Preparation and Characterization of Copper Imprinted PVA/Alginate Based Beads for Removal of Dyes from Aqueous Solution

Ishaku Hamidu Bingong

Submitted to the
Institute of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Master of Science
in
Chemistry

Eastern Mediterranean University
January 2020
Gazimağusa, North Cyprus

Approval of the Institute of Graduate Studies and Research

_____
Prof. Dr. Ali Hakan Ulusoy
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science in Chemistry.

_____
Prof. Dr. Izzet Sakalli
Chair, Department of Chemistry

We certify that we have read this thesis and that in our opinion it is fully adequate in scope and quality as a thesis for the degree of Master of Science in Chemistry.

_____
Prof. Dr. Mustafa Gazi
Supervisor

Examining Committee
_____

1. Prof. Dr. Mustafa Gazi   _____

2. Assoc. Prof. Dr. Sifa Dogan   _____

3. Assoc. Prof. Dr. Hayrettin Ozan Gulcan   _____

ABSTRACT

Cu(II)-imprinted polymeric beads were formed using PVA/SA and adsorption studies were carried out to check the effectiveness of the beads on dye and copper sorption. The adsorption studies were carried out by investigating the point zero charge of the beads which was at 3.04, effect of pH was investigated for methylene blue dye which pH 8 gave the best removal efficiency of about 98% and for copper, pH 5 gave the best removal efficiency, effect of dosage which an increase in dosage resulted to decreased removal efficiency so 0.1 g/L of the beads were used throughout for both adsorbates in this study, effect of initial concentration where removal efficiency increased with increase in initial adsorbate concentration, effect of time in which equilibrium was reached after 360 minutes for methylene blue dye sorption, effect of temperature which revealed that at higher temperatures, methylene blue dye removal efficiency decreased which implies that the adsorption process was exothermic while for copper, it showed it was endothermic. Adsorption kinetic studies were also carried out and it followed a pseudo-second order kinetics while isotherm studies revealed that the study is best described by the Freundlich isotherm which predicts heterogenous adsorption mechanism. From thermodynamic studies, it was deduced from ΔG^o and ΔH^o values that the process is spontaneous and exothermic for MB and spontaneous but endothermic for copper.

Keywords: Cu(II)-imprinted polymeric beads; Adsorption studies; Methylene blue dye; Copper; Adsorption kinetics; Isotherm studies.

ÖZ

PVA/SA kullanılarak Cu(II) izlenimli polimerik boncuklar oluşturuldu ve boncukların boya ve bakır emilimi üzerindeki etkinliğini kontrol etmek için adsorpsiyon çalışmaları yapıldı. Adsorpsiyon çalışmaları boncukların sıfır noktası yüküne pH 3.04 değerinde ulaşıldığını gösterdi. Metilen mavisi boyası için yapılan pH etkisi çalışması pH 8 değerinde 98% ile en iyi boya giderim verimliliğini gösterirken bakır için bu değer pH 5 olarak bulunmuştur. Dozajdaki artışın giderim etkinliğinin azalmasına yol açtığı ölçüldü ve bu nedenle her iki adsorbat için de boncuklar 0.1 g/L olacak miktarda kullanılmıştır. Giderim etkinliğinin adsorbat maddenin başlangıç konsantrasyonuna olan bağlılığının ölçüldüğü çalışmada giderim etkinliğinin başlangıç konsantrasyonundaki artışa bağlı olarak arttığını göstermiştir. Metilen mavisi boyası için yapılan süre etkisi çalışması 360 dakika sonra dengeye ulaşıldığını göstermiştir. Sıcaklığın giderim etkinliği üzerine olan etkisi ölçüldü ve yüksek sıcaklıklarda metilen mavisi boyasının gideriminin azaldığı görülüp metilen mavisi boyasının giderim işleminin ekzotermik olduğunu gösterirken bakır için ise bu işlemin endotermik olduğu görüldü. Adsorpsiyon kinetik çalışmaları da yapıldı ve sahte ikinci derece kinetiğe uyduğu hesaplandı, izoterm çalışmaları ise çalışmanın en iyi heterojen adsorpsiyon mekanizmasını öngören Freundlich izotermi tarafından tanımlandığını ortaya koydu. Termodinamik çalışmalardan elde edilen ΔG^o ve ΔH^o değerlerinin hesaplanması ve yorumlanması sonucu metilen mavisi boyasının gideriminin spontan ve ekzotermik ve bakır için spontan fakat endotermik olduğu çıkarılmıştır.

Anahtar kelimeler: Cu(II) izlenimli polimerik boncuklar; Adsorpsiyon çalışmaları;

Metilen mavisi boyası; Bakır; Adsorpsiyon kinetiği; Izoterm çalışmaları.

DEDICATION

This work is dedicated to God almighty and to my late parents Mr and
Mrs Hamidu Bingong.

ACKNOWLEDGEMENT

My gratitude goes to my supervisor in person of Prof. Dr. Mustafa Gazi for his advice, encouragement and supervision through this work. You have been a great mentor.

My gratitude also goes to chairman of Physics and Chemistry Department in person of Prof. Dr Izzet Sakali for always having a listening ear whenever I go to him. Also to my tutors in the chemistry program like Prof. Dr Osman Yilmaz and Prof . Dr Elvan Yilmaz; for your excellent tutoring and tutoring methods. I cannot also forget Prof. Dr Huriye Icil, Asst. Prof Mehmet Garip for your efforts in ensuring that I learn.

I will also be an ingrate if I do not appreciate the efforts of Asso. Prof Akeem Oladipo O. You are a rare gem sir. To Mrs Edith Ahaka Agboola, Faisal Mustafa and Khawla I also appreciate you.

To my friends and colleagues like Ezinne Favour, Blerta Totaj, Gabriel Joseph, Joshua Zoaka, John Wappa, Istifanus Halidu, Kingsley Opara, Innocent James, Aaron Daudu, Cahit, Pelin, Selma, Hoda, Farid, Taqwa, members of the Bethesda family and others too numerous to mention, you all are part of my success story. Thank you so much.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

INTRODUCTION

1.1 Background Information on Water Pollution

Water pollution is increasing at an alarming rate these days due to various natural and human activities. The widespread problem of water contamination has become a significant threat globally and jeopardizing public health (Erdem *et al*., 2018). It is worth stating that polluted water kills more people annually than political violence, war and many other forms of atrocities combined. According to the United Nation, an estimated 780 million people do not have access to useable and drinkable water due to water pollution (UN, 2013). Presently, we can only access nearly 1 per cent of the earth's freshwater even though the worldwide demand for fresh water is increasing yearly and has been projected to quadruple by 2050.

Industrial and other anthropogenic activities have been identified as key sources of pollutants contaminating the water streams (Huang *et al.*, 2015). Pollutants are toxic to the aquatic environment even at low concentrations and as such are detrimental to human health, aquatic species and other organisms (Hashemian *et al.,* 2015). The predominant industries involved in the discharge of these hazardous pollutants especially heavy metals, emerging pollutants and dyes include the mining, metallurgical, electroplating, battery manufacturing, textile, leather, paint, pharmaceutical and plastic and nuclear industries (Romero-González *et al.,* 2009).

As an illustration, water pollution can be represented as shown in Figure 1.1 which demonstrates the threat facing humans and aquatic species due to pollution.
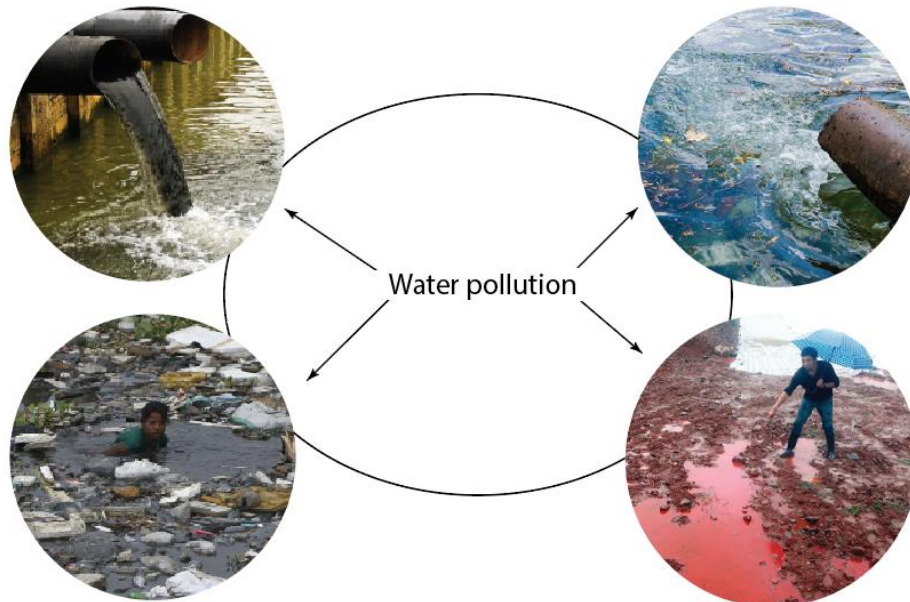
Figure 1.1: Representation of Water Pollution from Various Industries.

The problem of water pollution affects both developed and developing nations. This problem is notably high in developing countries due to many reasons including poor environmental policies, lack of technologies, increasing urbanization just to mention a few. As the developing nation urbanizes, their water bodies are getting polluted while only a tiny fraction is treated for human consumption. Dyes and heavy metals are the common pollutants released into the environment. The presence of heavy metals in industrial effluents has become a global concern because of the toxicity; non-biodegradability and their ability to accumulate in the body through the food chain (Tiwari and Kathane, 2015). Dyes, though used to beautify the world get to contaminate water bodies as they are used to whitewash the products from manufacturing industries such as textile, paper, plastic and dyestuff (Asfaram et al., 2015). Both dyes and heavy metals have adverse effects when they are present above

the maximum permissible limits set by regulatory agencies such as the Environmental Protection Agency.

1.2 Brief Information on Pollution by Heavy Metals and Dyes

The common heavy metals found in industrial effluents include arsenic, lead, copper, iron, cadmium and zinc (Hutton and Symon, 1986). Longterm exposure to even trace amounts of these heavy metals imposes significant negative effects on living organisms, could damage the nervous system, liver and distort brain function (Wadhawan *et al.,* 2020). This study is directed towards adsorptive removal of copper from synthetic copper contaminated water. Copper has its sources from textile, dyeing, petroleum, paper, metal finishing, electroplating and electronics and it is a very important nutrient for living beings but becomes harmful once it exceeds a concentration of 0.05mg/L which is the maximum permissible limit set according to Water Quality Act 1974 (Tiwari & Kathane 2015).

Copper, when present in excess (above the maximum permissible limit) brings about adverse effects such as dizziness, stomach aches, gastrointestinal disorders, headaches, liver and kidney damages and vomiting (He & Paul Chen 2014). The presence of copper above 1.0 mg/L brings about an accumulation of it in the liver of beings and leads to health issues such as Indian Childhood Cirrhosis; which is responsible for neurological disorders and psychiatric problems, Wilson's disease and fibrosis (Runnells *et al.,* 1992).

Dyes are used in beautifying the world since they come in different colours. However, once these dyes exceed a certain amount, they are detrimental to human health and could cause diseases such as deformity, mutation and even cancer

(Kadirvelu *et al.,* 2003). Dyes normally have a synthetic origin and complex aromatic molecular structures which could have their origin from coal-tar based hydrocarbons such as xylene, toluene, naphthalene, anthracene and benzene (Djelloul & Hamdaoui, 2014).

Dyes constitute a part of the pollutants found in the environment which are harmful. Different types of colours, dyes and pigments have found use in the textile industries worldwide (Park *et al.,* 2007). The uncontrolled discharge of dye wastewaters poses a serious threat to the environment as it has high COD values (Doğan *et al.,* 2009,)(Suteu & Rusu, 2012). When dyes or their degradation substances enter the human body, the toxins present adversely affect the health of people who come in contact with them (Kadirvelu *et al.,* 2003). As such, dye sorption is very important for water purification (Vilar *et al.,* 2007).

Dyes can be classified as cationic or anionic. In the current research, a cationic dye, methylene blue is the selected dye as a pollutant due to its high absorbance and excessive use in the textile industries. Methylene blue (MB) is widely used in the pharmaceutical, printing, textile, paper and food industries and has a high colour value and is considered a toxic colourant even at low concentrations (Roosta *et al.,* 2014). So in order to have safer and cleaner water being discharged to the environment, there is a need to remove methylene blue from wastewaters since it has the tendency to associate with oppositely charged surfaces (Singh *et al.,* 2011).

1.3 Common Methods for Treating Water Pollution

So many methods have been used in the treatment of water. These methods include biological methods, coagulation and flocculation (Liang *et al.,* 2014), membrane

filtration (Liang *et al.,* 2011), photo-catalysis (Pan and Zhu, 2010), chemical oxidation (Turgay *et al.,* 2011) and adsorption (Chaudhuri *et al.,* 2017). Of all these methods, adsorption is simple, flexible and relatively effective and non-selective (Zhao *et al.,* 2017). Therefore, adsorption technique using copper-imprinted polymeric beads was adopted during this research. The commonly used traditional and advanced treatment methods are depicted in Figure 1.2.
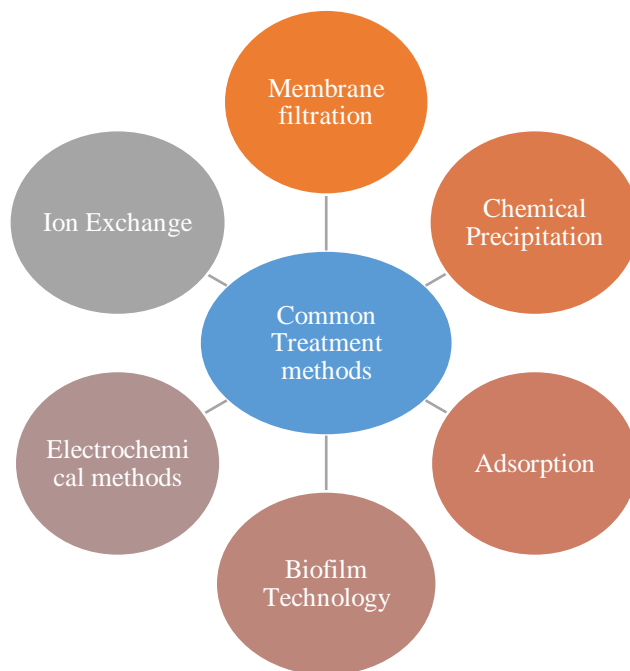
Figure 1.2: Treatment Methods for Water and Wastewater.

1.3.1 Chemical Precipitation

In this method, ions of heavy metals are removed from solution by their combination with inorganic ligands which gives rise to precipitates (Wang *et al.,* 2005). The equation below explains the process involved in this treatment method.

$$M^{2+} + 2OH^- \text{------} M(OH)_2 \qquad\qquad (1.1)$$

Where M^{2+} is the dissolved divalent metal ion, OH is the precipitant and $M(OH)_2$ is the insoluble metal hydroxide precipitate. The major disadvantage of this method is

that sludge production at higher metal concentration is large which requires separate sedimentation and filtration units (Bose *et al.*, 2002).

1.3.2 Electrochemical Method

Wastewaters from industries contain organic pollutants mostly in form of dyes and other dissolved solids, so electrochemical method of water treatment is a viable option. Electrochemical methods can take place in two ways which are:

    a. Conversion of non-biocompatible organics to biocompatible organics and

    b. Electrochemical combustion which oxidizes the organic substances present to CO_2.

Advantages of this treatment method are that it produces less voluminous sludge, has lower operational cost (Rajeshwar & Ibanez, 1997) and has no pH constraints *(*Jing *et al.,* 2013*)*(Subbaiah *et al.*, 2002). The disadvantage of this method is that electrolytic process in a continuous operational mode can be inhibited due to anode passivation and deposition of thick sludge on the electrodes (Sarode *et al.,* 2019).

1.3.3 Membrane Filtration

This is a technique which is applicable in separating out heavy metals and other contaminants from wastewaters and it functions by the application of hydraulic pressure as the driving force (Sarode *et al.,* 2019). Membrane filtration can occur through some filtration processes which are ultrafiltration, microfiltration, reverse osmosis, nanofiltration and electro-dialysis.

1.3.4 Ion Exchange Method

Ion exchange method of water treatment is a reversible chemical reaction in which dissolved heavy metals ions are eliminated from water by replacing them with other similarly charged ions (Vigneswaran *et al.,* 2005). It is used to remove heavy metals

from effluent flux. A good example of an exchanger is the mixed bed (an amphoteric ion exchanger) which is capable of exchanging both anions and cations. Fouling on the matrix which is caused by high concentration of target metal ions in wastewaters is a disadvantage of this method and in addition, it is a non-selective method and it is pH sensitive and as such it is not easy to be carried out (Sarode *et al.,* 2019).

1.3.5 Biofilm Technology

In this method, solid media are added to suspended growth reactors to provide means for the attachment of biofilm. This technology works at the same time for biomineralisation, bioaccumulation, biosorption and biodegradation (Pal *et al.,* 2010). A biofilm consists of microorganisms whose cells not only stick together but also stick to the surface more often and these cells are embedded in extracellular polymeric substances (mainly DNA proteins and polysaccharides) which are produced by the cell (López *et al.,* 2010). Water treated using this technology can be used for agricultural purposes or be released into the environment (Sarode *et al.,* 2019). Advantages of this technology are that it results in lower sludge production (Sarode *et al.,* 2019), requires less space, flexible to operate, has high active biomass concentration and is resistant to environmental changes (Wilderer *et al.,* 2001).

1.4 The Aims of the Research

The rapid growth of industries has increased the release of coloured pollutants and toxic heavy metals into the environment. Specifically, environmental pollution of water streams is a threatening global issue. Thus, to contribute to the body of knowledge regarding wastewater treatment, the current research aims to:

    I.   Prepare effective copper-imprinted polymeric beads for treatment of copper and dye polluted water.

II.   Characterize the synthesized polymeric beads using various commonly used techniques.

III.   Investigate the effect of various adsorption parameters on the performance of the synthesized adsorbent.

IV.   Establish the adsorption mechanism by elucidating the kinetic and isotherms data.

V.   Compare the efficiency and performance of the synthesized adsorbents with reported low-cost and commercial adsorbents.

VI.   Examine desorption efficiency, regeneration and reuse of the spent adsorbent under varying conditions in successive reuse cycles.

1.5 Thesis Outline

This thesis report is outlined in five sections. The first part of this thesis which is the introduction provides brief information regarding water pollution, common pollutants in the environment, environmental agency limits for heavy metals and examined the treatment methods for wastewater. Chapter 2 provides a detailed discussion on adsorption technology, its merit and drawbacks, literature reports on commonly used adsorbents, parameters influencing adsorption of pollutants from aqueous solutions and a brief mention of adsorption kinetics and mechanism. Chapter 3 provides the experimental procedures used and analytical techniques during the research. The experimental results obtained and the trend observed is discussed in chapter 4, the conclusion and general overview of the results are given in chapter 5 of this thesis report.

Chapter 2

LITERATURE REVIEW

2.1 Adsorption Technology

Adsorption is the adhesion of a material (adsorbate) onto the outer surface of an object (adsorbent) (Lynn Onnby, 2009). Adsorption is a treatment technique that has gained acceptance in recent years because it has the least operating cost and produces treated effluent of high quality (Sarode *et al.,* 2019). Adsorption is considered most appropriate because it can remove both organic and inorganic pollutants (Jing *et al.,* 2013). Also, adsorption is of great advantage as it is able to recover heavy metal, has high selectivity, simplicity in design and operation, meets strict discharge specifications and a lesser volume of sludge is produced (Chen *et al.,* 2010). For example, many researchers have investigated the removal of heavy metals such as chromium, mercury, lead, copper, cadmium, nickel and others (Erdem *et al.,* 2018). Adsorption has been used in the removal of metal ions and radionuclides, dyes, anions, and other pollutants (Jing *et al.,* 2013). Adsorption is mainly divided into two: physical adsorption (physisorption) and chemical adsorption (chemisorption) (Lynn Onnby, 2009).

2.1.1 Physisorption

This kind of adsorption takes place due to a form of attraction such as oppositely charged surface and adsorbate. In this, bond breaking cannot take place because the attraction does not result in chemical bond formation due to the low enthalpy values involved (Atkins *et al.,* 2018). Examples of these attractions are van der Waal forces,

chelation; which is the attraction between ligands and metal ions thereby forming a complex. The distance between the adsorbent and adsorbate is longer and therefore weak (Atkins *et al.,* 2018).

2.1.2 Chemisorption

In chemisorption, ions are held to the surface by a covalent bond. Enthalpy values are higher in chemisorption than in physisorption and the covalent bonds are stronger than the van der Waal forces in physisorption as well (Atkins *et al.,* 2018). In chemisorption, adsorbent-adsorbate distance is shorter.

2.2 Advantages and Disadvantages of Adsorption Technique

Adsorption is a technique that has found use in water treatment and other environmental remediation processes due to its high efficiency, low cost, ease of separation, easy handling and ability to reuse the materials used during the adsorption process (Bailey *et al.,* 1999). This technique is also being employed due to its simplicity and regenerative capacity and also has the ability to treat dyes in trace amounts (Gupta *et al.,* 2008). It is effective and efficient. In the adsorption technique, it is important to find an adsorbent that has high removal efficiency and is cost-effective (Tanhaei *et al.,* 2015).

The advantages of using adsorption technique far outweigh the disadvantages. The disadvantages of adsorption are the waste product formed and has weak selectivity in some cases (Sadegh & Ali, 2019).

2.3 Commonly used Adsorbents

An adsorbent is a solid material employed to collect or trap adsorbate molecules or species from a liquid or gas medium. Adsorbents are of different types. They could be natural zeolites or biosorbents. Natural zeolites are in abundance in nature and

have an excellent cation exchange capability and molecular sieve property. They have been used in the past in the treatment of contaminated water. Biosorbents are adsorbents which are used in biosorption and they are used mainly due to their abundance and good performance (Abbas *et al.,* 2014).

Adsorbents can also be classified into hydrophilic (polar surface) and hydrophobic (nonpolar surface) (LeVan *et al.,* 1997). The most common adsorbent used in the treatment of water is the activated carbon especially in the removal of heavy metal ions (Fu & Wang, 2011). Some carbon materials such as carbon nanotubes (CNTs) have shown greater adsorption capacities than the activated carbon (Xu *et al.,* 2012). Some other common adsorbents used for water treatment include biosorbents which are adsorbents that help in the removal of pollutants through biological means known as biosorption, natural zeolites which are crystalline hydrated aluminosilicates containing pores in its structure occupied by water, alkali and alkaline earth cations (Sarode *et al.,* 2019). Another class of adsorbents is the clay and it has found use due to its eco-friendliness, low cost since; they are available in nature and are non-toxic (Mittal *et al.,* 2010). The advantage of natural zeolites is that they are cost-effective as a result of their abundance in nature and in addition, they have high cation exchangeability and molecular sieve property (Sarode *et al.,* 2019).

2.4 Polymeric Adsorbents

Polymeric adsorbents are those adsorbents derived from polymeric materials. There is an interaction between the adsorbate and the hydrophilic functional groups present on the polymer backbone such as –OH (Hu *et al.,* 2018). The polymeric adsorbents could be in the form of membranes which can be prepared by surface modification (Salehi *et al.,* 2012), polymer coating or blending (Pan and Zhu 2010, Singh *et al.,*

2011) or polymer composting (Liang *et al.,* 2014, Turgay *et al.,* 2011). Other forms

could be imprinted polymeric adsorbents used for selective removal of ions from

waste waters. Examples of imprint andted polymeric adsorbents are Cr(III) ionic

imprinted PVA/SA porous membranes for selective adsorption of Cr(III) ions (Hua

Chen *et al.,* 2010), Cu(II)-imprinted PVA/PAA membrane (He and Chen 2014).

Table 2.1 shows a few polymeric adsorbents with the adsorbates they adsorbed.

Table 2.1:Some polymeric adsorbents with adsobates they adsorbed.

Polymeric adsorbent	Adsorbate	Removal efficiency (%) or uptake capacity(mg/g)	pH	Comments	Reference
Cu(III)-imprinted PVA/PAA membrane	Copper	95.6%	5	Very successful for copper adsorption	(He & Chen, 2014)
Cr (III)ionic imprinted PVA/SA membranes	Chromium ions	59.9 mg/g	6	high adsorption – desorption efficiencies	(Chen et al., 2010)
TA-PVA/SA	Methylene blue	147.06 mg/g	9	Easily recoverable adsorbentwith great potential for dye removal	(Hu et al., 2018)
PVA-ANM	Copper	98.7%	4	Highly efficient	(Tiwari & Kathane, 2015)
Nickel (II) methacrylic acid	Nickel	86.3 mg/g	7	High adsorption efficiency &shorter time to equilibrium	(Zhou et al., 2018)

In this research, focus is on the treatment of wastewater using Cu(II)-imprinted poly

(vinyl alcohol)/sodium alginate (PVA/SA) beads for dye removal and selective

removal of copper from wastewaters. This ion-selective imprinting technique is a

technique developed for the for the preparation of highly effective adsorbent in

which specific recognition capacity is given to host molecule by addition and extraction of template molecules or ions (Dakova *et al.,* 2007, Hoai *et al.,* 2010).

Poly (vinyl alcohol) (PVA) was chosen because PVA hydrogels have good mechanical strength, hydrophilicity (presence of –OH groups), chemical stability, high biocompatibility and are biodegradable (Li *et al.,* 2014). Sodium alginate (SA) is also blended with PVA since it is biocompatible, hydrophilic and relatively economical (Kim *et al.,* 2008). Copper-imprinted PVA/SA beads were prepared; its adsorption efficiency for the removal of cationic dye (MB) and copper ions from wastewater was investigated.

2.5 Factors Affecting Performance of Adsorbents

The performance adsorbents during adsorption depends on factors such as Ph of the solute, adsorbent dosage, temperature, initial concentration of the solute, contact time between the adsorbent and adsorbate. These are further discussed below.

2.5.1 pH

The performance of adsorbents is affected by whether the adsorbate is acidic or basic. The pH is used to know whether a solution is acidic or basic. It is the measure of the hydrogen ion concentration. Its values normally range from 0-14. Acidity decreases from zero as the numerical values increase and at pH 7, it is said to be neutral. As values increase after pH 7, basicity increases. It is represented by the equation below:

$$pH = -\log[H^+] \qquad\qquad (2.1)$$

An increase in pH values can cause a decrease in adsorption capacity which means that the adsorption is best in an acidic medium as reported for adsorption of Reactive Black 5 by chitin and chitosan where there was about 80% decrease observed

(Filipkowska *et al.,* 2010). Also, an increase in pH can cause an increase in adsorption capacity meaning that adsorption best occurs in a basic medium as in the case of MB adsorption by TA-PVA/SA where an increase from pH 2 to pH 10 increased adsorption amount from 49.3 to 143.0 mg/g (Hu *et al.,* 2018).

2.5.2 Dosage

Dosage greatly influences the performance of adsorbents. This refers to the amount of adsorbent in the solution. An increase in the dosage of adsorbent can cause either an increase or decrease in removal efficiency of the adsorbents. For example, an increase in the dose of Cr(III) ion imprinted PVA/SA membranes for selective removal of Cr(III) ions caused an increase in removal efficiency from 57.8 to 79.7% (Chen *et al.,* 2010) while an increase in dosage of TA-PVA/SA beads for MB removal caused a decrease from 147 to 84 mg/g (Hu *et al.,* 2018).

2.5.3 Temperature

Temperature plays an important role in the performance of adsorbents. An increase in temperature causes either an increase or decrease in adsorption capacity. The effect of temperature on adsorption tells whether an adsorption reaction is endothermic or exothermic in nature. As reported by (Chen *et al.,* 2010), an increase in temperature in adsorption of Cr(III) ions led to an increase in adsorption capacity which indicated that the adsorption process was endothermic. On the other hand, an increase in temperature from 293K to 313K led to a decrease in adsorption capacity in the removal of MB using TA-PVA/SA hydrogel beads form about 150 to 113 mg/g (Hu *et al.,* 2018).

2.5.4 Initial Concentration

Initial adsorbate concentration also affects the performance of adsorbents. To explore the adsorption capacity of adsorbents, an important information needed is the initial concentration (Ullah *et al.,* 2013). As reported by (Oladipo & Gazi, 2014), as initial CV concentration increased from 25 mg/L to 75 mg/L, removal efficiency for A-AAB, AB and AAB decreased from 96%, 80% and 65% to 55%, 35% and 19% respectively. Similar report also is obtained when initial concentration of Cr(III) ions was increased from 5 to 50 mg/L and its removal ability decreased from 99.1% to 59.8% as reported by (Chen *et al.,* 2010).

In the work reported by (Hu *et al.,* 2018), with increase in initial concentration of MB from 100 to 140 mg/L, there was a slight increase in removal amount from 137.1 to 139 mg/g.

2.5.5 Contact Time

Contact time plays a role also in checking the performance of adsorbents. It tells whether the adsorbent is able to remove the adsorbate to reach equilibrium. Removal amount tends to be high initially within a short period of time before it reaches a stage where it tends to be stable over longer period of time (He & Chen, 2014).

2.6 Adsorption Kinetics and Isotherms

These are models that are used in adsorption studies that help to determine reaction mechanisms and rates of reactions and how concentration, temperature and time all affect the rates of reactions.

2.6.1 Adsorption Kinetics

Kinetic studies are carried out to determine the rates of reactions under given set of conditions and how concentration and temperature influence the rate of reaction, the time required in attaining equilibrium during the process of adsorption.

The adsorptuion kinetics can be described using models. These models are pseudo-first order, pseudo-second order, elovich and intra-particle diffusion which has the Boyd model as an example (Kajjumba *et al.,* 2018). For this study, the pseudo-first order and pseudo-second order models will be considered.

- **Pseudo-First Order Model**

This model describes the adsorption of solute onto the adsorbent which follows a first order reaction mechanism. It can be represented by the equation:

$$\frac{q_t}{q_e} + \ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2.2)$$

Where q_e is equilibrium adsorption capacity, q_t is adsorbate adsorbed in time t and k_1 is rate constant per minute.

This model is also known as Lagergen model.

- **Pseudo-Second Order Model**

The assumption in this model is that solute adsorption rate is proportional to the available sites on the adsorbent. It also has it that the rate of reaction is dependent upon the amount of solute on the adsorbent surface (Tan & Hameed, 2017). The linear representation of the pseudo-second order is as seen below:

$$t/q_t = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2.3)$$

Where t is time, q_t is adsorbate adsorbed in time t, q_e is equilibrium adsorption capacity, k_2 is the rate constant.

It has been used to determine the adsorption capacity of an adsorbent and initial solute uptake.

- **Elovich Model**

This model gives further information that helps one to understand the nature of adsorption that occurs by chemisorption. The basic assumption here is that solute adsorption rate exponentially decreases as the adsorbed solute amount increases. The linear representation as equilibrium is approached is as seen below:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (2.4)$$

Where α is the initial adsorption rate in mg/g.min, β is desorption constant, t is time and q_t adsorbate adsorbed in time t.

Mass, surface diffusion, activation energy and deactivation energy can be predicted using this model.

2.6.2 Adsorption Isotherms

Adsorption isotherms are tools used to understand adsorption mechanism and to quantitatively determine under a given set of conditions, the amount of sample adsorbed (Piccin *et al.,* 2011). It describes the interaction between the adsorbent and the adsorbate. There are so many adsorption isotherm models which are described mathematically. These models are based on physical description of adsorption and desorption and also empirically which its intention is to be in tandem with experimental data (Piccin *et al.,* 2011).

The most commonly used adsorption isotherm models are Langmuir and Freundlich. Others are Temkin, Redlich-Peterson, Dubinin-Radushkevich, Harkins-Jura, Sips and Halsey isotherm models (Crini & Badot, 2008). For this work, Freundlich, Langmuir and Temkin will be studied.

- **Freunlich Isotherm**

The Freundlich isotherm is to determine the adsorption process. It is used for multilayer adsorption with interaction between adsorbed molecules and for heterogenous surface energy systems. The equation for Freundlich isotherm is as seen below:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{2.5}$$

Where K_F (mg/g)/(mg/L)$^{1/n}$ and n are the Freundlich constants which are respectively related to the adsorption capacity and adsorption intensity.

- **Langmuir Isotherm**

The Langmuir adsorption theory assumes that adsorption occurs at specific homogenous sites on the inside of the adsorbent and that no additional adsorption can occur once a specie has occupied a site. The Langmuir isotherm can be expressed using the equation below:

$$C_e/q_e = 1/K_L q_m + C_e/q_e \tag{2.6}$$

Where q_m (mg/g) is the maximum amount of specie adsorbed per unit weight and K_L (L/mg) is the constant that is related to the maximum removal energy C_e.

- **Temkin Isotherm**

The Temkin isotherm takes into account the effect of indirect adsorbate/adsorbate interaction in the adsorption process. The linear form this isotherm is seen below:

$$q_e = \frac{RT}{b_T}(\ln C_e + \ln K_T) \qquad\qquad (2.7)$$

where b is the Temkin constant which is related to the heat of sorption (Jmol[-1]), T is the absolute temperature, R is the universal gas constant and K_T is Temkin isotherm constant (Lg[-1]) (Samarghandi *et al.,* 2009).

2.7 Adsorption Mechanism

Adsorption mechanism refers to the process involved in the adsorption process. The adsorption is mainly classified into physical adsorption mechanism also known as (physisorption) and chemical adsorption mechanism also known as (chemisorption).

2.7.1 Physisorption

Physisorption occurs due to some kind of attraction between the adsorbate and the adsorbent. This could be as a result of opposite charges between the adsorbent surface and adsorbate. In physisorption, adsorbate identity is retained while being adsorbed because of the weak and long-range attractive forces such as the van der Waal forces of attraction (ATKINS & Paula, 2002). Chelation is an example of physisorption. Chelation refers to the attraction between a metal ion and ligands. Ligands are molecules or ions that produce a complex with a metal ion with the metal ion being central while the ligands are symmetrically formed around the metal ion (Jones *et al.,* 2000).
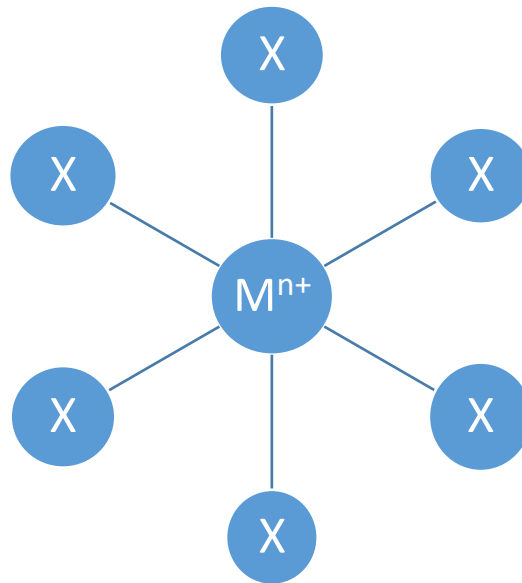
Figure 2.1: Schematic Diagram Showing the Process of Chelation

The figure shows the diagram relating to chelation mechanism where M is the metal, n is the valency of the metal and X represents the ligand.

By means of chelation, toxic metals are encapsulated and that reduces their toxicity when humans take them (Flora & Pachauri, 2010).

2.7.2 Chemisorption

Chemisorption is a term used to describe the adsorption process that takes place chemically. In chemisorption, adsorption is by means of chemical bond and the bonds responsible are the covalent bonds. When compared to physisorption, enthalpy values are higher and the adsorbent-adsorbate distance is shorter. An example of chemisorption is the use of thiol (SH) groups to enhance adsorption.

Chapter 3

EXPERIMENTAL

3.1 Reagents and Materials

All the chemicals used in this study are of analytical grade. Poly (vinyl alcohol), 98-99% hydrolysed, with average molecular weight (Mw) of 31,000-50,000 Da, was purchased from Aldrich Chemical Company USA. Sodium alginate with molecular mass 10,000-600,000 g/mol was purchased from AppliChem Panreac of ITW Reagents USA, Copper (II) nitrate {$Cu(NO_3)_2.3H_2O$} with molar mass 241.6 g/mol was purchased from Carlo Erba Reagents and glutaraldehyde (GLA) was purchased from Aldrich Chemical Company USA.

All these chemicals were used as received without further purification.

3.2 Preparation of Copper-Imprinted Polymeric Beads

0.5 g of Poly (vinyl alcohol) (PVA) was weighed and dissolved in 50 ml of distilled water and stirred at 400 rpm at 90°C for 30 minutes for it to dissolve completely and was allowed to cool. Then, 0.5 g of sodium alginate (SA) was also dissolved in 50 ml of distilled water and stirred for 4 h at 200 rpm at room temperature.10 g of Copper (II) nitrate trihydrate {$Cu(NO_3)_2.3H_2O$ } was dissolved in 50 ml of distilled water and stirred to dissolve.

10 ml of the prepared PVA solution was mixed with 10 ml of the prepared sodium alginate solution, and the mixture was dropped into the prepared aqueous copper (ll) nitrate trihydrate solution using a syringe. Subsequently, polymeric beads were

obtained and allowed to stay for one day in the solution. The mixture was filtered and the Cu-imprinted beads were collected in a beaker and 5 ml glutaraldehyde in 100 ml distilled water was added to the beads as a crosslinker and stirred at 200 rpm for 24 h. The Cu-imprinted gel beads were then obtained after filtration and washing. 2M HCl was added to the Cu-imprinted beads in a conical flask and stirred for 24 hours to remove the Cu template from the imprinted beads and the beads were washed with distilled water. The adsorbent is named *Cu-I* beads and used for adsorption studies. Figure 3 shows the *Cu-I* beads formed before and after removal of the copper template.
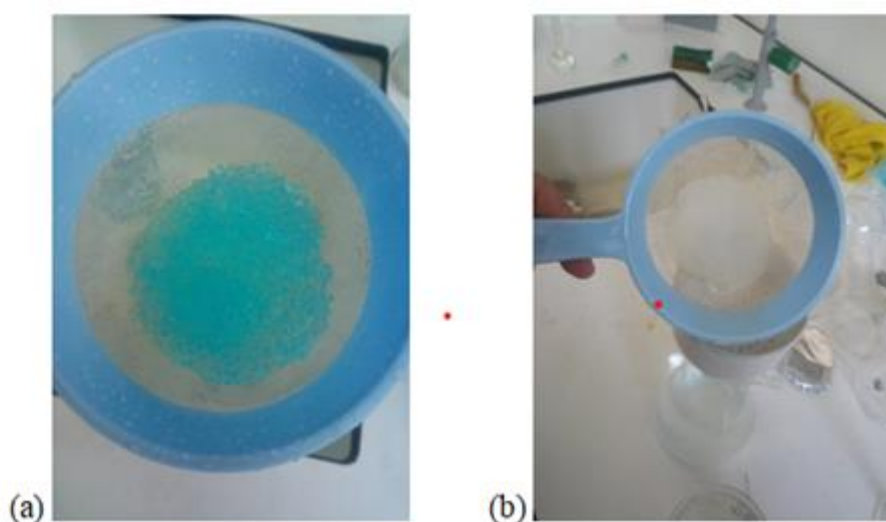

(a)   (b)

Figure 3.1: (a) *Cu-I* Beads from Copper Solution Before Removal of Template

3.3 Adsorbate and Adsorption Studies

Firstly, 1000 ppm stock solutions of MB and copper solutions were prepared by dissolving Y g of copper and MB in X L of distilled water. The standard solutions of each adsorbate were obtained by serial dilutions in the range of Y–X mg/L for the calibration curves. Known dosage of *Cu-I* beads were added separately to MB and copper solutions with varying concentrations in a batch adsorption system and

agitated for 24 hours. The pH of the solutions was adjusted using 0.1 M HCl and 0.1 M NaOH. After each adsorption experiment, the concentrations of the adsorbates (MB at a wavelength of 663 nm and copper at 630 nm) were calculated using the equation obtained from the calibration curves. Set of experiments were conducted to optimize the adsorption parameters and to compute the adsorption kinetics and isotherm constants.

The adsorption capacity of *Cu-I* beads is calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{3.1}$$

Where q_t is the amount of specie, C_0 is the initial concentration of specie, C_t is the concentration at time t, V is the volume in aqueos phase and m is the amount of adsorbent.

The removal efficiency of *Cu-I* beads is calculated as follows:

$$R_t = \frac{C_0 - C_t}{C_t} \times 100 \tag{3.2}$$

Typically, the following are done to establish the adsorption mechanism:

3.3.1 Point Zero Charge

Point zero charge of the beads were determined by weighing 0.1g of the beads and putting into 25 mL of NaCl solution of pH values from 2 to 10. This is to determine the medium in which the beads will function best.

3.3.2 Effect of pH

The effect of pH on dye adsorption was investigated by using pH values of 2, 3, 5, 6, 7, 8 and 9 with MB concentration at 20 mg/L, while for copper, the pH values were 2, 3, 5, 6 and 8 and concentration was at 400 mg/L. Dosage of 0.1g, volume of 25 mL, temperature of 25°C and time of 24 hours was same for both MB and copper.

These desired pH values were adjusted by using 0.1M HCl and 0.1M NaOH where necessary.

3.3.3 Effect of Dosage

After determining the best pH for adsorption (pH 8 for MB and pH 5 for copper), the effect of dosage was investigated using 0.1g, 0.25g, 0.5g, 1.0g and 1,5g of beads in 25 mL each for MB and 0.1g, 0.25g, 0.5g, 0.75g and 1.0g of beads in 25 mL each for copper. MB and copper concentrations were 20 mg/L and 400 mg/L respectively. Temperature of 25°C, and time of 24 hours were same for both MB and copper while pH values for MB and copper were pH 8 and pH 5 respectively.

3.3.4 Effect of Initial Concentration

This effect was investigated by using 25 mL each of 10, 20, 40, 60 and 100 mg/L solutions of MB all at pH 8 and 25 mL each of 200, 400, 600, 800 and 1000 mg/L soultions of copper all at pH5. Temperature of 25°C, dosage of 0.1g and time of 24 hours were same for both MB and copper.

3.3.5 Effect of Time

This effect was investigated by varying time (5, 15, 20, 180, 360, 720 and 1440 minutes) for MB and (5, 10, 20, 30, 60, 180, 360 and 720 minutes) for copper. Concentration of MB and copper were 100 mg/L and 600 mg/L respectively while pH of MB and copper were 8 and 5 respecctively. Temperature was at 25°C, dosage was at 0.1g and volume was 25 mL. for both MB and copper.

3.3.6 Effect of Temperature

This effect was investigated by carrying out adsorption at four different temperatures of 298K, 208K, 318K and 328K using 25 mL of 100 mg/L of MB solution each and 25 mg/L of 600 mg/L of copper solution each. Time for the adsorption for MB was

360 minutes while that of copper was 180 minutes, the dose for both MB and copper solutions was 0.1g while the pH of MB and copper were held at 8 and 5 respectively.

3.3.7 Choice of Solvent for Desorption

To determine the solvent suitable for desorption, 25ml for each of four solvents was used and 0.1g of MB adsorbed beads and 0.1g of copper adsorbed beads were put in these solvents. The solvents used are 0.2M HCl, 0.2M NaOH, distilled water and ethanol.

3.3.8 Reuse and Regeneration

The adsorption/desorption was carried out for four cycles to determine the reusability of the beads. This was achieved by using 0.1 g/L *Cu-I* beads in 100 mg/L solution of MB for adsorption and 0.1M HCl for desorption while for copper, it was achieved by using 0.1 g/L *Cu-I* beads in 1000 mg/L copper solution and desorption in 0.1M HCl.

3.4 Adsorption Kinetics and Isotherm Studies

To evaluate the adsorption mechanism of MB and copper, pseudo-first order and pseudo-second order kinetics were used to interpret the data obtained from experiment. The equation used for pseudo-first order kinetics calculation is given below:

$$\frac{q_t}{q_e} + \ln(q_e - q_t) = \ln q_e - k_1 t \tag{3.3}$$

The equation used for pseudo-second order kinetics calculation is given below:

$$t/q_t = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3.4}$$

For adsorption isotherm, models of Freundlich, Langmuir and Temkin were used to have better information on the dye and copper removal process.

3.5 Thermodynamic Studies

Thermodynamic properties of MB and copper adsorption was studied by calculating thermodynamic parameters such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) for temperature values of 298K, 308K, 318K and 328K. These thermodynamic parameters are expressed by the equations below:

$$K_c = {q_e}/{C_e} \tag{3.5}$$

$$\Delta G^o = -RT \ln K_c \tag{3.6}$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{3.7}$$

Where K_c is equilibrium constant, R is universal gas constant (8.314 J/mol K), q_e is the adsorption amount (mg/g), C_e is equilibrium concentration and T is for absolute temperature.

If ΔG° is negative, it means the reaction is spontaneous, if positive, it means the reaction is non-spontaneous. Once ΔS° is positive, it means that the system becomes more ordered and if negative, it is less ordered. For ΔH°, a negative value implies that the reaction is exothermic while a positive value implies that the reaction is endothermic.

Chapter 4

RESULTS AND DISCUSSIONS

4.1 FTIR Analysis and Point Zero Charge of *Cu-I* Beads

The pH point zero charge (pHz) of *Cu-I* beads was determined and the results obtained are depicted in Figure 4.1. As shown, pHz of the beads is 3.04 which suggest that the surface of the adsorbent is expected to be positively charged when the solution pH is lower than the pHz and becomes negatively charged when the solution pH is increased beyond the determined pHz.

The presence and interaction of the functional groups on the *Cu-I* beads before and after adsorption of MB and copper ions are examined using FTIR. Observed absorption bands are shown in Figure 4.2. From wavelength 3100 to 3700 cm^{-1}, broad and strong bands are observed which can be due to –O-H stretching vibrations (He & Chen, 2014). These –O-H are in the alcoholic groups found in poly (vinyl alcohol) and in the carboxyl groups in the sodium alginate. The peak at 1639 cm^{-1} in (a) which is attributed to the carboxylic group was observed to have shifted to 1602 cm^{-1} and 1594 cm^{-1} after it adsorbed MB and copper respectively which shows clearly that carboxyl groups participated in the adsorption for MB as reported by (Ovchinnikov *et al.,* 2016). Adsorption bands at 2961 cm^{-1} can be attributed to stretching vibrations of –C-H (Ovchinnikov *et al.,* 2016). The bands at 1393 and 1447 cm^{-1} are due to phenolic –OH stretching which were observed to have become more pronounced in (b) which later collapsed into a single band in (c). This indicates

that phenolic –OH groups participated in the adsorption. The band at 1268 cm^{-1} is attributed to C-O of the carboxylate anion. The band at 1287 cm^{-1} in (a) was observed to have shifted to 1306 cm^{-1} at in (c), it completely disappeared which is an indication that there is an complexation reaction between the copper and the beads. The –C=O stretching vibrations at (1065 cm^{-1}) in (a) slightly became narrower in (b) and (c).
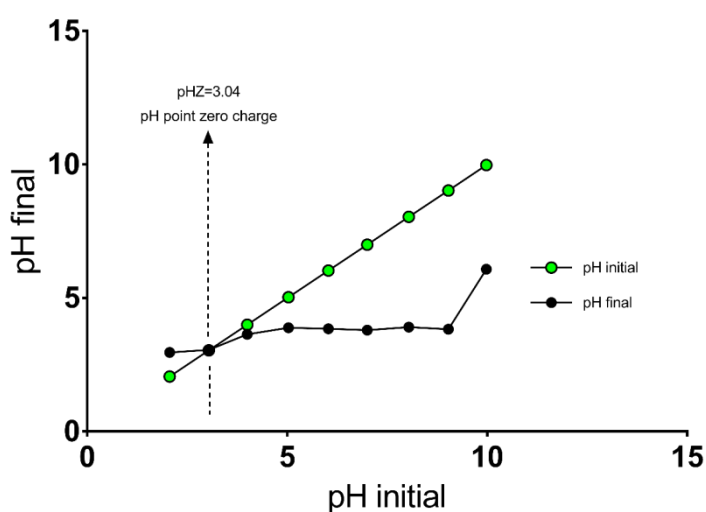

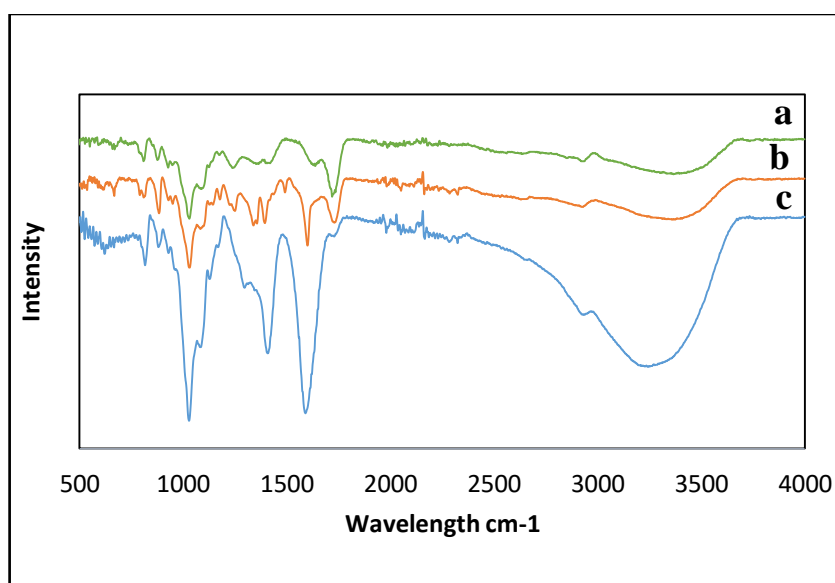Figure 4.1: pH Point Zero Charge of *Cu-I* Beads

Figure 4.2: FTIR Analyses of *Cu-I* Beads a) Before Adsorption, b) Beads Loaded by MB and c) Beads Loaded by Copper Ions

28

4.2 Effect of Adsorption Parameters on *Cu-I* Beads Efficiency

To optimize the adsorption efficiency and elucidate the performance of *Cu-I* beads for the adsorptive removal of the target adsorbates, the effects of various operational parameters are investigated. Results and trends observed in each case are reported and discussed. In order to determine the concentration of the adsorbate, calibration curves for both MB and copper ions are obtained under a range of concentration as shown in Figure 6 and 7, respectively. The concentration of the MB and copper ions remaining in the solution after adsorption was established using the calibration curve. For reproducibility, the average of duplicate experimental results is recorded.
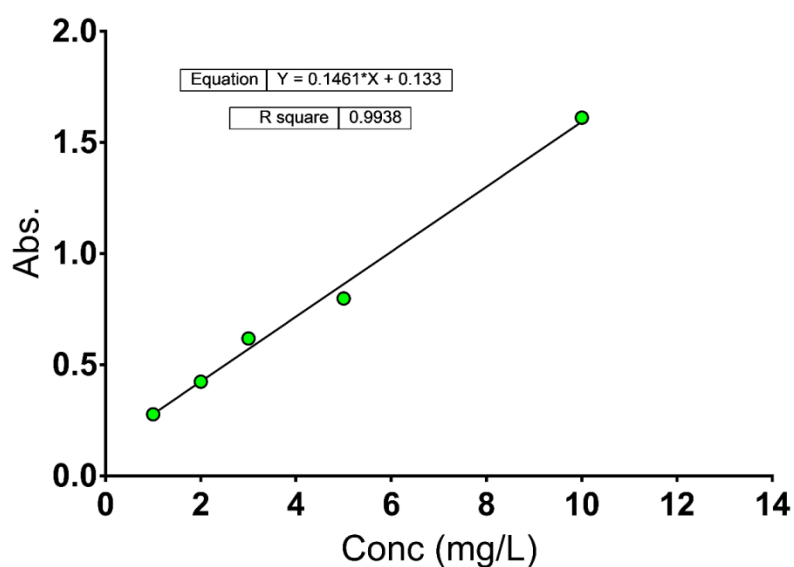

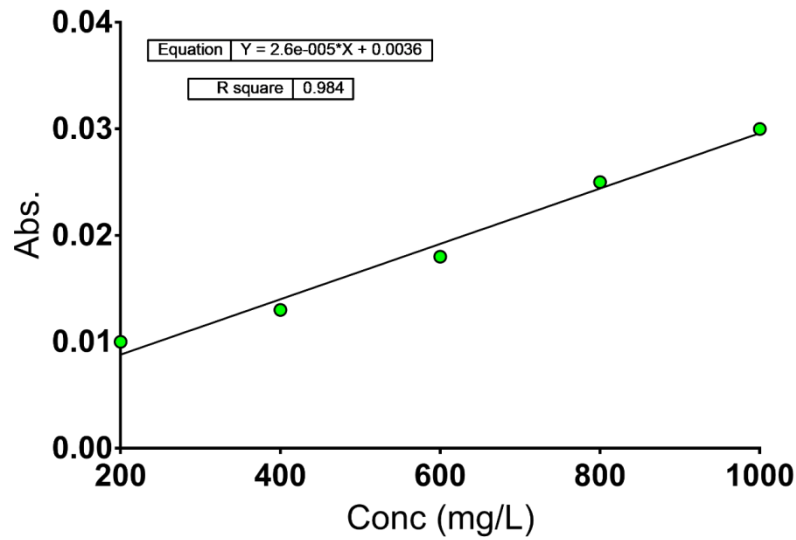| Equation | Y = 0.1461*X + 0.133 |
| R square | 0.9938 |

Figure 4.3: Calibration Curve for MB

Figure 4.4: Calibration Curve for Copper Ions

4.2.1 Solution pH

The solution pH is a very important parameter that influences the sorption performance of adsorbate in the solution. In general, the pH of the wastewater depends on the contents and factories discharging the effluents. Here, the performance of *Cu-I* beads under varying pH conditions is investigated and results shown in Figure 4.5 and 4.6. For MB adsorption, as expected, the maximum removal efficiency occurred at an alkaline pH. The removal efficiency increased from 48.5% to ~90% as the solution pH was increased from 2 to 3 after 24 h adsorption experiment. Notably, the removal efficiency decreased when the pH was increased to 5 and then maintained an increasing trend from pH 5 to 8 where a maximum removal of 98.9% was obtained. A similar adsorption trend is observed in the presence of copper ions.
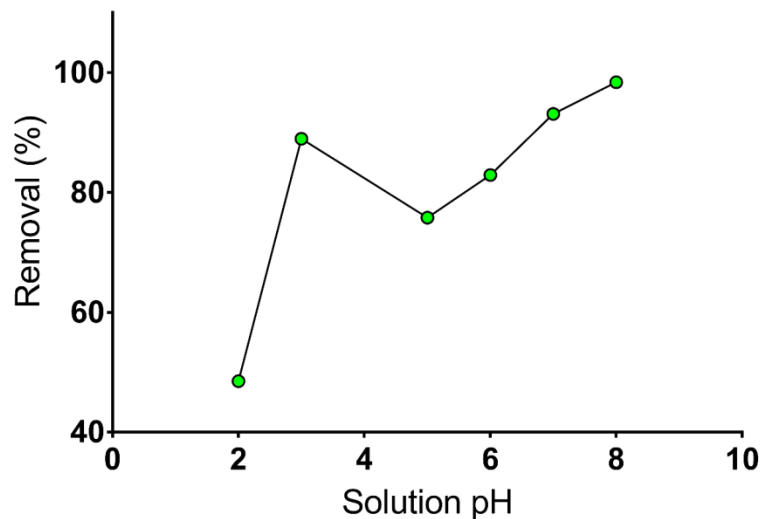
Figure 4.5: Influence of Solution pH on the Removal Efficiency of *Cu-I* Beads for MB
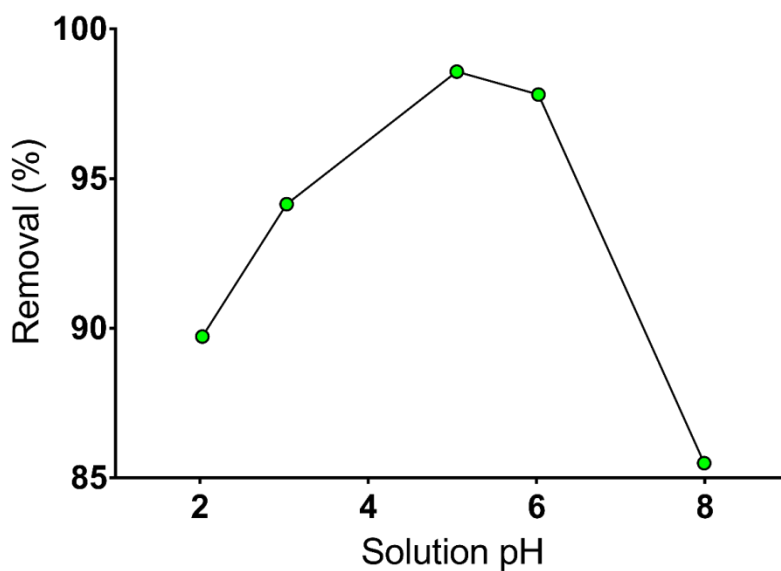

Figure 4.6: Influence of Solution pH on the Removal Efficiency of *Cu-I* Beads for Copper Ions

At acidic pH specifically, when the solution pH is less than the pHz, the surface of the *Cu-I* beads become more positive, resulting in less removal efficiency for cationic dye such as MB which is also positively charged and cationic metal ions (Cu^{2+}). The removal efficiency increased significantly when the solution pH was increased beyond the pHz due to the increases in the negative charges on the surface

of the *Cu-I* beads which is suitable for electrostatic attraction with the cationic adsorbates.

For copper ions, the *Cu-I* beads removal efficiency notably increased from 89.7% at pH to a maximum 98.6% at pH 5, while beyond pH 6, the removal efficiency decreased to 85.5% at pH 8. The decreasing trend observed at pH > 5 is ascribed to formation of metal hydroxides (Oladipo *et al.,* 2019). Generally, in copper solution various species including Cu^{2+}, $CuOH^+$, and $Cu(OH)_2$ exist depending on the pH range. At a very low pH, the solubility of the $Cu(OH)_2$ is high while Cu^{2+} becomes the dominant species in the solution. However, beyond pH 5; the concentration of $Cu(OH)_2$ increases and become the main species beyond pH 9 in the solution. Overall, the performance of *Cu-I* beads is quantifiable in a wider pH range as nearly 50% removal of MB was achieved even at acidic medium. Similar trends have been reported elsewhere (Oladipo *et al.,* 2019).

4.2.2 *Cu-I* Beads Dosage

When the dosage of *Cu-I* beads increased from 0.1 to 1.5 g/L, the MB removal efficiency decreased notably when the solution pH is 8 and the initial concentration of MB is 20 mg/L as shown in Figure 4.7. Similarly, the removal efficiency decreased for copper ions as noted in Figure 4.8 decreased from 95% to 68% when the Cu-I dosage increased from 0.1 g/L to 1.0 g/L, pH is 5 and initial concentration of copper is 400 mg/L. The observed decrease in the removal efficiency could be attributed to competition of adsorbed and incoming adsorbate species on the surface of the *Cu-I* beads. For MB, the removal efficiency decreased from 95% to 51% when the dosage of *Cu-I* beads was increased from 0.1 g/L to 1.5 g/L. Afterwards, *Cu-I* beads dosage of 0.1 g/L was utilized for further experiments.
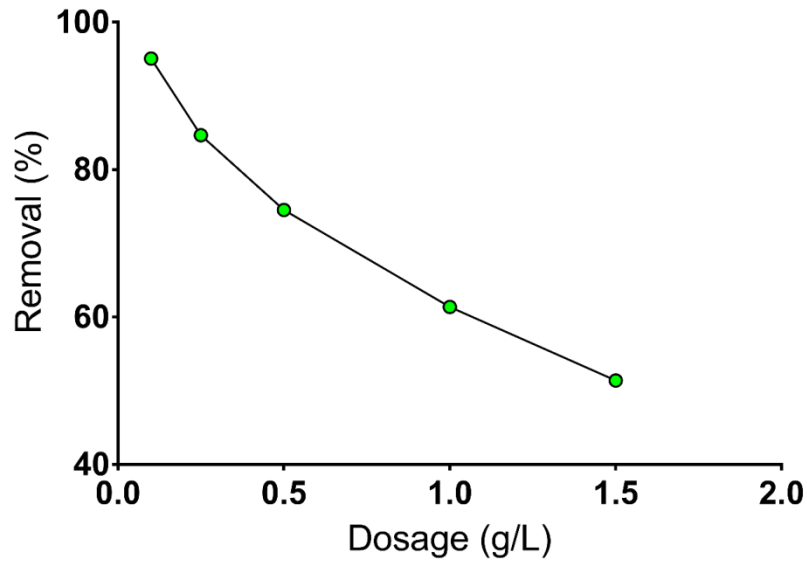
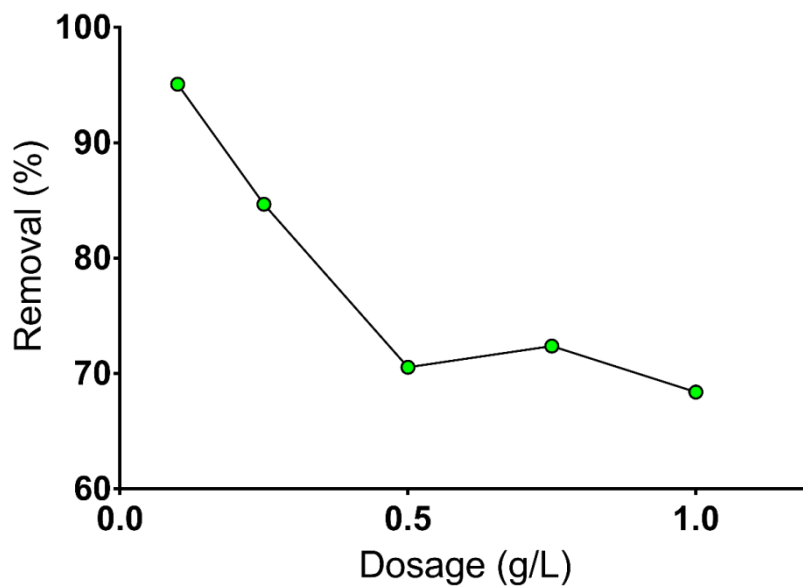Figure 4.7: Influence of Dosage of *Cu-I* Beads on the Removal Efficiency of MB

Figure 4.8: Influence of Dosage of *Cu-I* Beads on the Removal Efficiency of Copper Ions

4.2.3 Adsorbate Initial Concentration

The effects of the initial adsorbate concentration on the adsorption capacity of *Cu-I* beads were examined using concentrations in the range of 10 mg/L to 100 mg/L and 0.1 g/L dosage of *Cu-I* beads at pH 8 for MB and pH 5 for copper ions as represented in Figures 4.9 and 4.10. Obviously, the quantity of MB and copper ions adsorbed

increased as the initial concentration increased. Specifically, 2.38 mg/g of MB was adsorbed when its initial concentration was 10 mg/L and increased significantly to 21.65 mg/g when the MB concentration was increased to 100 mg/L. For copper, the quantity adsorbed increased from about 50 mg/g to 200 mg/g when the concentration of copper was increased from 200 mg/L to 600 mg/L which afterwards, there was no significant change even up to 1000 mg/L. The observed trend could be explained based on the fact that at a lower initial concentration fewer dye cations and copper species were available to be absorbed which increased as the concentration increases. Note that as the concentration is increasing the adsorption sites get filled with adsorbed adsorbate species and the number of available sites/pores decreased, hence the quantity of the adsorbate adsorbed is expected to level up as the initial concentration increased further (Hu *et al.,* 2018).
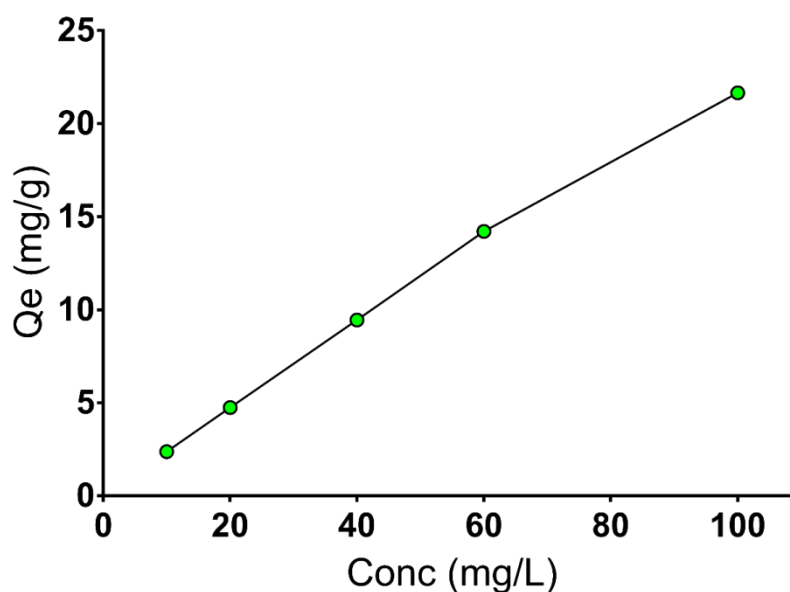

Figure 4.9: Influence of Initial Concentration of MB on Cu-I Beads Removal Efficiency
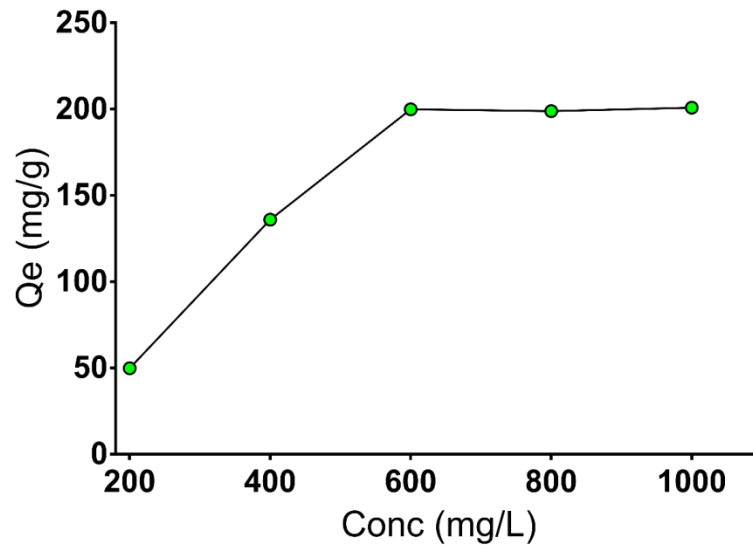
Figure 4.10: Influence of Initial Concentration of Copper Ions on *Cu-I* Beads Removal Efficiency

4.2.4 Contact Time and Solution Temperature

As depicted in Figures 4.11 and 4.12, the influences of the contact time of the *Cu-I* beads on the MB and copper ion removal at room temperature using 0.1 g/L of the adsorbent and 100 mg/L of the MB adsorbate and 600 mg/L of the copper adsorbate were investigated. As expected, the removal efficiency of *Cu-I* beads increased rapidly with increasing contact time but decreased notably after 360 min of contact with MB then reached equilibrium. The decreased removal efficiency is attributed to competition between the adsorbed MB species and the MB at the interface of the beads. Therefore, 360 min was selected as the optimal contact time for MB removal. For copper, the removal efficiency increased rapidly from about 40% at 5 minutes until it got to about 86% at 60 minutes after which there was no significant change even up to 720 minutes. The effects of solution temperature are shown in Figures 13 and 14 for MB and copper ions respectively. It is observed that the dye removal efficiency decreased from 89.9% to 83% as the solution temperature increased from 298 K to 328 K. The decreasing trend is ascribed to enthalpy and exothermic process

of adsorption(Hu *et al.,* 2018). For copper, the opposite was observed in this study. The removal efficiency increased from 45% to about 79% as solution temperature increased from 298K to 328K. This indicates that for this particular work, the process is endothermic. This was also reported by (Chen *et al.,* 2010) who used Cr (III) ionic imprinted PVA/SA membranes for Cr(III) removal.
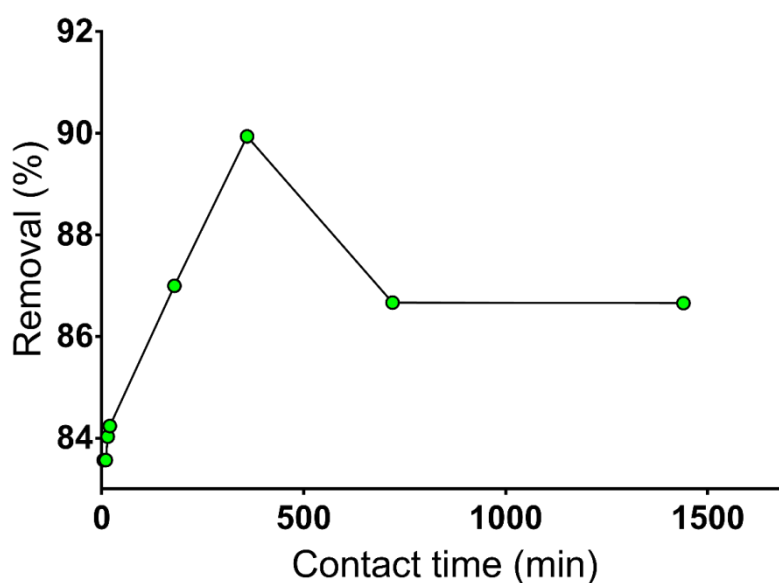

Figure 4.11: Influence of Contact Time of *Cu-I* Beads on MB Removal Efficiency
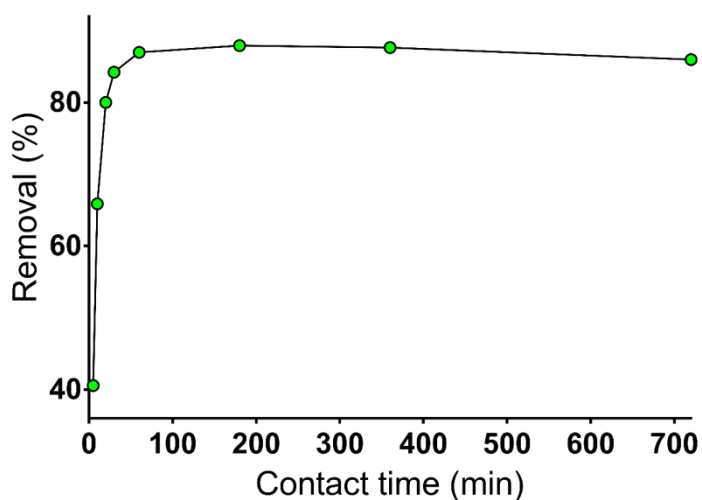

Figure 4.12: Influence of Contact Time of *Cu-I* Beads on Copper Ions Removal Efficiency
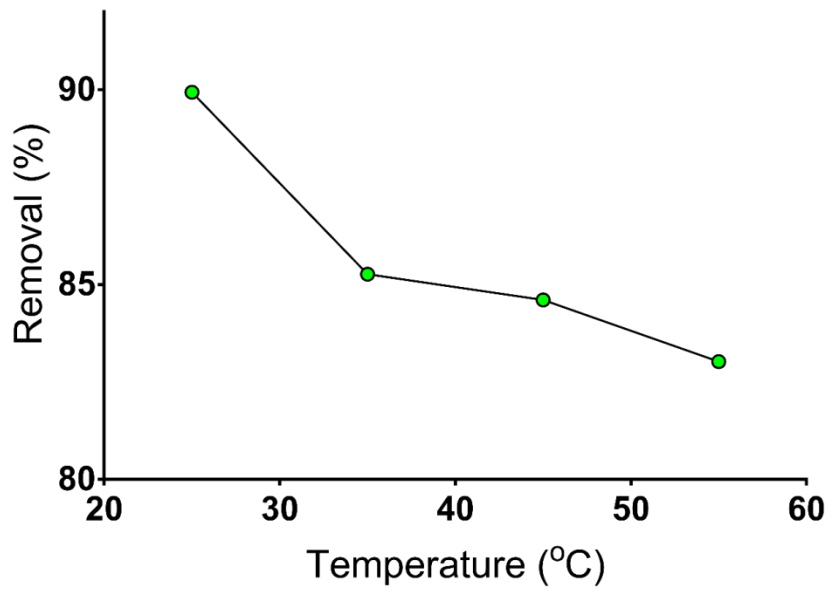
Figure 4.13: Influence of Solution Temperature on the Removal of MB by *Cu-I* Beads Efficiency

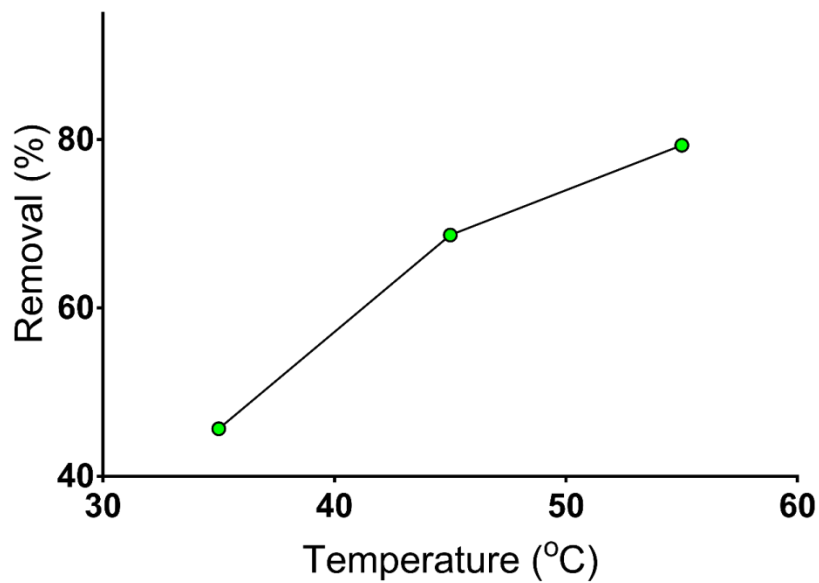Figure 4.14: Influence of Solution Temperature on Copper Ions Removal by *Cu-I* Beads

4.2.5 Adsorption Isotherm and Kinetics

Adsorption isotherm studies were conducted for MB and copper at pH 8 and pH 5 respectively. Figures 4.15, 4.16 and 4.17 represent the data obtained from experiment and curves with the isotherm models.
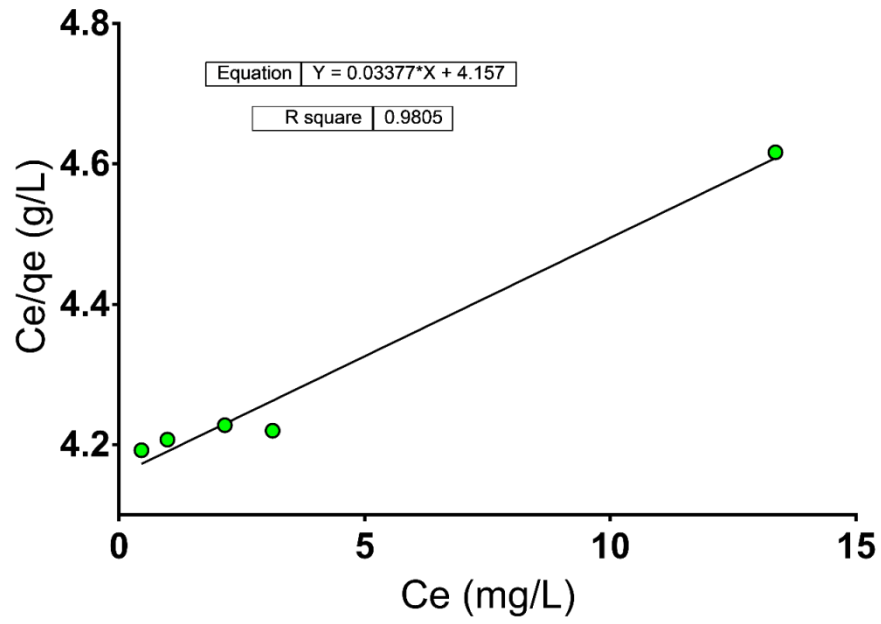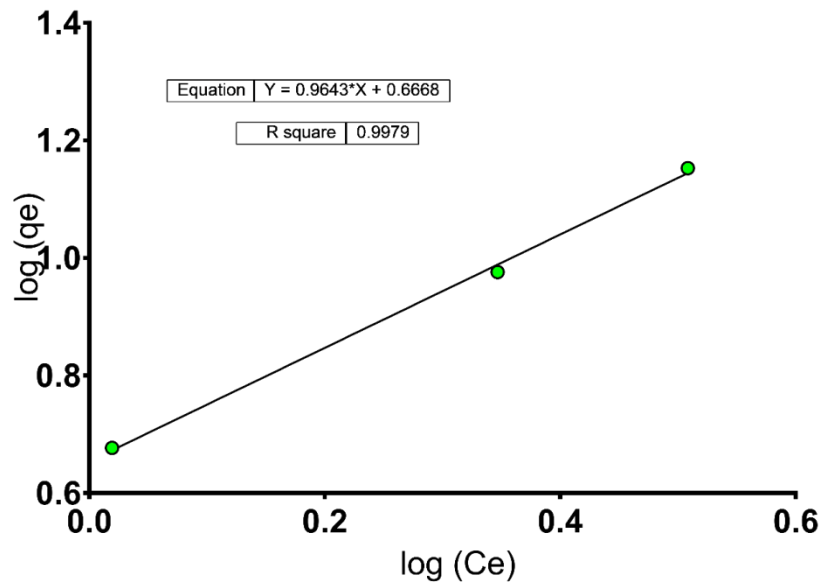
Figure 4.15: Freundlich Isotherm

Figure 4.16: Langmuir Isotherm
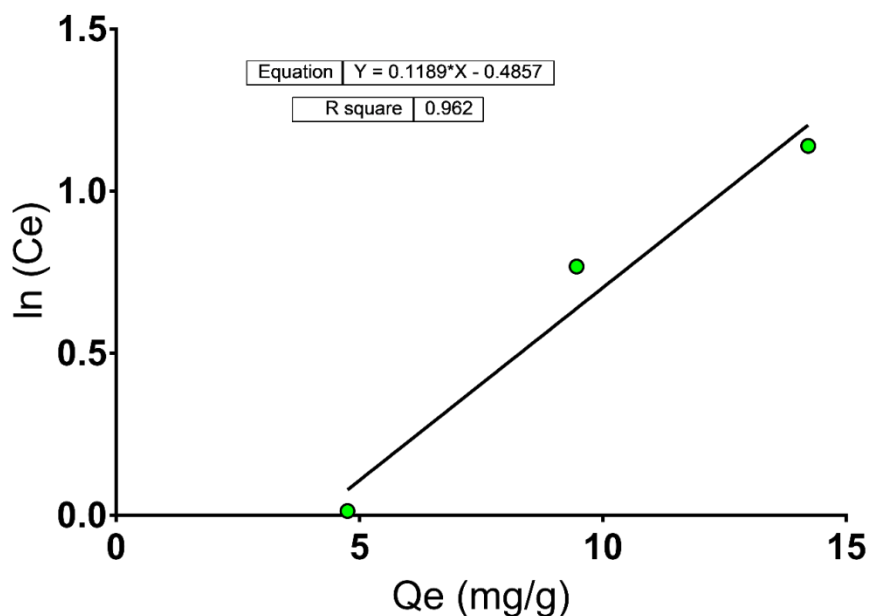
Figure 4.17: Temkin Isotherm

Table 4:1: Isotherm Parameters for MB and Copper Ions Removal by *Cu-I* Beads

Isotherms	Parameters	MB	Cu²⁺
Freundlich	$k_f(mg/g)(mg/L)^n$	4.765	5.651
	N	1.07	1.43
	Δq	4.64	3.36
	R^2	0.9969	0.9989
Langmuir	$q_m(mg/g)$	29.59	392.8
	b (L/mg)	0.008131	0.06789
	R_L	0.551–0.925	0.389–0.789
	Δq	5.94	8.28
	R^2	0.9805	0.9693
Temkin	$K_T(L/g)$	0.9999	0.7896
	b (kJ/mol)	20.32	54.89
	Δq	11.98	32.59
	R^2	0.9584	0.9439
Experimental			
	$q_e(mg/g)$	22.48	345.89

Note the concentration range of MB: 10–100 mg/L and copper ions: 200–1000 mg/L.

From the values above, the R^2 values from the three isotherm models, it shows clearly that for both MB and copper, the Freundlich adsorption isotherm had the

highest value which is the closest to 1 and means that is the isotherm that best predicts the adsorption process.
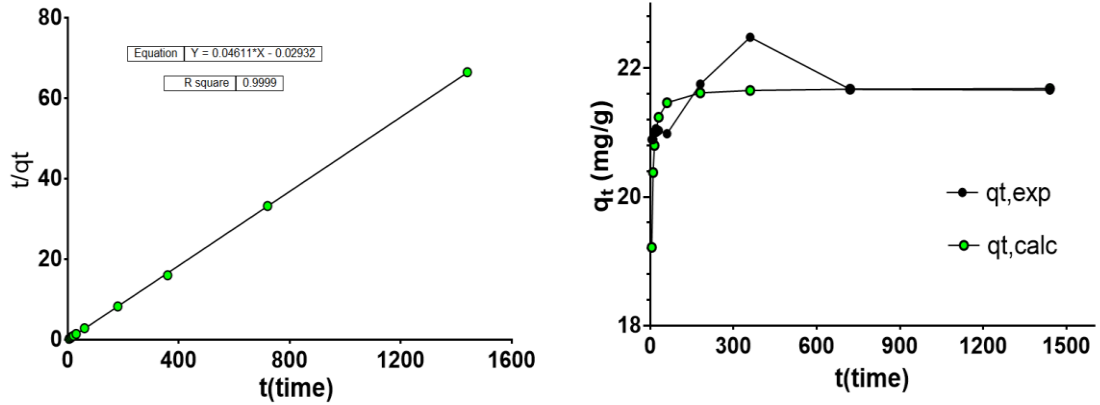

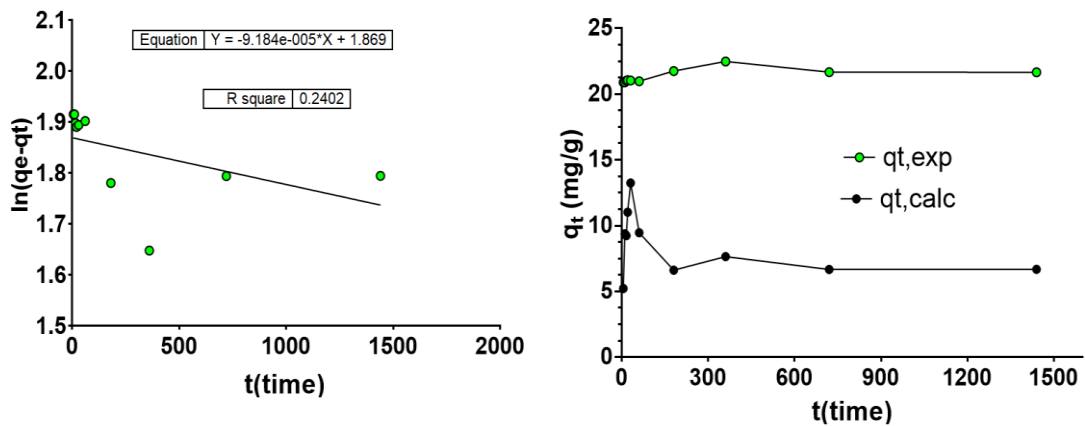Figure 4.18: Pseudo-Second Order Adsorption Kinetics for MB at pH 8 using 0.1 g of *Cu-I* Beads

Figure 4.19: Pseudo-First Order Adsorption Kinetics for MB at pH 8 using 0.1 g of *Cu-I* Beads.

40

Table 4.2: Kinetic parameters for MB and copper ions removal by Cu-I beads

Kinetic models	Parameters	MB	Cu^{2+}
	$q_{e,exp}$ (mg/g)	22.48	345.89
Elovich	α(mg/g min)	11.28	198.95
	β(g/mg)	6.36	11.4
	Δq_t	8.347	11.62
	R^2	0.9958	0.991
Pseudo-second-order	k_2(g/mg min)	0.07156	0.0036
	$q_{e,cal}$(mg/g)	21.69	328.9
	Δq_t	4.098	5.656
	R^2	0.9999	0.9976
Pseudo-first-order	k_1(1/min)	0.00009	0.0012
	$q_{e,cal}$(mg/g)	6.483	138.99
	Δq_t	15.95	45.96
	R^2	0.2402	0.789

Note the concentration range of MB: 10–100 mg/L and copper ions: 200–1000 mg/L.
$\Delta q_t = (q_t,exp - q_t,calc)^2$ where q_t,exp is quantity of adsorbate adsorbed at each time; $q_t,calc$ uptake calculated from the adsorption kinetic model and qe (mg/g) at 360 min.

For the Adsorption kinetics, the R^2 values for MB adsorption for pseudo-first order kinetics, pseudo-second order kinetics and Elovich are 0.2402, 0.9999 and 0.9958. From these values, it shows that for MB adsorption, a pseudo-second order id most favourable in the prediction of the adsorption process.

4.3 Thermodynamic Studies

Thermodynamic studies was carried out on adsorption process to determine whether the adsorption process was; endothermic or exothermic, there was increase or decrease in entropy and whether the reaction was spontaneous or non-spontaneous. Table shows the calculated results of thermodynamic parameters.

Table 2.3: Thermodynamic parameters for MB and Cu2+ removal from using 0.1 g *Cu−I* beads

Adsorbate	Temp. (K)	K_L	Slope	Intercept	R^2	$\Delta G°$ (kJmol^{-1})	$\Delta S°$ (kJmol^{-1})	$\Delta H°$ (kJmol^{-1})
MB								
	298	0.8040				-1.992		
	308	0.3696	0.0005	0.003	0.8486	-0.947	0.02494	-4.157
	318	0.3177				-0.839		
	328	0.2011				-0.548		
Cu^{2+}	308	0.2231				-0.571		
			-0.0001	0.0033	0.9997		0.02744	0.8314
	318	0.9163				-2.423		
	328	1.6094				-4.389		

‡Thermodynamic equilibrium constant KL=qe/ce.
For MB; pH =8, Conc = 100 mg/L and contact time = 6 h.
For Cu^{2+}; pH =5, Conc = 600 mg/L and contact time = 3 h.

From table 4.3, the values of $\Delta G°$ for MB and copper adsorption are all negative which implies that the adsorption process is spontaneous. However, in the case of MB, spontaneity decreased with increase in temperature while for copper, spontaneity increased with increase in temperature. For $\Delta S°$ values, in both cases were positive which means an increase in orderliness. For $\Delta H°$ values, for MB adsorption, it is -4.15 KJ/mol, which is an indication that the adsorption of MB is an exothermic process. For copper, the $\Delta H°$ value is 0.8314 which indicates that the copper adsorption in this study is an endothermic process.

4.4 Desorption Efficiency

Cu-I beads were used for MB adsorption and desorption four cycles in 0.2M HCl and it was observed that after the first cycle, 17 mg/g which was the highest. The second cycle was also good as 15 mg/g was also desorbed. On getting to the third and fourth cycle, the desorption reduced drastically to 2 mg/g and 1.8 mg/g. This is depicted in figure 4.20. For copper, the desorption effieciency was about 84% which decreased

to about 64% at the third cycle. On getting to the fourth cycle, about 43% was achieved which remained almost same at the fifth cycle as shown in figure 4.21.
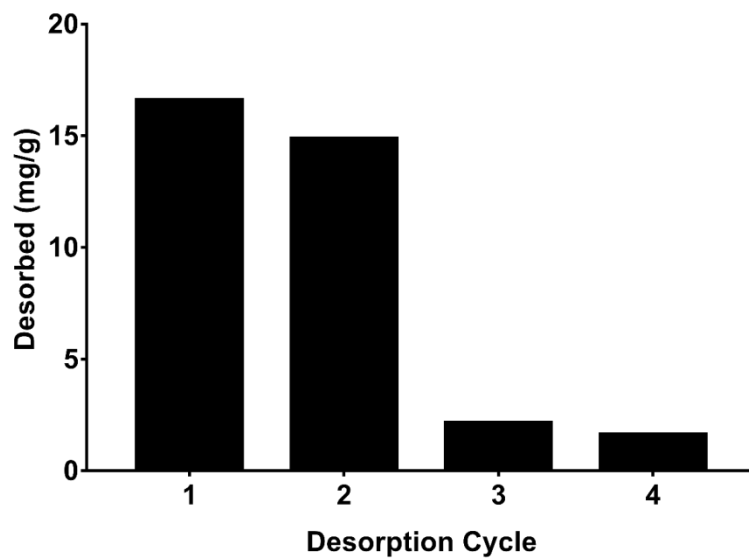

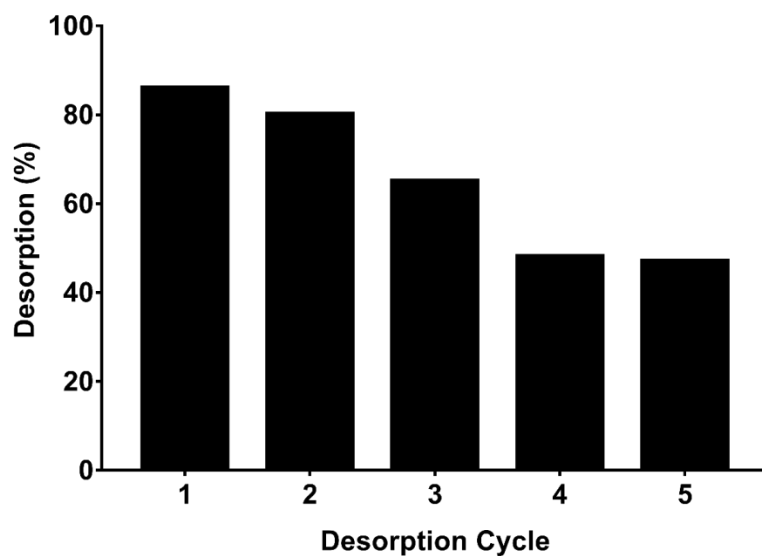Figure 4.20: Desorption of MB from Spent *Cu-I* Beads

Figure 4.21: Desorption Efficiency of Copper Ions from Spent *Cu-I* Beads.
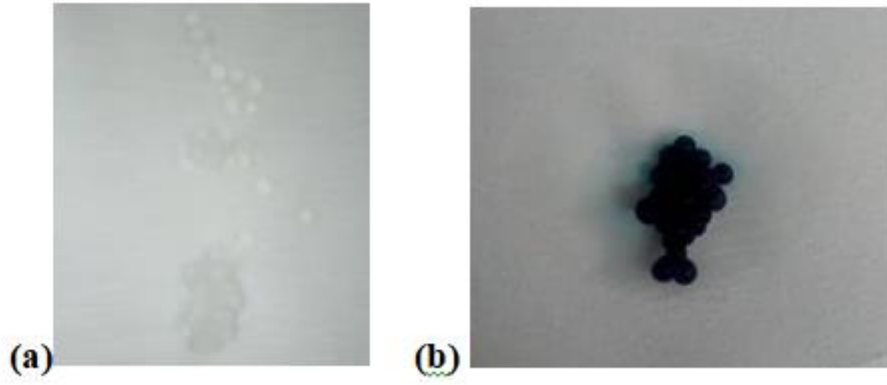
Figure 4.22: (a) Beads before MB adsorption (b) Beads after MB adsorption
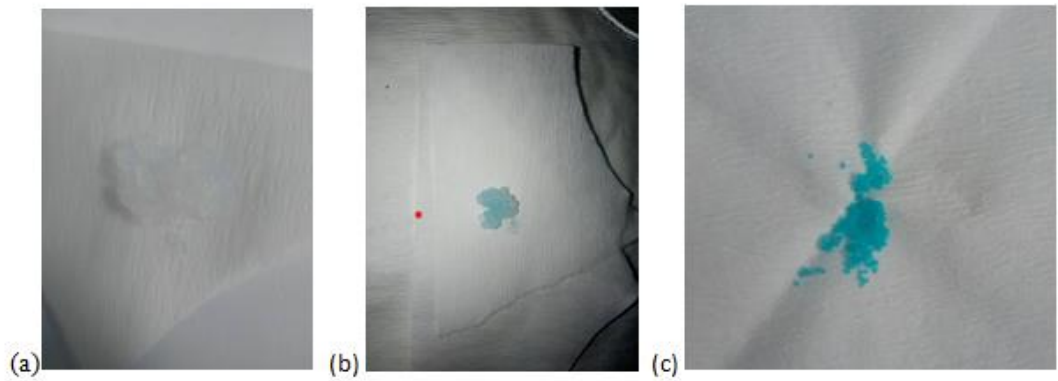
Figure 4..23: (a) *Cu-I* Beads Before Copper Adsorption (b) *Cu-I* Beads After Copper Adsorption (c) Dried *Cu-I* Beads After Copper Adsorption

Chapter 5

CONCLUSION

In this research, a copper-imprinted polyvinyl alcohol/sodium alginate beads named *Cu-I* beads were synthesized via a simple facile approach as reported in chapter 3. The functional groups present on the *Cu-I* beads are explicated and it was determined that the point zero charge of the adsorbent is 3.04. The efficiency of the *Cu-I* beads for the removal of methylene blue dye and copper ions from synthetic solutions under varying operation conditions is established. The results obtained are summarized as follows:

1. It was observed that the maximum MB removal efficiency occurred at the alkaline pH 8 where nearly 98% removal efficiency was obtained while that of copper, maximum removal was at pH 5, 98.6% removal efficiency was observed.

2. The *Cu-I* beads removal efficiency decreased as the dosage increased from 0.1 g/L to 1.5 g/L. for MB and it also decreased as dosage increased from 0.1 g/L to 1.0 g/L.

3. The removal efficiency increased with the contact time until it reached an equilibrium state at 360 mins for MB.

4. The *Cu-I* beads removal efficiency decreased as the solution temperature was increased from 298 to 328 K which is attributed to an exothermic adsorption behaviour while for copper, removal efficiency increased for same range of temperatures to indicate an endothermic adsorption behaviour for copper.

5. It was observed that the removal efficiency also increased with increases in the initial concentration of the adsorbate (both MB and copper).

6. Considering the R^2 of the isotherm equations, it is concluded that the experimental data can be explained better by the Freundlich isotherm which assumed heterogeneous adsorption mechanisms from green materials and used as an adsorbent for methylene blue dye removal.

7. Overall, the efficiency of the *Cu-I* beads is comparable to similar polymeric adsorbents reported in the literature. Further studies will be carried out to understand its performance in a multiple adsorbate system. Also, the adsorption mechanism in a single and multi-pollutant system will be further investigated to optimize its efficiency for industrial use.

REFERENCES

Abbas, S. H., Ismail, I. M., Mostafa, T. M., & Sulaymon, A. H. (2014). Biosorption of heavy metals: a review. *Journal of Chemical Science and Technology*, *3*(4), 74–102.

Asfaram, A., Ghaedi, M., Goudarzi, A., & Rajabi, M. (2015). Response surface methodology approach for optimization of simultaneous dye and metal ion ultrasound-assisted adsorption onto Mn doped Fe 3 O 4-NPs loaded on AC: kinetic and isothermal studies. *Dalton Transactions*, *44*(33), 14707–14723.

ATKINS, P., & Paula, D. E. (2002). J.(2002). *Physical Chemistry, 7th Ed. Freeman, New York*.

Bose, P., Bose, M. A., & Kumar, S. (2002). Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide. *Advances in Environmental Research*, *7*(1), 179–195.

Chen, J. H., Li, guo ping, Liu, qing lin, Ni, jian cong, Wu, wen bing, & Lin, jin mei. (2010). Cr (III) ionic imprinted polyvinyl alcohol/sodium alginate (PVA/SA) porous composite membranes for selective adsorption of Cr (III) ions. *Chemical Engineering Journal*, *165*(2), 465–473.

Crini, G., & Badot, P.-M. (2008). Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Progress in*

Polymer Science, *33*(4), 399–447.

Djelloul, C., & Hamdaoui, O. (2014). Removal of cationic dye from aqueous solution using melon peel as nonconventional low-cost sorbent. *Desalination and Water Treatment*, *52*(40–42), 7701–7710.

Doğan, M., Abak, H., & Alkan, M. (2009). Adsorption of methylene blue onto hazelnut shell: kinetics, mechanism and activation parameters. *Journal of Hazardous Materials*, *164*(1), 172–181.

Filipkowska, U., Rodziewicz, J., & Sobotka, R. (2010). Effect of pH value and adsorbent concentration on the effectiveness of adsorption onto chitin and chitosan. *Progress on Chemistry and Application of Chitin and Its Derivatives*, *15*, 79–86.

Flora, S. J. S., & Pachauri, V. (2010). Chelation in metal intoxication. *International Journal of Environmental Research and Public Health*, *7*(7), 2745–2788.

Gupta, V. K., Mittal, A., Kurup, L., & Mittal, J. (2008). Process development for removal and recovery of metanil yellow by adsorption on waste materials—bottom ash and de-oiled soya. *J. Hazard. Mater*, *151*(2–3), 834–845.

Hashemian, S., Saffari, H., & Ragabion, S. (2015). Adsorption of cobalt (II) from aqueous solutions by Fe 3 O 4/bentonite nanocomposite. *Water, Air, & Soil Pollution*, *226*(1), 2212.

He, J., & Chen, J. P. (2014). Cu(II)-imprinted poly(vinyl alcohol)/poly(acrylic acid) membrane for greater enhancement in sequestration of copper ion in the presence of competitive heavy metal ions: Material development, process demonstration, and study of mechanisms. *Industrial and Engineering Chemistry Research*, *53*(52), 20223–20233. https://doi.org/10.1021/ie5032875

Hu, T., Liu, Q., Gao, T., Dong, K., Wei, G., & Yao, J. (2018). Facile Preparation of Tannic Acid–Poly (vinyl alcohol)/Sodium Alginate Hydrogel Beads for Methylene Blue Removal from Simulated Solution. *ACS Omega*, *3*(7), 7523–7531.

Jing, G., Wang, L., Yu, H., Amer, W. A., & Zhang, L. (2013). Recent progress on study of hybrid hydrogels for water treatment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *416*(1), 86–94. https://doi.org/10.1016/j.colsurfa.2012.09.043

Jones, L., Hoeger, C., Atkins, P., & Schoenfield-Tacher, R. (2000). *Chemistry: Molecules, Matter, and Change Media Activities Book: Integrating Media in Learning* (Vol. 2). Macmillan.

Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N., & Pattabhi, S. (2003). Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresource Technology*, *87*(1), 129–132.

Kajjumba, G. W., Emik, S., Öngen, A., Özcan, H. K., & Aydın, S. (2018). Modelling

of adsorption kinetic processes—errors, theory and application. In *Advanced sorption process applications*. IntechOpen.

López, D., Vlamakis, H., & Kolter, R. (2010). *Biofilms. Cold Spring Harb. Perspect. Biol. 2: a000398.*

Mittal, A., Mittal, J., Malviya, A., & Gupta, V. K. (2010). Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. *Journal of Colloid and Interface Science*, *344*(2), 497–507.

Oladipo, A. A., Ahaka, E. O., & Gazi, M. (2019). High adsorptive potential of calcined magnetic biochar derived from banana peels for Cu 2+, Hg 2+, and Zn 2+ ions removal in single and ternary systems. *Environmental Science and Pollution Research*, *26*(31), 31887–31899.

Oladipo, A. A., & Gazi, M. (2014). Enhanced removal of crystal violet by low cost alginate/acid activated bentonite composite beads: optimization and modelling using non-linear regression technique. *Journal of Water Process Engineering*, *2*, 43–52.

Ovchinnikov, O. V, Evtukhova, A. V, Kondratenko, T. S., Smirnov, M. S., Khokhlov, V. Y., & Erina, O. V. (2016). Manifestation of intermolecular interactions in FTIR spectra of methylene blue molecules. *Vibrational Spectroscopy*, *86*, 181–189.

Pal, S., Sarkar, U., & Dasgupta, D. (2010). Dynamic simulation of secondary

treatment processes using trickling filters in a sewage treatment works in Howrah, west Bengal, India. *Desalination*, *253*(1–3), 135–140.

Park, C., Lee, M., Lee, B., Kim, S.-W., Chase, H. A., Lee, J., & Kim, S. (2007). Biodegradation and biosorption for decolorization of synthetic dyes by Funalia trogii. *Biochemical Engineering Journal*, *36*(1), 59–65.

Piccin, J. S., Dotto, G. L., & Pinto, L. A. A. (2011). Adsorption isotherms and thermochemical data of FD&C Red n 40 binding by chitosan. *Braz. J. Chem. Eng*, 295–304.

Rajeshwar, K., & Ibanez, J. G. (1997). *Environmental electrochemistry: Fundamentals and applications in pollution sensors and abatement*. Elsevier.

Romero-González, J., Walton, J. C., Peralta-Videa, J. R., Rodríguez, E., Romero, J., & Gardea-Torresdey, J. L. (2009). Modeling the adsorption of Cr (III) from aqueous solution onto Agave lechuguilla biomass: study of the advective and dispersive transport. *Journal of Hazardous Materials*, *161*(1), 360–365.

Sadegh, H., & Ali, G. A. M. (2019). Potential applications of nanomaterials in wastewater treatment: nanoadsorbents performance. In *Advanced Treatment Techniques for Industrial Wastewater* (pp. 51–61). IGI Global.

Samarghandi, M. R., Hadi, M., Moayedi, S., & BARJESTEH, A. F. (2009). *Two-parameter isotherms of methyl orange sorption by pinecone derived activated carbon*.

Sarode, S., Upadhyay, P., Khosa, M. A., Mak, T., Shakir, A., Song, S., & Ullah, A. (2019). Overview of wastewater treatment methods with special focus on biopolymer chitin-chitosan. *International Journal of Biological Macromolecules*, *121*, 1086–1100.

Subbaiah, T., Mallick, S. C., Mishra, K. G., Sanjay, K., & Das, R. P. (2002). Electrochemical precipitation of nickel hydroxide. *Journal of Power Sources*, *112*(2), 562–569.

Suteu, D., & Rusu, L. (2012). Removal of methylene blue dye from aqueous solution using seashell wastes as biosorbent. *Environmental Engineering & Management Journal (EEMJ)*, *11*(11).

Tan, K. L., & Hameed, B. H. (2017). Insight into the adsorption kinetics models for the removal of contaminants from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers*, *74*, 25–48.

Tiwari, A., & Kathane, P. (2015). Adsorption of Cu2+ ions onto polyvinyl alcohol-alginate bound nano magnetite microspheres: A kinetic and thermodynamic study. *International Research Journal of Environment Sciences*, *4*(4), 12–21.

Ullah, I., Nadeem, R., Iqbal, M., & Manzoor, Q. (2013). Biosorption of chromium onto native and immobilized sugarcane bagasse waste biomass. *Ecological Engineering*, *60*, 99–107.

Vigneswaran, S., Ngo, H. H., Chaudhary, D. S., & Hung, Y.-T. (2005).

Physicochemical treatment processes for water reuse. In *Physicochemical treatment processes* (pp. 635–676). Springer.

Vilar, V. J. P., Botelho, C. M. S., & Boaventura, R. A. R. (2007). Methylene blue adsorption by algal biomass based materials: biosorbents characterization and process behaviour. *Journal of Hazardous Materials*, *147*(1–2), 120–132.

Wadhawan, S., Jain, A., Nayyar, J., & Mehta, S. K. (2020). Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: A review. *Journal of Water Process Engineering*, *33*, 101038.

Wang, L. K., Vaccari, D. A., Li, Y., & Shammas, N. K. (2005). Chemical precipitation. In *Physicochemical treatment processes* (pp. 141–197). Springer.

Wilderer, P. A., Irvine, R. L., & Goronszy, M. C. (2001). *Sequencing batch reactor technology*. IWA publishing.

Zhou, Z., Kong, D., Zhu, H., Wang, N., Wang, Z., Wang, Q., Liu, W., Li, Q., Zhang, W., & Ren, Z. (2018). Preparation and adsorption characteristics of an ion-imprinted polymer for fast removal of Ni (II) ions from aqueous solution. *Journal of Hazardous Materials*, *341*, 355–364.