

THE ADSORPTION OF Cu(II) IONS BY POLYANILINE GRAFTED CHITOSAN BEADS

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Dissertation submitted for the degree of Masters

In Chemical Engineering at the Vaal University of Technology

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DECLARATION

I, igberase Ephraim declare that the material in this dissertation is my work, except where it is otherwise stated.

This work has not been submitted to another university for any other degree.

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ABSTRACT

This work investigates the possible use of chitosan beads and polyaniline grafted chitosan beads (PGCB) for the adsorption of copper ions from copper contaminated water. For this purpose chitosan flakes were converted to chitosan beads. However, a variable from a number of reaction variables (aniline concentration, chitosan concentration, temperature, acid concentration, reaction time and initiator concentration) was varied while others was kept constant, in an attempt to determine the best conditions for grafting of polyaniline onto chitosan beads. Percentage (%) grafting and % efficiency were key parameters used to determine such conditions. The chitosan beads and PGCB were characterized using physical techniques such as Fourier transformed infra red (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM). The beads were used as an adsorbent for copper ions removal. The effect of pH on the removal rate of copper (II) by PGCB was investigated on by varying the pH values from pH 3 to 8 at an initial concentration of 40 mg/l. The effect of contact time, initial concentration and temperature was also investigated. The Langmuir and Freundlich model were used to describe adsorption isotherms for chitosan beads and PGCB, with correlation coefficient (R^2) as the determining factor of best fit model. The thermodynamics of adsorption of copper (II) onto PGCB was described by parameters such as standard Gibb's free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) while the pseudo first-order and pseudo second-order kinetic model was used to describe kinetic data for the PGCB, with R^2 and chi-square test (χ^2) as the determinant factor of best fit model. From the desorption studies, the effect of eluants (HCl and HNO₃) and contact time on percentage desorption of PGCB loaded copper (II) ion was investigated upon. In determining the reusability of the PGCB loaded copper (II) ion, three cycles of adsorption/desorption studies was carried out.

The results obtained from determining the best conditions for grafting polyaniline onto chitosan beads revealed the following grafting conditions; [Aniline] 0.1 g/l, [temperature] 35°C, [chitosan] 0.45 g/l, [HCl] 0.4 g/l, [(NH₄)₂S₂O₈] 0.35 g/l, and [time] 1 h. These conditions were applied in the grafting of polyaniline onto chitosan beads. FTIR analysis showed increase intensity in the grafted beads which provided evidence of grafting, XRD measurement showed a decrease in crystallinity in the PGCB as against the partial crystalline nature of chitosan. In SEM analysis, evidence of grafting was revealed by the closed gap between the polysaccharide

particles in the PGCB. From the investigation carried out on the effect of pH on the percentage removal of Cu(II) ions by PGCB, the optimal pH value was found to be pH 5 with a percentage removal of 100% and this value was used for all adsorption experiment. Also from the investigation performed on the effect of contact time and initial concentration, it was observed that there was a sharp increase in the amount of Cu(II) ions adsorbed by PGCB up until contact time of 30 min and thereafter, it increases gradually. From the experiment carried out on the effect of temperature on adsorption capacity, there was an increase in adsorption capacity with increase in temperature. Moreover, at temperatures of 25°C, 35 °C and 45°C the Langmuir model gave the best fit for the chitosan beads having R^2 values that are equal and greater than 0.942 in contrast to Freundlich having R^2 values that is equal and greater than 0.932. The maximum adsorption capacity (Q_m) from Langmuir model at these temperatures were 30.3 mg/g, 47.6 mg/g and 52.6 mg/g respectively. Also, the Langmuir model gave the best fit for the PGCB having R^2 values that are equal and greater than 0.956 in contrast to Freundlich model with R^2 values that is equal and greater than 0.935. The Q_m from Langmuir model at these temperatures were 80.3 mg/g, 90.9 mg/g and 100 mg/g respectively. The values of Q_m for PGCB appears to be significantly higher when compared to that of chitosan beads and this makes PGCB a better adsorbent than chitosan beads.

From the thermodynamic studies carried out on PGCB, the values of ΔG° were negative and this denotes that the adsorption of copper ions onto PGCB is favorable and spontaneous, the positive value of ΔH° shows the adsorption process is endothermic and the positive value of ΔS° illustrate increased randomness at the solid-liquid interface during the adsorption process. Also, from the kinetic studies carried out on the PGCB, the pseudo second-order kinetic model best described the kinetic data having R^2 values that are equal and greater than 0.994 in contrast to the pseudo first-order kinetic model with R^2 values that is equal and greater than 0.913. The χ^2 values for the pseudo first-order and pseudo second-order kinetic model were similar; however, there was a large difference for q_e between the calculated (q_{eCal}) values of the first-order kinetic model and experimental (q_{eExp}) values. In the case of the pseudo second-order model, the calculated q_e values agree very well with the experimental data.

Desorption of the metal ions from PGCB was efficient. 0.5 M HCl was successfully used in desorbing the beads loaded with copper ions and a percentage desorption of 97.1% was achieved

at contact time of 180 min. PGCB were successfully re-used for adsorption/desorption studies were a Q_m of 83.3 mg/g, 83.3 mg/g and 76.9 mg/g was achieved in the first, second and third cycle respectively.

Table of Contents

| | |
|--|------|
| DECLARATION | ii |
| ACKNOWLEDGEMENT | iii |
| ABSTRACT | iv |
| LIST OF TABLES | xi |
| LIST OF FIGURES | xiii |
| Nomenclature..... | xv |
| CHAPTER ONE..... | 1 |
| 1 Introduction | 1 |
| 1.1 Problem statement | 3 |
| 1.2 Objective | 3 |
| 1.2.1 Specific objectives | 3 |
| 1.3 Research values | 4 |
| 1.4 Project Scope..... | 4 |
| REFERENCE | 5 |
| | |
| CHAPTER TWO | 7 |
| 2.1 ADSORBENT | 7 |
| 2.1.1 Activated carbon | 7 |
| 2.1.2 Zeolite | 7 |
| 2.1.3 Peat..... | 8 |
| 2.1.4 Chitin and Chitosan..... | 9 |
| 2.1.4.1 Purification of Chitin and chitosan production | 10 |
| 2.2 Physico-chemical properties of chitosan | 12 |
| 2.2.1 Degree of deacetylation..... | 12 |
| 2.2.2 Molecular weight | 12 |
| 2.2.3 Solubility | 13 |
| 2.2.4 Crystallinity | 13 |
| 2.3 Modification of chitosan..... | 14 |
| 2.3.1 Grafting initiated by free radicals | 15 |

| | |
|--|----|
| 2.3.2 Radiation initiated grafting | 17 |
| 2.4 Reaction mechanism of chitosan..... | 17 |
| 2.5 Adsorption process | 18 |
| 2.5.1 Factors affecting the adsorption of Cu(II) ions | 20 |
| 2.5.1.1 Solution pH | 21 |
| 2.5.1.2 Contact time and initial concentration..... | 22 |
| 2.5.2 Adsorption Isotherms | 23 |
| 2.5.2.1 Langmuir model | 23 |
| 2.5.2.2 Freundlich model..... | 24 |
| 2.5.3 Thermodynamic parameters of adsorption | 24 |
| 2.5.4 Kinetic studies | 26 |
| 2.5.5 Error analysis | 27 |
| 2.6 Regeneration | 27 |
| 2.7 Conclusion | 28 |
| REFERENCE | 29 |
| | |
| CHAPTER 3 | 37 |
| 3.1 Introduction..... | 37 |
| 3.2 Experimental | 37 |
| 3.2.1 Materials..... | 37 |
| 3.2.2 Formation of chitosan beads..... | 37 |
| 3.2.3 Determination of best conditions for grafting polyaniline onto chitosan beads..... | 38 |
| 3.2.3.1 Effect of contact time | 39 |
| 3.2.3.2 Effect of Aniline concentration | 39 |
| 3.2.3.3 Effect of Initiator concentration | 40 |
| 3.2.3.4 Effect of chitosan concentration..... | 40 |
| 3.2.3.5 Effect of acid concentration | 40 |
| 3.2.3.6 Effect of temperature | 41 |
| 3.2.4 Characterization of the beads | 41 |
| 3.2.4.1 Infrared measurement | 41 |
| 3.2.4.2 XRD measurement | 42 |

| | | |
|---------|--|----|
| 3.2.4.3 | SEM measurement | 42 |
| 3.3 | Result/discussion | 43 |
| 3.3.1 | Determination of best conditions for grafting polianiline onto chitosan beads..... | 43 |
| 3.3.1.1 | Effect of contact time | 43 |
| 3.3.1.2 | Effect of aniline concentration | 44 |
| 3.3.1.3 | Effect of initiator concentration | 45 |
| 3.3.1.4 | Effect of chitosan concentration..... | 46 |
| 3.3.1.5 | Effect of acid concentration | 47 |
| 3.3.1.6 | Effect of temperature | 48 |
| 3.3.2 | Grafting of chitosan beads..... | 49 |
| 3.3.3 | Characterization | 49 |
| 3.3.3.1 | IR spectra | 49 |
| 3.3.3.2 | XRD spectra..... | 50 |
| 3.3.3.3 | SEM morphology | 52 |
| | REFERENCE | 53 |
| | | |
| | CHAPTER FOUR..... | 55 |
| 4.1. | Introduction..... | 55 |
| 4.2 | Experimental | 55 |
| 4.2.1 | Materials..... | 55 |
| 4.2.2 | Adsorption experiments | 55 |
| 4.2.2.1 | Effect of pH on Cu(II) ion removal by PGCB | 55 |
| 4.2.2.2 | Isotherm experiment | 56 |
| 4.2.2.3 | Kinetic experiment | 56 |
| 4.2.3 | Desorption Experiment | 57 |
| 4.3 | Results/discussion | 57 |
| 4.3.1 | Effect of pH | 57 |
| 4.3.2 | Effect of contact time and initial concentration..... | 58 |
| 4.3.3 | Effect of temperature..... | 59 |
| 4.3.4 | Adsorption isotherm parameters | 60 |
| 4.3.5 | Maximum adsorption capacity comparison | 62 |

| | | |
|--------|--|----|
| 4.3.6 | Thermodynamics parameters..... | 63 |
| 4.3.7 | Kinetic parameters | 64 |
| 4.4.1 | Effect of desorbing copper ions by HCl and HNO ₃ systems..... | 66 |
| 4.4.2. | Effect of contact time on percentage desorption of copper..... | 67 |
| 4.4.3 | Effect of adsorbent re-use on maximum adsorption capacity | 68 |
| 4.5 | CONCLUSION | 69 |
| | REFERENCE | 70 |
| | | |
| | CHAPTER FIVE | 72 |
| | CONCLUSION AND RECOMMENDATION..... | 72 |
| 5.1 | INTRODUCTION..... | 72 |
| 5.1.1 | General conclusion..... | 72 |
| 5.1.2 | Specific observation..... | 72 |
| | Appendix A: Experimental and calculated data on graft copolymerization | 74 |
| | Appendix B: Experimental data for the effect of pH on Cu(II) ions removal by PGCB at a concentration of 40 mg/l..... | 77 |
| | Appendix C: Experimental data for Isothermal studies | 78 |
| | Appendix D: Langmuir and Freundlich plot at temperatures of 25°C, 35 °C and 45 °C..... | 81 |
| | | 81 |
| | Appendix E: Data for thermodynamics study | 83 |
| | Appendix F: Data for kinetic studies at a temperature of 25°C and pH 5..... | 84 |
| | Appendix G: Pseudo first and pseudo second order kinetic plot at different concentration | 86 |
| | Appendix H: Experimental data for desorption studies | 87 |
| | Appendix I: Chitosan beads production | 89 |

LIST OF TABLES

| | |
|--|----|
| Table 2. 1: Characteristics of Physical adsorption and Chemical adsorption | 20 |
| Table 4. 1: Langmuir and Freundlich isotherm parameters at different temperature. | 62 |
| Table 4. 2: Comparison of adsorption capacity of copper (II) with other absorbent | 63 |
| Table 4. 3: Thermodynamic parameters for the adsorption of copper ions onto PGCB at an initial concentration of 200 mg/l | 64 |
| Table 4. 4: Kinetic parameters for the adsorption of copper onto PGCB at a pH of 5. | 66 |
| Table 4. 5: Adsorption and desorption behavior of copper ions on PGCB at a temperature of 25°C, pH of 4 and contact time of 150 min. | 69 |
| Table A- 1: Data obtained from the grafting of polyaniline onto chitosan showing the effect of time on graft copolymerization at fixed concentration of chitosan (0.45 g/l), ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.1 g/l), at 25°C. | 74 |
| Table A- 2: Data obtained from the grafting of polyaniline onto chitosan showing the effect of aniline concentration on graft copolymerization at fixed concentration of chitosan (0.45 g/l), ammonium persulfate (0.35 g/l), HCl (0.1 g/l), for 1 h at 25°C. | 74 |
| Table A- 3: Data obtained from the grafting of polyaniline onto chitosan showing the effect of initiator concentration on graft copolymerization at fixed concentration of chitosan (0.45 g/l), aniline (0.1 g/l), HCl (0.1 g/l), for 1 h at 25°C. | 75 |
| Table A- 4: Data obtained from the grafting of polyaniline onto chitosan showing the effect of varying chitosan concentration on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.1 g/l), for 1 h at 25°C..... | 75 |
| Table A- 5: Data obtained from the grafting of polyaniline onto chitosan showing the effect of acid concentration on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), chitosan (0.45 g/l) for 1 h at 25°C..... | 76 |
| Table A- 6: Data obtained from the grafting of polyaniline onto chitosan showing the effect of varying temperature on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), chitosan (0.45 g/l), HCl (0.1 g/l) for 1 h. | 76 |
| Table C- 1: Adsorption data for un-grafted chitosan beads at 25°C for 150 min | 78 |
| Table C- 2: Adsorption data for un-grafted chitosan beads at 35°C for 150 min | 78 |
| Table C- 3: Adsorption data for un-grafted chitosan beads at 45°C for 150 min | 79 |
| Table C- 4: Adsorption data for grafted chitosan beads at 25°C for 150 min | 79 |
| Table C- 5: Adsorption data for grafted chitosan beads at 35°C for 150 min | 80 |
| Table C- 6: Adsorption data for grafted chitosan beads at 45°C for 150 min | 80 |
| Table E- 1: Adsorption data for thermodynamic study at an initial concentration of 200 mg/l.... | 83 |

| | |
|--|----|
| Table F- 1: Adsorption data for kinetic studies at an initial concentration of 40 mg/l | 84 |
| Table F- 2: Adsorption data for kinetic studies at an initial concentration of 80 mg/l | 84 |
| Table F- 3: Adsorption data for kinetic studies at an initial concentration of 120 mg/l | 84 |
| Table F- 4: Adsorption data for kinetic studies at an initial concentration of 200 mg/l | 85 |
| Table F- 5: Adsorption data for kinetic studies at an initial concentration of 320 mg/l | 85 |
| Table F- 6: Adsorption data for kinetic studies at an initial concentration of 400 mg/l | 85 |
| | |
| Table H- 1: Experimental data showing the effect of varying the concentrations of HCl/HNO ₃ system at an initial concentration of 40 mg/l. | 87 |
| Table H- 2: Experimental data showing the effect of time on percentage desorption of copper. . | 87 |
| Table H- 3: Data for first cycle | 88 |
| Table H- 4: Data for second cycle | 88 |
| Table H- 5: Data for third cycle | 88 |

LIST OF FIGURES

| | |
|--|----|
| Figure 2. 1: Structure of chitin..... | 10 |
| Figure 2. 2: The structure of chitosan. | 10 |
| Figure 2. 3: Schematic representation of chitin and chitosan preparation from the basic raw material. | 12 |
| Figure 2. 4: Graft copolymerization of polyaniline onto chitosan..... | 16 |
| Figure 2. 5: Formation of chitosan chelates with copper ions binding with amino groups | 18 |
| | |
| Figure 3. 1: Set-up for the production of chitosan beads. | 38 |
| Figure 3. 2: The effect of time on graft copolymerization at fixed concentration of chitosan (0.45 g/l), ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.1 g/l), at 25°C. | 44 |
| Figure 3. 3: The effect of aniline concentration on graft copolymerization at fixed concentration of chitosan (0.45 g/l), ammonium persulfate (0.35 g/l), HCl (0.1 g/l), for 1 h at 25°C. | 45 |
| Figure 3. 4: The effect of initiator mass on graft copolymerization at fixed concentration of chitosan (0.45 g/l), aniline (0.1 g/l), HCl (0.1 g/l), for 1 h at 25°C. | 46 |
| Figure 3. 5: The effect of chitosan concentration on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.1 g/l), for 1 h at 25°C. | 47 |
| Figure 3. 6: The effect of acid concentration on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), chitosan (0.45 g/l) for 1 h at 25°C. | 48 |
| Figure 3. 7: The effect of temperature on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.4 g/l), chitosan (0.45 g/l) for 1 h. | 49 |
| Figure 3. 8: IR spectrum of chitosan beads and PGCB..... | 50 |
| Figure 3. 9a: XRD spectra of chitosan beads. | 51 |
| | |
| Figure 4. 1: Effect of pH on percentage removal of Cu(II) ions by PGCB at an initial concentration of 40 mg/l. | 58 |
| Figure 4. 2: Effect of contact time and initial concentration. | 59 |
| Figure 4. 3: Effect of temperature on adsorption capacity of PGCB..... | 60 |
| Figure 4. 4: Thermodynamic plot of LnK against 1/T for PGCB..... | 64 |
| Figure 4. 5: Effect of varying the concentrations of HCl/HNO ₃ system. | 67 |
| Figure 4. 6: Effect of contact time on percentage desorption..... | 68 |
| | |
| Figure D- 1: Langmuir plot for chitosan beads | 82 |
| Figure D-2: Freundlich plot for chitosan beads..... | 82 |
| Figure D-3: Langmuir plot for PGCB..... | 83 |
| Figure D-4: Freundlich plot for PGCB | 83 |
| Figure G- 1: Pseudo first order kinetic model plot | 87 |

Figure G- 2: Pseudo second order kinetic model plot.....87

Nomenclature

| | |
|------------------|--|
| PGCB | polyaniline graft chitosan beads |
| Q_m | maximum adsorption capacity from Langmuir (mg/g) |
| q_e | amount adsorbed at equilibrium (mg/g) |
| C_e | final concentration of a solution (mg/l) |
| b | heat of adsorption (l/mg) |
| n | adsorption intensity (l/mg) |
| R | gas constant defined by 8.3145 J/mol.K |
| K_1 | pseudo first order rate constant (min) |
| K_2 | pseudo second order rate constant (g/mg.min) |
| K_f | adsorption capacity from Freundlich (mg/g) |
| X^2 | chi square test |
| ΔG° | Gibb's free energy change (KJ/mol) |
| ΔH° | enthalpy change (KJ/mol) |
| ΔS° | enthropy change (KJ/molK) |
| DD | degree of deacetylation |
| APS | ammonium persulfate |
| CAN | ceric ammonium nitrate |
| PPS | potassium persulfate |
| TCPB | thiocarbonation-potassium bromate |
| MAA | methyl methacrylate |
| Vac | vinyl acetate |
| SEC | size exclusion chromatography |
| GPC | gel permeation chromatography |
| GFC | gel filtration chromatography |
| IR | refractive index |
| MALLS | multi-angle light scattering |
| FTIR | Fourier transform infrared |
| SEM | scanning electron microscope |
| XRD | x-ray diffraction |

CHAPTER ONE

1 INTRODUCTION

Water conservation and management have been a universal issue while trying to satisfy the needs of people. South Africa is situated in a region that lacks sufficient useable water to meet the needs of the people especially those in the rural areas. (DWAF, 2002). In South Africa, the majority of people make use of water from streams and wells, which are often polluted with heavy metal ions. The major sources of these metal ions are industries such as mining, metal-plating, pharmaceutical, electrical device manufacturing and pest-control. This development has produced quite a number of physical and chemical pollutants that find their way into water bodies. Copper for example is used extensively in the electrical industry and in the manufacture of fungicides. Although copper can be an essential element for human beings in trace amount due to the fact that human body can regulate the trace level haemostatically, it can also be toxic when large dosage is ingested (Li and Bai, 2005). The maximum contaminant level for Cu(II) in industrial effluent as suggested by United States Environmental Protection Agency (USEPA) is 1.3 mg/l (Hasan et al., 2008). Therefore, it is necessary to develop a method that can efficiently remove copper ions from water and at the same time recover them in their pure form for potential reuse to avoid the problem of second pollution. Copper ions can be removed from water or wastewater physically or chemically due to the fact that they are un-biodegradable.

However, several techniques have been proposed for the removal of copper ions from water and wastewater including chemical precipitation, membrane filtration, ion exchange, electrolysis and adsorption (Cheung et al., 2002; Ola, 2007). Most of these methods are inefficient when it comes to treating water with low metal concentration. For example, precipitation method is limited by; low efficiency, labour-intensive operation, cost and lack of selectivity of the precipitation process (Tarley and Arruda, 2004). In the case of membrane filtration which is often guided by the membrane pore, it is inefficient in meeting the requirement of low metal concentration and the other disadvantage is the cost of the membrane which is very expensive. Recent studies have shown adsorption to be the most promising technique for metal ions removal due to convenience, easy operation, simplicity of design and can remove different type of pollutants (Bhatnagar and Minocha, 2006). Adsorbents such as chitosan, chitin, activated carbon, peat and zeolite have been used in the past for adsorption of heavy metal ions (Amuda and Ibrahim, 2006). In this

study, chitosan based adsorbent was given attention for copper ion removal due to chitosan wide availability and unique chemical and biological properties such as biocompatibility, biodegradability, high mechanical strength, good film-forming properties and low cost (Jenkins and Hudson, 2002). Chitosan is a polymer derived from N-deacetylation of chitin (Park et al., 2001), a naturally occurring polysaccharide obtained from crustaceans i.e. shrimps and crabs, and fungal biomass. This polymer is well established as an excellent natural adsorbent for metal ions removal due to the presences of the amino ($-NH_2$) and hydroxyl ($-OH$) groups. These groups serve as the coordination and binding sites (Nghah and Fatinathan, 2008). However, Chitosan is an adsorptive polymer that is used in the form of flakes, beads and membranes. It was reported in literature that, when using chitosan flakes for adsorption, metal ions do not penetrate the particle completely and the metal ions adsorbs near the outer surface of the particle (Guibal et al., 1998). As metal ions penetrate the porous particle and are adsorbed onto the amine sites from the outer surface inwards, the formation of adsorbed metal ions clusters may constrict or completely block pores, rendering amine sites deep in the interior of the particle inaccessible for heavy metal ion adsorption (Rorrer et al., 1993), resulting in relatively poor adsorption capacities. Therefore, most researchers have given attention to the transformation of chitosan flakes to chitosan beads (Osifo et al., 2009). This transformation is necessary for ease of handling and easier diffusion of target metal ions to adsorption site.

However, several grafting of chemicals with chitosan beads have been reported in literature to create additional adsorption site, thereby improving its adsorption performance in the process. Such chemicals include; polyaniline, polyvinylacetate, methyl methacrylate and acrylonitrile. In this work, polyaniline was chosen to be grafted on the backbone of chitosan beads because it is a promising organic polymer which has attracted attention of many researchers due to the combination of unique properties like simple preparation and doping procedure, good environmental stability, and low cost. The presence of amine functional group in polyaniline allows the chemical to be applied in modification reaction (Thangarathinavelu et al., 1994).

In a previous study, a comparison study of adsorption of Cr(VI) from aqueous solutions onto alkyl-substituted polyaniline/chitosan composite was done by Yavuz et al., (2011). In this study, polyaniline was grafted onto chitosan beads and in the new matrix, it is expected that more sites

responsible for copper ions uptake will be created due to the grafting of additional functional group (-NH₂) onto the backbone of chitosan beads.

1.1 Problem statement

Among the existing heavy metals, special attention has been given to copper, the reason being that their presence and accumulation in humans body can cause hepatic and renal damage, mucosal irritation and corrosion and possible signs of gastro intestinal disturbance (Ola, 2007). However, Industrial wastewater containing copper are common because these metals are used in a large number of industries such as metal-plating, mining, electric device manufacturing, pest control and pharmaceutical. At present copper ion have polluted our waters, soils and food chain due to uncontrolled disposal (Cheung, et al., 2002). It is therefore necessary to control the emissions of copper ions in the environment.

Moreover, materials with high binding capacity have been studied as absorbents to remove copper ions from contaminated water and industrial effluents, particularly chitosan. It has been found that gel formulation, cross-linking and grafting usually open chitosan network for increased metal ions uptake (Bayrammoglu et al., 2002). In this study, the challenge is to develop an adsorbent that has the following properties: high adsorption rate, low cost, high environmental stability and mechanical strength, which will improve the performance of chitosan in adsorption processes.

1.2 Objective

This research focuses on the adsorption of copper ions from contaminated water using PGCB.

1.2.1 Specific objectives

- a) To determine the best conditions for grafting of polyaniline onto chitosan beads.
- b) To characterize the chitosan beads and PGCB using analytical methods such as FTIR, XRD and SEM.
- c) To determine equilibrium and kinetic parameters of the PGCB.
- d) To compare the adsorption capacity of the PGCB with that of some other adsorbents.
- e) To use the copper loaded PGCB in desorption studies.

1.3 Research values

The grafting of polyaniline onto chitosan beads will contribute meaningfully towards the removal of copper ions from water and industrial effluents. Since excessive intake of copper ions is toxic and is a source of human carcinogen, there is need for this clean up technology. However, this new technology from creative ideas can increase and improve research in the department of chemical engineering.

1.4 Project Scope

This work covers the formulation of chitosan beads from chitosan flakes, the determination of best conditions for grafting of polyaniline onto chitosan beads and grafting of the beads in an attempt to enhance the removal of copper ions from contaminated water. It also covers characterization and adsorption/desorption studies. On this note it reports; introduction, problem statement, objective, research values. It also reports some of the adsorbents used treatment of contaminated water, characterization, physico-chemical properties of chitosan, modification of chitosan, reaction mechanism of chitosan, adsorption process and regeneration. Chapter one and two introduces and motivates this process.

Chapter three, deals with the experiment performed on; the formation of beads, determination of best condition for grafting of polyaniline onto chitosan beads, characterization of the beads and the discussion of the results obtained during the experiment

Chapter four covers, the experiment performed on; adsorption/desorption studies, and the discussion of the results obtained during the experiment. It also covers the use of model in explaining adsorption data. Chapter five deal with conclusions/recommendation.

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CHAPTER TWO

2.1 ADSORBENT

The usefulness of an adsorbent in adsorption process depends on the composition, type of functional groups present at the surface, degree of polarity, surface area and hydrophilicity. Adsorbent are solid material that are used as the adsorbing phase in adsorption processes. Most researchers have focused on adsorbent that are able to remove heavy metal ions at a very low cost. Bailey et al., (1999) reported that an adsorbent can be considered a low cost material if it requires little processing and it is abundant in nature. Hence cost is an important parameter when choosing an adsorbing material. Over the years quite a number of non conventional adsorbent have been used in the removal of copper ions from water and wastewater, such as activated carbon, zeolite, peat, chitin and chitosan (Zawani et al., 2009). These listed non conventional adsorbents are discussed below.

2.1.1 Activated carbon

Activated carbon is one of the earliest non conventional adsorbent used for numerous application including water treatment processes. Roa et al., (2006) used this adsorbent in the removal of copper ions from aqueous solution, were a maximum adsorption capacity of 20.8 mg/g was obtained from equilibrium studies. Activated carbon can be produced from a variety of raw materials such as coal, wood, nut shells cocoa-nut, and petroleum-based products. Two steps are involved in the activation process; firstly, the material is heated to a high temperature of 590°C in the absence of air, carbon and ash are left. Secondly, carbon is then activated by applying steam, air or carbon dioxide at higher temperature to increase the surface area (Rao et al., 2006). The adsorption qualities of the carbon produced is favored by the temperature involve, amount of oxygen present and the type of feedstock. Though activated carbon is an excellent adsorbent due to its strong affinity to organic compounds, its high cost limits the use in water treatment (Gaikwad, 2011).

2.1.2 Zeolite

Zeolite is a non conventional low cost adsorbent that can also be used to remove contaminant from water and wastewater. It is a porous aluminosilicate with different cavity structures. Their

structures are made up of three dimensional frameworks, having a negatively charged lattice and this charge is balance by cations in solutions. Zeolite consists of a number of species and the most abundant of them is clinoptilolite (Crini, 2005). This adsorbent have been studied extensively by researchers due to its ability of removing trace quantities of heavy metal ions from aqueous solution by making use of ion exchange phenomenon (Peri et al., 2004). One of the major limitations of using zeolite as an adsorbent is their low permeability, also the adsorption mechanism of zeolite is complex because of their porous structure and inner and outer charged surface (Calzaferri et al., 2000). The use of zeolite as an adsorbent in the removal of copper ions from contaminated water was reported by Ouki and Kavanagh, (1997). In his report the maximum adsorption capacity from equilibrium studies was found to be 5.10 mg/g.

2.1.3 Peat

Peat on the other hand, is also a non conventional low cost adsorbent used in the treatment of contaminated water. Peat is a porous and complex soil material with organic matter present in all the stages of organic breakdown and can be divided into four groups; herbaceous peat, woody peat, moss peat, and sedimentary peat (Crini, 2005). This adsorptive material that occurs naturally is cheap, readily available and produces high adsorption efficiency. Peat is compose of humic acid, lignin, cellulose, and fulvic, these composition possesses functional group that are polar such as ketones, alcohols, carboxylic acids that can be involve in chemical adsorption (Ho and Mckay, 1998).

Despite the fact that peat is used as an adsorbent, there are still some shortcomings that limit its application in adsorption processes such as high affinity for water and low mechanical strength (Crini, 2005). These limitations can be reduced by chemical pretreatment and the formation of immobilized biomass beads that can increase its adsorption efficiency. Over the years a great number of tests have been performed on the adsorption of copper ions using peat that has been pretreated. Yahya and Rosebi, (2010), reported that peat can be a good copper removal medium when it is treated with a suitable amount of hydrochloric acid. Chen et al., (1990), however reported the removal of copper ions from aqueous solution by peat. In his report the maximum adsorption capacity from equilibrium studies was found to be 19.6 mg/g.

2.1.4 Chitin and Chitosan

Among various adsorbents, chitin is the second most abundant organic material after cellulose. It occurs in marine invertebrates, especially in crustacean, mollusc's and also in insects, where it is a constituent of the exoskeleton, and in some fungi, where it is the principal fibrillar polymer in the cell wall. The constituent monosaccharide units in chitin (2-acetamido-2-deoxy-b-D-glucose) are linked together by β -(1 \rightarrow 4) glycosidic bonds. The structure of chitin constitutes a network of organized fibres and this structure has rigidity and resistance to organisms that contain it (Merzendorfer and Zimoch, 2003). Chitin is highly hydrophobic and is insoluble in water and organic solvents. It is soluble in hexafluoroisopropanol, hexafluoroacetone, chloroalcohols in conjugation with aqueous solutions of mineral acids and dimethylacetamide containing 5% lithium chloride (Kumar 2000). The use of chitin for copper ion removal from seawater was reported by Davila and millero (1989).

The removal of acetyl functional group present in chitin produces chitosan by a process called alkaline deacetylation of chitin. This acetyl group present in chitin can hinder the accessibility of metal ions to adsorption site. Chitosan contains 2-amino-2-deoxy-D-glucopyranose which is also linked together by β -(1 \rightarrow 4) glycosidic bonds. Owing to its unique characteristics such as antimicrobial activity, biocompatibility, non-toxicity and biodegradability, chitosan can be applied in many fields, such as wastewater treatment, pharmaceutical and medical applications, environmental protection, textiles, biotechnology, cosmetics, food processing and agriculture. However, in the manufacture of chitosan, flakes are normally obtained but this formulation is not efficient in adsorption processes due to its poor adsorption characteristics which may result to low adsorption capacity. To overcome this problem of poor adsorption performance, flakes are converted into chitosan beads. Chitosan bears two types of reactive groups which will enable the easy occurrence of graft copolymerization, namely; the amino group and the hydroxyl group. This polymer is soluble in dilute acids such as acetic acid and formic acid. The chemical structure of chitin and chitosan are shown in Figure 2.1 and 2.2 respectively.

Various studies on chitin and chitosan have been conducted over the years. Chen et al., (2008) reported that chitosan is more efficient than chitin in adsorption process due to the free amino groups present on chitosan chain. Moreover, the use of chitosan beads for the adsorption of copper (II) ions from contaminated water was reported by Wan et al., (2004). In his study, the

maximum adsorption capacity obtained from equilibrium studies was 33.4 mg/g. Findon et al., (1993), also investigated the adsorption of copper (II) using chitosan beads as an adsorbent, he reported 59 mg/g as the maximum adsorption capacity from equilibrium studies. The difference in maximum adsorption capacity from both studies may be attributed to; the degree of deacetylation, pH value and method of preparation of chitosan beads.

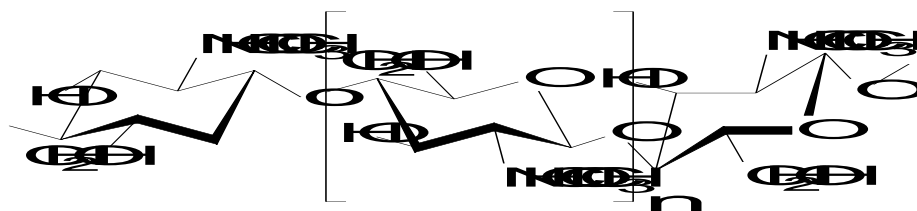


Figure 2. 1: Structure of chitin.

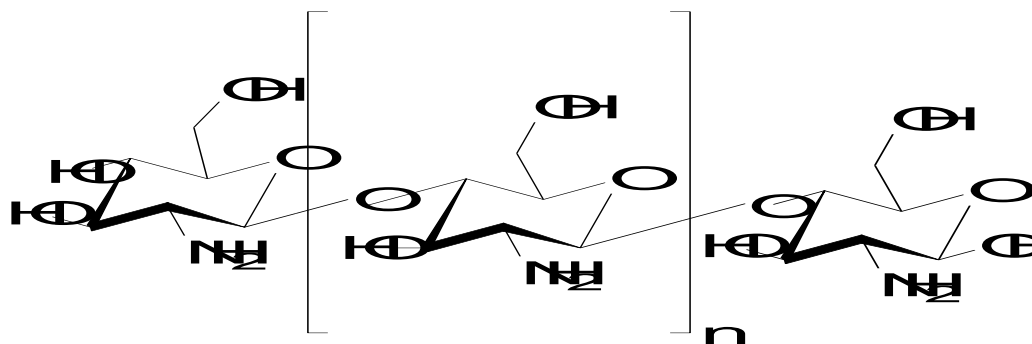


Figure 2. 2: The structure of chitosan.

2.1.4.1 Purification of Chitin and chitosan production

The exoskeleton of crustaceans such as shrimp and crabs constitutes the major sources of material for the preparation of chitin. Chitin is closely associated with proteins, an inorganic material which is mainly calcium carbonate (CaCO_3) pigments and lipids hydroxide (Inmaculada et al., 2009). Demineralization is one of the most frequently used methods in removing impurities present in chitin and demineralization is carried out by treatment with dilute hydrochloric acid (HCl) and deproteinization by treatment with sodium hydroxide (NaOH) (Inmaculada et al., 2009), but other methods may be used and the order in which these steps are carried out varies with different researchers, although in most instances deproteinization has been carried out prior to demineralization. The processing of crustacean shells mainly involves the removal of proteins and the dissolution of CaCO_3 which is present in crab shells at high

concentrations. The resulting chitin is deacetylated in 40% sodium hydroxide at 120°C for 1 to 5 h. This treatment produces 70% deacetylated chitosan (Kumar, 2000). Figure 2.3 gives a schematic representation of chitin and chitosan preparation from the basic raw material.

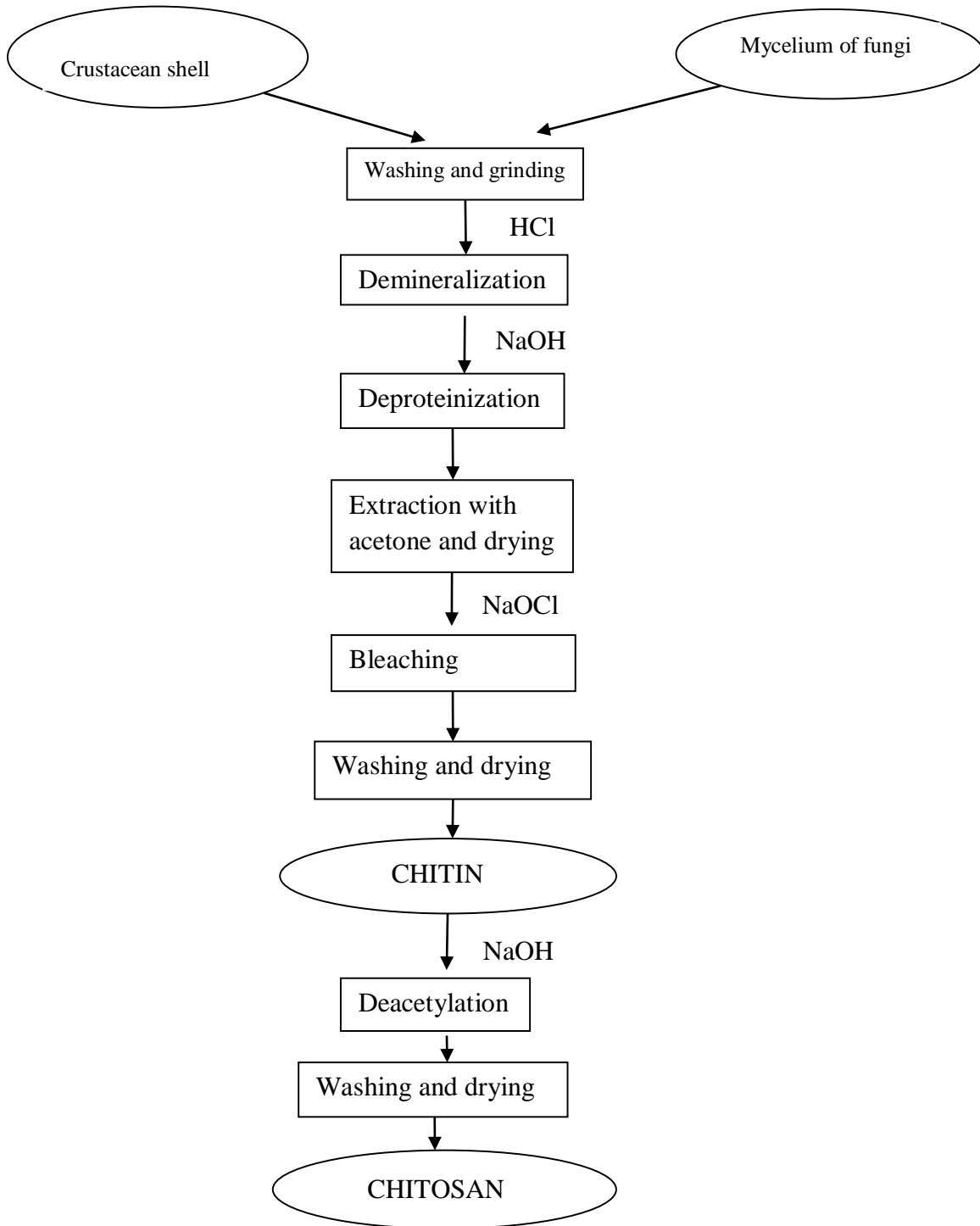


Figure 2. 3: Schematic representation of chitin and chitosan preparation from the basic raw material.

2.2 Physico-chemical properties of chitosan

Chitosan is a safe, non-toxic, biocompatible and biodegradable natural polymer, and is capable of forming chelates with many transitional metal ions such as copper. The physico-chemical properties of chitosan that could influence adsorption are; degree of deacetylation, molecular weight, solubility and crystallinity. They are therefore discussed below.

2.2.1 Degree of deacetylation

The major reaction carried out on chitin is deacetylation. In order to obtain a partially deacetylated chitin known as chitosan, thermal treatment in the presence of strong alkali conditions is needed (Inmaculada et al., 2009). Amino group (-NH₂) is left behind when acetyl functional group is removed from the molecular chain of chitin, this amino group is responsible for chitosan versatility and uniqueness during adsorption processes. The degree of deacetylation (DD) of chitin can be increased or decreased, for example, increase in temperature or strength of sodium hydroxide solution could enhance the removal of acetyl groups found in chitin, which results in a wide range of chitosan molecules with different properties and hence its applications (Hong and Samuel, 1995). Since the degree of deacetylation depends mainly on two important factors: the method of purification and reaction conditions, therefore, it is necessary to characterize chitosan before utilization (Pradip et al., 2004).

Various methods have been reported for the determination of the degree of deacetylation of chitosan. These methods include ninhydrin test (Mohammed, 2010), nuclear magnetic resonance spectroscopy (Shi-Hui et al., 2005), infrared spectroscopy (Delphine et al., 2004), Methods like nuclear magnetic resonance spectroscopy are too tedious, costly for normal analysis, or destructive to the sample as in the case of Ninhydrin Test. From literature, the DD values of chitosan appeared to be highly associated with the analytical methods employed.

2.2.2 Molecular weight

Chitosan is a bio-polymer of high molecular weight. The polymer weight may control the solubility of chitosan. Solubilisation can occur by protonation of the NH₂ group on the C₂

position of the D-glucosamine repeated unit (Rinaudo, 2006). The source of raw material and the method of preparation are basic factors in determining the molecular weight of chitosan. The average molecular weight of chitin is 1.03×10^6 KDa to 2.5×10^6 KDa but the N-deacetylation reaction reduces this to 1×10^5 KDa to 5×10^5 KDa (Pillai et al., 2009).

Stulik et al., (2003) reported the use of size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC), or gel filtration chromatography (GFC) for the study of molecular weight of synthetic polymers, biopolymers and natural polymers. To enhance the efficiency of separation, the smaller molecular weight components should enter the stationary phase. SEC is used to determine quantitatively the molecular weight differences between two lots of the polymers, or quantitatively determine the number, weight, and average molecular weight. Other detectors include differential refractive index (IR) and multi-angle light scattering (MALLS). With the IR detector, molecular weight is determined by standard curves generated with polymers of defined molecular weight. With the MALLS detector, molecular weight is determined directly based on light scattering.

2.2.3 Solubility

Chitosan is soluble in dilute acid solutions such as acetic acid, lactic acid, formic acid and hydrochloric acid at a pH below 6. However, the solubility of chitosan generally increases as the pH decreases. This is due to the fact that at a low pH the amino group of chitosan becomes protonated which results to a water-soluble cationic polyelectrolyte. Moreover, increasing the pH level to above 6 may result to the deprotonation of the amine group of chitosan (Domard and Domard, 2002). Chitosan solubility in acid solution is used to reduce its crystallinity by converting chitosan flakes to beads. This physical form of modification has been found to improve the adsorption kinetics and adsorption capacity of chitosan (Guibal, 2004).

2.2.4 Crystallinity

The three structural forms of chitosan; crystal, non-crystal and hydrated can be examined easily by measuring the X-ray diffraction pattern of a chitosan sample. The crystallinity of chitosan can control the accessibility of copper ions to adsorption site. Dissolving chitosan in acid solutions, formation of gel beads, and grafting has been considered the most convenient method of reducing its crystallinity (Guibal, 2004).

2.3 Modification of chitosan

Chitosan versatility allows the polymer to be easily modified in an attempt to change or enhance the properties of chitosan in adsorption. Modification of chitosan is of two types; namely, physical and chemical modification. Guibal, et al., (2004) reported that chitosan modification is a common way to regulate the reactivity of the polymer or increase the adsorption kinetics depending on the field of application.

Physically modified forms of chitosan include powders, nano particles, gel beads, sponge, honey comb and fibers or hollow fibers. (Juang et al., 2001; Wu et al., 2001; Calvo et al., 1997; Vincent and guibal, 2001; Amaike et al., 1998; Yoshida et al., 1993).

However, in these forms chitosan can only be soluble in dilute acid solutions and this limits its application. Therefore a number of chemical modification such as nitration, phosphorylation, sulphation, cross-linking and graft copolymerization have been developed to change its solubility properties in water or acidic solutions and to create additional adsorption site, thereby improving the target metal adsorption properties (Pengju et al., 2009). In this study, graft copolymerization method of modifying chitosan was applied due to the fact that graft copolymerization is anticipated to be quite promising for developing sophisticated material and can enlarge the field of the potential application of the polymer (Olteanu, 2007). Zohuriaan, (2005) also reported that graft copolymerization is expected to be one of the most promising approaches to a wide variety of molecular designs which will lead to novel types of hybrid materials, composed of natural polysaccharide and synthetic materials.

Graft copolymerization is the production of a branched macro-molecule with a high molecular weight backbone of one polymeric species, to which a second polymer is attached (grafted) at intervals. In a graft copolymerization reaction percentage (%) grafting and % efficiency are basic parameters used in determining the best conditions for grafting. These parameters are influenced greatly by reaction variables such as reaction temperature, reaction time, initiator type, monomer concentration, acid concentration and concentration of the adsorbent. Percentage grafting describes the amount of polyaniline grafted on the backbone of chitosan and percentage efficiency indicates the efficiency of conversion of aniline to polyaniline. In most cases of

application, the purpose of graft copolymerization is to improve adsorption. The grafting of new functional groups onto the backbone of chitosan has produced a great number of chitosan derivatives with the aim of increasing the adsorption capacity of chitosan. Li et al., (2005) used this method to improve the removal of mercury ions from contaminated water by grafting polyacrylamide onto chitosan beads. Holme and Hall (1991) reported the grafting of carboxylic functions onto chitosan backbone, as a way of increasing the adsorption properties of chitosan. Chang and Chen, (2005) prepared chitosan-bound Fe_2O_4 nano-particles by grafting Fe_2O_4 onto the backbone of chitosan as a magnetic adsorbent for the removal of copper ions and it was reported that the adsorption rate was fast and equilibrium was achieved within one minute due to absence of internal diffusion resistance.

One of the factors that can improve graft copolymerization is the type of initiator used during grafting and quite a number have been developed over the years, such as ammonium persulfate (APS), potassium persulfate (PPS) and ceric ammonium nitrate (CAN). (Pedram et al., 2000; Don et al., 2002; Caner et al., 1998). These initiators are responsible to initiate the grafting process. In most studies, ammonium persulfate (APS) was used as an initiator in the grafting reaction due to its low cost when compared to other initiators. Most of the reactions occur through free radicals and radiation to produce graft copolymer.

2.3.1 Grafting initiated by free radicals

In recent years, graft copolymerization of vinyl monomers onto chitosan using free radicals has attracted the interest of many researchers, owing to the fact that this technique enables the formation of new polymer materials with desired properties (High adsorption capacity, improved mechanical strength, environmental stability and low cost). Carbonylmethyl chitosan-grafted-methyl methacrylate (MAA) was prepared by using APS as an initiator in an aqueous solution; the effects of APS, MAA, reaction time and temperature on graft copolymerization were studied by determining the percentage grafting and grafting efficiency. It was observed that graft copolymerization is greatly influenced by the initiator concentration, monomer concentration, reaction time and temperature, and the material formed after grafting had a better water solubility property (Sun et al., 2003). Tiwari and Singh, (2007), prepared chitosan-grafted-polyaniline by reacting chitosan in aqueous acid solution with aniline using APS initiator as shown in Figure 2.4. They also reported that a chain mechanism is involved in polyaniline graft chitosan, due to

the formation of sulfate radicals which are known chain carriers for graft copolymerization. However, persulfate stimulates the polymerization of aniline through a medium of cationic radicals to produce free polyaniline and polyaniline radicals, chitosan macro radicals and polyaniline radicals then combine to form polyaniline graft chitosan.

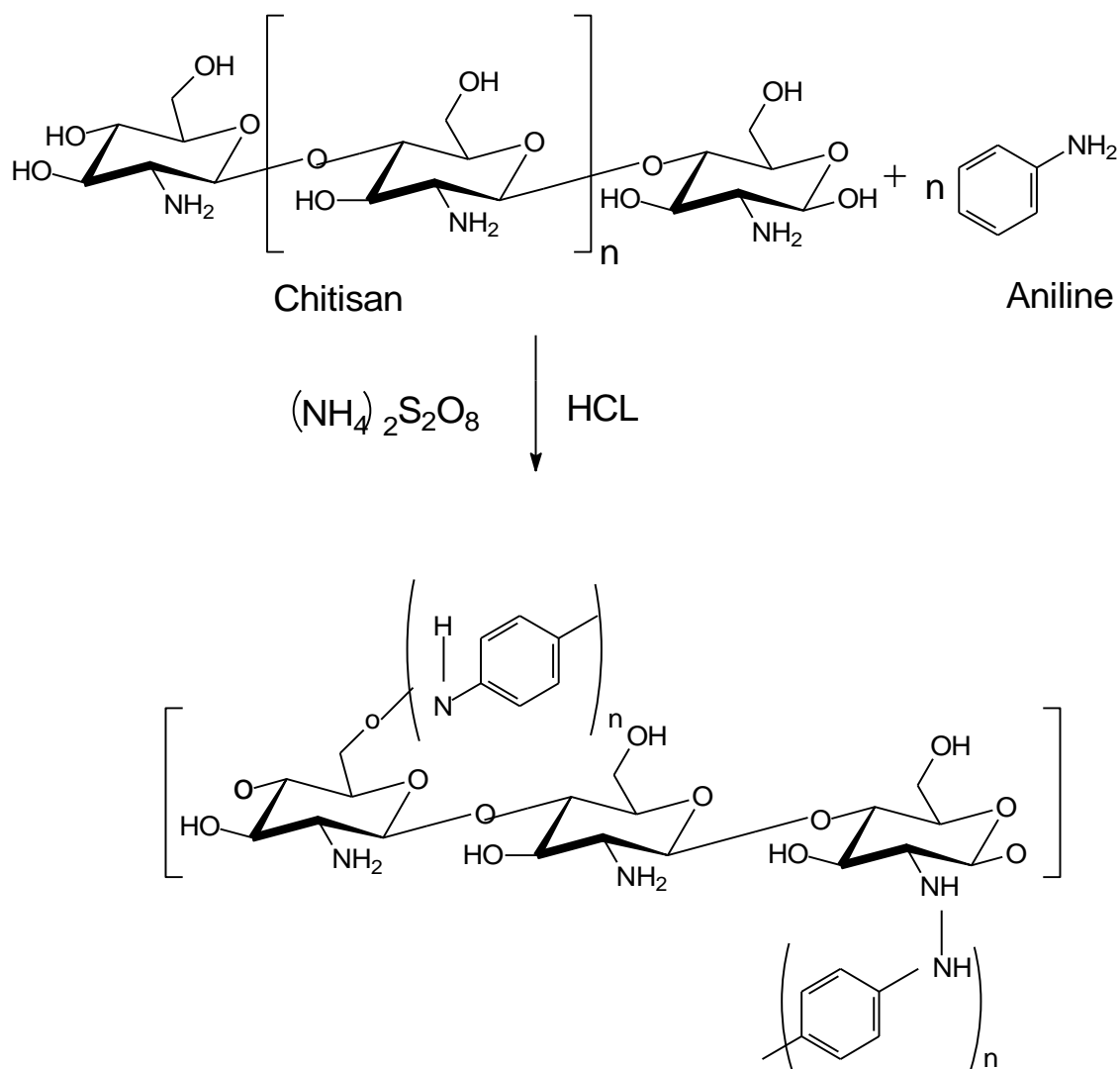


Figure 2. 4: Graft copolymerization of polyaniline onto chitosan.

Another method of carrying out graft copolymerization of vinyl monomer onto chitosan is by the use of redox initiator systems, such as ceric ammonium nitrate (CAN) and potassium persulfate (PPS). This procedure has been used by researchers to produce free radical sites onto many kinds of polymers. Vinyl acetate (VAc) was graft copolymerized onto chitosan by Don et al., (2002), using CAN initiator system in dispersion medium at 60°C. They observed that the monomer

conversion is between 70-80 % after 2 h of reaction. The experimental result showed that chitosan macromolecules not only took part in the graft copolymerization reaction but also served as a surfactant which provided the stability of the dispersed particles. Pedram and Retuert, (1996) carried out the modification of chitosan by grafting of vinyl pyrrolidone in a homogeneous phase using PPS as redox. The effect of reaction variables such as monomer concentration, initiator concentration, reaction time and temperature were studied extensively. The polymer formed after grafting was found to be insoluble in dilute organic and inorganic acids. This proves that the grafted chitosan has high hydrophobic characteristics when compared to the un-grafted. However, this hydrophobic characteristic of the grafted chitosan can expand the polymer network for easy diffusion of the target metal ions to adsorption site.

2.3.2 Radiation initiated grafting

In recent years, researchers have developed interest in the use of radiation as a method to graft natural polymers. An efficient method for initiating radical graft copolymerization onto polysaccharides is through the use of high energy radiation such as beta ray (β), gamma ray (γ) and X-ray. Pengfei et al., (2001) reported the grafting of polystyrene onto chitin and chitosan using ^{60}Co γ -irradiation at room temperature. The effect of reaction variables such as adsorbed dose, solvent and oxygen was studied. It was observed that oxygen delayed the reaction process but did not inhibit it completely and the grafting yield increased with increase in adsorbed dose.

Hegazy, (2012), however gave a report on the use of radiation initiated grafting in adsorption. In his study, acrylic acid was grafted onto non-woven polypropylene sheets using gamma rays as an initiator for the removal of Copper, nickel and cobalt from wastewater. He reported that the non-woven polypropylene sheets had strong affinity towards copper, nickel and cobalt.

2.4 Reaction mechanism of chitosan

Most authors agree that amine groups are the main reactive sites for metal ions, though hydroxyl groups especially in the C-3 position may contribute to adsorption of metal ions. These reactive groups may interact with metal ions through different mechanisms depending on factors such as the type of metal, the pH, and the matrix of the solution. The free electron doublet of nitrogen on amine groups is responsible for the adsorption of metal cations at pH near neutrality, and at lower pH value, where protonation of the amine group takes place; the polymer attains cationic

groups which can bind anions through electrostatic interactions (Guibal, 2004). However, the other mechanism reported by Guibal, (2004) in a review is the chelation of metal cations by ligands in solution and formation of metal anions, which turns the chelation of chitosan to an electrostatic attraction mechanism on protonated amine groups of the polymer. This mechanism is based on the theory of hard and soft acids and bases which defines the ability of ions to interact or enter into coordinate bonding with other ions or with ligands. However, some contradictory hypotheses have been proposed for the interpretation of uptake mechanisms. They can be classified in two groups; the bridge model and the pendant model. In the bridge model, metal ions are bound with several amine groups from the same chain or from different chains, through inter or intra-molecular complexation as opposed to the pendant model, in which the metal ion is bound to an amine group in a pendant trend. Whatever be the mechanism and way (chelation versus electrostatic attraction), the adsorption of a metal by chitosan depends on fraction of deacetylated units (free amine groups), polymer chain length, crystallinity, molecular weight, conditioning of polymers, physical form of chitosan, solution pH, type and concentration of the acid used for solution, composition of solution, metal ion selectivity and speciation. Moreover, of the free amino groups only some are accessible to metal binding, since some of these amine sites are involved in hydrogen bonds (Mourya et al., 2010). The chelation of copper ion may result in the formation of complexes with a release of hydrogen ion, as shown in figure 2.5.

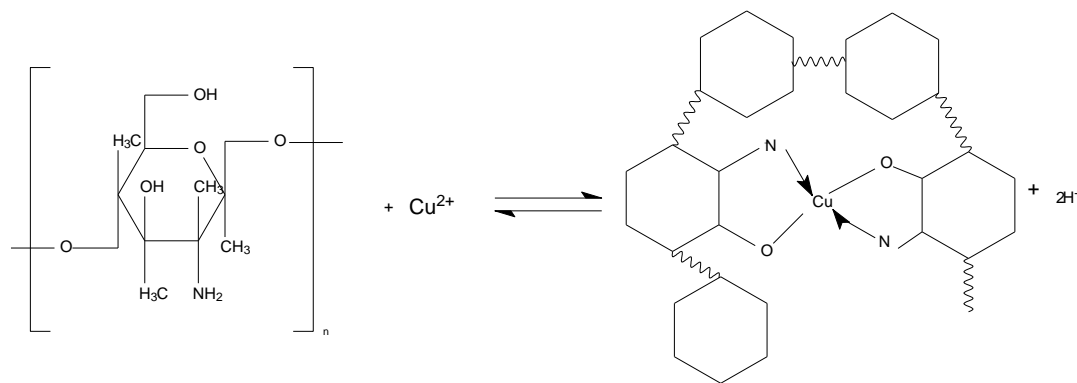


Figure 2. 5: Formation of chitosan chelates with copper ions binding with amino groups (Gerente et al., 2007).

2.5 Adsorption process

Adsorption is a process of attracting and retaining the molecules of a substance on the surface of a solid. Adsorption is termed mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase. Adsorption can occur on the outer surface of the adsorbent and in the macropores, mesopores, micropores, and submicropores. However, the surface area of the macro and mesopores is small compared with the surface area of the micropores and submicropores and the amount of material adsorbed there is usually considered negligible. Depending on the nature of force existing between adsorbate molecule (metal ion) and adsorbent, adsorption can be classified into two categories namely; physical adsorption (physisorption) and chemical adsorption (chemisorption). The characteristics of these two kinds of forces are given in Table 2.1.

Physical adsorption (physisorption) is due to operation of weak forces that exist between molecules, also known as vander waal's adsorption. The energy of interaction between the adsorbate and adsorbent has the same order of magnitude, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed. In this case, low temperature is favors adsorption. However, the physisorption decreases with increase temperatures. In physical adsorption, equilibrium is established between the adsorbate and the fluid phase resulting in multilayer adsorption. Physical adsorption is relatively non specific due to the operation of weak forces of attraction between molecules. The adsorbed molecule is not affixed to a particular site on the solid surface, but is free to move about over the surface. Physical adsorption is basically reversible in nature. In this case, the adsorbed species are chemically identical with those in the fluid phase, so that the chemical nature of the fluid is not altered by adsorption and subsequent desorption; as a result, it is not specific in nature (Mohammed, 2011).

Table 2. 1: Characteristics of Physical adsorption and Chemical adsorption.

| Physical adsorption | Chemical adsorption |
|---|---|
| Low heat of adsorption usually in the range of 20-40 KJ/mol | High heat of adsorption in the range of 50-400 kJ/mol |
| Force of attraction is Vander Waal's forces. | Forces of attraction are chemical bond forces. |
| It is reversible | It is irreversible |
| It is usually takes place at low temperature and decreases with increasing temperature. | It takes place at high temperature. |
| It is related to the case of liquefaction of the gas. | It is not related. |
| It forms multimolecular layers. | It forms monomolecular layers. |
| It does not require any activation energy. | It requires high activation energy. |
| High pressure is favorable. Decrease of pressure causes desorption | High pressure is favorable. Decrease of pressure does not cause desorption. |

Chemical adsorption (chemisorption) is also based on electrostatic force, in chemisorptions; the forces of attraction that exist between adsorbate molecules and adsorbent are most likely to be the same strength as chemical bonds. Therefore, the energy of chemisorption is considered like chemical reactions. It may be exothermic or endothermic processes ranging from very small to very large energy magnitudes. The elementary step in chemical adsorption often involves large activation energy. This means that the true equilibrium may be achieved slowly. However, a spontaneous process requires a negative free energy (ΔG) value, because, the translational freedom of the adsorbate is reduced when it is adsorbed (Mohammed, 2011).

2.5.1 Factors affecting the adsorption of Cu(II) ions

In general, the adsorption of metal ions is known to proceed through the following steps

- (I) Transfer of metal ions from bulk solution to adsorbent surface, which is usually mentioned as diffusion.

- (2) Migration of metal ions into pores.
- (3) Interaction of metal ions with available sites on the interior surface of pores.

Normally, the driving force for the adsorption process is the concentration difference between the metal ions in the solution at any time and metal ions in the solution at equilibrium (C_0-C_e) (Mohammed, 2011). However, there are some important factors affecting adsorption and these factors are discussed below.

2.5.1.1 Solution pH

The pH of a solution is an important parameter that affects the rate of copper ion removal, because it affects the solubility of the metal ions, concentration of counter ions on the functional groups of the adsorbent and the degree of ionization of the metal ions during reaction. Adsorbent has active sites capable of binding metal ions thus it is regarded as a complex ion exchanger similar to a commercial resin. Such bond formation could be accompanied by displacement of protons and is dependent in part on the extent of protonation which is determined by the pH (Karthika et al., (2010).

However, various investigations have been going on over the years to determine the effect of pH on adsorption. Popuri et al., (2009) investigated the effect of pH on adsorption of nickel (II) and Copper(II) ions by chitosan coated polyvinyl chloride beads, at a pH range of 1 to 6. The results indicated that maximum uptake of Cu(II) took place at pH 4 while the maximum uptake of Ni(II) took place at pH 5. This observation was attributed by the workers to increased concentration of hydrogen ions at lower pH which compete along with Cu(II) and Ni(II) ions for binding sites.

Moreover, Tumin et al., (2008) conducted a study on the effect of pH on the removal of Cu(II) by activated carbon at a pH range of 2 to 8. It was observed from the study that the uptake of Cu(II) increased appreciably from pH 2 to 6, further increase in pH led to a decrease in the adsorption capacity. This observation was attributed to the fact that at lower pH values the surface of the adsorbent is surrounded by hydrogen ions, thereby preventing Cu(II) ions from approaching binding sites of the adsorbent, and as the pH is increased slightly up to pH 6 more negatively charged surface becomes available, facilitating greater copper removal. Increasing the pH value above pH 6 resulted in the decrease in adsorption capacity, and this observation was reported to be due to the occurrence of copper precipitation.

2.5.1.2 Contact time and initial concentration

The time it takes Cu(II) ions to reach equilibrium is of great importance in adsorption experiment because it depends on the system used. Consequently, it is important to establish the time dependant of such system under various process conditions (Chiban et al., 2012).

The effect of contact time on Cu(II) ions removal by activated carbon was investigated upon at various initial concentration by Arivoli et al., (2011). They reported that percentage removal of Cu(II) ions decreased with increase in initial Cu(II) ions concentration, but the actual amount of Cu(II) ions adsorbed per unit mass of carbon increased with increase in metal ion concentration. This means that adsorption is highly dependent on the initial Cu(II) concentration. This observation was attributed to the fact that at lower concentration, the ratio of the initial number of Cu(II) ions to the available surface area is low, subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available site of adsorption becomes fewer and hence percentage of removal of copper ions is independent upon initial concentration. They also reported that equilibrium was established at contact time 60 minutes at all concentrations.

2.5.1.3 Temperature

Among the process parameters frequently investigated in the literature, temperature is shown to affect adsorption capacity. When adsorption capacity increased with temperature, the process is termed endothermic, and when adsorption capacity decreases with temperature the process is called exothermic. The thermodynamic parameters present the essential parameters for subsequent engineering evaluation on the ultimate uptake of the adsorbents, and, hopefully, also provide insights to the adsorption mechanisms thus applied for further use in process modification and optimization (Chiban et al., 2012). However, with respect to the relationship between temperature and adsorption capacity. Han et al., (2006) stated that the increasing adsorption capacity of the adsorbent with temperature is attributable to the enlargement of pores and or the activation of the adsorbent surface.

Moreover, Ho and Ofomaja (2006) investigated the effect of temperature on adsorption capacity of copper ion onto palm kernel fiber at a temperature range of 299 to 399 K. The result obtained from the investigation showed increase in adsorption capacity of copper ion as the reaction temperature is increased from 299 to 399 K. This observation was attributed by the workers to; increased mobility of copper ion as the temperature rises. They also reported that the reaction of copper ions and surface functional groups is enhanced by increased temperature of reaction, and that the trend (increase in adsorption capacity with increase in temperature) suggests that a chemisorption reaction or an activated adsorption between copper ions and functional groups on palm kernel fibre surface involving valences forces through sharing or exchange of electrons between palm kernel fibre and copper ions occurs.

2.5.2 Adsorption Isotherms

Adsorption Isotherms gives a description of how metal ions interact with adsorbents and are important in optimizing the use of adsorbents (Li and bai, 2005). Adsorption isotherms are the basic requirement for the design of an adsorption system; in other to optimize the design of an adsorption system it is important to establish a correlation that is appropriate for the equilibrium adsorption curve. In any given system an accurate mathematical analysis of equilibrium adsorption capacity is necessary for prediction of adsorption parameters. Over the years, a number of isotherm models have been developed to analyze experimental data, such as Langmuir, Freundlich, Bet, Toth, Temkin, Redlich, Peterson, Sips, Frumkin, Harkins-Jura, Halsey, Henderson and Dubinin-Radushkevich isotherms (Oubagaranadin et al., 2007). However, the most frequently used isotherm models applied in a solid/liquid system are the Langmuir and Freundlich model (Madhukar and Mahajan, 2011).

2.5.2.1 Langmuir model

The Langmuir model is the most popular model commonly used in describing adsorption isotherms. It explains descriptively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and no further binding takes place once a saturation value is reached (Zawani, et al., 2009). This model is based on the fact that every adsorption site is identical and energetically equivalent, and assumes that the adsorption occurs at specific homogeneous sites

on the adsorbent and this is used successfully in monolayer adsorption processes (Hena, 2010). This model is described in the non-linear and linear form in equations 2.3 and 2.4 respectively.

$$q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (\text{Non-linear form}) \quad (2.3)$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \quad (\text{Linear form}) \quad (2.4)$$

Where C_e is the equilibrium concentration (mg/l) and q_e the amount adsorbed at equilibrium (mg/g). The Langmuir constant Q_m (mg/g) represent the maximum adsorption capacity and b (l/mg) relates to the rate adsorption. Higher values of b indicate much stronger affinity of metal ion adsorption. (Mohammed, 2011).

2.5.2.2 Freundlich model

The empirical Freundlich isotherm is based on the equilibrium relationship between heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption (Ola, 2007). This model is described in the non-linear and linear form in equations 2.5 and 2.6 respectively.

$$q_e = K_f C_e^{1/n} \quad (\text{Non-Linear form}) \quad (2.5)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (\text{Linear form}) \quad (2.6)$$

K_f and n of the Freundlich model are constant representing the adsorption capacity and adsorption intensity respectively. Under normal adsorption conditions, the values of n should be in the range of 1 to 10 (Liu et al., 2011).

2.5.3 Thermodynamic parameters of adsorption

When designing an adsorption system the designer should put into consideration the change in the reaction and this change requires an idea of thermodynamics. The original ideal of thermodynamics is based on the assumption that in a system that is kept isolated, where energy cannot be gained or lost to the surroundings, the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order

to decide what processes will occur spontaneously (Ho and Ofomaja, 2005). The entropy and enthalpy change, associated with the process can be calculated from equation 2.7.

$$\ln K = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2.7)$$

The Gibbs free energy change, ΔG° , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity (Ho and ofomaja, 2005). The free energy of the adsorption reaction, considering the adsorption equilibrium constant, K, is given by equation 2.8.

$$\Delta G^\circ = -RT \ln K \quad (2.8)$$

Putting the relationship between free energy change and equilibrium constant (K) into consideration. The change in K with temperature can be obtained in the differential form in equation 2.9.

$$d \ln K = \frac{\Delta H^\circ}{RT^2} \quad (2.9)$$

On integrating, the integrated form of equation 2.9 is shown in equation 2.10.

$$\ln K = \frac{\Delta H^\circ}{RT} + Y \quad (2.10)$$

Where Y is a constant. Equation 2.11 is obtained from rearranging equation 2.10

$$-RT \ln K = \Delta H^\circ + RTY \quad (2.11)$$

Assuming,

$$\Delta S^\circ = RY \quad (2.12)$$

Substituting equations (2.8) and (2.12) into equation (2.11), ΔG° becomes

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.13)$$

The equilibrium constant 'K' as defined mathematically by Liu et al., (2011) is given in equation 2.14.

$$K = \frac{q_e}{C_e} \quad (2.14)$$

Where q_e is amount of copper ions adsorbed on the adsorbent in mg/g and C_e is the equilibrium concentration in mg/l. The gas constant R is defined by 8.3145 J/mol. K; T is the temperature of the solution in Kelvin; ΔS° is the entropy change while ΔH° is the enthalpy change. ΔH° and ΔS° can be calculated from the slope and intercept of a plot of $\ln K$ as a function of $1/T$.

2.5.4 Kinetic studies

An ideal adsorbent for the removal of heavy metal ions should not only have a large adsorbate loading but a fast rate of adsorption also (Madhukar and Mahajan, 2011). Adsorption kinetics describes how fast the chemical reaction occurs and also gives information on the factors affecting the rate of reaction. Most studies apply the pseudo-first order kinetics of lagargren, (1898), and the pseudo-second order kinetic model that was introduced by Ho and McKay, (1998), to describe kinetic data. These models are used to analyze the controlling mechanism of adsorption process.

A kinetic model for the adsorption analysis that is proceeded by diffusion through a boundary will most likely follow the pseudo-first order equation of lagargren (Ofomaja et al., 2010).

$$\frac{dq}{dt} = K_1(q_e - q) \quad (2.15)$$

Where q_e and q_t represents the amount of copper ions absorbed on the adsorbent (mg/g) at equilibrium and time t , respectively. K_1 is the rate constant of the pseudo-first order kinetics. Considering the initial conditions of $q_t = 0$ at $t = 0$, the integrated rate law will follow the linearized form in equation (2.16).

$$\log(q_e - q_t) = \log(q_e) - t \frac{K_1}{2.303} \quad (2.16)$$

The value of adsorption rate constant, K_1 can be calculated from the straight line plot of $\log(q_e - q_t)$ versus t .

The pseudo-second order chemisorptions kinetic is expressed in is non-linear form in equation (2.17)

$$\frac{dq}{dt} = K_2(q_e - q)^2 \quad (2.17)$$

Where K_2 is the rate constant for a pseudo-second order model and the definitions of q_e and q_t remains the same.

Separating the variables in equation (2.17) gives:

$$\frac{dq}{(q_e - q)^2} = K_2 dt \quad (2.18)$$

Integrating with respect to the boundary conditions $t=0$ to $t=t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \quad (2.19)$$

Equation (2.19) is the integrated rate law for a pseudo-second order kinetic model, and can be rearranged to obtain:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (2.20)$$

The slope and intercept of the linear plot of t/q versus t , gives the values of q_e and K_2 respectively.

2.5.5 Error analysis

The Chi-square test is a non-linear method of describing experimental data besides the linear coefficient of determination (R^2). The Chi-square statistic is the sum of the squares of the differences between the experimental data and data obtained by calculating from models, divided by the corresponding data obtained by calculating from models (Ho and Ofomaja, 2005). This is expressed mathematically in Equation 2.21.

$$\chi^2 = \sum \frac{(q_{e(Exp)} - q_{e(Cal)})^2}{q_{e(Cal)}} \quad (2.21)$$

Where $q_{e(Exp)}$ (experimental q_e) is the amount adsorbed at equilibrium in mg/g and $q_{e(Cal)}$ (calculated q_e) is the calculated amount from the kinetic model. If the data from the model is similar to the experimental data, χ^2 will be a smaller number and if they are different, χ^2 will be a bigger number. It is therefore necessary to analyze the data set on the non-linear Chi-square test to confirm the best-fit kinetic model for adsorption system.

However, in the case of the linear correlation coefficient method of determining best fit data, the nearer R^2 value is to one the more the best fit of experimental data will be to the model equation.

2.6 Regeneration

Metal recovery from loaded sorbent is important for proper disposal and also for the re-use of the sorbent. One of the major advantages of using chitosan as an adsorbent is the ease of recovery of adsorbed metal ions. Adsorbent re-use helps keep the process cost down and for this reason it is necessary to desorb the sorbed pollutant metal ions and to regenerate the adsorbent for another cycle of use. However, due to biodegradability characteristic of chitosan, it may not undergo continuous recycling (Crini, 2005)

The mechanism of adsorption involve in the uptake of metal ion can provide an orientation for the design of the desorption strategy (Volesky, 2001). Since pH is an important factor in metal binding, a change in pH can allow the metal to desorb, using the appropriate eluent for the desorption process is necessary in order to ensure the undiminished adsorption performance of the chitosan beads that was regenerated. Li et al., (2005), reported the uses of eluents such as hydrochloric acid, and nitric acid and perchloric acid for desorption of mercury, in his report the percentage desorption were above 96% for each eluent used. However, wankasi et al., (2005) also gave a report on desorption of copper ions from nipa palm using hydrochloric acid as eluant. In his report copper showed an increase rate of desorption as contact time was increased, and maximum desorption percentage of 63.7% was attained at time 140 min. They also reported that a 100% desorption can be achieved if the contact time is increased.

2.7 Conclusion

A critical study of relevant literature proves that chitosan has the ability to remove copper (II) ions from water and wastewater. The transformation of chitosan flakes to beads is necessary for ease of handling and easier diffusion to sites responsible for adsorption. It is generally believed that the amine group is responsible for metal adsorption. After grafting, more amine group is produced on the backbone of chitosan beads which eventually increase the adsorption performance of chitosan based material. However, it is possible to recycle chitosan beads and to regenerate the adsorbed metal ions for effective disposal so as to avoid second pollution.

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CHAPTER 3

3.1 INTRODUCTION

This section covers the conversion of chitosan flakes to beads, determination of best conditions for grafting polyaniline onto chitosan beads, characterization of the beads and the discussion of the results obtained during the experiment.

However, the conversion of flakes to beads is a physical form of modification which is essential for easy handling and easier diffusion to adsorption site. Determination of best conditions is expected to provide favorable conditions for grafting of polyaniline onto chitosan beads. The experimental data is presented in Appendix A (Table A-1 to A-6). % grafting and % efficiency were parameters applied in determining such conditions. The analytical techniques applied in this study are; Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) and scanning electron microscopy (SEM), and is expected that these techniques will provide evidence that polyaniline was successfully grafted onto chitosan beads.

3.2 Experimental

3.2.1 Materials

The chitosan flakes with average molecular weight 400kDa and a degree of deacetylation of 74% was obtained from Labchem (pty) Ltd. Chitosan flakes were used to prepare the beads. Aniline (99.5%, extra pure) was purchased from AEC AMERSHAM (PTY) LTD, and was used without any further purification. Ammonium persulfate (>98%), ethanol (>99%), hydrochloric acid (99%), 1-Methyl-2-pyrrolidinone (>99%), sodium hydroxide (>99%), acetic acid (>99%) were all purchased from Sigma-Aldrich.

3.2.2 Formation of chitosan beads

Chitosan beads were prepared by the method applied by Rorrer *et al.*, (1993). Chitosan solution was made by dissolving 75.3 g of chitosan flakes in 1 L of 3.0% (v/v) acetic acid solution. A polystyrene sieve with a mesh size of 100 μ m was used to remove impurities from the dissolve chitosan solution.

The filtrate was pumped with a peristaltic pump (Watson Marlow 313S) through a 140 mm glass pipette with a 25 mm long capillary tip, having an inner diameter of 0.9 mm, into 2 L of a prepared 1.0 M NaOH solution. A regulating nub in the peristaltic pump was used to control the rate at which the chitosan solution passes through the capillary tip. The formation of gel beads is said to take place when the chitosan solution comes in contact with the sodium hydroxide solution. The produced beads and aqueous sodium hydroxide solutions were continuously stirred with a magnetic stirrer for 12 h, after which the beads were washed with dionized water to obtain a constant neutral pH. Figure 3.1 shows a schematic experimental set-up for the production process.

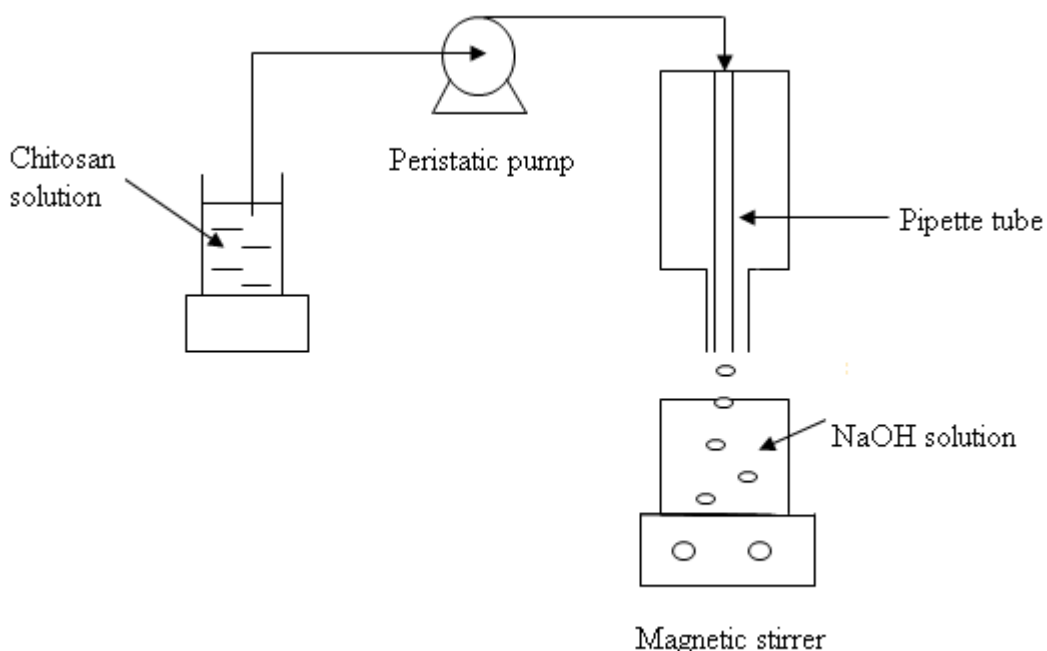


Figure 3. 1: Set-up for the production of chitosan beads.

3.2.3 Determination of best conditions for grafting polyaniline onto chitosan beads

In an attempt to determine the best conditions for grafting polyaniline onto chitosan beads, reaction variables such as chitosan concentration, aniline concentration, acid concentration, initiator concentration, reaction temperature and contact time were varied under certain range of values; chitosan concentration [0.45-1.50] g/l, aniline concentration [0.05-0.3] g/l, acid concentration [0.1-0.4] g/l, initiator concentration [0.20-0.35] g/l, reaction temperature [25-40] °C and contact time [30-120] min. The amount of polyaniline grafted onto chitosan beads and

efficiency of conversion of aniline onto polyaniline were calculated from the increase in weight of the chitosan beads, based on % grafting and % efficiency as given by Sun et al., (2003). These equations are shown in equations 3.1 and 3.2.

$$\%Grafti[\%G]=\frac{W_1-W_0}{W_0}\times 100 \quad (3.1)$$

$$\%Efficiency[\%E]=\frac{W_1-W_0}{W_2}\times 100 \quad (3.2)$$

Where W_1 , W_0 and W_2 denote, respectively, the weights of PGCB, chitosan beads, and monomer charged respectively.

In determining the best conditions, one variable was varied while others are fixed or kept constant. This experimental procedure is described as follows;

3.2.3.1 Effect of contact time

0.45 g/l of chitosan beads and 0.1 g/l of aniline were transferred into a series of 200 mL round-bottom flask containing 0.1 g/l HCl, and content was continuously stirred by a magnetic stirrer. After 30 minutes, 0.35 g/l of ammonium persulfate was added to each of the flask, and this was taken as zero time (30 minutes stirring time was not added to the grafting time). Grafting time was set at 30, 60, 90 and 120 min respectively for each of the four flasks, and at a temperature of 25°C. The PGCB was washed with N-methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer was rinsed with distilled and oven dried for one hour at a temperature of 50°C. Percentage grafting and % efficiency were calculated by the equation in 3.1 and 3.2 respectively.

3.2.3.2 Effect of Aniline concentration

Aniline concentration at various values of 0.05, 0.1, 0.2 and 0.3 g/l was transferred into a series of 200 mL round-bottom flask containing 0.1 g/l HCl. Subsequently, 0.45g/l of chitosan concentration was added to each of the four flasks, and content was continuously stirred by a magnetic stirrer. After 30 minutes, 0.35 g/l of ammonium persulfate was added to the reactive mediums and this was taken as zero time (30 minutes stirring time was not added to the grafting time). Grafting was allowed to take place for an hour at 25°C. The PGCB was washed with N-

methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer was rinsed with distilled and oven dried for one hour at a temperature of 50°C. Percentage grafting and % efficiency were calculated by the equation in 3.1 and 3.2 respectively.

3.2.3.3 Effect of Initiator concentration

0.45 g/l of chitosan beads and 0.1 g/l of aniline were transferred into a series of 200 mL round-bottom flask containing 0.1 g/l HCl, and content was continuously stirred by a magnetic stirrer. After 30 minutes, various concentrations consisting of 0.20, 0.25, 0.30 and 0.35 g/l ammonium persulfate were added to each of the four flasks respectively, and this was taken as zero time (30 minutes stirring time was not added to the grafting time). Grafting was allowed to take place for an hour at 25°C. The PGCB was washed with N-methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer was rinsed with distilled and oven dried for one hour at a temperature of 50°C. Percentage grafting and % efficiency were calculated by the equation in 3.1 and 3.2 respectively.

3.2.3.4 Effect of chitosan concentration

Chitosan concentration at various values of 0.45, 0.90, 1.25 and 1.50 g/l was transferred into a series of 200 mL round-bottom flask containing 0.1 g/l HCl. Subsequently, 0.1 g/l of aniline concentration was added to each of the four flasks, and content was continuously stirred by a magnetic stirrer. After 30 minutes, 0.35 g/l of ammonium persulfate was added to the reactive mediums and this was taken as zero time (30 minutes stirring time was not added to the grafting time). Grafting was allowed to take place for an hour at 25°C. The PGCB was washed with N-methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer was rinsed with distilled and oven dried for one hour at a temperature of 50°C. Percentage grafting and % efficiency were calculated by the equation in 3.1 and 3.2 respectively.

3.2.3.5 Effect of acid concentration

0.45 g/l of chitosan beads and 0.1 g/l of aniline were transferred into a series of 200 mL round-bottom flask containing various acid concentrations of 0.10, 0.20, 0.30 and 0.40 g/l HCl respectively, and content was continuously stirred by a magnetic stirrer. After 30 minutes, 0.35 g/l ammonium persulfate was added to each of the four flasks respectively, and this was taken as

zero time (30 minutes stirring time was not added to the grafting time). Grafting was allowed to take place for an hour at 25°C. The PGCB was washed with N-methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer was rinsed with distilled water and oven dried for one hour at a temperature of 50°C. Percentage grafting and % efficiency were calculated by the equation in 3.1 and 3.2 respectively.

3.2.3.6 Effect of temperature

0.45 g/l of chitosan beads and 0.1 g/l of aniline were transferred into a series of 200 mL round-bottom flask containing 0.40 g/l HCl respectively, and content was continuously stirred by a magnetic stirrer. After 30 minutes, 0.35 g/l ammonium persulfate was added to each of the three flasks respectively, and this was taken as zero time (30 minutes stirring time was not added to the grafting time). Grafting was allowed to take place for an hour at temperatures of 25, 35 and 45°C for each of the flasks. The PGCB was washed with N-methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer was rinsed with distilled water and oven dried for one hour at a temperature of 50°C. Percentage grafting and % efficiency were calculated by the equation in 3.1 and 3.2 respectively.

3.2.4 Characterization of the beads

3.2.4.1 Infrared measurement

This technique is used to obtain an infrared spectrum of absorption, photoconductivity and emission of a solid, liquid or gas. An FTIR spectrometer collects data in a wide range of spectral. The aim of any absorption spectrum is to measure how well a sample adsorbs light at each wavelength. This method is used mainly to identify bonds, structures, and functional group in organic and inorganic compounds. It can be used for both qualitative and quantitative analysis in identifying molecules, compounds, and to determine the presence or absence of some types of bonds and functional groups. For example: nitrogen-hydrogen (N-H), carbon-hydrogen (C-H), nitrogen-oxygen (N-O), and oxygen-hydrogen (O-H). IR spectra can also identify the positions in which the functional groups are attached. The reason is that vibration frequencies differ when functional group are attached at different sides in molecules and when illuminated by IR radiation the functional groups will vibrate and energy will be absorbed. Each bending and

stretching vibration mode of a functional group will adsorb at a particular frequency (Dinger, 2005).

Approximately 0.45 g Chitosan beads and PGCB was separately weighed, oven dried overnight at 60°C and blended to its powdered form. The blended beads were measured with a shimadzu FTIR, model 8300 (Kyoto, Japan).

3.2.4.2 XRD measurement

X-ray diffraction analysis is method by which multiple beams of X-ray create a three dimensional picture of the density of electrons of any crystalline structure. The primary purpose is to examine the crystalline nature of solids such as ceramics, metals, geological materials, electronic materials, organics and polymers. These materials may exist in powders, single crystals, multilayer crystals, thin films and sheet depending on the individual requirement. The theoretical basis of X-ray diffraction stands on Bragg's equation and is given by equation 3.3.

$$n \lambda = 2d \sin \Theta \quad 3.3$$

Where n is the order of reflection and n can be any positive integer (1, 2, 3, 4, 5.....), λ is the wavelength, d is the distance between parallel lattice planes and Θ is the angle of incident beam, this angle is also known as Bragg's angle.

Approximately 0.45 g Chitosan beads and PGCB was separately weighed, oven dried overnight at 60°C and blended to its powdered form. The blended beads were measured with a shimadzu XRD, model 7000.

3.2.4.3 SEM measurement

This is an electron microscope that produces images of a sample by scanning it with a beam of electron. SEM is commonly used in studying structure, surfaces, morphologies and forms of material. This analysis is conducted in a vacuum environment and all non-conductive samples must be coated with electrically conductive coatings such as gold and carbon before they can be observed in SEM (Dinger, 2005).

Approximately 0.45 g Chitosan beads and PGCB was separately weighed and bisected in order to get a clear vision of the inner fibres. The bisected beads were coated with gold and measured with a Jeol 733, superprobe.

3.3 Results/discussion

3.3.1 Determination of best conditions for grafting polyaniline onto chitosan beads

3.3.1.1 Effect of contact time

In Figure 3.2, % grafting and % efficiency increased with increase in contact time from 30 min to 60 min and decreased thereafter. At contact time of 30 min, 60 min, 90 min and 120 min, the % grafting and % efficiency were 70.2%, 90.5%, 70.2%, 55% and 48.8%, 60.1%, 48.8%, 42.5% respectively. The best grafting condition was attained at time 1 h with % grafting and % efficiency as 90.5% and 60.1% respectively. This observation is due to the fact that at the initial stage there was more active site available for grafting and the decrease that was observed from contact time 60 min to 120 min may be due to the reduction in free radicals available for grafting. This reduction in free radicals during the reaction terminated the grafting chains at time 60 min, thereby causing a decrease in % grafting and % efficiency with increase of time. In an earlier study by Mishra et al., (2008), on the effect of time on graft copolymerization of vinyl formamide onto chitosan using a time range of 60 min to 180 min. Maximum % grafting and % efficiency were obtained as 95.8% and 70.7% at contact time of 60 min, after which it experiences a decrease. However, this finding is in contrast to the report presented by Ibrahim et al., (2012) on the effect of reaction period (time) on graft copolymerization of methyl methacrylate onto oil palm empty fruit bunch fiber. In his report % grafting maintained the same level from time 2 h with a value of 220.6% while % efficiency had a decrease at time 90 min with a maximum of 50%.

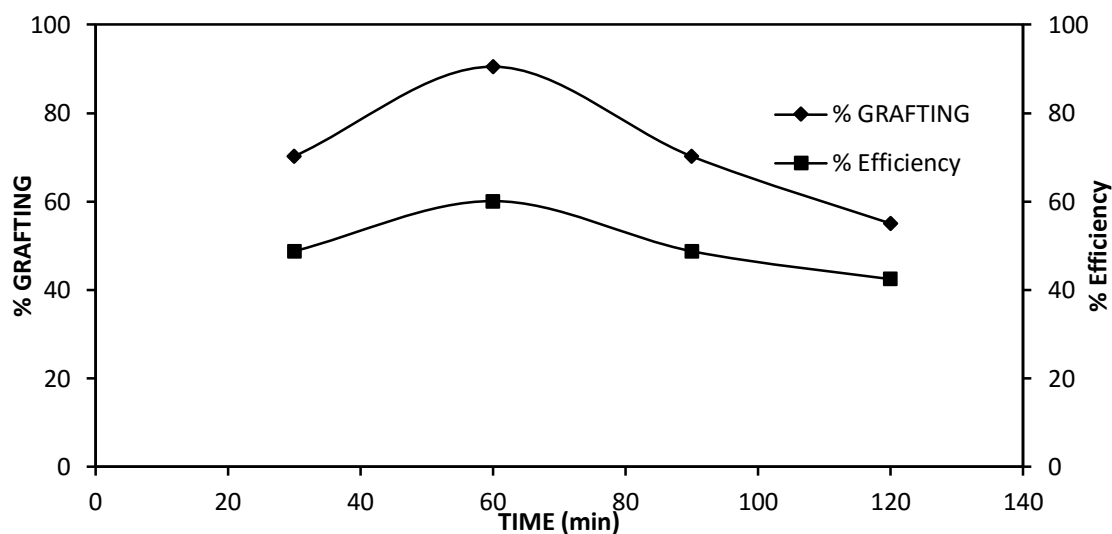


Figure 3. 2: The effect of time on graft copolymerization at fixed concentration of chitosan (0.45 g/l), ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.1 g/l), at 25°C.

3.3.1.2 Effect of aniline concentration

Figure 3.3 shows the result obtained in varying the aniline concentration. At aniline concentrations of 0.05 g/l, 0.1 g/l, 0.2 g/l, 0.3 g/l, the corresponding % grafting and % efficiency were 90%, 110%, 90.7%, 60.2% and 60.1%, 67.8%, 60.1%, 45.3% respectively. The best aniline concentration was found to be 0.1 g/l with % grafting and % efficiency of 110% and 67.8% respectively. Findings may be attributed to the availability of active site in the chitosan backbone at the initial stage and the decrease may be due to the termination of grafting chain which prevents the diffusion of ammonium persulfate for further grafting. Khullar et al., (2008) gave a similar report in which there was an increase in % grafting and % efficiency, reaching a maximum value of 168.3% and 95.8% respectively, thereafter it experiences a decrease. Tiwari and Sighn (2007) also gave a similar finding on the effect of aniline concentration on graft copolymerization of polyaniline onto chitosan, in his report, maximum % grafting and % efficiency was obtained as 180% and 84% after which it start to decrease.

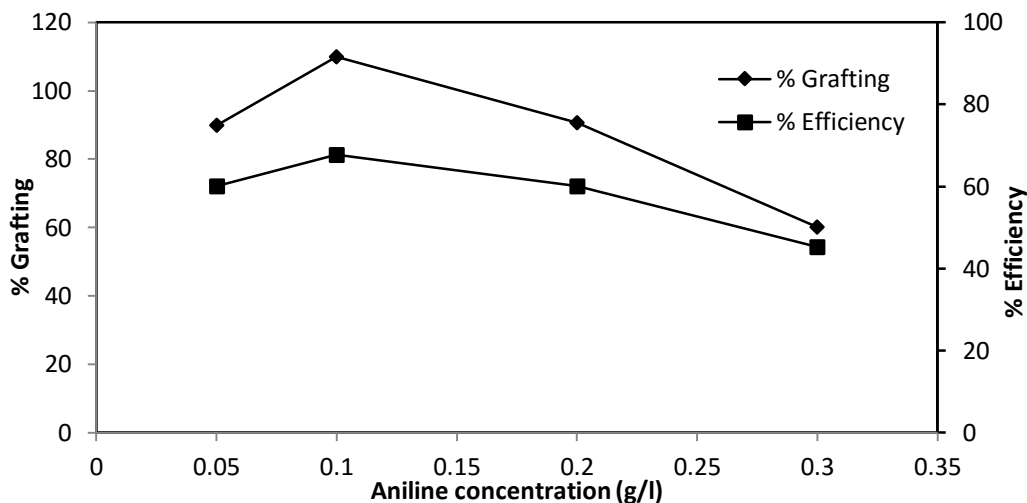


Figure 3. 3: The effect of aniline concentration on graft copolymerization at fixed concentration of chitosan (0.45 g/l), ammonium persulfate (0.35 g/l), HCl (0.1 g/l), for 1 h at 25°C.

3.3.1.3 Effect of initiator concentration

Figure 3.4 gives the result obtained in varying the initiator concentration. Increasing the initiator concentration at various values of 0.2 g/l, 0.25 g/l, 0.30 g/l, 0.35 g/l gave a corresponding increase in % grafting and % efficiency as 115%, 130%, 148.5%, 161.1% and 68.5%, 72.1%, 78%, 82.7%. The best grafting condition was attained at a concentration of 0.35 g/l of ammonium persulfate (initiator) with % grafting and % efficiency as 161.1% and 82.7% respectively, This increment may be due to sulphate radical which activated the backbone of chitosan, thereby creating more active sites for grafting within the ammonium persulfate range. Tiwari and Singh, (2007) gave a similar observation on the effect of initiator on graft copolymerization of polyaniline onto chitosan. In his report, the maximum % grafting and % efficiency were obtained as 110% and 80% within the initiator concentration range of $2.5 \cdot 10^{-2}$ M- $12.5 \cdot 10^{-2}$ M. However, the report presented by Pati and Nayak, (2012) on the effect of initiator concentration on graft copolymerization of methyl acrylate onto chitosan was in contrast to this study. In his report % grafting and % efficiency had an increase with optimum value of 60% and 55% respectively at an initiator concentration of 0.06 M and beyond this concentration value, % grafting and % efficiency experienced a decrease. Based on the observation of Pati and Nayak, (2012), the decrease may be due to ceric ion (the initiator) which is capable of terminating grafting chains at a higher initiator concentration.

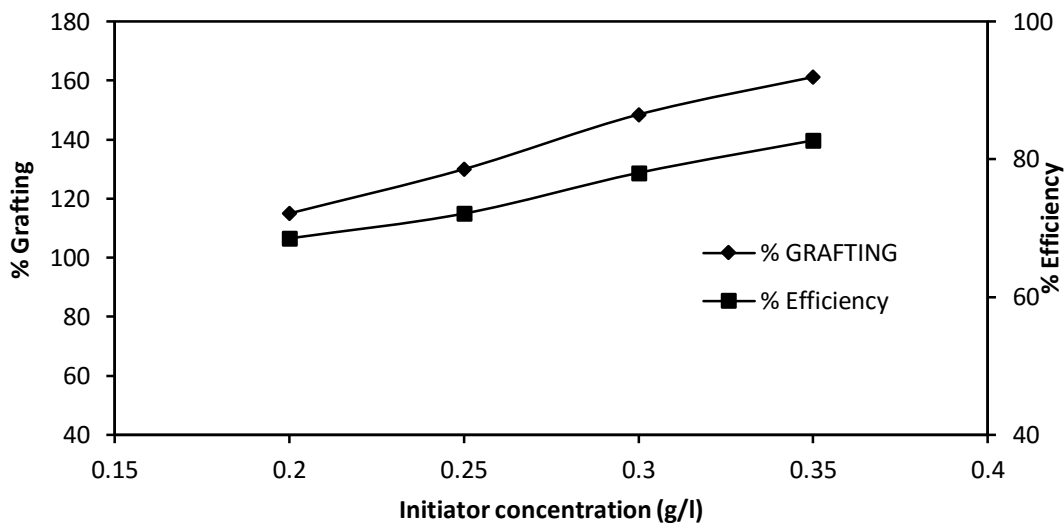


Figure 3. 4: The effect of initiator mass on graft copolymerization at fixed concentration of chitosan (0.45 g/l), aniline (0.1 g/l), HCl (0.1 g/l), for 1 h at 25°C.

3.3.1.4 Effect of chitosan concentration

Figure 3.5 gives the result obtained in varying chitosan concentration at various concentration values of 0.45 g/l, 0.90 g/l, 1.25 g/l, 1.5 g/l. The % grafting and % efficiency at these values were 165.2%, 144.5%, 120%, 105.5% and 83.4%, 76.9%, 69.5%, 66.2% respectively. It was observed in this figure that there was a decrease in % grafting and % efficiency with increase in the concentration of chitosan. The best grafting condition was attained at a concentration of 0.45 g/l of chitosan with % grafting and % efficiency as 165.2% and 83.4% respectively. This observation may be attributed to the fact that as the chitosan concentration is increasing, stirring becomes difficult due to increase in the viscosity of the system and this can cause hindrance to the activation of site responsible for grafting. A different report was presented by Pengju et al., (2009) on the effect of chitosan concentration on graft copolymerization of acrylonitrile onto chitosan. In his study, % grafting and % efficiency experienced an increase within the range of chitosan concentration of 4 g/l – 20 g/l, reaching a maximum of 130% and 41% respectively. He reported that with increase in chitosan concentration the total number of amine groups responsible for grafting also increases thereby increasing % grafting and % efficiency. However, this report was in contrast to the finding reported by Tiwari and Singh, (2007) on the effect of chitosan concentration on graft copolymerization of polyaniline onto chitosan. In his report %

grafting and % efficiency had a decrease within the chitosan concentration range of 1 g/l - 5 g/l. The best grafting condition was attained at a concentration of 1 g/l of chitosan with % grafting and % efficiency as 180% and 84% respectively. This finding favors well with this present study.

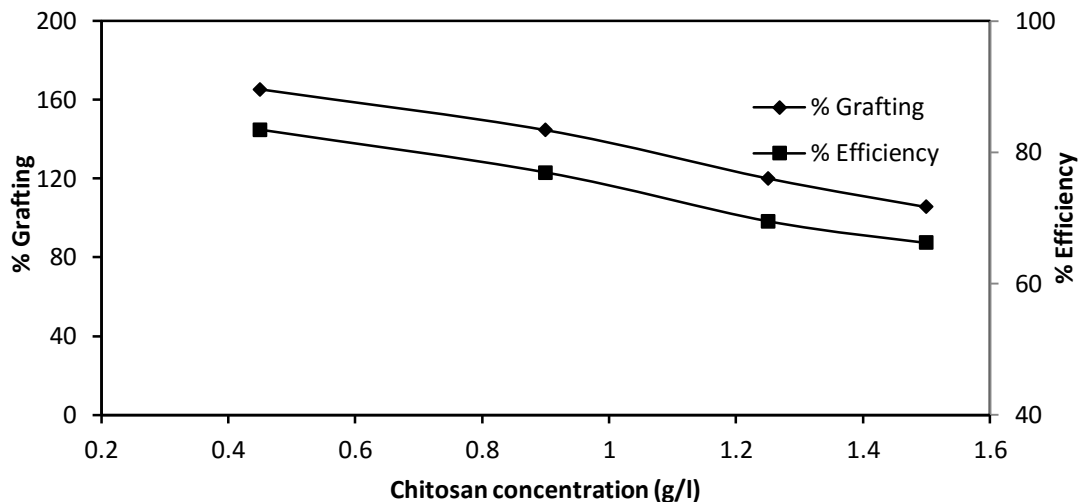


Figure 3. 5: The effect of chitosan concentration on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.1 g/l), for 1 h at 25°C.

3.3.1.5 Effect of acid concentration

Figure 3.6, gives the result of varying acid concentration. However, at concentration values of 0.1 g/l, 0.2 g/l, 0.3g/l, 0.4 g/l, the corresponding % grafting and % efficiency were 168.4%, 180.2%, 193.6%, 205% and 84%, 86.4%, 88%, 91.2%. The best grafting condition was attained at an acid concentration of 0.4 g/l with % grafting and % efficiency as 205%% and 91.2% respectively, This finding may be due to the fact that more polyaniline radicals were produced and these radicals activated the backbone of chitosan and created more active sites for grafting within the acid concentration range. However, a different finding was reported by Mishra et al., (2008), on the effect of sulphuric acid on graft copolymerization of vinyl formamide onto chitosan at an acid concentration range of 2×10^{-3} mol/dm³- 10×10^{-3} mol/dm³. The best grafting condition was attained at an acid concentration of 2×10^{-3} mol/dm³ with % grafting and % efficiency as 182.2% and 90.6% respectively. This finding was attributed by the workers to the fact that the initiator (Bromide) used produced more oxygen which acted as a scavenger for free radicals, causing a decreasing trend for % grafting and % efficiency. Srivastava et al., (2009)

gave a report on the effect of sulfuric acid on graft copolymerization of acrylamide onto guar gum. This report is however similar to this present study. In his report % grafting and % efficiency was increasing within the acid concentration range. The best grafting condition was attained at an acid concentration of $55 \times 10^{-2} \text{ mol/dm}^3$ with % grafting and % efficiency as 168.4% and 67.4% respectively.

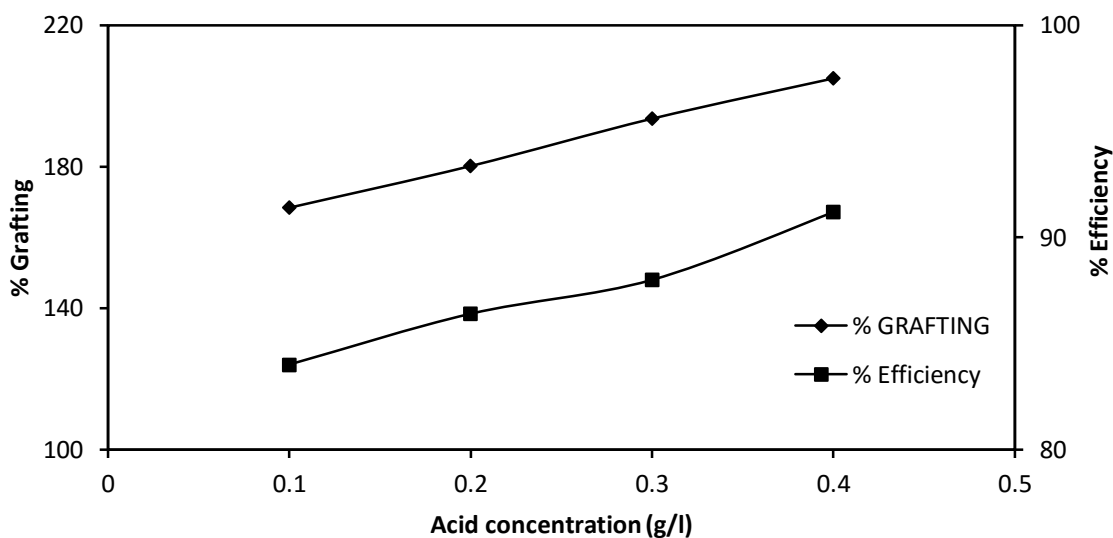


Figure 3. 6: The effect of acid concentration on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), chitosan (0.45 g/l) for 1 h at 25°C.

3.3.1.6 Effect of temperature

Figure 3.7 shows the result obtained in varying of temperature, in this figure, percentage grafting and % efficiency increased at the initial stage from 25°C to 35°C and decreased thereafter, the best temperature was found to be 35°C with % grafting and % efficiency of 219.2% and 93.9% respectively. This finding may be due to the fact that at temperatures below 35°C, the decomposition of thermally dissociating initiator increases and this create more active site for grafting (Zuhuriaan, 2005). However temperatures higher than the optimum temperature will produce low-graft polymer (Soleimani et al., 2012), and in this study the best temperature is 35°C and further increase in temperature lead to termination of grafted chain which caused a decrease in % grafting and % efficiency. In a similar study presented by Fares and Al-Taani, (2003), on the effect of temperature on graft copolymerization of methyl methacrylate onto

chitosan and at a temperature range of 30°C-55°C, maximum % grafting and % efficiency were found to be 70.2% and 16.7% respectively, at a temperature of 30°C.

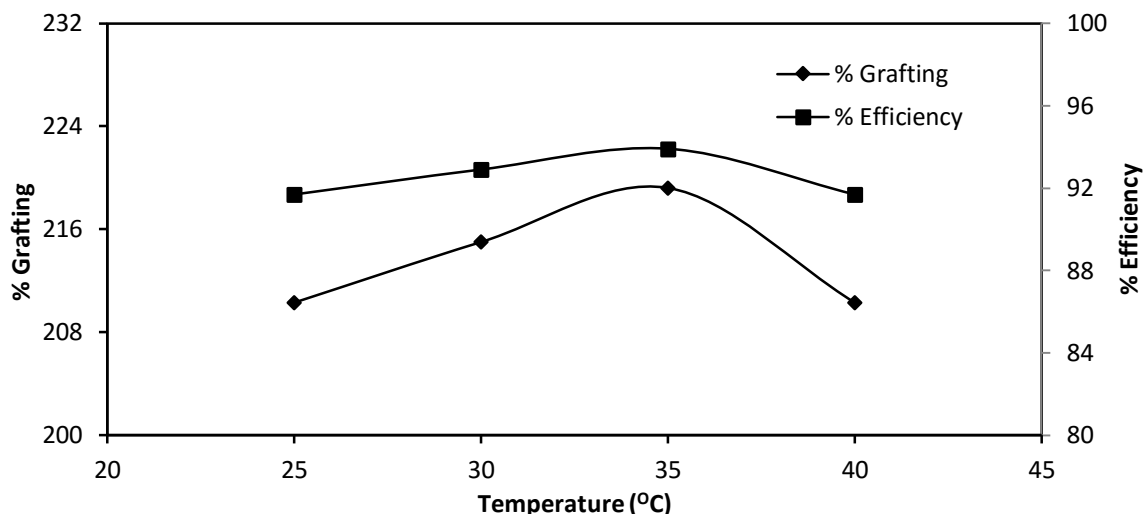


Figure 3. 7: The effect of temperature on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.4 g/l), chitosan (0.45 g/l) for 1 h.

3.3.2 Grafting of chitosan beads

0.45 g/l of chitosan beads and 0.1 g/l of aniline were transferred into 200 mL of 0.4 g/l HCl in a round-bottom flask and content was continuously stirred by a magnetic stirrer. After 30 minutes, 0.35 g of ammonium persulfate was added to the reactive medium and this was taken as zero time (30 minutes stirring time was not added to the grafting time). Grafting was allowed to take place for an hour at 35°C. The PGCB was washed with N-methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer was rinsed with distilled water and ready to be used.

3.3.3 Characterization

3.3.3.1 IR spectra

The infrared red spectroscopy was used to confirm graft copolymerization reaction of polyaniline onto chitosan. The IR spectra of chitosan showed a broad band at 3458.27 cm^{-1} due to NH_2 stretching vibration (Yavuz et al., 2011). The absorption band at 1059.59 cm^{-1} and 1020.36 cm^{-1} both corresponds to C-O stretching vibration (Abhishek et al., 2011). The peak at 1684 cm^{-1} was

assigned to the stretching vibration of C=O, While the N=O stretching vibration correlated with a wavelength of 1578.82 cm^{-1} . The sharp peaks at wavelength 1455.72 cm^{-1} , 1373.84 cm^{-1} and 848.06 cm^{-1} , is attributed to CH_2 bending vibration, CH_3 bending vibration and C-H bending vibration of monomer molecule respectively. (Mishra et al., 2008; Tiwari and Singh, 2007; Abhishek et al., 2011).

The IR spectra of PGCB showed increase in intensity at peaks $1150.09\text{ (cm}^{-1})$ 1507.69 cm^{-1} 1263.32 cm^{-1} and 1377.23 cm^{-1} corresponding to C-O stretching vibration, N-H bending vibration, C-N stretching vibration and N-O stretching vibration (Mishra et al., 2008), as shown in Figure 4.8, indicating that grafting has taken place. The shifting of band from 3458.27 cm^{-1} in the spectra of chitosan to 3367.66 cm^{-1} in PGCB may be attributed to the hydrogen bonding between chitosan and imine group of the grafted chain of polyaniline (Tiwari and Singh, 2007).

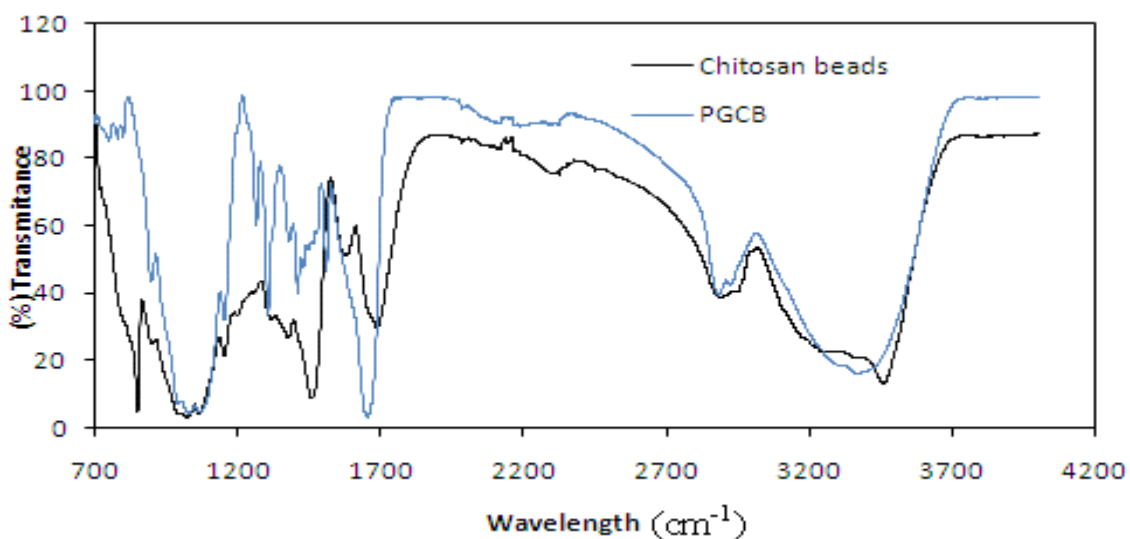


Figure 3. 8: IR spectrum of chitosan beads and PGCB.

3.3.3.2 XRD spectra

The crystallinity of chitosan and PGCB was investigated by X-ray diffraction method. Chitosan is a partially crystalline polymer, and this crystalline nature exhibited by chitosan is mainly due to the accumulation of linear chains in the structure of the polymer (Fares and Al-Taani, 2003). However, this crystallinity makes some group inaccessible to the target metal ions (Sewvandi and Adikary, 2011). In this study polyaniline was grafted to chitosan beads to reduce its

crystallinity and hence expand the polymer network for easy accessibility of copper ions to adsorption site.

In Figures 4.9a and b, the strong reflection at $2\Theta=20^\circ$ correspond to 110 planes of chitosan (Jolanta et al., 2010). Moreover, from Figure 4.8a the intensity of chitosan at around $2\Theta=20^\circ$ is 440 Angstrom units and as expected on grafting polyaniline onto chitosan the intensity ratio was reduced to about 213 Angstrom units (Figure 4.8b), indicating the decrease of crystallinity in PGCB. This finding is due to the fact that some of the crystalline chains have been destroyed during grafting process. In a similar study by Nagahama et al., (2009), there was a decrease in the intensity ratio when gelatin membrane was grafted to chitosan and this decrease denotes a reduction in the crystallinity of the polymer. Also in a report by Fares and Al-Taani, (2003) the intensity ratio of chitosan was up to 1200 Angstrom units and upon grafting with ethyl methacrylate (EMA) the intensity ratio was reduced to 800 Angstrom units.

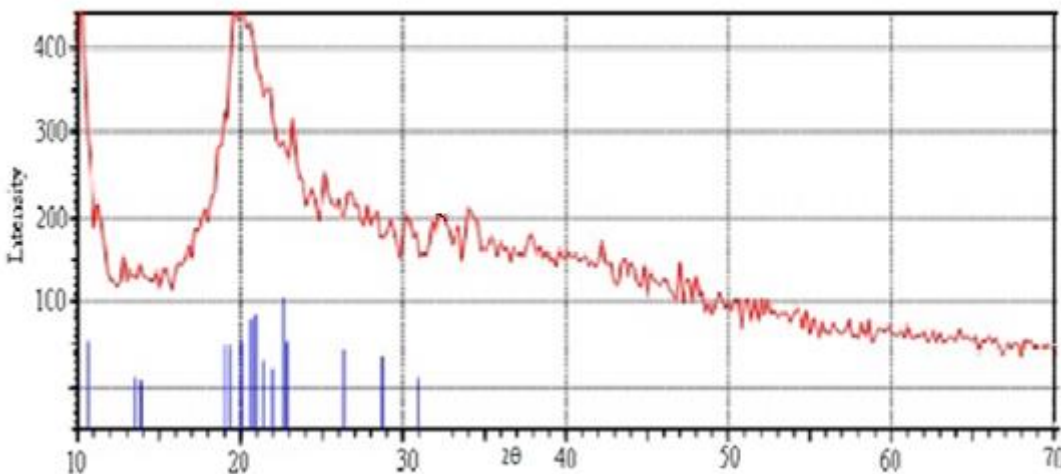


Figure 3. 9a: XRD spectra of chitosan beads.

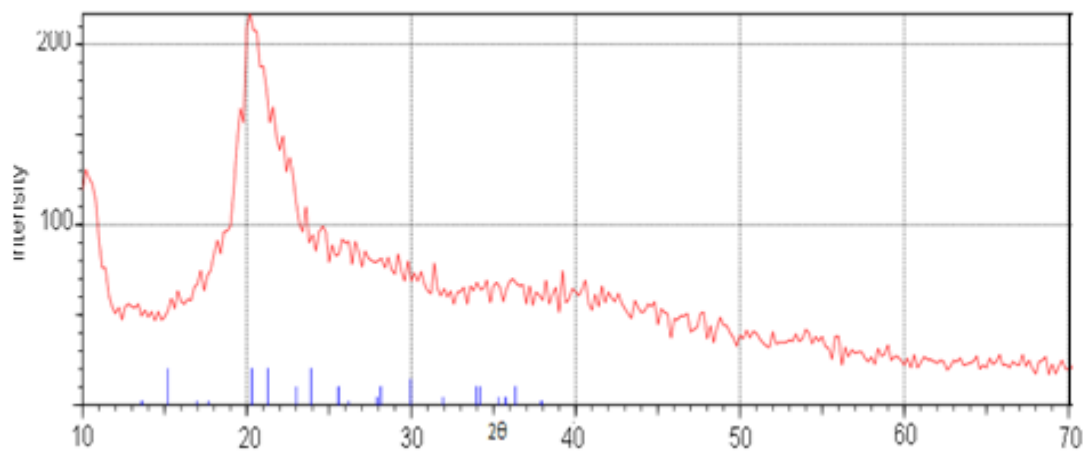


Figure 3.9b: XRD spectra of PGCB.

3.3.3.3 SEM morphology

The morphology of chitosan beads and PGCB was studied by Scanning Electron Microscope (SEM). SEM images with magnification of 300 μm are shown in Figure 4.9a and b, and it clearly reveals the polysaccharide nature of chitosan having a network of organized fibres. The gaps between polysaccharide particles have been closed as shown in figure 4.9b, indicating the evidence of grafting. Kelesoglu, (2007) gave a similar finding in his report.

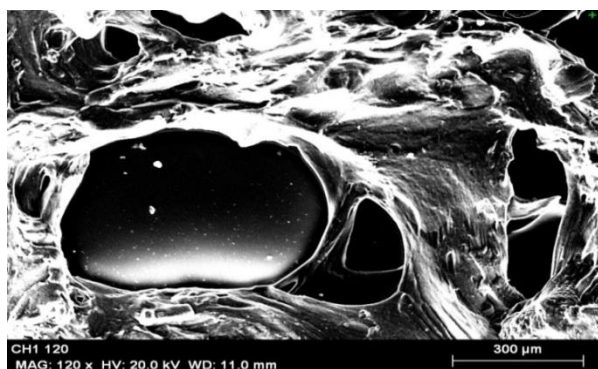


Figure 3.10a: SEM morphology of chitosan beads

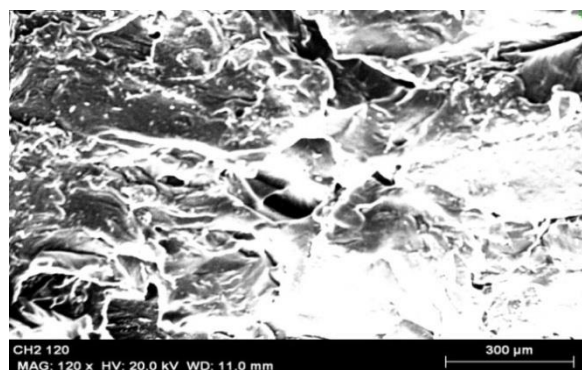


Figure 3.10b: SEM morphology of PGCB.

3.3.4 Conclusion

The best condition obtained in this chapter were used in the grafting of polyaniline onto chitosan beads and such conditions were; [Aniline] 0.1 g/l, [temperature] 35°C, [chitosan] 0.45 g/l, [HCl] 0.4 g/l, $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ 0.35 g/l, and [time] 1 h.

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CHAPTER FOUR

4.1. INTRODUCTION

This section covers adsorption/desorption studies using the beads prepared in chapter 3 and the discussion of the results obtained during the investigation. However, the effect of pH, contact time, initial concentration and temperature on adsorption was examined. The Langmuir and Freundlich model was used to interpret adsorption isotherm data while the Pseudo-first order and Pseudo-second model was applied in the interpretation of kinetic data. Thermodynamics of adsorption of Cu(II) onto PGCB was explained by the Gibb's free energy, entropy and enthalpy change. Three cycles of regeneration of copper loaded PGCB experiment was carried out. Other experiments carried out on desorption studies include; effect of desorbing copper ions using HCl and HNO₃ system and effect of contact time on percentage desorption of copper ions.

Subsequently, it is expected from the investigation that the PGCB will adsorb copper ion effectively at an optimum pH. It is also expected from the desorption studies that, Cu(II) ions will desorb effectively using the appropriate eluant, right concentration of eluant and reaction time, and the regenerated beads can be used successfully for subsequent removal of Cu(II) ions.

4.2 Experimental

4.2.1 Materials

Chitosan beads, solution of Cu(II) ion was prepared by dissolving a weighed quantity of CuSO₄.5H₂O (>99%) which was obtained from Labchem. Distilled water was produced with a pure water distiller (Ultima 888 water distiller) in the chemical engineering laboratory, hydrochloric acid (99%), sodium hydroxide (>99%), acetic acid (>99%) were all purchased from Sigma-Aldrich. The pH of the solution was measured with a pH meter (Hanna HI 8421).

4.2.2 Adsorption experiments

4.2.2.1 Effect of pH on Cu(II) ion removal by PGCB

A copper solution with a concentration of 40 mg/l was prepared from a stock solution obtained by dissolving 3.932 g of copper ions in 1 L of distilled water. A mass of 0.45 g of PGCB was each transferred into eight (8) Erlenmeyer flask, then samples of 100 ml from the 40 mg/l

concentration was measured into each flask. The pH of the samples was adjusted by 0.1 M HCl and 0.1 M NaOH to various pH values in the range of pH 3 to 8. The flasks were placed in a labcon incubator and shaken for 150 min. The temperature and agitation speed were fixed at 25 °C and 120 rpm respectively. After equilibrium, a clear metal solution was taken and analyzed with atomic adsorption spectrophotometer to determine the amount of metal ion adsorbed

4.2.2.2 Isotherm experiment

Isotherm studies were carried out by transferring 0.45 g of chitosan beads and 0.45 g of PGCB, separately into a series of 250 mL Erlenmeyer flasks, each of the flasks was filled with 100 mL of Cu(II) solution with different initial concentrations of 40 mg/l, 80 mg/l, 120 mg/l, 200 mg/l, 320 mg/l and 400 mg/l. These initial concentrations were prepared from a stock solution and then adjusted to optimum pH of 5. In order to attain equilibrium, the Erlenmeyer flasks were placed in a labcon incubator for 150 min, the agitation speed was at 120 rpm. Isotherms were conducted at temperatures of 25°C, 35 °C and 45 °C respectively. However, thermodynamics was investigated at an initial concentration of 200 mg/l. The effect of temperature on maximum adsorption capacity was studied at these ranges of temperatures.

After equilibrium, a clear metal solution was taken and analyzed with atomic adsorption spectrophotometer (Varian SpectrAA-10). To determine the amount of metal ion adsorbed. The equilibrium adsorption capacity was calculated from the mass balance equation as shown in equation 4.1.

$$q_e = \frac{(C_0 - C_e)}{M} \times V \quad (4.1)$$

Where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e is the initial and equilibrium concentration (mg/l) of heavy metal ion in solution respectively, while V (mL) is the volume and M (g) is the weight of the adsorbent.

4.2.2.3 Kinetic experiment

0.45 g of PGCB was mixed with 100 mL of Cu(II) solution in a series of 250 mL Erlenmeyer flasks having different initial concentrations of 40 mg/l, 80 mg/l, 120 mg/l, 200 mg/l, 320 mg/l and 400 mg/l. These initial concentrations were prepared from a stock solution and then adjusted to optimum pH of 5. In order to attain equilibrium, the Erlenmeyer flasks were placed in a labcon

incubator, the solutions were shaken at 120 rpm and the temperature fixed at 25°C. Samples was taken at interval of 30 min, 60 min, 90 min, 120 min and 150 min and analyzed with atomic adsorption spectrophotometer for their metal ions removal. The effect of contact time and initial concentration on copper ion removal was studied at these ranges of time and concentration.

4.2.3 Desorption Experiment

After adsorption, the grafted beads loaded with copper ions were washed with distilled water before treating it with 50 mL of 0.01 M, 0.05 M, 0.1 M and 0.5 M HCl/HNO₃ system at a pH of 4 and contact time of 200 min. This was done in other to study the effect of desorbing copper ions by dilute HCl and HNO₃. In other to study the effect of contact time on percentage desorption, copper ions was desorb with 0.5 M HCl and measured with atomic adsorption spectrometer at contact time of 30 min, 60 min, 90 min 120 min, 150 min and 180 min. The percentage desorption was calculated by equation 4.2.

$$\%desorption = \frac{C_e}{C_o} \times 100 \quad 4.2$$

Were C_e represents the final copper ion concentration in the desorption medium in mg/l and C_o represent the initial concentration of copper ion.

In order to determine the possible re-use of the beads, the treated adsorbent was again rinsed with distilled water and mixed with 100 mL of Cu(II) solution with different initial concentrations of 40 mg/l - 400 mg/l, and transferred into a 250 mL Erlenmeyer flask, placed in a labcon incubator. The temperature and pH of the mixture was maintained at 25°C and 5 respectively. After equilibrium has taken place for 150 min, a clear metal solution was collected and analyzed with atomic adsorption spectrophotometer for their metal ion removal. Adsorption-desorption process was conducted for 3 consecutive cycles.

4.3 Results/discussion

4.3.1 Effect of pH

In an attempt to determine the optimum pH for the adsorption of Cu(II) ions onto PGCB, the percentage removal of Cu(II) ion as a function of hydrogen ion concentration was examined at an initial concentration of 40 mg/l. The experimental data is found in Appendix B. In Figure

4.10, the percentage removal of Cu(II) ions were 60.3%, 88%, 100%, 93.3%, 39.4% and 36% at pH values of 3, 4, 5, 6, 7, and 8 respectively. However, the PGCB adsorbent showed a decrease in the removal rate of Cu(II) ions at lower pH conditions. This may be due to the competitions between the hydrogen ions and Cu(II) ions on the adsorption site. This competition actually caused a low level of Cu(II) removal from PGCB at lower pH. The optimum pH was found to be pH 5 with a maximum percentage removal of 100%. Moreover, increasing the pH above 6 resulted to the precipitation of insoluble copper hydroxide, causing a decrease in the removal of Cu(II) ions. A similar trend was reported by Liu et al., (2011) on the removal of Cu(II) and Cd(II) from aqueous solutions by polyaniline on sawdust.

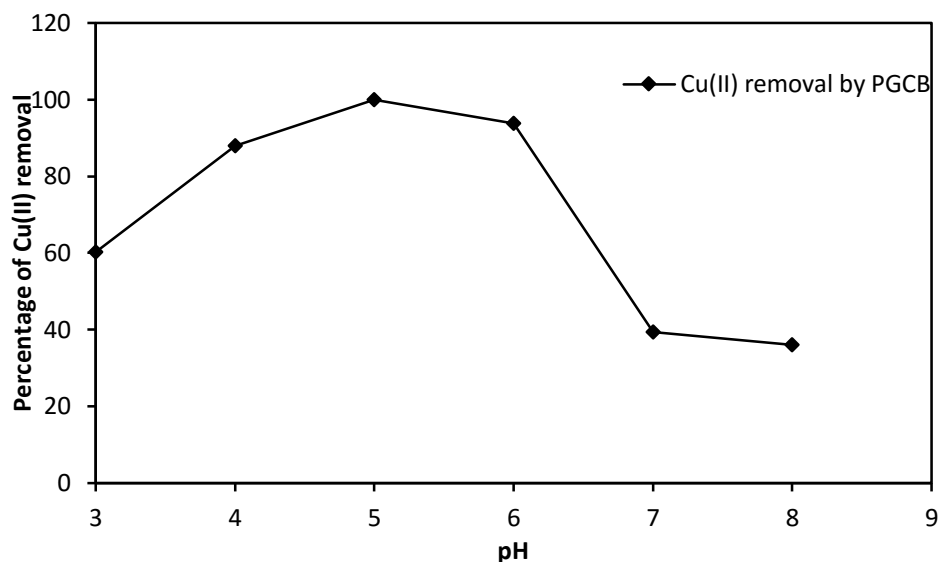


Figure 4. 1: Effect of pH on percentage removal of Cu(II) ions by PGCB at an initial concentration of 40 mg/l.

4.3.2 Effect of contact time and initial concentration

Adsorption of copper ions onto PGCB was investigated as a function of time at various initial concentrations of 40 mg/l, 80 mg/l, 120 mg/l, 200 mg/l, 320 mg/l and 400 mg/l, as shown in figure 4.11. During the first 30 min the amount adsorbed at equilibrium is said to proceed faster with time and then onwards increases slightly, until it reaches equilibrium. However, at lower initial concentration of 40 mg/l, 80 mg/l, 120 mg/l, 200 mg/l, equilibrium was said to occur at contact time of 90 min, also, at higher initial concentration of 320 mg/l and 400 mg/l, equilibrium was said to occur at contact time of 120 min. This observation may be due to the fact

that at lower initial Cu(II) ion concentration, sufficient sites responsible for adsorption of Cu(II) ion are available. Moreover, as the concentration of Cu(II) ions increases, the numbers of Cu(II) ions becomes relatively higher compared to availability of adsorption sites. Hence, the rate of removal of Cu(II) ion is dependent on the initial concentration of Cu(II) ions and also decrease with increase in concentration of Cu(II) ions. A similar trend was reported by (Jin and Bay, 2002; Liu et al., 2011; Ola, 2007).

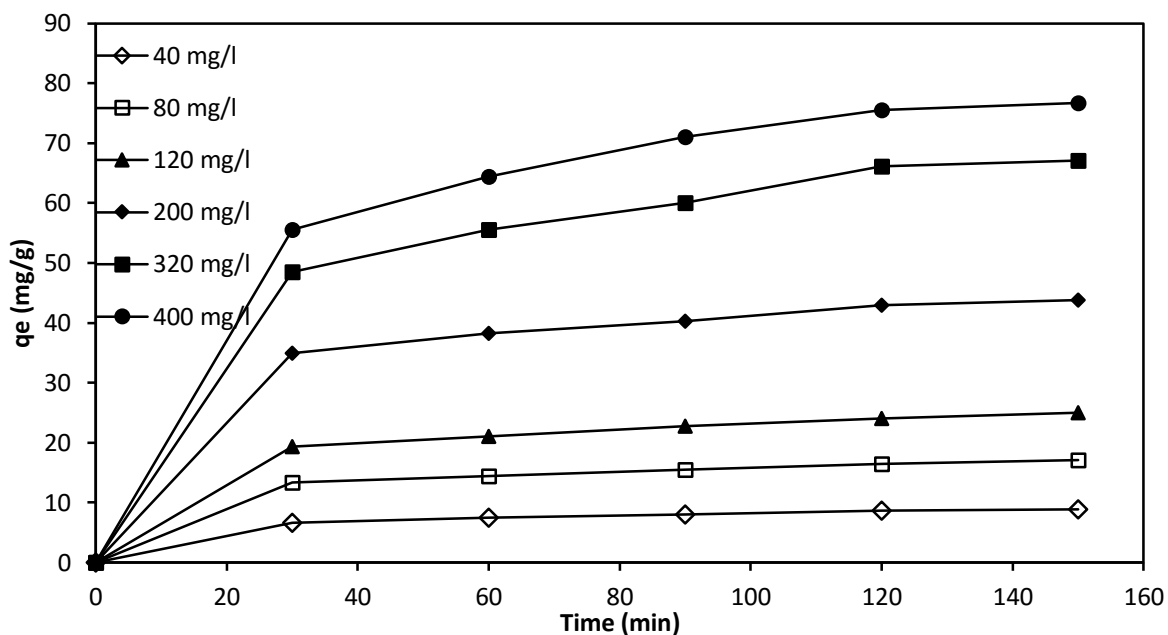


Figure 4. 2: Effect of contact time and initial concentration.

4.3.3 Effect of temperature

Figure 4.12 shows the effect of temperature on maximum adsorption capacity (Q_m) of PGCB and it was observed that an increase in temperature from 25°C to 45°C gave a corresponding increase in the adsorption capacity from 83.3 mg/g to 100 mg/g. This increase in adsorption capacity with increase in temperature indicates that the adsorption process is endothermic in nature. This trend (increase in adsorption capacity with increase in temperature) strongly suggests that the adsorption process is chemisorptions. A similar report was given by Kannambaa et al., (2010), in his report, the Q_m of the modified chitosan beads for copper ions increased from 12.24 mg/g to 14.78 mg/g as the temperature was increased from 20°C to 50°C.

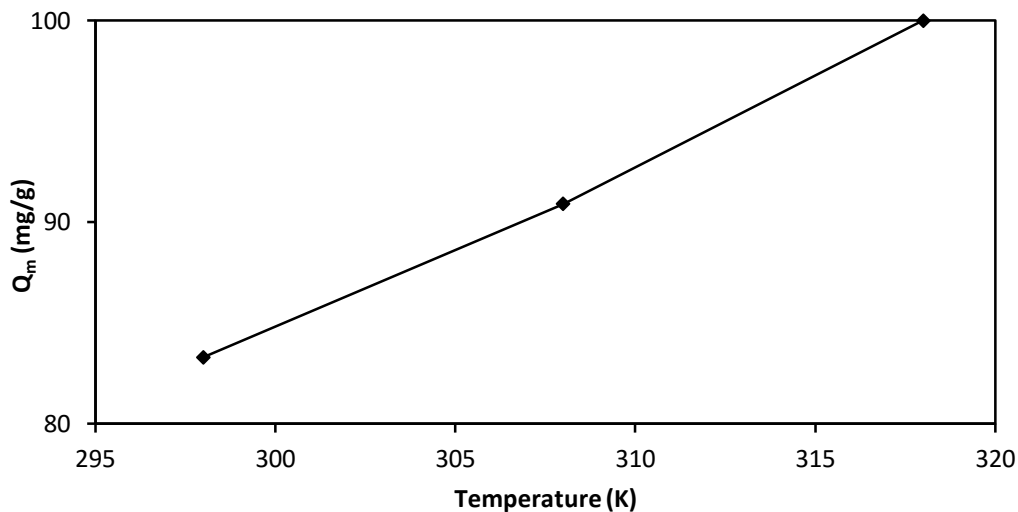


Figure 4. 3: Effect of temperature on adsorption capacity of PGCB.

4.3.4 Adsorption isotherm parameters

The Langmuir and Freundlich model were used to determine the appropriate isotherm for copper onto chitosan beads and PGCB. These models were described in their linear form in equation 2.4 and 2.6 respectively. Experimental data used to obtain the appropriate isotherms are found in Appendix C (Table C-1 to C-6). The parameters of the two models at different temperatures (25°C, 35°C and 45°C), were calculated from the slope and intercepts of C_e/q_e versus C_e and $\log q_e$ versus $\log C_e$ plots and the results are shown in Table 4.1.

From table 4.1, the Langmuir parameters for chitosan beads at temperatures of 25°C 35°C and 45°C indicated the following; that Q_m (mg/g) has values of 30.3, 47.6 and 52.6, b (l/mg) has values 0.011, 0.014 and 0.014, and R^2 has values of 0.971, 0.942 and 0.943 respectively. The values $1/n$ from the Freundlich model for copper ion adsorption onto chitosan beads are 0.539, 0.544 and 0.579 and this values lies between the favorable condition of $0.1 < \frac{1}{n} < 1$, indicating that copper ion adsorption onto chitosan beads is favorable. The K_F (mg/g) values were found to be 1.19, 2.06 and 3.44 and R^2 values were 0.969, 0.932 and 0.950. The closer R^2 is to I the more the best fit model. The R^2 values of the Langmuir model were all equal and greater than 0.942 and this is in contrast to the R^2 values obtained from the Freundlich model (equal and greater than 0.932) and hence the Langmuir model best describe the adsorption isotherm of chitosan

beads. The Langmuir model however supports the existence of monolayer coverage on the adsorption site of chitosan beads. The Langmuir and Freundlich plot for chitosan beads at temperatures of 25°C, 35°C and 45°C is shown in Appendix D (Figure D-1 to D-2).

However, from table 4.1 also, the Langmuir parameters for PGCB at temperatures of 25°C 35°C 45°C, indicated the following; that Q_m has values of 83.3 mg/g, 90.9 mg/g and 100 mg/g. The values of b (0.070, 0.20 and 0.32) in mg/g were increasing with increase in temperature and higher values of b denotes high adsorption affinity for copper ions (Ola, 2007), and R^2 values were 0.988, 0.956 and 0.957 respectively. Moreover, the Freundlich parameters indicated the following; the values $1/n$ for copper ion adsorption onto PGCB are 0.396, 0.429 and 0.510 and this values lies between the favorable condition of $0.1 < \frac{1}{n} < 1$, indicating that copper ion adsorption onto PGCB is also favorable. The K_F (mg/g) values were 12.27, 17.70 and 19.63 and the R^2 values obtained were 0.985, 0.935 and 0.953. The correlation coefficient (R^2) of the Langmuir model were all equal and greater than 0.956 and this is in contrast to the R^2 values obtained from the Freundlich model (equal and greater than 0.935) and hence the Langmuir model best describe the adsorption isotherm of PGCB. This also indicates monolayer coverage on the adsorption site of PGCB and hence the adsorption process is thus called chemisorptions. The Langmuir and Freundlich plot for PGCB at temperatures of 25°C, 35°C and 45°C is shown in Appendix D (Figure D-3 to D-4).

Table 4. 1: Langmuir and Freundlich isotherm parameters at different temperature.

| Sample | Isotherm model | Parameters | 25°C | 35°C | 45°C |
|----------------|----------------|--------------|-------|-------|-------|
| Chitosan beads | Langmuir | Q_m (mg/g) | 30.3 | 47.6 | 52.6 |
| | | b (l/mg) | 0.011 | 0.014 | 0.014 |
| | | R^2 | 0.971 | 0.942 | 0.943 |
| | Freundlich | $1/n$ | 0.539 | 0.544 | 0.579 |
| | | K_F (mg/g) | 1.19 | 2.06 | 3.44 |
| | | R^2 | 0.969 | 0.932 | 0.950 |
| PGCB | Langmuir | Q_m (mg/g) | 83.3 | 90.9 | 100 |
| | | b (l/mg) | 0.070 | 0.20 | 0.32 |
| | | R^2 | 0.988 | 0.956 | 0.957 |
| | Freundlich | $1/n$ | 0.396 | 0.429 | 0.510 |
| | | K_F (mg/g) | 12.27 | 17.70 | 19.63 |
| | | R^2 | 0.985 | 0.935 | 0.953 |

4.3.5 Maximum adsorption capacity comparison

The maximum adsorption capacity obtained in this present investigation in comparison with that reported from literature for the adsorption of copper ions onto several adsorbent (Table 4.2) strongly reveal that chitosan beads and PGCB were a better adsorbent and as such were highly effective in the removal of copper ions.

Table 4. 2: Comparison of adsorption capacity of copper (II) with other adsorbent using Langmuir model.

| Heavy metal | Adsorbent | Adsorption capacity (mg/g) | Reference |
|-------------|---|-------------------------------|----------------------------|
| Copper (II) | Activated carbon | 21.5 | Rivera et al., (2003). |
| | Waste slurry | 20.97 | Lee and Davis, (2001). |
| | Green algae | 32.6 | Ola, (2007). |
| | Carrot residue | 32.74 | Ola, (2007). |
| | Rice bran | 33.58 | Wang and Qin, (2005). |
| | Wheat shell | 10.84 | Basci et al., (2004). |
| | Wood sawdust | 5.73 | Kalavathy et al., (2005). |
| | Bagasse fly ash | 2.26 | Gupta and Ali, (2000). |
| | Chitosan | 30.3 | This study |
| | Polyaniline grafted - Chitosan beads | 83.3 | This study |
| | Sawdust | 13.8 | Ajmal et al., 1998. |
| | Scolecite | 4.2 | Bosso and Enzweiler, 2002. |
| | Peanut hull | 21.25 | Zhu et al., 2009 |

4.3.6 Thermodynamics parameters

The plot of $\ln K$ against $1/T$ for PGCB is shown in figure 4.13. The experimental data can be found in Appendix E. Table 4.3 gives the values of the parameters for thermodynamic studies. The free energy change (ΔG°) obtained during the absorption reaction at temperatures of 25°C, 35°C and 45°C were all negative (-1.86 KJ/mol, -5.53 KJ/mol, and -6.90 KJ/mol), and this indicates that the adsorption of copper onto PGCB is spontaneous and favorable. A similar finding was reported by Zawani et al., (2009). The positive value of ΔH° (+52.67 KJ/mol) indicates that the adsorption process is endothermic in nature. This finding is in agreement to the result presented by Liu et al., (2011). The positive value of ΔS° (+0.19 KJ/mol) indicates the increased randomness at the solid-solution interface during the adsorption of copper onto PGCB (Liu et al., 2011).

Table 4. 3: Thermodynamic parameters for the adsorption of copper ions onto PGCB at an initial concentration of 200 mg/l.

| Temperature (K) | Thermodynamic parameters | | | |
|-----------------|------------------------------|------------------------------|-------------------------------|-------|
| | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (kJ/molK) | R^2 |
| 298 | -1.86 | | | |
| 308 | -5.53 | +52.67 | +0.19 | 0.990 |
| 318 | -6.90 | | | |

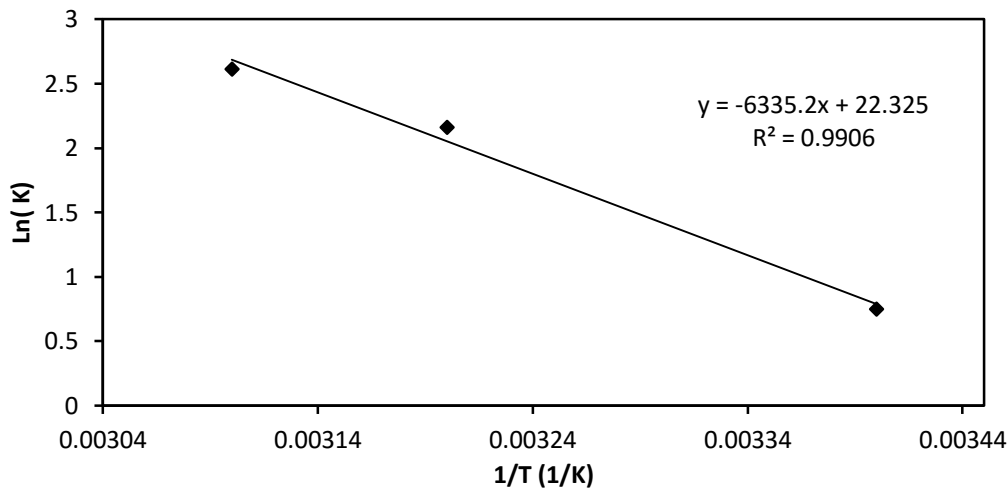


Figure 4. 4: Thermodynamic plot of $\ln K$ against $1/T$ for PGCB.

4.3.7 Kinetic parameters

The kinetics of adsorption is used to investigate the time course of copper adsorption onto PGCB. It is also important to determine whether the behavior of copper uptake onto the beads can be explained by a predictive model. The data obtained from the experiment carried out as shown in Appendix F (Table F-1 to F-6), were used to study the kinetics of copper ion adsorption onto PGCB.

The pseudo-first order and pseudo-second order model (Equations 2.16 and 2.20) was used to fit the kinetic data. Recent studies have shown that the pseudo-second order kinetic model gives a better fit for adsorption data (Sag and Aytay, 2002). Table 4.4 gives the values of the parameters for a pseudo-first and second order kinetic model, and it was observed that the correlation coefficients for

the straight plot of t/q_t against t from the pseudo-second order rate law are equal and greater than 0.994, in contrast to the correlation coefficient (≥ 0.896) of the pseudo-first order kinetic model obtained from the linear plot of $\log (q_e - q_t)$ against t . This linear correlation coefficient method of determination of best fit model suggests that the adsorption of copper ions onto PGCB is a pseudo-second order reaction model. The straight line plot of the pseudo first and pseudo second order kinetic model is presented in Appendix G (Figure G-1 to G-2).

To further investigate kinetic data the chi-square test (χ^2) of statistical analysis was applied. It was observed also in Table 4.4 that the values of χ^2 for the pseudo first-order kinetic model and pseudo second-order kinetic model were similar. For example at a concentration of 40 mg/l the χ^2 for pseudo first-order and pseudo second-order kinetic model were 0.03 and 0.11 respectively. However, there was a large difference for q_e values obtained by calculating from pseudo first-order kinetic model and experimental values. For example, at 40 mg/l the value of $q_{e(\text{Cal})}$ from pseudo first-order kinetic model is 5.57 mg/g and the value of $q_{e(\text{Exp})}$ is 8.89 mg/g and these values are further from each other. In the case of the pseudo second-order model, the $q_{e\text{Cal}}$ values agree very well with the experimental data, such that from pseudo second-order model at 40 mg/l the $q_{e\text{Cal}}$ value is 9.90 mg/g and this value is very close to $q_{e\text{Exp}}$ which is having a value of 8.89 mg/g. This suggests that the adsorption of copper ions onto PGCB is a pseudo-second order reaction model, and this model is based on the assumption that the rate limiting step may be chemical adsorption or chemisorption involving valence forces through exchange of electrons between adsorbate (copper ions) and adsorbent (PGCB), provides best correlation of data (Ho and Mckay, 1999).

Table 4. 4: Kinetic parameters for the adsorption of copper onto PGCB at a pH of 5.

| Metal ion | First-order kinetic model | | | | | Second-order kinetic model | | | | |
|-----------|---------------------------|-------------------------|-----------------------------|----------------|----------------|-------------------------------|------------------------------|-------------------------------|----------------|----------------|
| | Mg/l | K ₁ (min) | q _{e(Cal)} mg/g | χ ² | R ² | q _{e(Exp)} (mg/g) | K ₂ (g/mg.min) | q _{e(Cal)} (mg/g) | R ² | χ ² |
| Cu | 40 | 0.020 | 5.57 | 0.03 | 0.913 | 8.89 | 5.93x10 ⁻³ | 9.90 | 0.997 | 0.11 |
| | 80 | 0.016 | 7.13 | 0.07 | 0.973 | 17.31 | 3.34x10 ⁻³ | 18.87 | 0.995 | 0.19 |
| | 120 | 0.020 | 11.25 | 0.03 | 0.973 | 25.34 | 2.31x10 ⁻³ | 27.78 | 0.997 | 0.30 |
| | 200 | 0.020 | 19.10 | 0.05 | 0.943 | 44.44 | 1.38x10 ⁻³ | 50.00 | 0.997 | 0.43 |
| | 320 | 0.030 | 52.60 | 0.10 | 0.896 | 67.78 | 6.31x10 ⁻⁴ | 76.90 | 0.996 | 0.91 |
| | 400 | 0.020 | 53.30 | 0.14 | 0.962 | 83.22 | 3.76x10 ⁻⁴ | 100.0 | 0.994 | 0.77 |

4.4 Desorption studies

4.4.1 Effect of desorbing copper ions by HCl and HNO₃ systems

The effect of using HCl/HNO₃ system to desorb copper ions was investigated at a concentration range of 0.01 M, 0.05 M, 0.1 M, 0.5 M and 0.9 M and contact time of 200 mins. The experimental data is found in Appendix H (Table H-1). It was observed in Figure 4.14 that using the HCl system for desorption at concentration range of 0.01M to 0.5 M, there was an increase in percentage desorption as follows 50.1%, 76.8%, 88.2% and 97.1%, after which percentage desorption decrease to 74.6% at a concentration of 0.9 M. The use of HNO₃ system gave an increase as follows 39.6%, 55.4%, 68.7% and 79.4%, at concentration of 0.01M to 0.5 M. With a further increase in the concentration of HNO₃ to 0.9 M gave a reduction in percentage desorption to 50.8%. On comparing the two systems one can say that the 0.5 M HCl system is an effective method of desorbing copper ions, since maximum desorption of 97.1% was attained at a concentration of 0.5 M, in contrast to the HNO₃ system which gave a desorption percentage of 79.4%. From this result one can say conclusively that for effective desorption of copper ions using PGCB, factors such as appropriate eluant, right concentration of eluant and time of desorption needs to be considered. In a similar study from literature by Liu et al., (2011), eluants such as HCl and HNO₃ were used with concentration range of 0.5 M to 2 M to desorb copper ion from polyaniline on sawdust. Maximum desorption of 95.4% and 78.1% was obtained for HCl and HNO₃ system respectively at a concentration of 2 M.

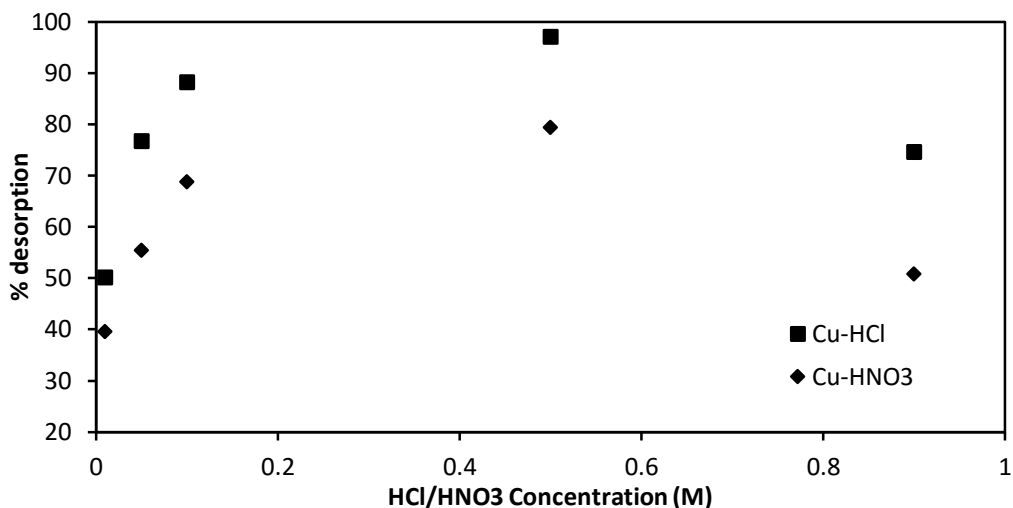


Figure 4. 5: Effect of varying the concentrations of HCl/HNO₃ system.

4.4.2. Effect of contact time on percentage desorption of copper.

Figure 4.15 gives the result from desorbing Cu(II) ion using 0.5M hydrochloric acid (eluant) and analysis was taken at different time interval to determine the amount in concentration that was desorbed. The experimental data is found in Appendix H (Table H-2). In this figure, at contact time of 30 min, 60 min, 90 min, 120 min, 150 min and 180 min there was a corresponding increase in percentage desorption from 37.5%, 51.40%, 78.30%, 90.20%, 97.10% and 97.10% respectively. At contact time of 150 min and 180 min, maximum desorption of 97.10% was obtained. This observation may be due to the chemisorptions nature of the adsorption process.

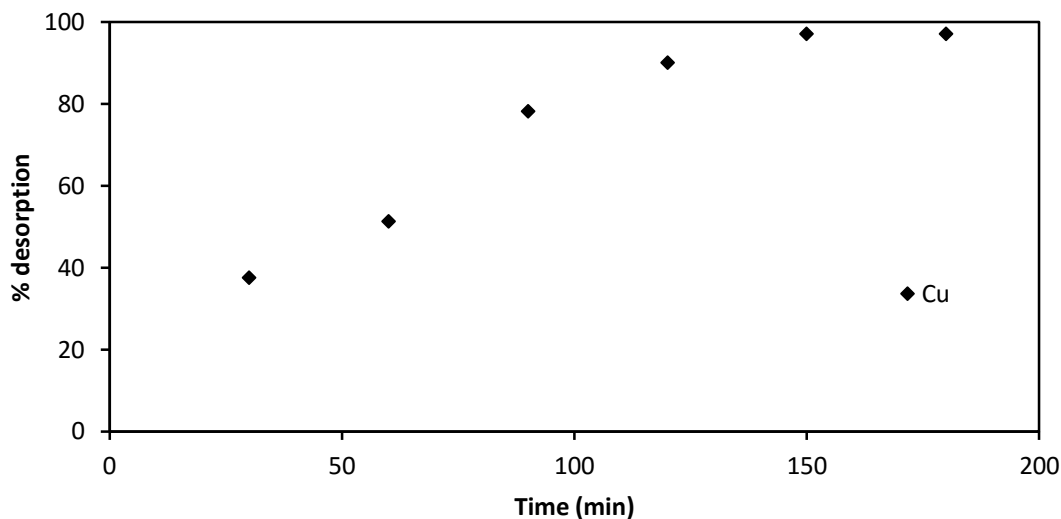


Figure 4. 6: Effect of contact time on percentage desorption.

4.4.3 Effect of adsorbent re-use on maximum adsorption capacity

In an attempt to determine the reusability of PGCB for copper ions adsorption, three successive cycles of adsorption and desorption studies was carried out and the experimental data is seen in appendix H (Table H-3 to H-5).

After the first and second cycle of adsorption and desorption studies the maximum adsorption capacity (83.3 mg/g) was not affected with 0.0 % and 4.4% loss in the mass of the beads and this development in the maximum adsorption capacity may be due to acid treatment during the desorption of copper that cause the opening of pore spaces in the surface of the beads. These findings are presented in Table 4.5.

In the third cycle of desorption, an 8.9% loss in the mass of the beads was observed and there was a decrease in the maximum adsorption capacity (76.9 mg/g), this decrease may be due to their biodegradability characteristics that restrict continuous recycling (Shetty, 2006).

Table 4. 5: Adsorption and desorption behavior of copper ions on PGCB at a temperature of 25°C, pH of 4 and contact time of 150 min.

| | Mass of wet beads (g) | % mass loss | Maximum adsorption capacity (mg/g) | R ² |
|-----------|-----------------------|-------------|------------------------------------|----------------|
| Cycle I | 0.45 | 0.0 | 83.3 | 0.965 |
| Cycle II | 0.43 | 4.4 | 83.3 | 0.963 |
| Cycle III | 0.41 | 8.9 | 76.9 | 0.954 |

4.5 CONCLUSION

The Langmuir model was shown to successfully describe the adsorption isotherms of copper (II) onto chitosan and PGCB. This model assumes that adsorption takes place at specific homogenous sites on both beads. However, the pseudo second-order was able to describe the kinetics of copper ion adsorption; both the linear correlation coefficient method of determination and the chi square test were in favor of this model.

Three cycles of adsorption/desorption experiment were performed, although there was a 4.4% loss in the mass of PGCB in the second cycle, the maximum adsorption capacity was not affected and in the third cycle, a little drop in the maximum adsorption capacity was observed. This development can help minimize the process cost.

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CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 INTRODUCTION

The use of chitosan to treat wastewater has grown mainly because of its high adsorption capacity when compared to other low cost adsorbent. Chitosan is a nontoxic, biodegradable, hydrophilic, and biocompatible polymer which has the ability to form complex with copper ions due to the presence of amino group in the polymer. These amino groups are capable of reacting with copper ions in the solution by chelation and electrostatic attraction. In this work, modification methods such as transformation of chitosan flakes to chitosan beads and grafting of the beads were actualized, and this was done to increase the pores spaces and thereby allowing easy accessibility of copper ions to adsorption site.

5.1.1 General conclusion

With reference to the problem statement that was presented in 1.1, it is concluded that an adsorbent (PGCB) with desirable properties was developed successfully, whose adsorption capacity (83.3 mg/g) was more than twice that of the chitosan beads (30.3 mg/g) at 25°C. However, it is therefore necessary to develop the PGCB beads into an industrially applicable adsorbent for the removal of copper ions from water and wastewater. Evidence of this can be seen in the adsorption studies where 100% removal of copper ions from solution was achieved at an initial concentration of 40 mg/l. Further evidence was revealed were the regenerated PGCB was used in re-adsorption without any loss in maximum adsorption capacity in the first and second cycle of adsorption/desorption studies.

5.1.2 Specific observation

5.1.2.1 From the results obtained from optimizing the beads, the following conditions for grafting polyaniline onto chitosan was found; [Aniline] 0.1 g/l, [temperature] 35°C, [chitosan] 0.45 g/l, [HCl] 0.4 g/l, [(NH₄)₂S₂O₈] 0.35 g/l, and [time] 1 h.

5.1.2.2 Based on the results obtained from characterizing the beads, evidence of grafting was noticed as follow; FTIR analysis of the PGCB produced increase in intensity at

wavelength around 1150 cm^{-1} to 1400 cm^{-1} in contrast to the low intensity produced by chitosan beads. XRD analysis showed a decrease in crystallinity of PGCB as against that of the chitosan beads. SEM morphology revealed that the gaps between the polysaccharide particles were closed, which is an evidence of successful grafting.

5.1.2.3 From the investigation carried out on the effect of temperature on adsorption capacity, one can say that adsorption of copper ions onto PGCB is temperature dependent, and hence follows a chemisorptions reaction.

5.1.2.4 The Langmuir model described successfully the adsorption isotherms of chitosan beads and PGCB and hence indicates monolayer coverage for both beads.

5.1.2.5 The maximum adsorption capacity of copper (II) for chitosan and PGCB was found to be higher than some literature values that were obtained under comparable conditions.

5.1.2.6 Kinetics of adsorption was described best by the pseudo second-order kinetic model. Both the correlation coefficient (R^2) test and the chi-square test (χ^2) were in favor of this model.

5.1.2.7 The investigation carried out on thermodynamics, clearly revealed that the adsorption process of PGCB is spontaneous and favorable. Also, there was increased randomness at the solid-solution interface during the adsorption reaction.

5.1.2.8 Evidence was found that using the right eluant, proper concentration and reaction time will determine how efficient copper ions will desorb from the PGCB.

5.1.3 Recommendation

After much consideration, the following recommendations are made;

5.1.3.1 Different sizes of chitosan beads should be produced before grafting. In an attempt to determine what size of the beads will best adsorb Cu(II) ion the most.

5.1.3.2 A column study should be performed on the PGCB in comparison to this study.

Appendix A: Experimental and calculated data on graft copolymerization

Table A- 1: Data obtained from the grafting of polyaniline onto chitosan showing the effect of time on graft copolymerization at fixed concentration of chitosan (0.45 g/l), ammonium persulfate (0.35 g/l), aniline (0.1 g/l), HCl (0.1 g/l), at 25°C.

$W_o = 0.45$ g/l

| Time (minute) | Mass of monomer charged (g/l) | Mass of PGCB (g/l) | % Grafting | % Efficiency |
|---------------|-------------------------------|--------------------|------------|--------------|
| 30 | 0.648 | 0.766 | 70.2 | 48.8 |
| 60 | 0.677 | 0.857 | 90.5 | 60.1 |
| 90 | 0.648 | 0.766 | 70.2 | 48.8 |
| 120 | 0.584 | 0.698 | 55 | 42.5 |

Table A- 2: Data obtained from the grafting of polyaniline onto chitosan showing the effect of aniline concentration on graft copolymerization at fixed concentration of chitosan (0.45 g/l), ammonium persulfate (0.35 g/l), HCl (0.1 g/l), for 1 h at 25°C.

$W_o = 0.45$ g/l

| Aniline Concentration (g/l) | Mass of monomer charged (g/l) | Mass of PGCB (g/l) | % Grafting | % Efficiency |
|-----------------------------|-------------------------------|--------------------|------------|--------------|
| 0.05 | 0.677 | 0.857 | 90 | 60.1 |
| 0.1 | 0.730 | 0.945 | 110 | 67.8 |
| 0.2 | 0.677 | 0.857 | 90.7 | 60.1 |
| 0.3 | 0.157 | 0.721 | 60.2 | 45.3 |

Table A- 3: Data obtained from the grafting of polyaniline onto chitosan showing the effect of initiator concentration on graft copolymerization at fixed concentration of chitosan (0.45 g/l), aniline (0.1 (g/l), HCl (0.1 g/l), for 1 h at 25°C.

$W_o = 0.45$ g/l

| Initiator mass (g) | Mass of monomer charged (g/l) | Mass of PGCB (g/l) | % Grafting | % Efficiency |
|--------------------|-------------------------------|--------------------|------------|--------------|
| 0.20 | 0.756 | 0.968 | 115 | 68.5 |
| 0.25 | 0.811 | 1.035 | 130 | 72.1 |
| 0.30 | 0.856 | 1.118 | 148.5 | 78 |
| 0.35 | 0.877 | 1.175 | 161.1 | 82.7 |

Table A- 4: Data obtained from the grafting of polyaniline onto chitosan showing the effect of varying chitosan concentration on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 (g/l), HCl (0.1 g/l), for 1 h at 25°C.

$W_o = 0.45$ g/l

| Chitosan concentration (g/l) | Mass of monomer charged (g/l) | Mass of PGCB (g/l) | % Grafting | % Efficiency |
|------------------------------|-------------------------------|--------------------|------------|--------------|
| 0.45 | 0.891 | 1.193 | 165.2 | 83.4 |
| 0.90 | 0.845 | 1.10 | 144.5 | 76.9 |
| 1.25 | 0.777 | 0.990 | 120 | 69.5 |
| 1.50 | 0.718 | 0.925 | 105.5 | 66.2 |

Table A- 5: Data obtained from the grafting of polyaniline onto chitosan showing the effect of acid concentration on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), chitosan (0.45 g/l) for 1 h at 25° C.

$W_o = 0.45 \text{ g/l}$

| Acid Conc (g/l) | Mass of monomer charged (g/l) | Mass of PGCB (g/l) | % Grafting | % Efficiency |
|-----------------|-------------------------------|--------------------|------------|--------------|
| 0.1 | 0.90 | 1.208 | 168.4 | 84 |
| 0.2 | 0.939 | 1.261 | 180.2 | 86.4 |
| 0.3 | 0.99 | 1.321 | 193.6 | 88 |
| 0.4 | 1.012 | 1.373 | 205 | 91.2 |

Table A- 6: Data obtained from the grafting of polyaniline onto chitosan showing the effect of varying temperature on graft copolymerization at fixed concentration of ammonium persulfate (0.35 g/l), aniline (0.1 g/l), chitosan (0.45 g/l), HCl (0.1 g/l) for 1 h.

$W_o = 0.45 \text{ g/l}$

| Temp (°C) | W_2 (g/l) | W_1 (g/l) | % Grafting | % Efficiency |
|-----------|-------------|-------------|------------|--------------|
| 25 | 1.031 | 1.395 | 210.1 | 91.7 |
| 30 | 1.041 | 1.418 | 215 | 92.9 |
| 35 | 1.050 | 1.436 | 219.2 | 93.9 |
| 40 | 1.032 | 1.396 | 210.3 | 91.7 |

Appendix B: Experimental data for the effect of pH on Cu(II) ions removal by PGCB at a concentration of 40 mg/l.

| pH | Final concentration (mg/l) | Percentage removal |
|----|----------------------------|--------------------|
| 3 | 15.88 | 60.30 |
| 4 | 4.80 | 88 |
| 5 | 0.0 | 100 |
| 6 | 2.68 | 93.30 |
| 7 | 24.24 | 39.40 |
| 8 | 25.60 | 36 |

Appendix C: Experimental data for Isothermal studies

Table C- 1: Adsorption data for un-grafted chitosan beads at 25°C for 150 min

| Co (mg/l) | Ce (mg/l) | Co-Ce | Vol (mL) | qe (mg/g) | % removal | Ce/qe (g/l) | logqe | logCe |
|--------------|--------------|-------|-------------|--------------|--------------|----------------|-------|-------|
| 40 | 17 | 23 | 0.1 | 5.11 | 57.5 | 3.33 | 0.71 | 1.23 |
| 80 | 38.9 | 41.1 | 0.1 | 9.13 | 51.38 | 4.26 | 0.96 | 1.59 |
| 120 | 69.2 | 50.8 | 0.1 | 11.29 | 42.33 | 6.13 | 1.05 | 1.84 |
| 200 | 120 | 80 | 0.1 | 17.78 | 40 | 6.75 | 1.25 | 2.08 |
| 320 | 215 | 105 | 0.1 | 23.33 | 32.81 | 9.21 | 1.37 | 2.33 |
| 400 | 300 | 100 | 0.1 | 22.22 | 25 | 13.50 | 1.35 | 2.48 |

Table C- 2: Adsorption data for un-grafted chitosan beads at 35°C for 150 min

| Co (mg/l) | Ce (mg/l) | Co-Ce | Vol (mL) | qe (mg/g) | % removal | Ce/qe (g/l) | logqe | logCe |
|--------------|--------------|-------|-------------|--------------|--------------|----------------|-------|-------|
| 40 | 9.3 | 30.7 | 0.1 | 6.82 | 76.75 | 1.36 | 0.83 | 0.97 |
| 80 | 30.1 | 49.9 | 0.1 | 11.09 | 62.38 | 2.71 | 1.04 | 1.48 |
| 120 | 44.7 | 75.3 | 0.1 | 16.73 | 62.75 | 2.67 | 1.22 | 1.65 |
| 200 | 70 | 130 | 0.1 | 28.89 | 65 | 2.42 | 1.46 | 1.85 |
| 320 | 179.8 | 140.2 | 0.1 | 31.16 | 43.81 | 5.77 | 1.49 | 2.25 |
| 400 | 230.2 | 169.8 | 0.1 | 37.73 | 42.45 | 6.1 | 1.58 | 2.36 |

Table C- 3: Adsorption data for un-grafted chitosan beads at 45°C for 150 min

| Co (mg/l) | Ce (mg/l) | Co-Ce | Vol (mL) | qe (mg/g) | % removal | Ce/qe (g/l) | logqe | logCe |
|--------------|--------------|-------|-------------|--------------|--------------|----------------|-------|-------|
| 40 | 10 | 30 | 0.1 | 6.67 | 75 | 1.5 | 0.82 | 1.0 |
| 80 | 24 | 56 | 0.1 | 12.44 | 70 | 1.93 | 1.09 | 1.38 |
| 120 | 41.9 | 78.1 | 0.1 | 17.36 | 65.08 | 2.41 | 1.24 | 1.62 |
| 200 | 67 | 133 | 0.1 | 29.56 | 66.5 | 2.27 | 1.47 | 1.83 |
| 320 | 172.6 | 147.4 | 0.1 | 32.76 | 46.06 | 5.27 | 1.52 | 2.24 |
| 400 | 210 | 190 | 0.1 | 42.22 | 47.5 | 4.97 | 1.63 | 2.32 |

Table C- 4: Adsorption data for grafted chitosan beads at 25°C for 150 min

| Co (mg/l) | Ce (mg/l) | Co-Ce | Vol (mL) | qe (mg/g) | % removal | Ce/qe (g/l) | logCe | logqe |
|--------------|--------------|-------|-------------|--------------|--------------|----------------|-------|-------|
| 40 | 0 | 40 | 0.1 | 8.89 | 100 | - | - | 0.95 |
| 80 | 2.2 | 77.8 | 0.1 | 17.29 | 97.25 | 0.13 | 0.34 | 1.24 |
| 120 | 7.4 | 112.6 | 0.1 | 25.02 | 93.83 | 0.30 | 0.87 | 1.40 |
| 200 | 19 | 181 | 0.1 | 40.22 | 90.5 | 0.47 | 1.28 | 1.60 |
| 320 | 45 | 275 | 0.1 | 61.11 | 85.94 | 0.74 | 1.65 | 1.79 |
| 400 | 90.1 | 309.9 | 0.1 | 68.87 | 77.48 | 1.31 | 1.95 | 1.84 |

Table C- 5: Adsorption data for grafted chitosan beads at 35°C for 150 min

| Co (mg/l) | Ce (mg/l) | Co-Ce | Vol (mL) | qe (mg/g) | % removal | Ce/qe (g/l) | logCe | logqe |
|--------------|--------------|-------|-------------|--------------|--------------|----------------|-------|-------|
| 40 | 0 | 40 | 0.1 | 8.89 | 100 | - | - | 0.95 |
| 80 | 0 | 80 | 0.1 | 17.78 | 100 | - | - | 1.25 |
| 120 | 4 | 116 | 0.1 | 25.78 | 96.67 | 0.16 | 0.60 | 1.41 |
| 200 | 5 | 195 | 0.1 | 43.33 | 95.5 | 0.12 | 0.70 | 1.64 |
| 320 | 18 | 298 | 0.1 | 67 | 94.3 | 0.27 | 1.26 | 1.83 |
| 400 | 40 | 360 | 0.1 | 80 | 90 | 0.5 | 1.60 | 1.90 |

Table C- 6: Adsorption data for grafted chitosan beads at 45°C for 150 min

| Co (mg/l) | Ce (mg/l) | Co-Ce | Vol (mL) | qe (mg/g) | % removal | Ce/qe (g/l) | logCe | logqe |
|--------------|--------------|-------|-------------|--------------|--------------|----------------|-------|-------|
| 40 | 0 | 40 | 0.1 | 8.89 | 100 | - | - | 0.95 |
| 80 | 0 | 80 | 0.1 | 17.78 | 100 | - | - | 1.25 |
| 120 | 2 | 118 | 0.1 | 26.22 | 98.33 | 0.06 | 0.08 | 1.42 |
| 200 | 3.2 | 176.8 | 0.1 | 43.73 | 98.40 | 0.11 | 0.07 | 1.64 |
| 320 | 10 | 310 | 0.1 | 68.89 | 96.88 | 0.15 | 1 | 1.84 |
| 400 | 22 | 378 | 0.1 | 84 | 94.50 | 0.26 | 1.34 | 1.92 |

Appendix D: Langmuir and Freundlich plot at temperatures of 25°C, 35 °C and 45 °C.

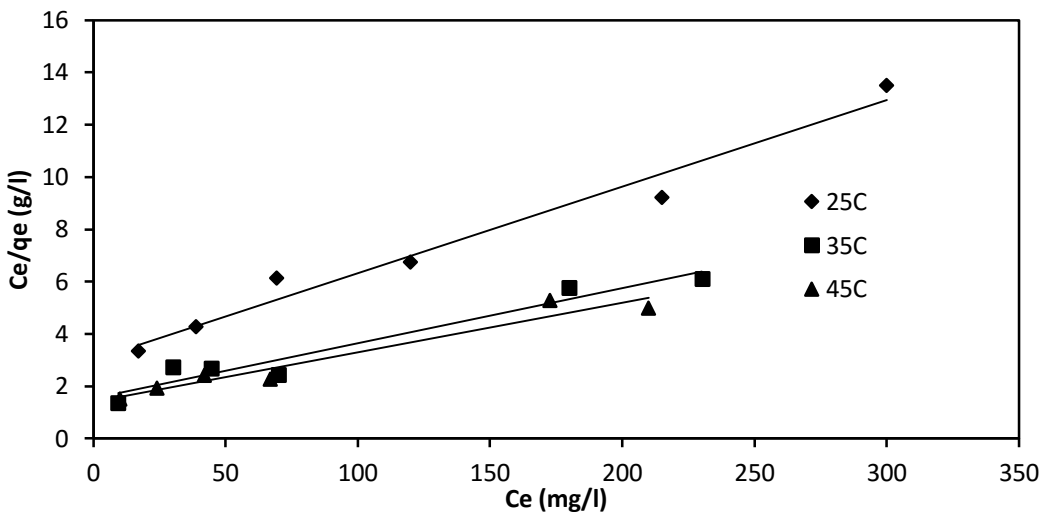


Figure D-1: Langmuir plot for chitosan beads

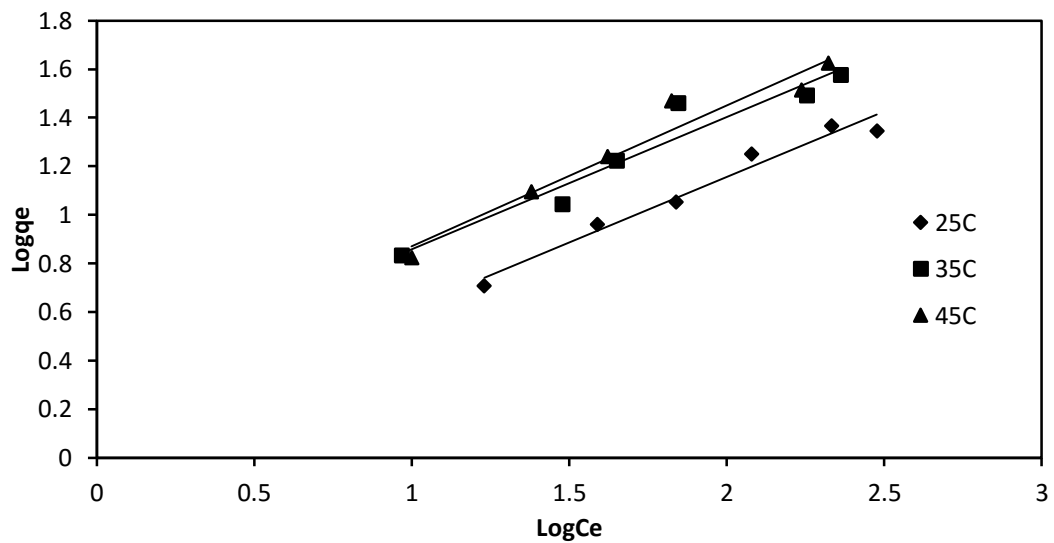


Figure D-2: Freundlich plot for chitosan beads.

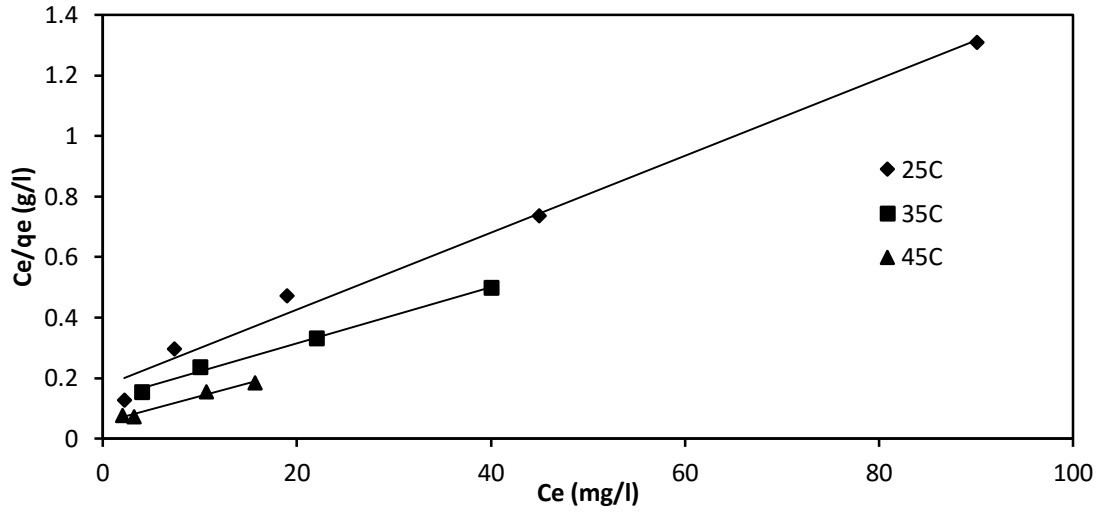


Figure D-3: Langmuir plot for chitosan beads

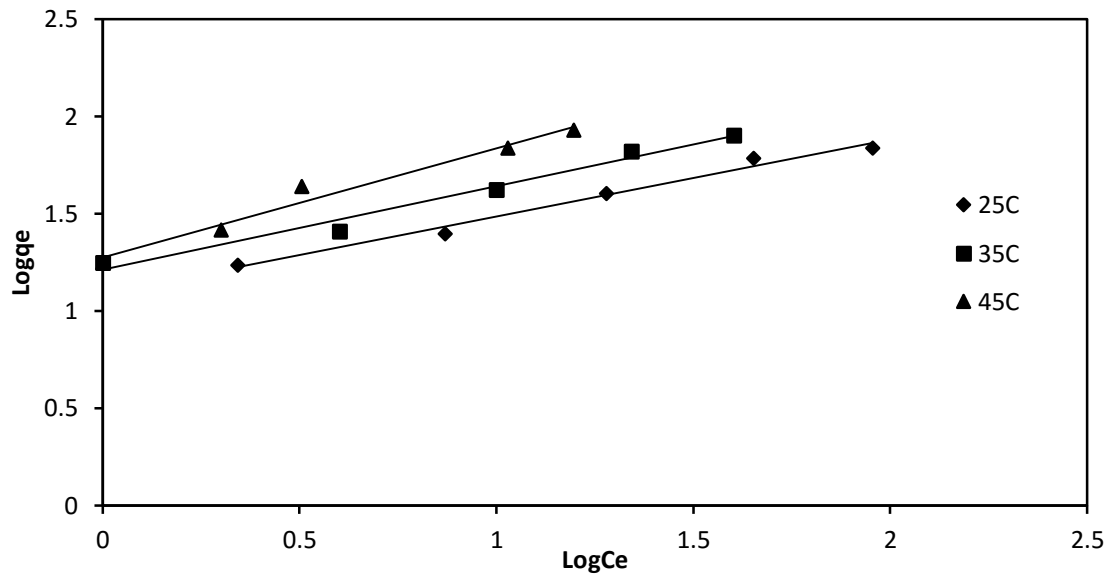


Figure D-4: Freundlich plot for PGCB.

Appendix E: Data for thermodynamics study

Table E- 1: Adsorption data for thermodynamic study at an initial concentration of 200 mg/l

| T (K) | 1/T (K ⁻¹) | Ce (mg/l) | qe (mg/g) | qe/Ce (g/l) | Ln qe/Ce |
|-------|------------------------|-----------|-----------|-------------|----------|
| 298 | 0.0034 | 19 | 40.22 | 2.12 | 0.75 |
| 308 | 0.0032 | 5 | 43.33 | 8.67 | 2.16 |
| 318 | 0.0031 | 3.2 | 43.73 | 13.67 | 2.61 |

Appendix F: Data for kinetic studies at a temperature of 25°C and pH 5.

Table F- 1: Adsorption data for kinetic studies at an initial concentration of 40 mg/l

| Time (min) | Ce (mg/l) | qt (mg/g) | qe-qt | Log(qe-qt) | t/qt | % Removal |
|------------|-----------|-----------|-------|------------|-------|-----------|
| 30 | 10 | 6.67 | 2.22 | 0.35 | 4.5 | 75 |
| 60 | 6.3 | 7.49 | 1.4 | 0.15 | 8.01 | 84.25 |
| 90 | 4 | 8 | 0.89 | -0.05 | 11.25 | 90 |
| 120 | 1 | 8.67 | 0.22 | -0.65 | 13.85 | 97.5 |
| 150 | 0 | 8.89 | | | 16.88 | 100 |

Table F- 2: Adsorption data for kinetic studies at an initial concentration of 80 mg/l

| Time (min) | Ce (mg/l) | qt (mg/g) | qe-qt | Log(qe-qt) | t/qt | % Removal |
|------------|-----------|-----------|-------|------------|------|-----------|
| 30 | 20.1 | 13.31 | 3.98 | 0.60 | 2.25 | 74.88 |
| 60 | 15.1 | 14.42 | 2.887 | 0.46 | 4.16 | 81.13 |
| 90 | 10.2 | 15.51 | 1.78 | 0.25 | 5.80 | 87.25 |
| 120 | 6.2 | 16.4 | 0.89 | -0.05 | 7.32 | 92.25 |
| 150 | 2.2 | 17.28 | | | 8.68 | 97.25 |

Table F- 3: Adsorption data for kinetic studies at an initial concentration of 120 mg/l

| Time (min) | Ce (mg/l) | qt (mg/g) | qe-qt | Log(qe-qt) | t/qt | % Removal |
|------------|-----------|-----------|-------|------------|------|-----------|
| 30 | 33 | 19.33 | 5.69 | 0.76 | 1.55 | 72.5 |
| 60 | 25.4 | 21.02 | 4 | 0.60 | 2.85 | 78.83 |
| 90 | 17.4 | 22.8 | 2.22 | 0.35 | 3.95 | 85.5 |
| 120 | 12 | 24 | 1.02 | 0.01 | 5 | 90 |
| 150 | 7.4 | 25.02 | | | 5.99 | 93.83 |

Table F- 4: Adsorption data for kinetic studies at an initial concentration of 200 mg/l

| Time (min) | Ce (mg/l) | qt (mg/g) | qe-qt | Log(qe-qt) | t/qt | % Removal |
|------------|-----------|-----------|-------|------------|------|-----------|
| 30 | 43 | 34.89 | 9.56 | 0.98 | 0.86 | 78 |
| 60 | 28 | 38.22 | 6.22 | 0.79 | 1.57 | 86 |
| 90 | 19 | 40.22 | 4.22 | 0.63 | 2.24 | 90.5 |
| 120 | 7 | 42.89 | 1.56 | 0.19 | 2.80 | 96.5 |
| 150 | 0 | 43.78 | | | 3.38 | 100 |

Table F- 5: Adsorption data for kinetic studies at an initial concentration of 320 mg/l

| Time (min) | Ce (mg/l) | qt (mg/g) | qe-qt | Log(qe-qt) | t/qt | % Removal |
|------------|-----------|-----------|-------|------------|------|-----------|
| 30 | 102 | 48.44 | 19.33 | 1.29 | 0.62 | 68.13 |
| 60 | 70 | 55.56 | 12.22 | 1.09 | 1.08 | 78.13 |
| 90 | 49.8 | 60.04 | 7.73 | 0.89 | 1.50 | 84.44 |
| 120 | 22.4 | 66.13 | 1.64 | 0.21 | 1.81 | 93 |
| 150 | 15 | 67.11 | | | 2.21 | 95.31 |

Table F- 6: Adsorption data for kinetic studies at an initial concentration of 400 mg/l

| Time (min) | Ce (mg/l) | qt (mg/g) | qe-qt | Log(qe-qt) | t/qt | % Removal |
|------------|-----------|-----------|-------|------------|------|-----------|
| 30 | 150 | 55.56 | 26.67 | 1.43 | 0.54 | 62.5 |
| 60 | 1110 | 64.44 | 17.78 | 1.25 | 0.59 | 72.5 |
| 90 | 80.1 | 71.08 | 11.13 | 1.05 | 0.89 | 79.98 |
| 120 | 50 | 75.56 | 4.44 | 0.65 | 1.56 | 87.5 |
| 150 | 30 | 76.67 | | | 2.74 | 92.5 |

Appendix G: Pseudo first and pseudo second order kinetic plot at different concentration

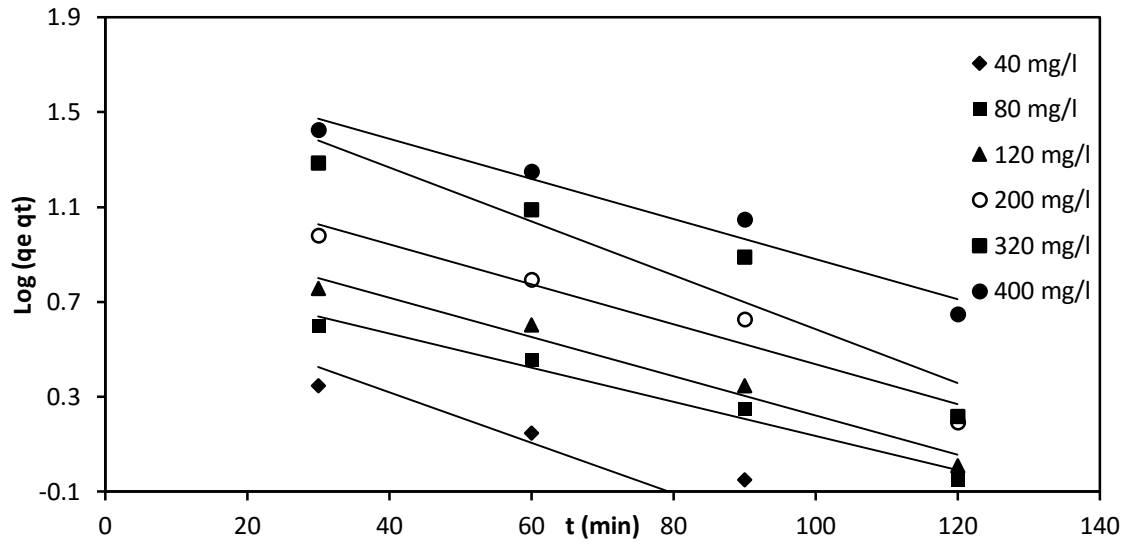


Figure G- 1: Pseudo first order kinetic model plot

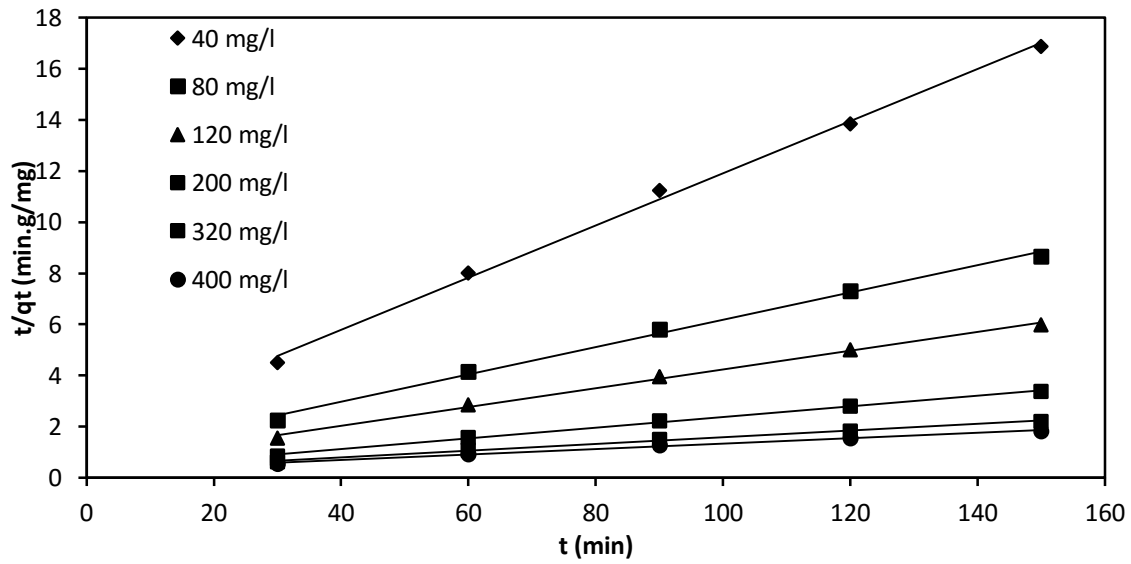


Figure G- 2: Pseudo second order kinetic model plot

Appendix H: Experimental data for desorption studies

Table H- 1: Experimental data showing the effect of varying the concentrations of HCl/HNO₃ system at an initial concentration of 40 mg/l.

| HCl Conc | Amount desorb (mg/l) | Percentage desorption | HNO ₃ Conc | Amount desorb (mg/l) | Percentage desorption |
|----------|----------------------|-----------------------|-----------------------|----------------------|-----------------------|
| 0.01 | 20.04 | 50.10 | 0.01 | 15.84 | 39.60 |
| 0.05 | 30.56 | 76.80 | 0.05 | 22.16 | 55.40 |
| 0.1 | 35.28 | 88.20 | 0.1 | 27.48 | 68.70 |
| 0.5 | 38.84 | 97.10 | 0.5 | 31.76 | 79.40 |
| 0.9 | 29.84 | 74.60 | 0.9 | 20.32 | 50.80 |

Table H- 2: Experimental data showing the effect of time on percentage desorption of copper.

| Time (min) | Initial conc (mg/l) | Final conc (mg/l) | % desorption |
|------------|---------------------|-------------------|--------------|
| 30 | 40 | 14.28 | 35.7 |
| 60 | 40 | 20.56 | 51.40 |
| 90 | 40 | 31.32 | 78.30 |
| 120 | 40 | 36.08 | 90.20 |
| 150 | 40 | 38.84 | 97.10 |
| 180 | 40 | 38.84 | 97.10 |

Table H- 3: Data for first cycle

| Co | Ce | Co-Ce | qe | Ce/qe | % Removal |
|-----|------|--------|-------|-------|-----------|
| 40 | 0 | 40 | 8.89 | 0 | 100 |
| 80 | 2.1 | 77.90 | 17.31 | 0.12 | 97.38 |
| 120 | 6.4 | 113.60 | 25.24 | 0.25 | 94.67 |
| 200 | 16.9 | 183.1 | 40.69 | 0.42 | 91.55 |
| 320 | 35 | 285 | 63.33 | 0.55 | 89.06 |
| 400 | 76.1 | 323.9 | 71.97 | 1.06 | 80.98 |

Table H- 4: Data for second cycle

| Co | Ce | Co-Ce | qe | Ce/qe | % Removal |
|-----|------|-------|-------|-------|-----------|
| 40 | 0 | 40 | 8.89 | 0 | 100 |
| 80 | 2.1 | 77.9 | 17.31 | 0.12 | 97.38 |
| 120 | 6.9 | 113.1 | 25.13 | 0.27 | 94.25 |
| 200 | 17.2 | 182.8 | 40.62 | 0.42 | 91.4 |
| 320 | 36.2 | 283.8 | 63.07 | 0.57 | 88.69 |
| 400 | 77.5 | 322.5 | 71.67 | 1.08 | 80.63 |

Table H- 5: Data for third cycle

| Co | Ce | Co-Ce | qe | Ce/qe | % Removal |
|-----|-------|-------|-------|-------|-----------|
| 40 | 8 | 32 | 7.11 | 1.13 | 80 |
| 80 | 20.3 | 59.7 | 13.27 | 1.53 | 74.63 |
| 120 | 35 | 85 | 18.89 | 1.85 | 70.83 |
| 200 | 71.5 | 128.5 | 28.56 | 2.50 | 64.25 |
| 320 | 130 | 190 | 42.22 | 3.08 | 59.38 |
| 400 | 172.6 | 227.4 | 50.53 | 3.42 | 56.85 |

Appendix I: Chitosan beads production

