4}$ 13211 0.96 0.00958 2526.54 0.99</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.46×10$^{-4}$ 31973</td>
<td>0.99 1.06×10$^{-4}$ 12535 0.89 0.00963 1233.54 0.99</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>7.92×10$^{-4}$ 31709</td>
<td>0.98 1.93×10$^{-4}$ 14192 0.92 0.0170 815.561 0.98</td>
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<table>
<thead>
<tr>
<th>Initial Cr(VI) concentration (mg/L)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.44×10$^{-4}$ 32744</td>
<td>0.99 1.48×10$^{-4}$ 13211 0.96 0.00958 2526.54 0.99</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>2.93×10$^{-3}$ 43350</td>
<td>0.99 9.91×10$^{-3}$ 14952 0.95 0.00964 2200.21 0.99</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>1.8×10$^{-5}$ 67974</td>
<td>0.99 6.24×10$^{-5}$ 23475 0.95 0.0134 1520.99 0.99</td>
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</tr>
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</table>

<table>
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<tr>
<th>Environmental sample</th>
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</thead>
<tbody>
<tr>
<td>1.59×10$^{-3}$</td>
<td>24438</td>
<td>0.99 7.48×10$^{-4}$ 7695 0.99 0.0087 7404.32 0.99</td>
<td></td>
</tr>
</tbody>
</table>

5.3.5.3.  **Yoon-Nelson model**

This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent (Bhaumik et al., 2013b, Chen et al., 2012, Setshedhi et al., 2014). Yoon–Nelson model for a single component system can be expressed as:
\[
\frac{c_t}{c_0-c_t} = \exp(k_{YN} t - \tau k_{YN}) \tag{5-7}
\]

where \( k_{YN} \) is the rate constant in \((\text{min}^{-1})\), \( \tau \) is the time required for 50% adsorbate breakthrough (min) and \( t \) is the processing time (min). Results listed in Table 5.4 indicate that \( k_{YN} \) values increases with an increase in flowrate and in initial concentration for Cr(VI) adsorption whilst \( \tau \) values are observed to increase for an increase in adsorbent mass.

Table 5-5. Thomas, Adams–Bohart and Yoon–Nelson models constants for the V(V) adsorption

<table>
<thead>
<tr>
<th>Mass of adsorbent (g)</th>
<th>Thomas Model Parameters</th>
<th>Bohart-Adams Model Parameters</th>
<th>Yoon-Nelson Model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_{Th} ) (mL/min)</td>
<td>( q_0 ) (mg/g)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>1</td>
<td>9.79 \times 10^{-5}</td>
<td>46818</td>
<td>0.99</td>
</tr>
<tr>
<td>2.5</td>
<td>4.23 \times 10^{-5}</td>
<td>46390</td>
<td>0.99</td>
</tr>
<tr>
<td>5</td>
<td>4.53 \times 10^{-5}</td>
<td>31523</td>
<td>0.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
<th>Thomas Model Parameters</th>
<th>Bohart-Adams Model Parameters</th>
<th>Yoon-Nelson Model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>9.79 \times 10^{-5}</td>
<td>46390</td>
<td>0.99</td>
</tr>
<tr>
<td>3</td>
<td>5.37 \times 10^{-5}</td>
<td>55412</td>
<td>0.99</td>
</tr>
<tr>
<td>4.5</td>
<td>9.79 \times 10^{-5}</td>
<td>62030</td>
<td>0.97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial V(V) concentration (mg/L)</th>
<th>Thomas Model Parameters</th>
<th>Bohart-Adams Model Parameters</th>
<th>Yoon-Nelson Model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>4.23 \times 10^{-5}</td>
<td>46390</td>
<td>0.99</td>
</tr>
<tr>
<td>63</td>
<td>5.75 \times 10^{-5}</td>
<td>32108</td>
<td>0.99</td>
</tr>
<tr>
<td>84</td>
<td>4.74 \times 10^{-5}</td>
<td>27075</td>
<td>0.99</td>
</tr>
</tbody>
</table>
For V(V) results listed in Table 5.5 indicate that the $k_{YN}$ values increase when flowrate and initial V(V) concentration are increased while it decrease when the adsorbent bed mass is increased. $\tau$ values are observed to increase with an increase in adsorbent mass and decreases when the initial V(V) and flow rate are increased. The Yoon–Nelson model fitted very well the experimental breakthrough data as a consequence the $R^2$ values are 0.99.

5.4. Conclusions

Removal of Cr(VI) and V(V) using magnetic zeolite polypyrrole composite in dynamic column studies was investigated by varying the process variables such as bed mass of the adsorbent, initial Cr(VI) and V(V) concentrations and flowrate. The performance of the column was better at lower flow rate and initial metal ion concentration and higher bed mass. Low values of AER and large bed volumes were observed at lower metal ion concentration and higher bed mass for Cr(VI) and V(V) removal indicating good performance. However better performance was observed at higher flow rate for chromium and lower flow rate for vanadium. Thomas, Bohart–Adams and Yoon–Nelson mathematical models were used to interpret the experimental breakthrough curves. Both Yoon–Nelson and Thomas models were found to describe breakthrough curves well under all different experimental conditions. This study has shown that MZPPY can be used to treat water contaminated with both Cr(VI) and V(V) in fixed bed operation mode.
CHAPTER 6

Adsorptive removal of manganese from aqueous solution using batch and column studies

Abstract
Improper disposal of toxic wastes from mining and chemical process industries can yield higher manganese concentrations well above those normally found in environmental water. Bentonite/Natural zeolite as a potential adsorbent for manganese was prepared. Mn(II) adsorption onto bentonite/zeolite (B/Z) from aqueous solutions was explored using batch and packed-bed column studies. The effectiveness of B/Z as an adsorbent for Mn(II) removal was evaluated as a function of solution pH, initial Mn(II) concentration, temperature, bed mass and time. Batch adsorption isotherm data at solution pH of 6, was satisfactorily described by the Freudlich isotherm model, while the kinetic data fitted well with the pseudo second order kinetic model. Sorption of Mn(II) onto B/Z results showed that the presence of co-existing ions there was as significant effect on Mn(II) removal. At breakthrough point, high bed volumes and low AER values were attained at lower flow rate, lower initial manganese concentration and higher adsorbent bed mass. Thomas and Yoon–Nelson models fitted experimental breakthrough curves well compared to Bohart–Adams.

6. Introduction

South Africa has the world’s largest resources of manganese which is estimated to be around 80%. Manganese is used in the manufacture of iron and steel alloys, batteries, glass and fireworks, a significant fertilizer for plants, food additive for stocks and catalyst for organic synthesis (Li et al., 2010). Manganese is also found in the effluents of mine waters, either neutral or acid (AMD) (Silva et al., 2012). Mn is one of the most widely used metals in the world and one of the important indexes of water pollutants (Ma et al., 2013).
Manganese occurs naturally in many surface water and groundwater sources and in soils that may erode manganese into waters. Improper disposal of dry-cell batteries or other toxic wastes from industries can yield higher manganese concentrations well above those normally found in environmental water (WHO, 2011) and cause significant harm to public health (Frisbie et al., 2012). Manganese at lower doses is an essential nutrient for humans and animals. Manganese at elevated concentrations is a powerful neurotoxin which affects the nervous system and causes learning disabilities and intellectual impairment in children (Bouchard et al., 2007, Bouchard et al., 2011). Manganese intoxication is also linked to Mn induced Parkinsonism (Lucchini et al., 2009, Aschner et al., 2009), low fetal weight (Grazuleviciene et al., 2009, Zota et al., 2009), infant mortality (Hafeman et al., 2007, Spangler and Spangler, 2009) and increased cancer rates (Spangler and Reid, 2010).

Several treatment methods to remove Mn from mining and industrial wastewaters have been reported. Mn in wastewater are commonly removed by precipitation (Pakarinen and Paatero, 2011, Silva et al., 2010, Silva et al., 2012, Zhang et al., 2010b, Nishimura and Umetsu, 2001), ion-exchange (White and Asfar-Siddique, 1997), oxidation and filtration (Roccaro et al., 2007, Piispanen and Sallanko, 2010), coagulation and flocculation (Fu-Wang et al., 2009), biosorption (Vijayaraghavan et al., 2011) and adsorption (Al-Rashdi et al., 2011). A lot of efforts have been made on the development of new technologies in which technological, environmental and economic constraints are taken into consideration. The technologies have to avoid generation of secondary waste and involve materials that can be recycled and reused on an industrial scale (Ngomsik et al., 2006).
Adsorption compared with other methods appears to be an attractive process in view of its efficiency and capacity of removing heavy metal ions over wide range of pH and to a much lower level, ability to remove complex forms of metals that is generally not possibly by other methods. It is also environmentally friendly, cost effective and easy to operate compared to other processes with which it can be applied in the treatment of acid mine and heavy metal containing wastewater (Rao et al., 2010). Various low-cost materials have been studied for Mn such as agricultural wastes (Li et al., 2010, Adeogun et al., 2013, García-Mendieta et al., 2012, Ali and Saeed, 2015) and natural materials (Taffarel and Rubio, 2010) (Ates, 2014, Belviso et al., 2014, Shavandi et al., 2012, Dawodu and Akpomie, 2014, Cvetković et al., 2010) locally available in certain regions. The abundance, versatility and low cost of natural clays make them attractive as adsorbents (Vhahangwele and Mugera, 2015). Clays are widely used of clays because of their high specific area, high chemical and mechanical stability, and variety of surface and structural properties. The adsorption ability clay is determined by the chemical nature and pore structure (Kubilay et al., 2007). Zeolites have been widely used in adsorption of heavy metals due to their unique physical and chemical properties (Dimirkou and Doula, 2008). Bentonite is known as a clay material consisting essentially of smectite mineral of the montmorillonite group (Erdem et al., 2009). Bentonite possess a net negative structural charge attributed to isomorphic substitution of cations in crystal lattice which gives them the ability to attract and hold cations such as toxic heavy metals (Kubilay et al., 2007, El-Korashy et al., 2016). However it is well-known that Ca-bentonite has lower sorption capacity of heavy metals and in order to enhance the capacity the use of zeolite has been proposed (Du et al., 2015, Hong et al., 2012).
To reduce the hazards associated with manganese in aqueous wastes, natural zeolite and bentonite is considered to be one of the most viable options. Consequently this study explores the application of natural zeolite/bentonite (B/Z) clay as an adsorbent for remediation of Mn(II) ions in aqueous solution in batch and continuous fixed bed modes.

6.1. Materials and Methods

6.1.1. Chemicals and reagents

Natural zeolite was provided by Ajax Industries (Cape Town, South Africa). Bentonite calcium clay with particle size < 53 µm was provided by GW Mineral Resources (Wadeville South Africa). Hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from Sigma Aldrich. Manganese (II) nitrate tetrahydrate (Mn(NO$_3$)$_2$.4H$_2$O) was used to prepare a stock solution of 1000 mg/L of Mn(II). Acid mine drainage sample was collected from a gold mine in West Rand (South Africa).

6.1.2. Methods

Zeolite was crushed to < 160 µm and then conditioned with 1 M NaCl. Calcium bentonite and conditioned zeolite were physically mixed at a ratio 1:1 to prepare a Calcium Bentonite/Zeolite (B/Z) adsorbent. Finally, the material was used for characterization and adsorption studies. Fourier transform infrared spectroscopy (FTIR) was done on a Perkin Elmer Spectrum 100 spectrophotometer. X-ray diffraction (XRD) patterns measurements were performed on a PANalytical X’Pert PRO-diffractometer using Cu Kα radiation (wavelength, $\lambda$ = 1.5406 Å) with variable slits at 45 kV/40 mA.
6.1.3. Batch adsorption experiments

6.1.3.1. Effect of pH and sorbent dosage

Batch adsorption experiments were performed by contacting B/Z adsorbent with 60 mL Mn(II) solution in 100 mL plastic bottles. The samples were agitated for 24 h at 150 rpm in a temperature controlled thermostatic shaker. The effect of the composition of the clay adsorbent was tested at pH 6 with synthetic water containing 50 mg/L of Mn(II), while the effect of pH of acid mine water containing 25 mg/L Mn(II) ions was done at different solution pH using 1 g of the adsorbent at 25°C. The samples were then filtered, using 0.45 um Whattsman filter paper and the filtrate analyzed using an inductively couple plasma-emission spectroscopy (ICP-OES) for manganese residual. The effect of adsorbent dosage on the removal of Mn (II) was explored by varying the mass of the B/Z adsorbent from 0.05 to 0.8 g using 60 mL of AMD solution (25 mg/L) at pH 6. The removal efficiency of Mn(II) was determined by the following equation.

\[
\% \text{removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100
\]  

(6-1)

where \(C_o\) and \(C_e\) are the initial and equilibrium concentrations (mg/L) of Mn(II), respectively.

6.1.3.2. Kinetics and equilibrium isotherm studies

Kinetic studies for adsorption of Mn(II) were carried out at pH 6 in a 1 L batch reactor. 4 g of B/Z was added to the 1000 mL of synthetic solutions with initial concentrations of 65, 100, and 200 mg/L. The studies were also conducted on AMD sample containing initial
concentrations of 25, 34, and 45 mg/L of Mn(II) ions. The reactor was stirred at a constant stirring speed of 150 rpm with an overhead stirrer. A 5 mL sample solution was withdrawn at predetermined time intervals from the reaction mixture and filtered through a syringe filter and analyzed for residual Mn(II) concentrations. Amount of manganese adsorbed was calculated using the following equation

\[ q_t = \frac{C_0 - C_t}{m} \times V \]  

(6-2)

where \( C_t \) (mg/L) is the manganese residual concentration at time \( t \) and \( q_t \) (mg/g) is the time dependent amount of manganese adsorbed per unit mass of adsorbent.

Adsorption isotherms were generated by contacting 0.4 g of adsorbent with 60 mL of Mn(II) containing synthetic solution ranging from 50 to 300 mg/L in 100 mL plastic sample bottles at pH 6. The samples were shaken for 24 h at varying temperatures (298 K, 308 K and 318 K) at 150 rpm. The equilibrium sorption capacity of the adsorbent was calculated by following equation

\[ q_e = \frac{C_0 - C_e}{m} \times V \]  

(6-3)

where \( q_e \) (mg/g) is the equilibrium amount of Mn(II) adsorbed per unit mass \( (m) \) of adsorbent.

6.1.3.3. Effect of co-existing ions and desorption studies

Usually industrial wastewater discharges may contain other ions which may have competitive effect on Mn(II) adsorption. It is very important to investigate the competitive effect of coexisting ions on Mn(II) removal. 60 mL of 50 mg/L Mn(II) solutions containing 50 mg/L of
various components (Mg$^{2+}$, Fe$^{2+}$ and Al$^{3+}$) were contacted with 0.4 g of B/Z adsorbent at pH 6 for 24 hrs. At the end of the adsorption experiment, the residual concentration of Mn (II) was determined.

The reusability of B/Z adsorbent was investigated by performing adsorption-desorption studies. Initially, equilibrium experiments were carried out at 25 ° C using 0.4 g of B/Z adsorbent which was contacted with 60 mL of 50 mg/L solution containing Mn(II) at pH 6. Thereafter desorption experiments were performed by contacting Mn(II) loaded adsorbent with HNO$_3$, HCl, NaCl, NaOH and deionized H$_2$O as potential eluents at different concentrations (0.1, 0.5 and 1 M). Then the adsorbent was washed and reused. To investigate the reusability of the adsorbent, four adsorption-desorption cycles were performed.

6.1.4. Column studies

Continuous fixed bed column adsorption studies were performed using a lab scale columns to evaluate the performance of the adsorbent for Mn(II) removal from aqueous solutions. For this a cylindrical perspex glass tube of 3.4 cm internal diameter and a height of 30 cm were used as an adsorption column. The column was packed with bentonite/zeolite adsorbent between glass wool and supported by inert glass beads. The influent Mn(II) solution was pumped in an upward flow through the packed bed using a peristaltic pump. Subsequently, the effluent samples were collected at predetermined time intervals and were analyzed for Mn(II). To evaluate the performance of the bed three main parameters that affect the shape of the breakthrough curves were investigated namely; the flow rate, bed mass and initial influent concentration.
6.1.4.1. Effect of bed mass, flow rate and initial concentration

The effect of bed mass was evaluated by varying the B/Z adsorbent media mass from 5 g to 15 g, with 50 mg/L initial Mn(II) concentration at pH 6 and a flow rate of 5 mL/min. The effect of initial Mn(II) concentration was evaluated by varying the initial Mn(II) concentration between 50 mg/L and 150 mg/L at pH 6, while keeping the bed mass and flow rate constant at 10 g and 5 mL/min, respectively. The effect flow rate was assessed by pumping water vertically upward at a flow rate of 2.5, 5.0 and 7.5 mL/min, while the initial Mn(II) concentration, pH 6 and bed mass (10 g) were kept constant. The acid mine drainage (AMD) sample with Mn(II) concentration of 25 mg/L was also treated using a packed column. The AMD sample was pumped vertically upward at a flow rate of 5 mL/min through columns packed with 10 g bentonite/zeolite clay.

6.2. Results and discussions

6.2.1. Characterization

The x-ray diffraction pattern in Figure 6-1. (a) of the natural zeolite shows peaks of major intensity corresponding to clinoptilolite (C) which are observed at 10, 11.4, 17.4, 23, 26, 28.2, 30.2 and 32° at 2θ (Olad and Naseri, 2010, Nezamzadeh-Ejhieh and Khorsandi, 2014). The XRD pattern of natural Ca-bentonite is given in Figure 6.1. (b). The figure indicates that the clay is composed mainly of montmorillonite (M) component which are seen at 5.76, 17.60, 19.84, and 34.80° (2θ) (Caglar et al., 2009). Other species present in small quantities are dolomite and quartz. Ca-Bentonite/Zeolite x-ray diffraction pattern indicates that the clay contains both clinoptilolite (C) and montmorillonite (M) component Figure 6.1. (c)) and that there was no change in the crystalline structure of the adsorbent before and after adsorption.
FTIR spectra of bentonite/zeolite before and after adsorption are shown in Figure 6-2. A band at 3611 cm$^{-1}$ is assigned to acidic hydroxyls Si–O(H)–Al group, while a band at 3402 cm$^{-1}$ is due to the vibration of the bonds O–H–O. A band at 1625 cm$^{-1}$ is connected to deformation vibration of absorbed water (Setsshed et al., 2013). A band at 1116 cm$^{-1}$ is due to the asymmetric valence vibrations in tetrahedra SiO$_4$ (Duranoğlu et al., 2012). An intense peak is observed at 986 cm$^{-1}$ due to the Si–O–Si stretching modes (Caglar et al., 2009). New peaks and at 1003, 930, 856 and 783 cm$^{-1}$ are observed after adsorption suggesting that Mn(II) interact
with functional groups present in the adsorbent and it is evident that the structure of the adsorbent was altered due chemical adsorption process.

Figure 6-2. FTIR spectra of the bentonite/zeolite (a) before and (b) after adsorption with Mn(II) ions.

6.2.2. Effect of sorbent dosage and pH

A comparative study was conducted to investigate the removal percentages of zeolite, bentonite and the mixture of zeolite and bentonite at different mixing ratios. From the results in Figure 6-3 it is evident that the highest removal efficiency of 99% was achieved when the bentonite and zeolite was physically mixed at a ratio of 1:1. For bentonite and zeolite only, the removal efficiencies recorded were 37% and 59%, respectively.
The solution pH is a significant parameter because it can influence the solubility of the metal ions and induce some chemical reactions, such as hydrolysis, complexation, and precipitation reactions during the adsorption process (Islam et al., 2015). The pH of the solution was varied from 2 to 8 to investigate the effect of pH on Mn(II) ion adsorption. The results in Figure 6-4 indicate that Mn(II) removal increased with an increase in initial solution pH. The removal efficiency increased from 8.7 % to 77.9 % when the pH was increased from 2 to 8. At lower pH values the solution creates repulsive forces between H\(^+\) and Mn(II) ions resulting in low metal uptake. As the pH in the solution was increased, the competition from H\(^+\) ions decreased and the removal efficiency of Mn(II) increased (Masukume et al., 2014). High pH values can cause manganese ion to precipitate hence pH of 6 was chosen as optimum pH.
Figure 6-4. The effect of pH on the adsorption of Mn(II) by B/Z adsorbent.

It is important to study the effect of adsorbent dose to determine the optimum amount of B/Z adsorbent for a given initial concentration for effective adsorption of manganese. The results in Figure 6-5. show that the removal efficiency of Mn(II) was increased from 69% at 0.2 g to 85% at 0.8 g. An increase in the adsorbent dosage resulted in a corresponding increase in Mn(II) ion removal owing to an increase in the number of active sites available for the manganese ions to interact with. As the adsorbent dosage is increased the adsorption capacity of the adsorbent is decreased mainly because of unsaturation of adsorption sites through the adsorption process. At 0.4 g removal percentage was 76.32% which was subsequently used for other tests to be conducted.
6.2.3. Effect of co-existing ions and desorption studies

Most wastewaters contain various kinds of ions including magnesium, aluminum and iron and sulphates. The adsorption of Mn (II) onto the B/Z was explored in the presence of co-existing ions. Results in Figure 6-6 indicate that there is a decrease in Mn(II) adsorption capacity in the presence of coexisting ions. The adsorption capacity were found to be 3.2; 4.8; 5.5 and 1.35 mg/g for such as Fe\(^{2+}\), Mg\(^{2+}\), Al\(^{2+}\) and SO\(_4\)^{2-} respectively compared to 7.1 mg/g in the absence of these ions. According to the Irving-Williams series, that is, the order of complex stabilities order, Mn\(^{2+}\) must be the least adsorbed metal ion, because the Mn(II) oxidation states are not very stable (Güzel et al., 2008).
The reusability of the adsorbent is very important for economic and environmental impact. The best eluent to desorption of Mn(II) was found to be NaCl compared to other eluents used and the results are presented in Figure 6.7, NaCl showed that it can efficiently desorb 76.6% of manganese from the adsorbent.

![Graph](image)

**Figure 6-6.** Effect of coexisting ions on the adsorption of Mn(II) onto B/Z.

The reusability of the adsorbent is shown in Figure 6-8 and it was observed that the removal efficiency of B/Z decreased remarkably from 95% to 73% in second cycle and further decreased to 48.6 and 31.4% in the third and fourth cycle, respectively. The clays are abundantly available and based on the reusability studies desorption studies might not be cost effective.
Figure 6-7. The effect of desorption on Mn(II) from the adsorbent using different eluent at three different concentrations

Figure 6-8. Adsorption–desorption cycles on the adsorption of Mn (II) onto B/Z.
6.2.4. *Adsorption kinetics of Mn(II) onto B/Z adsorbent*

The rate at which adsorption process take place is very important when designing batch adsorption process. The adsorption kinetic studies of synthetic water at three different initial Mn(II) concentrations are presented in Figure 6-9. Adsorption kinetics data of Mn(II) was very rapid at the initial stage of adsorption and then progressed at a slower rate to reach the final equilibrium stage. Such rapid uptake is indication of readily available and accessible adsorption sites in the adsorption media.

![Adsorption kinetics plot of Mn (II) onto B/Z at three different initial manganese ion concentrations.](image)

Figure 6-9. Adsorption kinetics plot of Mn (II) onto B/Z at three different initial manganese ion concentrations.
The adsorption kinetic data was analyzed using non-linear method on Origin 9.1 software by pseudo-first (Tseng et al., 2010), pseudo-second order (Ho and McKay, 2000) and Elovich (Chien and Clayton, 1980) kinetic models. Based on the correlation coefficient the pseudo-second-order equation was found to be the best fit for the test results. The pseudo second order adsorption capacities predicted were consistent with the experimental data results. The pseudo-first, pseudo second order rate parameters and Elovich rate parameters for manganese adsorption are listed in Table 6-1. The constants $k_1$ and $k_2$ indicating the adsorption rate, were found to decrease slightly when the initial concentration of Mn (II) increased from 50 to 200 mg/L. The values of $k_1$ are found to be 0.039 – 0.024 (1/min) while values of $k_2$ are 0.003-0.001 (g-mg/min) for initial concentrations of 50 to 200 mg/L. The experimental data fitted to pseudo first and pseudo second order kinetic models as well as Elovich kinetic model.

Table 6-1. Kinetics parameters for Mn(II) adsorption onto B/Z adsorbent using synthetic water

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>Pseudo-first –order model</th>
<th>Pseudo-second –order model</th>
<th>Elovich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (L/min)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>50</td>
<td>0.038</td>
<td>12.58</td>
<td>0.98</td>
</tr>
<tr>
<td>100</td>
<td>0.029</td>
<td>15.56</td>
<td>0.98</td>
</tr>
<tr>
<td>200</td>
<td>0.024</td>
<td>18.77</td>
<td>0.97</td>
</tr>
</tbody>
</table>
Table 6-2. Kinetics parameters for Mn(II) adsorption onto B/Z adsorbent using AMD water samples

<table>
<thead>
<tr>
<th>$C_o$ (mg/L)</th>
<th>Pseudo-first –order model</th>
<th>Pseudo-second –order model</th>
<th>Elovich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (L/min)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>25</td>
<td>0.031</td>
<td>3.41</td>
<td>0.99</td>
</tr>
<tr>
<td>34</td>
<td>0.053</td>
<td>3.93</td>
<td>0.99</td>
</tr>
<tr>
<td>45</td>
<td>0.069</td>
<td>5.74</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Figure 6-10. Adsorption kinetics plot of Mn (II) onto B/Z using AMD samples with experimental data fitted to Pseudo first and second order kinetic models as well as Elovich kinetic model.
The kinetic data of AMD water samples are presented in Figure 6-10. It is also observed that the adsorption kinetics data of Mn (II) is very rapid at the initial stage of adsorption and then progressed at a slower rate to reach the final equilibrium stage. The kinetic model that best describes the kinetic adsorption data was assessed by considering the correlation coefficient ($R^2$) and according to the $R^2$ values, it is suggested that the adsorption kinetic data of AMD samples are best described by both pseudo first and pseudo second-order models. The kinetic parameters are summarized in Table 6.2.

6.2.5. Adsorption isotherm

Adsorption isotherm is used to represent how Mn(II) interacts with the adsorbent. Langmuir and Freundlich isotherms have been applied for the analysis of equilibrium data. Langmuir isotherm refers to homogeneous adsorption process, where all adsorption sites possess equivalent affinity for the adsorbate and each adsorbate molecule has constant enthalpies and sorption activation energy (Foo and Hameed, 2010, Sun et al., 2014b). Freundlich model describes the non-ideal and reversible adsorption and is widely applied in multilayer sorption on heterogeneous surfaces where the adsorption heat and affinities are distributed non-uniformly (Foo and Hameed, 2010, Sun et al., 2014b). Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate (Setsshedhi et al., 2013). The adsorption isotherm of Mn (II) was studied to evaluate the material adsorption capacity at temperatures 298, 308 and 318 K. The results are given in Figure 6-11. It is observed that the adsorption capacity of Mn (II) ions increased with an increase in Mn (II) concentration and temperature. The manganese adsorption capacity of the B/Z adsorbent was found to be within the range of 4.8 – 16.6 mg/g. Table 6.3 represents a comparison of adsorption capacity with some other clay adsorbents previously reported. A direct comparison of adsorbents is difficult because of the different applied
experimental condition. The adsorption capacity for most natural clays for removal of manganese have low adsorption capacity as seen in Table 6.3 and the adsorption for this study was also very low.

Table 6-3. Maximum sorption capacities of Mn ions on clay mineral

<table>
<thead>
<tr>
<th>Clay Sorbent</th>
<th>pH</th>
<th>Adsorption capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg/g</td>
<td></td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>7.53</td>
<td>7.69</td>
<td>(Doula, 2006)</td>
</tr>
<tr>
<td>Fe- Clinoptilolite</td>
<td>8.14</td>
<td>27.1</td>
<td>Dimirkou and Doula, 2008</td>
</tr>
<tr>
<td>Serbian natural zeolite</td>
<td>5.5</td>
<td>10</td>
<td>(Rajic et al., 2009)</td>
</tr>
<tr>
<td>Brazilian vermiculite</td>
<td>6.4</td>
<td>31.53</td>
<td>(da Fonseca et al., 2006)</td>
</tr>
<tr>
<td>Kaolite</td>
<td>N/a</td>
<td>0.446</td>
<td>(Yavuz et al., 2003)</td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>6</td>
<td>7.69</td>
<td>(Ates, 2014)</td>
</tr>
<tr>
<td>Al-Natural zeolite</td>
<td>6</td>
<td>25.12</td>
<td>(Ates, 2014)</td>
</tr>
<tr>
<td>NH₄-Natural zeolite</td>
<td>6</td>
<td>24.33</td>
<td>(Ates, 2014)</td>
</tr>
<tr>
<td>Turkey natural zeolite</td>
<td>2.5</td>
<td>0.37</td>
<td>(Motsi et al., 2009)</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>Natural zeolite – Slovakia</td>
<td>7</td>
<td>0.076</td>
<td>(Shavandi et al., 2012)</td>
</tr>
<tr>
<td>Lignite</td>
<td>6</td>
<td>3.4 - 18.7</td>
<td>(Mohan and Chander, 2006)</td>
</tr>
<tr>
<td>Natural Bentonite/Zeolite</td>
<td>6</td>
<td>4.8-16.6</td>
<td>This study</td>
</tr>
</tbody>
</table>

n/a : not available
The equilibrium data were further fitted to Freundlich and Langmuir isotherms. The Freundlich model described the equilibrium data satisfactorily based on the correlation factor $R^2$.

Figure 6-11. Equilibrium isotherms of Mn(II) adsorption nonlinear onto B/Z adsorbent.

The isotherm parameters are presented Table 6-4. The constant related to the adsorption capacity $K_F$, was found to be 3.31, 4.34 and 4.88 for 298 K, 308 K, and 318 K, respectively. The $K_F$ values confirm that adsorption is favored at high temperature. The heterogeneity coefficient,
on the other hand is 0.324, 0.289 and 0.302 for 298 K, 308 K, and 318 K, respectively. The $1/n$ values suggest heterogeneous sorption sites.

Table 6-4. Langmuir and Freundlich isotherms parameters for Mn(II) adsorption onto B/Z adsorbent

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_o$ (mg/g)</td>
<td>$b$ (L/mg)</td>
</tr>
<tr>
<td>298 K</td>
<td>16.85</td>
<td>0.06</td>
</tr>
<tr>
<td>308 K</td>
<td>17.68</td>
<td>0.09</td>
</tr>
<tr>
<td>318 K</td>
<td>21.51</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The thermodynamic parameters such as changes in entropy and enthalpy for the adsorption of manganese over the sorption media were determined by

$$\ln \frac{m Q_e}{C_e} = \frac{\Delta S^0}{R} + \frac{-\Delta H^0}{R T}$$

where $m$ is the adsorbent dose (g/L), $Q_e$ is the amount of manganese adsorbed per unit mass of adsorbent (mg/g), $C_e$ is the equilibrium concentration (mg/L) and $T$ is the temperature in K. The ratio $m Q_e/C_e$ is referred to as adsorption affinity (Bhaumik et al., 2011a). The changes in enthalpy ($\Delta H^0$) and the entropy ($\Delta S^0$) for the adsorption of manganese onto bentonite/zeolite adsorbent were obtained from the plot of $\ln(m Q_e/C_e)$ vs $1/T$ and the values are 17.05 kJ/mol and 32.09 J/mol K, respectively. The positive value of $\Delta H^0$ indicate an endothermic adsorption
process while the positive value of $\Delta S^\circ$ suggests an increased randomness state at the solid-solution interface (Hu et al., 2014; Bhaumik et al., 2011a).

The change in standard Gibbs energy ($\Delta G^\circ$) was computed from the values of change $\Delta H^\circ$ and $\Delta S^\circ$ and found to decrease from 7.5 kJ/mol at 298 K to 6.8 kJ/mol at 318 K, which presumes to a spontaneous process.

### 6.2.6. Column studies

When designing adsorption fixed bed columns for water treatment operating parameters such as bed mass, flow rate and initial metal ion concentration are of high significance. In this study the effects of these parameters for adsorption of Mn(II) by bentonite zeolite were investigated. The main objective of operating adsorption fixed bed columns is to reduce the concentration of a given contaminant to a level lower than maximum allowable concentration. The capacity of the bed at breakthrough point is determined from the following equation:

$$q_b = \frac{c_0}{m} \int_0^{V_b} \left(1 - \frac{c_t}{c_0}\right) dV$$  \hspace{1cm} (6-5)

For a given bed mass the adsorption performance is directly related to the number of bed volumes processed before the breakthrough point (point when Mn (II) concentration in the effluent is $\leq 1$ mg/L) is reached (Bhaumik et al., 2013b, Setshedie et al., 2014, Mthombeni et al., 2012). The number of bed volumes at breakthrough is given by the following equation:

$$BV = \frac{Volume\ of\ water\ at\ breakthrough\ point(L)}{Volume\ of\ adsorbent\ bed(L)}$$  \hspace{1cm} (6-6)
The rate of at which the adsorbent becomes exhausted during the continuous column operation is used to indicate how often the material is replaced and the operating costs involved. The adsorbent exhaustion rate (AER) is defined as the mass of adsorbent material exhausted per volume of water treated at breakthrough point (Onyango et al., 2009, Bhaumik et al., 2013b, Setshed et al., 2014, Mthombeni et al., 2012) and is expressed as:

\[
AER = \frac{\text{Mass of adsorbent material (g) in column}}{\text{Volume of water treated (L)}}
\]  

(6-7)

Low value of AER implies good performance of the bed and is considered the main performance indicator for comparing different operating conditions.

6.2.7. Effect of bed mass

To evaluate the effect of bed mass on Mn(II) adsorption, the influent concentration of manganese and flow rate were kept constant at 50 mg/L and 5mL/min, respectively, while bed masses were 5; 10 and 15 g. By increasing the bed mass of the bentonite-zeolite adsorbent and fixing the flow rate and initial Mn(II) concentration in the influent, the amount of active sites in the material and the contact time between the adsorbent and manganese ions are increased. The effect of bed mass is shown in Figure 6-12 as breakthrough curves (BTCs). From the results it can be observed that the breakthrough time increases with increasing bed mass. The experimental breakthrough time increases from 180 to 360 min with an increase in bed mass from 5 to 10 g. The adsorbent is saturated faster at low bed mass due to less active sites for manganese to adsorb; which results in an early breakthrough point. At higher bed mass there are more active sites for adsorption which results in late breakthrough time. Meanwhile, the volumes processed at breakthrough point were 0.9, 0.9, and 1.8 L and for 5; 10; 15 g, respectively. This is agreement with late breakthrough time observed at increased mass increases.
Figure 6-12. Effect of mass on breakthrough curves for adsorption of Mn (II) onto B/Z adsorbent at a flow rate of 5mL/min and initial concentration of 50 mg/L

6.2.8. Effect of flowrate

Water contaminated with 50 mg/L Mn(II) ions was pumped in an upward flow mode at an average volumetric flow rate of 2.5; 5 and 7.5 mL/min while the bed mass was maintained at 10g. The results in Figure 6-13 show that more processing time was required for lower flow rate for breakthrough to be reached. The volume processed at breakthrough point was found to be 2.25; 1.5; and 1.8 with corresponding bed volumes of 55; 37; and 44 for 2.5, 5 and 7.5 mL/min, respectively.
Figure 6-13. Effect of flowrate on breakthrough curves for adsorption of Mn (II) onto B/Z adsorbent at a bed mass of 10 g and initial concentration of 50 mg/L.

The AER values obtained are 4.44; 6.67 and 5.56 g/L at the flow 2.5; 5 and 7.5 mL/min, respectively. The decrease in bed performance with an increase in flow rate maybe due to the increase in the movement of mass transfer zone, which results in a decrease in adsorbent–adsorbate contact time. Therefore, adsorbate does not have enough time to penetrate and diffuse into the pores of the adsorbent thus limiting equilibrium to occur (Setshedhi et al., 2014, Bhaumik et al., 2013b, Masukume et al., 2014). From the AER and BV values is noticed that there was no proper trend visible.
6.2.9. **Effect of initial concentration**

The metal ion concentration in contaminated water can vary depending on the nature of the source water. It is very important to know how an adsorbent will perform under such conditions. Consequently, the influent contaminated water at three initial concentrations of 50; 100 and 150 mg/L were used, while a bed mass of 10 g and a flow rate of 5 mL/min was maintained throughout the experimental run. The breakthrough curves obtained from the test are shown in Figure 6-14. It is observed that the breakthrough point decreases with an increase in initial Mn (II) concentration. Volume of processed water at breakthrough point decreased with an increase in initial Mn(II) concentration and were 1.5; 0.6; and 0.3 for 50; 100; and 150 mg/L, respectively. At higher initial concentration binding sites are saturated faster which results in an earlier breakthrough point. Moreover at high initial metal concentrations, increased driving force for mass transfer leads to faster saturation of the adsorbent's active sites, resulting in an increase in the adsorbent exhaustion rate (Chen et al., 2012). The bed volumes at breakthrough point were volumes are 37; 15; and 7 L at the initial at concentrations of 50; 100 and 150 mg/L, respectively. The AER values obtained are 6.67; 16.67 and 33.33 for 50; 100 and 150 mg/L, respectively.
Figure 6-14. Effect of initial concentration on breakthrough curves for adsorption of Mn (II) onto B/Z adsorbent at a bed mass of 10 g and flowrate of 5 mL/min

High values of AER at higher initial manganese ion concentration indicates that in operation the bentonite/zeolite adsorbent will need to be replaced at a higher frequency when processing water containing higher initial manganese concentration. This indicates that the poor column performance of B/Z adsorbent.

6.2.10. Removal of Mn (II) from Acid mine water sample

Bentonite-zeolite sample was employed for adsorption of Mn(II) from real acid mine water sample collected from Gold mine in Randfontein (South Africa). The sample was pretreated with
lime at the treatment plant and contained 25 mg/L of Mn(II) at pH 6. Table 6.6 shows the concentrations of ions in mine water used in this study.

Table 6-5. Summary of results at breakthrough point

<table>
<thead>
<tr>
<th>Time at breakthrough point $t_b$ (min)</th>
<th>Capacity mg/g</th>
<th>Volumes processed at breakthrough</th>
<th>Bed volume processed L</th>
<th>AER g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of B/Z adsorbent (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>180</td>
<td>8.82</td>
<td>0.9</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>300</td>
<td>7.35</td>
<td>1.5</td>
<td>37</td>
</tr>
<tr>
<td>15</td>
<td>360</td>
<td>5.88</td>
<td>1.8</td>
<td>29</td>
</tr>
<tr>
<td>Flow rate (mL/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>900</td>
<td>11.03</td>
<td>2.25</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>7.35</td>
<td>1.5</td>
<td>37</td>
</tr>
<tr>
<td>7.5</td>
<td>240</td>
<td>8.82</td>
<td>1.8</td>
<td>44</td>
</tr>
<tr>
<td>Initial Mn (II) concentration (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>7.35</td>
<td>1.5</td>
<td>37</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
<td>2.94</td>
<td>0.6</td>
<td>15</td>
</tr>
<tr>
<td>150</td>
<td>60</td>
<td>1.47</td>
<td>0.3</td>
<td>7</td>
</tr>
<tr>
<td>Acid mine drainage</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>4.41</td>
<td>0.9</td>
<td>22</td>
<td>11.11</td>
</tr>
</tbody>
</table>
Table 6-6. Chemical composition of mine water.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>5</td>
<td>mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>6.43</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>25</td>
<td>mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>17</td>
<td>mg/L</td>
</tr>
<tr>
<td>Sulphate</td>
<td>985</td>
<td>mg/L</td>
</tr>
<tr>
<td>Aluminium</td>
<td>7</td>
<td>mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>11.45</td>
<td>mg/L</td>
</tr>
</tbody>
</table>

Figure 6-15. Breakthrough curve for Mn(II) removal from mine water using bentonite/zeolite clay
Figure 6-15 presents the breakthrough behavior of Mn(II) removal from mine water. The breakthrough point was observed to be reached after 180 min with the volume of water processed at breakthrough found to be 0.9 L using 10 g adsorbent mass at a flowrate of 5mL/min. The breakthrough point was expected to be reached at a much later time due reduced concentration of manganese in the mine water, but due to coexisting competing ions in the water removal of Mn (II) was impacted and the breakthrough point was reached much faster. High values of AER as a performance indicator shows poor performance of B/Z adsorbent for the removal of Mn(II) under all experimental conditions.

6.3. Breakthrough curves modelling

To model the breakthrough behaviors of Mn(II) adsorption onto the bentonite-zeolite adsorbent three mathematical equations; Yoon–Nelson, Thomas and Bohart–Adams were used to match and model experimental data.

6.3.1. Thomas model

Thomas model is the most commonly and widely used model to describe the performance theory of the sorption process in fixed-bed column. Thomas model is developed on the assumption that (1) the adsorption is not limited by chemical interactions but by mass transfer at the interface and (2) the experimental data follows Langmuir isotherms and second-order kinetics (Foo et al., 2013, Wang et al., 2015, Nguyen et al., 2015a). The model can be described by the following expression:

\[
\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{K_T q_0 m}{v - k_T C_0 t}\right)}
\]  

(6-8)
where \( k_{Th} \) is the Thomas rate constant (mL/min mg), \( q_o \) is the adsorption capacity (mg/g), \( C_o \) is the inlet Mn(II) ions concentration (mg/L), \( C_t \) is the outlet Mn(II) ions concentration at time \( t \) (mg/L), \( m \) is the mass of adsorbent (g), \( v \) is the feed flow rate (mL/min), and \( t \) is time (min).

The results are listed in Table 6.7. It is observed that the \( k_{Th} \) values decrease and \( q_o \) values increase with an increase in both the adsorbent bed mass and initial Mn (II) concentration. While the value of \( k_{Th} \) increased as the flow rate is increased. Based on the high correlation coefficients the model described the experimental data well, which indicates that the external and internal diffusions are not the limiting step (Chen et al., 2012, Setshedi et al., 2014).

### 6.3.2. Bohart–Adams model

This model is based on the surface reaction theory which is a fundamental equation, describing the relationship between \( C_t/C_0 \) and \( t \) in a continuous system (Bohart and Adams, 1920). The model assumes that equilibrium is not instant and the adsorption rate is controlled by external mass transfer (Quintelas et al., 2013, Nguyen et al., 2015a). The model can be expressed as:

\[
\frac{C_t}{C_0} = \exp \left( k_{AB} C_0 t - k_{AB} N_0 \frac{z}{U_0} \right)
\]

where \( k_{BA} \) is the kinetic constant (L/mg min), \( N_o \) is the saturation concentration (mg/L), \( z \) is the bed depth of the fixed bed column (cm) and \( U_0 \) is the superficial velocity (cm/min) defined as the ratio of the volumetric flow rate \( v \) (cm³/min) to the cross-sectional area of the bed (cm²). The values of \( k_{BA} \) and \( N_o \) are listed in Table 6.7. The experimental breakthrough curves are not described well by the Bohart–Adams model as shown by the low regression values. It is observed that the values of \( k_{BA} \) decreases with an increase in bed mass and increase with increase initial concentrations no specific trend was followed with an increase in flow and flowrates.
Table 6-7. Thomas, Adams–Bohart and Yoon–Nelson models constants for Mn(II) adsorption onto B/Z adsorbent.

<table>
<thead>
<tr>
<th>Mass of adsorbent (g)</th>
<th>Thomas Model Parameters</th>
<th>Bohart-Adams Model Parameters</th>
<th>Yoon-Nelson Model Parameters</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>1.65×10^{-4} 18529.8</td>
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<td>3.8×10^{-5} 1681.9 0.82</td>
<td>0.00713 559.2 0.99</td>
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<tr>
<td>15</td>
<td>1.19×10^{-4} 10575.1</td>
<td>3.79×10^{-5} 805.4 0.82</td>
<td>0.00593 634.5 0.96</td>
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</table>

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
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<th>Yoon-Nelson Model Parameters</th>
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<tr>
<td>2.5</td>
<td>8.53×10^{-5} 16928.5</td>
<td>2.4×10^{-5} 1708.8 0.91</td>
<td>0.00426 1354.29 0.99</td>
</tr>
<tr>
<td>5</td>
<td>1.43×10^{-4} 13979.6</td>
<td>3.8×10^{-5} 1681.9 0.82</td>
<td>0.00713 559.2 0.99</td>
</tr>
<tr>
<td>7.5</td>
<td>1.84×10^{-4} 20199.9</td>
<td>3.45×10^{-5} 2521.9 0.79</td>
<td>0.00922 538.665 0.99</td>
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</table>

<table>
<thead>
<tr>
<th>Initial Mn(II) concentration (mg/L)</th>
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<th>Bohart-Adams Model Parameters</th>
<th>Yoon-Nelson Model Parameters</th>
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</thead>
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<tr>
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<td>9.×10^{-5} 20506.2 0.97</td>
<td>0.0148 273.418 0.99</td>
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<table>
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<td>0.00854 293 431.81 0.99</td>
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6.3.3. Yoon–Nelson model

(Yoon and Nelson, 1984) developed a adsorption kinetic model for a fixed bed based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule
is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent (Bhaumik et al., 2013b). Yoon–Nelson model for a single component system can be expressed as:

\[
\frac{C_t}{C_0 - C_t} = \exp(k_{YN} t - \tau k_{YN})
\]  

(6-10)

where \( k_{YN} \) is the rate constant in \( \text{min}^{-1} \), \( \tau \) is the time required for 50% adsorbate breakthrough (min) and \( t \) is the processing time (min). The Yoon–Nelson model fitted very well to the experimental breakthrough curves based on the regression correlation coefficient which indicate that mass transport through a fixed bed of B/Z adsorbent follows the assumption of the Yoon–Nelson model. The results in Table 6.7 indicate that rate constant \( k_{YN} \) values decrease with an increase in bed mass, whilst \( \tau \) values are observed to increase. Also \( k_{YN} \) values increase with an increase in flowrate and in initial concentration. The time required to reach 50% Mn initial concentration, \( t_{0.5} \), significantly decreases with the increase of initial Mn(II) concentration and flow rate.

4. Conclusion

The removal of Mn(II) ion from aqueous solution was carried out in a batch and column adsorption systems using calcium bentonite/zeolite adsorbent. The adsorption capacity was found to be depended on the initial concentration and temperature. Adsorption of Mn(II) ions increased with an increase in temperature and initial concentration. The sorption kinetics of Mn (II) was described by the pseudo-second-order kinetic model. The equilibrium data fitted well to the Freundlich model. Adsorption of manganese in the presence of other coexisting ions such as Fe\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\) and SO\(_4^{2-}\) was significantly affected. Parameters such as bed mass, initial
Mn(II) concentration, and flow rate were evaluated for column studies. The performance of the column sorption process was found to be better at lower flow rate and initial Mn(II) concentration and higher bed mass. At breakthrough point, high bed volumes and low AER values were attained at lower flow rate, lower initial manganese concentration and higher adsorbent bed mass, which indicated a good bed performance. Thomas and Yoon–Nelson models fitted experimental breakthrough curves well compared to Bohart–Adams. High values of AER in column studies and low adsorption capacity in batch studies indicated that B/Z effectiveness in treating water contaminated with Mn is very low. However the material can be used to polish water in further treatments.
CHAPTER 7

Conclusions and Recommendations

This study was carried out to prepare and apply zeolite-bentonite and zeolite polymer based nanocomposites for the removal of metal ions in aqueous solution. MZPPY was successfully synthesized, characterized and used as an adsorbent for the removal of Cr(VI) and V(V) from aqueous solution. B/Z adsorbent was prepared for this study and the performance for adsorption of Mn(II) was evaluated. The sorption performance of MZPPY and B/Z for Cr(VI), V(V) and Mn(II) from aqueous solutions was evaluated in both batch and continuous column sorption modes. The results indicated that removal efficiency of Cr(VI), V(V) and Mn(II) ions are dependent on pH, initial concentration, contact time, temperature. The highest removal efficiency was observed at pH values of 2, 4-5 and 6 for Cr(VI), V(V) and Mn(II) ions, respectively. The sorption kinetic data of Cr(VI), V(V) and Mn(II) ions fitted to the pseudo – second order model. The equilibrium data of Cr(VI) and V(V) ions fitted well to the Langmuir isotherm model. The Langmuir adsorption capacity for Cr(VI) sorption increased from 344.83 to 434.78 mg/g with an increase in temperature from 298 K to 318 K. While the Langmuir maximum adsorption capacity for V(V) sorption increased with an increase in temperature from 65.1 to 75.0 mg/g when temperature was increased from 298 K to 318 K. The Freundlich model described the equilibrium data of Mn(II) adsorption satisfactorily. Thermodynamic parameters confirmed that the adsorption process is spontaneous, endothermic in nature and marked with an increased randomness at solid–liquid interface. Removal of Cr(VI), V(V) and Mn(II) using MZPPY and B/Z in dynamic column studies was investigated by varying the process variables such as bed mass of the adsorbent, initial Cr(VI), V(V) and Mn(II) concentrations and flowrate.
Thomas, Bohart–Adams and Yoon–Nelson mathematical models were used to interpret the experimental breakthrough curves. Both Yoon–Nelson and Thomas models were found to describe breakthrough curves well under all different experimental conditions. The performance of the column was better at lower flow rate and initial metal ion concentration and higher bed mass. Low values of AER and large bed volumes were observed at lower metal ion concentration and higher bed mass for Cr (VI) removal indicating good performance. The adsorption capacity in batch studies of B/Z for Mn(II) sorption was found to be very low and the high values of AER in column studies indicated that B/Z effectiveness in treating water contaminated with Mn is very low.

Based on the excellent performance of MZPPY as an adsorbent for Cr and V it is recommended that the adsorbent media be pelletized and the adsorption process scaled up to simulate industrial applications. Other heavy metals that are available within the industrial water should be also be studied using MZPPY adsorbent. Environmental water from various sources should also be tested. A comparative economic evaluation should be conducted between treatment strategies that are currently used in South Africa with the adsorption treatment using MZPPY. To reduce the cost of preparing the adsorbent it is recommended that the study to conduct to determine if the amount of pyrrole added to polymerize the media can be reduced without affecting the adsorption capacity of the composite.
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## APPENDIX

### Equilibrium isotherms for Cr(VI)

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<th>Initial Cr (VI) concentration mg/L</th>
<th>25 °C Ce mg/L</th>
<th>35 °C Ce mg/L</th>
<th>45 °C Ce mg/L</th>
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### Kinetics Cr(VI)

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<td>Time (min)</td>
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<td>5 g Ct mg/L</td>
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Column Cr(VI) studies
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### Vanadium equilibrium isotherm data

### Vanadium kinetics

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