OPTIMIZATION STUDIES OF PROCESS PARAMETERS FOR THE ADSORPTION OF COPPER AND ARSENIC IONS FROM SIMULATED WASTE WATER USING CHITOSAN AND CHITOSAN – ZEOLITE BEADS

BY

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NOVEMBER, 2019

ABSTRACT

This research presents the "Optimization Studies of Process Parameters for the Adsorption of Copper and Arsenic Ions from Simulated Waste Water using Chitosan and Chitosan – Zeolite Beads" which was achieved by developing adsorbents of chitosan and chitosan – zeolite composite beads under acidic and alkaline conditions such as acetic acid and sodium hydroxide mediums. The prepared adsorbents were characterized using X - Ray Diffraction, Brunauer Emmett Test, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. The SEM result of chitosan Zeolite has homogenous, cubic crystals and smooth flaky surface evenly distributed in the composite while that of Chitosan beads surface was relatively rough, irregular in shapes and shows presence of agglomerate particles. The mean crystallite size of Chitosan-Zeolite and Chitosan beads were obtained as 41.64 and 74.45 nm. And the BET result shows that the surface area of the Chitosan and Chitosan-Zeolite beads were found to be 376.40 m^2/g and 691.10 m^2/g respectively. Using the central composite design, the effect of the parameters such as adsorbent dosage, initial concentration, temperature and time on the adsorption rate of the heavy metal (Copper and arsenic) from the simulated waste water was investigated. The optimal conditions obtained for both adsorbents (chitosan beads and chitosan – zeolite beads) on copper removal were 0.5g, 0.5M, 50°C and 80mins which translated to 98.03 and 99.78% removal and which also resulted to 96.22 and 99.10% removal respectively. The combined effect of adsorbent dosage and temperature and the combined effect of temperature and time from the four parameters studied for Chitosan beads were found to have the greatest impact on Copper and Arsenic removal while the combined effect of initial concentration and time and that of adsorbent dosage and initial concentration were also found to have the greatest impact on both Copper and Arsenic removal based on their F- values which were found to be (7.27 for Cu and 9.58 for As) removal using Chitosan beads while (17.20 for Cu and 8.69 for As) removal for Chitosan – Zeolite beads . IR spectrum analysis suggested the different functional groups which are present in the Chitosan and Chitosan- Zeolite beads to be -CONH-, -CH₂ and -CH₃, C-O, stretching N-H bending, -NHC00CH₃ and -NH bending. Batch adsorption studies on Chitosan- Zeolite beads for Copper and Arsenic removal showed significant effects on the variables adsorbent dosage, equilibrium time (90 min), initial metals concentration, pH and temperature. The results provide a good indication of the different operating conditions that would be required for efficient removal of Copper and Arsenic from aqueous solution. The isotherm parameters obtained from models revealed that Langmuir was the best isotherm that best described the adsorption process with the highest respective Correlation Coefficient R^2 value of 0.998 and 0.981 for Copper and Arsenic removal on Chitosan-Zeolite beads. The Copper and Arsenic adsorption process on Chitosan- Zeolite beads kinetics data were best modelled by pseudo second order kinetics with the R^2 value 0.999 even at different temperatures. The thermodynamic constants, ΔG , ΔH and ΔS of the adsorption process showed that adsorption of the both metal on the adsorbent were endothermic, spontaneous and is built on the principle of physical adsorption which is caused by van der waals forces a relatively weak bond.

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Plate

I Types of adsorption

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LIST OF ABBREVIATIONS

- BET Brauner Emette Teller
- CH Chitosan Beads
- CH-Z Chitosan Zeolite Beads
- FTIR Fourier Transform Infra-red
- SEM Scanning Electron Microscopy
- XRD X-Ray Diffraction

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

In recent years there has been an increase in the release of heavy metals into the surroundings leading to the contamination of ground water as a result of advancement in industrialization and urbanization. This has led to a great problem of environmental pollution worldwide (Gupta *et al.*, 2011). The presence of heavy metals in minute concentrations plays an important role in the metabolic activities and growth of plants and animals. However, increased concentrations of heavy metals may have several toxicological effects on many life forms (Pahlavanzadeh *et al.*, 2012).

The most hazardous chemical industries are those that deals with heavy metals such as chromium (Cr), Nickel(Ni), Cadium (Cd), Arsenic (As), Lead (Pb) and Copper (Cu). These industries (Example is the metallurgical industries i.e steel industries, and the non – ferrous mining industries) released large amount of heavy metals which contaminates potable clean water and kill aquatic organism due to their high rates of solubility.

As reported by (Mabrouk *et.*, *al* 2010), the adsorption of heavy metals at concentrations above threshold limit into food chains by ingestion can result to serious health related problems. Hence, the treatment of heavy metal contaminated wastewater is a very important step prior to the emission or release to the environment.

Conventional treatment processes such as ion exchange, electrochemical removal and precipitation can be employed in the elimination of heavy metal from inorganic effluent. It is noteworthy to mention that each of these processes have their various disadvantages which includes: creation of toxic sludge, partial removal and sometimes high energy consumption. (Auta and Hammed, 2011).

Recent study for the quest of effective and inexpensive technologies which utilized low cost adsorbent has been intensified. One of such alternative for effluent treatment is adsorption (Auta and Hammed,2011). Adsorption process is a suitable technique for inorganic and organic pollutants removal from wastewater, because of the significant advantages like low-cost, availability, profitability, ease of operation, efficiency, and effectiveness than other techniques (Sarra *et al.*, 2014; Gupta *et al.*, 2011). Adsorption process involves separation of a substance from one phase and its accumulation at another surface. This technique is easy to operate and equally effective in the removal of toxic pollutants, even at low concentrations (Amuda and Edewor, 2013). Though many techniques can be used for the treatment of inorganic effluent, the ideal treatment should not only be suitable, appropriate and applicable to the local conditions but also able to meet the Maximum Contaminant Level (MCL) standards established.

The various adsorbent may be in different forms which could be organic or may have biological origin, minerals, industrial byproduct, biomass, polymeric materials and agricultural waste (Kumari *et al.*, 2016). The commercial activated carbon most widely used as an adsorbent has become economically less feasible owing to its relatively high cost. Recently, different low cost bio sorbent sourced from natural materials and biological wastes

from industrial processes has been studied for the development of cheap and effective metal sorbents (Sethu *et al.*, 2010). Among these low cost adsorbents, chitosan has the highest sorption capacity for several metal ions (Amuda *et al.*, 2013).

Chitosan is obtained from Chitin (2-acetamido-2deoxy- d-glucose-(N-accetylglucan) which is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps (Amuda *et al.*, 2013). It has been reported that approximately 49000 tons of scales per year rounding up to about 2% of fish weight are produced during de – scaling process of fish (Boddu *et al.*, 2008). Fish scales contains connecting tissues, protein, collagen embodied with calcium salt such as calcium carbonate and phosphate, 41% - 84% protein content (Boddu *et al.*, 2008).

Chitin is one of the most abundant and most important natural polysaccharide which has been described to be produced on a yearly basis as much as cellulose found in shells and cell walls of fungi (Zakaria *et al.*, 2011).

Zeolites are crystalline in nature, could be found naturally in the earth's crust or sodium silicate and also can be synthesized under hydrothermal conditions from solutions sodium aluminate. Usually crystalline aluminosilicates with pores of molecular dimensions with high surface area and ordered pore structure. Zeolite which is a multi – purpose material normally source from clay is mostly for engineering purposes one which is adsorption owing to the fact that its molecules have similar diameter order, diameter larger than pore diameter or aperture are separated from entering the pores. However, it is only zeolites that are technically well – prepared that can give optimum performance during its application.

Yang and Zall (1984) reported that chitosan can chelate five to six times greater concentrations of metals than chitin. They further reported this property to be related to the free amino groups exposed in chitosan because of deacetylation of chitin. Chitosan is slightly soluble at low P^H and possesses problems for developing commercial applications. Also, the active binding sites of chitosan are not readily available for sorption. The sites are reported to be soft and have a tendency to agglomerate or form gel in aqueous solutions. Transport of metal contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications. Ascertaining the best operating condition and optimal percentage removal of Copper and Arsenic using Chitosan and Chitosan – Zeolite beads from simulated waste water based on process parameters such as time, adsorbent dosage, initial concentration and temperature so as to ascertain necessitated this research study Also, investigating the mechanism of adsorption kinetics and thermodynamic studies gave an insight of the entire process.

1.2 Statement of the Research Problem

Water pollution is a source of danger to the health of people living in developing countries such as Nigeria. However, industrially generated waste water containing heavy metals such as (Cr), Nickel (Ni), Cadmium (Cd), Arsenic (As), Lead (Pb) and Copper (Cu), Iron (Fe) and Zinc (Zn) have been reported to be potentially harmful and not eco-friendly to the human body system, this is due to their unique composition and content, and if not properly treated or recycled prior to the release for domestic usage , it ultimately results in various health related issues such as cardiomyopathy, Anemia, kidney damage, memory loss, edema, horizontal lines on nails and miscarriages in women.

There is the need for further studies on how these harmful metals could efficiently or totally eliminated using better and readily available adsorbents such Chitosan and Zeolite. Other techniques used for removal of heavy metals are rather inadequate, expensive and generate lot sludge.

1.3 Justification for the Study

Research interest arise as a result of production of alternative adsorbents to replace the expensive adsorbents. Besides, using other techniques for the removal of heavy metal with low concentration apart from them not being suitable also generates a lot of sludge. In view of these, recent study suggests that the use of naturally occurring material like chitosan, zeolite as adsorbents for the remov of heavy metals will be adequate and give remarkable efficiency owing to its regenerating ability, high adsorption capacity, economically viable and also help to reduce the negative effect of this toxic metal in the environment. Consequently, chitosan offers a lot of promising benefits for wastewater treatment and applications today.

1.6 Aims and Objectives of the Study

The aim of this research is to develop chitosan beads and chitosan – zeolite composite beads for the removal copper and arsenic from simulated wastewater. The objectives of the study are to :

 Develop adsorbent using chitosan and chitosan – zeolite beads under alkaline and acidic conditions.

- Characterize adsorbents using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier transformation infrared (FT-IR) for crystal size, surface morphology and surface functional groups respectively.
- 3. Determine the percentage removal of Copper and Arsenic using the developed adsorbents based on time, temperature, initial concentration and adsorbent dosage.
- 4. Carry out the Kinetic, Thermodynamic, and Isotherm study of the heavy metals removal from simulated wastewater using the developed adsorbents.
- 5. Determine Optimal conditions to obtain the highest percent removal of Copper and Arsenic using Central Composite Design (CCD).

1.7 Scope of the Study

This research was limited to development of adsorbents (Chitosan Beads and Chitosan– Zeolite Beads), characterized and forming of composite. The developed chitosan composite was optimized and used for removal of heavy metals from simulated wastewater. Adsorption isotherms, kinetic and thermodynamic study were also carried out.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Heavy Metals

Heavy metals contamination has been a serious environmental concern due to its toxicity, persistency and accumulation. This contamination has increased over decades due to increase in population, which has increased the consumption rate and has led to rapid industrialization. Through industrial processes, heavy metals are released into the air, soil, and water (Deniz *et al.*, 2012). It has been consistently desired that the heavy metals concentrations be reduced at threshold limits in industrial and municipal effluents before ultimate disposal into the environment (Muthusamy *et al.*, 2012).

Researchers have developed various methods such as chemical precipitation, coagulation, adsorption, ion exchange and membrane filtration for the removal of heavy metals from wastewater (Deniz *et al.*, 2012).

2.2 Copper

Copper is classified as a heavy metal that is not poisonous in its metallic form which makes it useful for most industrial applications. As explained by World Health Organization 1998; (Lwin *et al.*, 2008) copper possess high thermal and electrical conductivity, it also has high resistance to corrosion which gives it an excellent property to be used as combustion source such as municipal incinerators, gasoline, diesel, lubricating oil tires, brakes of vehicles and burning of coal. Although, some of its salts are poisonous such as the sulphates form and the sub acetate. Copper sulphate is bluish in colour and crystalline in nature with a metal taste in small dosage (0.5g) but acts as an irritant large dosage (Blasi *et., al* 2007).

Copper toxicity is said to be a condition in which its retention in the lever occurs, it then stops the ability of the liver to detoxify the increased copper level in the body system which in turn affects organs like reproductive systems, connective tissues, adrenal functions ability of a growing child to learn. (Blasi *et., al* 2007).

2.2.1 Chemistry of copper

The commonest ore is chalcopyrite, CuFeS₂, a brass yellow ore that accounts for approximately 50% of the world's copper deposits. Numerous other copper ores of varying colors and compositions exist. Examples are malachite, $Cu_2CO_3(OH)_2$ bright green ore, and the red ore cuprite, Cu₂O. Copper occurs in biological systems as a part of the prosthetic group of certain proteins. (Wayne, 2000).

2.2.2 Uses of copper metal

The electrical industry is the beneficiary of most of the world's copper output. The metal is used in the manufacture of electrical apparatus such as cathodes and wires. Other uses include: Roofing -Utensils -Coins -Metal work -Plumbing -Refrigerator and Air Conditioning coils -Alloys e.g. bronze, brass.

2.2.3 Uses of copper compounds

Copper compounds have their most extensive use in Agriculture. Since the discovery of their toxicity to certain insects, fungi and algae these compounds have been used in insecticides, fungicides and to prevent algal development in potable water reservoirs. They are therefore used in the control of animal and plant diseases. Fertilizers are also often supplemented with copper compounds, e.g. copper sulphate, in order to increase soil fertility and thus boost crop

growth, copper compounds are also used in photography and as colorants for glass and porcelain. (Wayne, 2000).

2.3. Chemistry of Arsenic

2.3.1.1 Arsenic forms and mobility

Occurrence of arsenic is rarely in a free state, it is largely found together with sulphur, oxygen, and iron (Chen and Chung, 2006). In natural water, arsenic combines with oxygen to form inorganic pentavalent arsenate and trivalent arsenite (Fan *et al.*, 2012). Different from other heavy metalloids and oxy-anion-forming elements, arsenic mobilization can be at the pH values typically found in surface and ground waters (pH 6.5 to 8.5) and under both oxidizing and reducing conditions (Gupta *et al.*, 2010). Arsenic unlike other oxyanion-forming elements are found within the μ g/L range, while other oxyanion can be found within the mg/L range (Blasi *et al.*, 2007).

Arsenic occur in the environment in varying oxidation states (-3, 0, +3 and +5), frequently as sulfides or metal arsenides or arsenates (Pahlavanzadeh *et al.*, 2012). In ground water its major forms are inorganic oxy-anions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)) (Blasi *et al.*, 2007).

The toxicity of various arsenic groups varies in the order arsenite> arsenate > monomethylarsonate > dimethylarsinate. Trivalent arsenic is about 60 times more toxic than arsenic in the oxidized pentavalent state, and inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds (Ferguson and Hering, 2006). The organic forms of arsenic are much more unimportant and are found frequently in surface waters or in areas severely affected by industrial pollution (Balarama *et al.*, 2001). Risks of arsenic related

diseases have been reported to be on the increase and associated with ingestion of drinkingwater at concentrations of $< 50 \mu g/L$ (Pahlavanzadeh *et al.*, 2012).

2.4 Determination Heavy Metals using UV Spectrophotometer

Spectrophotometry is the quantitative measurement of the transmission properties of a material as a function of wavelength. It generally involves spectrophotometry that deals with visible light, near-ultraviolet, and near-infrared, but does not cover time-resolved spectroscopic techniques compared to the general term Electromagnetic Spectrophotometry uses photometers that can measure a light beam's intensity as a function of its colour (wavelength) known as spectrophotometers. Important features of spectrophotometers are spectral bandwidth, (the range of colours it can transmit through the test sample), and the percentage of sample-transmission, and the logarithmic range of sample-absorption and sometimes a percentage of reflectance measurement.

A spectrophotometer is commonly used for the measurement of transmittance or reflectance of solutions, transparent or opaque solids, such as polished glass, or gases. However they can also be designed for the measurement of diffusivity on any of the listed light ranges that can cover around 200 nm - 2500 nm using different controls and calibrations. Within these ranges of light, calibrations are needed on the machine using standards that vary in type depending on the wavelength of the photometric determination (He *et al.*, 1999).

2.5 Importance of Chitosan Immobilisation for Arsenic Removal

Systematic investigation on the studies of arsenic uptake from aqueous solutions by chitosan and chitosan nanoparticles are listed in Table 2.1

Product	References
Chitosan without modifications (CH)	Elson et al., (1980) Chen and Chung, (2006).
Chitosan bead	
impregnated with	Guibal et al., 1999, Dambies et al., (2000).
Molybdate (MICB)	Miller and Zimmerman 2010 Miller et al. (2011)
Titanium dioxide (TICB)	Miller and Zimmerman, 2010, Miller <i>et al.</i> , (2011).
Chitosan beads impregnated with	
iron (FICB)	Liu et al., 2010, Gang et al., (2010).
Iron coated chitosan flakes (ICF)	Gupta <i>et al.</i> , (2009).
Zerovalent iron encapsulated chitosan nanospheres (ZIEN)	Gupta <i>et al.</i> , (2012).
-	Dos Santos et al., (2011).
Iron cross-linked chitosan (F-CH)	
	Liu <i>et al.</i> , (2011).
Iron impregnated chitosan beads impegnated with As(III) (As-ICR)	
	Chassary et al., 2004, Singh et al., (2011).
Glutaraldehyde cross-linked chitosan (GLU-CH)	
	Wei <i>et al.</i> , (2011).
N-Methylglucamine immobilized on	
crosslinked chitosan beads (MG-CH)	Boddu <i>et al.</i> , (2008).
Chitosan-coated ceramic alumina	
(CH-CA)	$C_{\text{constraint}}$ (2011)
GS)	Gupta <i>et al.</i> , (2011).
Chitosan immobilized sodium silicate (CH-SS)	Boyaci et al., (2010)

Table 2.1 Chitosan and Chitosan Nanoparticles used for Arsenic uptake from Water

Crude chitosan is hardly use for arsenic adsorption from water. Often times chitosan derivatives, obtained through chemical and physical modifications, cross-linking, modifying its physical structure, immobilizing it on insoluble supports, or impregnating it with metals are preferred. This is due to poor stability of chitosan at the pH optimal for arsenic removal (Chen *et al.*, 2006); reduced accessibility of chitosan active sites (Dambies *et al.*, 2002); the

supposed low sorptive capacity of chitosan especially for As(III) (Gupta and Sankararamakrisham, 2010); poor physical structure of chitosan for continuous-flow treatment plant applications (Liu *et al.*, 2011); and difficulty to define a standard raw chitosan because of heterogeneities related to its deacetylation degree (Gupta *et al.*, 2011). Having stated that the capacity of chitosan for interacting with anions is related to the protonation of its amine groups, the latter is also responsible for its solubility. It can be important to modify the polymer to obtain a molecule of low solubility, which can be used in acidic conditions. Such a result is reached by cross-linking chitosan, generally using glutaraldehyde (Dambies *et al.*, 2000).

The process takes place through the formation of a base between the coupling agent and some amino and hydroxyl groups of chitosan. This produces a closed network that increases the chemical stability of chitosan (Boyaci et al., 2010). Another reason for chitosan modification is related to the low porosity (Guibal et al., 1999) and residual crystallinity (Gupta et al., 2012) of the raw molecule, which represents an obstacle for the diffusion mechanisms governing the adsorption process. This also limits the number of available active sites to the external layers of the polymer. Both cross-linking and chitosan gel beads manufacturing are able to increase the porosity and reduce the crystallinity of the raw molecule (Gang *et al.*, 2010), although cross-linking operations could restrict the accessibility of internal sites or reduce the segment mobility (Dos santo et al., 2011). Chitosan immobilization onto a supporting surface is another way to increase the surface area of the sorbent. In this case, the molecular mobility of the chitosan is not affected, while the number of available and accessible active sites is increased (Gupta et al., 2009). Physical modification is also aimed at improving mechanical resistance (Wei et al., 2011). Application of chitosan powder or flakes in column studies demonstrates, in fact, a rapid drop of available hydraulic charge, which does not allow correct hydrodynamic working conditions. Metal impregnation is proposed to increase arsenic uptake capacity and favour chitosan selectivity over other metal ions and co-ions. The metals employed are those like molybdenum and iron, which are known to form complexes with arsenate ions and for their strong affinity for chitosan (Liu *et al.*,2010).

The same effect is obtained by immobilizing N-methylglucamine on chitosan beads because the N-methylglucamine moiety is known for its capacity to remove arsenic (Miller *et al.*, 2011).

Titanium dioxide impregnation is also used (Boddu *et al.*, 2008) to oxidize As(III) to As(V), which is normally removed more efficiently by chitosan, also chitosan can be impregnated with iron alumina, or mix metals.

2.6 Sorption Efficiency of Copper and Arsenic

This is the ability of impregnated or immobilize chitosan to take up arsenic and other pollutants from ground waters and waste waters. While the initial attempts to use chitosan for arsenic removal from aqueous solutions did not reach quantitative values (Chassaey *et al.*, 2004), later research carried out using either raw chitosan or chitosan-modified materials attained quite good results, as indicated in Table 2.4. The table shows the maximum value of arsenic sorption capacity for various adsorbents.

Product	As(V)(mg	As(III)(mgg ⁻¹)	MMAA	DMAA	References
	g-1)		$(mg g^{-1})$	$(mg g^{-1})$	
		1.92	8 /	8 /	Elson et al. (1090)
Сп	—a	1.85			EISOII <i>et al.</i> , (1980)
	—a				Kartal and Imamura, 2005)
	0.73				$C_{\text{constant}} = \left(-\frac{1}{2} \left(2005 \right) \right)$
	1.94				Gerente <i>et al.</i> , (2005)
	14.16				Chen and Chung, (2006)
	14.16				Kwok et al., (2009)
	4.02				Kwok and (McKay, 2010)
					Gerente et al., (2010)
MICB					Guibal et al., (1999)
		69			Dambies et al., (2000)
		80			Dambies et al., (2002)
		1.98			Chassary et al., (2004)
					Chen et al., (2008)
TICB	4.9	6.4			Miller and
	—b	—b			Zimmerman, (2010)
					Miller et al., (2011)
FICB	4.28				^e Liu et al., (2010)
	22.6	6.48			Gang et al., (2010)
	25.8				Gupta and Sankararamakrishnan, (2010)
ICF	16.5	22.5			Gupta et al., (2009)
ZIEN	119	94			Gupta et al., (2012)

 Table 2.2: Arsenic Sorption Capacity of Chitosan and Chitosan Derivatives

		4			
Product	As(V)(mg g ^{_1})	As(III)(mgg ⁻¹)	MMAA (mg g ⁻¹)	$DMAA (mg g^{-1})$	References
As-ICR	9.35				Liu et al., (2011)
	4.45				Liu et al., (2011)
GLU-	—b	—b			Chassary et al., (2004)
СН	270				Singh et al., (2011)
MG-CH	69.28		15	7.1	Wei et al. (2011)
					Wei et al., (2011)
CH-CA	96.48	56.50			Boddu et al., (2008)
CH-GS	23	17			Gupta et al., (2011)
CH-SS	—c				Boyaci et al., (2010)

Table 2.2a: Arsenic Sorption Capacity of Chitosan and Chitosan Derivatives

2.7 Some Earlier Facts of Chitin

Chitin came into being in 1823 when Frenchman Oldier boiled the wing of insects with potassium hydroxide only to obtain a non-soluble substance which subsequently was named Chitin. The term chitosan was given to de- acetylated chitin by Hoppe Seiler in 1894 (Divya and Jisha, 2017).

Chitin is naturally formed in the invertebrates and lower plants. It is the second most abundant material on earth after cellulose. Chitin $(C_8H_{13}O_5N)_n$, a long-chain polymer of N-acetylglucosamine, is a derivative of glucose. It is a primary component of cell walls in fungi, the exoskeletons of arthropods, such as crustaceans (e.g., crabs, lobsters and shrimps) and insects, the radulae of molluscs, cephalopod beaks, and the scales of fish and lissamphibians. (Tang *et al.*, 2015).

Chitin, poly (b-(1-4)-N-acetyl-D-glucosamine), is a natural polysaccharide of major importance, first identified in the year 1884 (Rinaudo, 2006). Among the novel families of biological macromolecules, whose relevance is becoming increasing evident are chitin and its main derivative, Chitosan, the deacetylated form of chitin, is a polysaccharide formed primarily of repeating units of β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucose or D-glucosamine).

Chitosan is a natural polysaccharide comprising of copolymers of glucosamine and *N*-acetyl glucosamine, and can be obtained by the partial deacetylation of chitin. Only with the advent of bio-technology in 1859 was the process of deriving Chitosan from Chitin made possible. Chitosan was discovered in 1859 by Professor C. Rouget. Chitosan has been regarded as a source of potential bioactive material. It is the main and most important derivative of Chitin for industrial consumption, since it is soluble in acidic aqueous systems and, by extension, in human body (Gang, 2010). From Chitosan, many more derivatives are obtained, each with its own unique characteristics.

Chitosan a biopolymer, which is extracted from crustacean shells or from fungal biomass, has structure of chitin and chitosan derivatives represented schematically in Figure 2.1 and Figure 2.2.



Figure 2.1: Chemical Structure of Chitin (Lamprecht et al., 2001).



Figure 2.2: Chemical Structure of Chitosan (Lamprecht et al., 2001).

Chitosan is insoluble in most organic solvents and in water at neutral. However, it dissolves in acidic solutions (Jegadeesan *et al.*, 2010). There exist more than 200 Potential and usual applications of chitin, chitosan and their derivatives (Kato *et al.*, 2002). It is the second-most abundant high molecular-weight biopolymers and is recognized as versatile, environmentally friendly raw materials (Zhang and Friedrich, 2005). Chitin is the major component in the shell of the shrimps, and crabs, cartilage of the squid, and outer cover of insects. It also occurs as ordered crystalline micro fibrils forming structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast. It is also extracted from a number of other living organisms in the lower plant and animal kingdoms, serving in many functions where reinforcement and strength are required (Rossman, 2006).

In General, the shell of selected crustacean was reported to consist of 30-40% protein, 30-50 % calcium carbonate and calcium phosphate, and 20-30 % chitin (Diebold, 2003). Depending on the processing method used to derive the chitin (Harish and Tharanathan, 2003), and also depending on the source, its degree of deacetylation may range from 30% to 95% (Lee *et al.*, 2004).

Chitin and its deacetylated derivative chitosan are natural polymers composed of randomly distributed β (1-4) - linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Chitin is insoluble in aqueous media while chitosan is soluble in acidic conditions due to the free protonable amino groups present in the D- glucosamine units. Due to their natural origin, both chitin and chitosan cannot be defined by a unique chemical structure but as a family of polymers that present a high variability in their chemical and physical properties. Chitosan is a natural polysaccharide comprising of copolymers of glucosamine and *N*-acetyl glucosamine, and can be obtained by the partial deacetylation of chitin (Aravind *et al.*, 2009).

2.8 Chitosan Applications and its Derivatives

Chitosan has been widely used in diverse fields, ranging from waste management to food processing, medicine and biotechnology (López-León *et al.*, 2005). In agriculture, the use of chitosan has been established to improve the yield of rice and orchid production (Miller and Zimmerman, 2010). Also in the paper industry, biodegradable chitosan can strengthen recycled paper and increase the environmental friendliness of packaging and other products (Huang and Fu, 1984). More so in the field of photography, chitosan has been used as a fixing

agent for the acid dyes in gelatin and also acts as an acid to improve diffusion which is an important step in the development of photographs (Arai *et al.*, 2001).

Chitosan and its derivatives have also been used in the field of medicine for wound dressing to enhance healing and burn treatment. Surgical gauze, coated with chitin demonstrated a substantially greater amount of activity more than the uncoated control group (Konstantinou and Albanis, 2004). More so, due to the ability of chitosan to form tough, water absorbent and biocompatible films it is applied to treat burns (Konstantinou and Albanis, 2004).

2.9 Nanoparticles from Chitosan

A portion of chitosan undergoes extensive crosslinking to yield modified chitosan whose properties are different from those of native chitosan. Polymer crosslinking leads to the formation of a permanent covalent network, which may allow the free diffusion of water/bioactive materials and also enhance mechanical properties of a polymer. The antimicrobial, biocompatible, and biodegradable properties of chitosan make it an ideal candidate for the applications on polymeric film, protective food coating and controlled released drug carrier. In view of its hydrophilicity, excellent film-forming ability, good mechanical properties, and high chemical reactivity, chitosan can be an excellent candidate for affinity membranes. Until now, chitosan membranes have been used for active films in food area pervaporation, and Inorganic particles as well known to enhance the mechanical and tribological properties of polymers, and this issue has been widely investigated. Reducing the particle size to a nano-scale level is suggested to improve significantly the composite efficiency; nanoparticle-filled polymers, the so-called polymer nanocomposites, are very promising materials for various applications (Tchounwou *et al.*, 2003).

2.10 Methods of Preparation of Chitosan Nanoparticles

Nanoparticles are defined as particulate dispersions or solid particles with a size in the range of 1-100 nm. Methods, such as the emulsion method, ionic gelation method (Liu, *et al.*, 2005), reverse micellar method, self-assembling method (Li – Ming *et al.*, 2011), have been used Coated chitosan is finally obtained by dissolving the polymer into oxalic acid and by adding to the solution the used inert material (Tao *et al.*, 2007) to prepare chitosan nanoparticles.

2.10.1 Emulsion droplet coalescence

This method is a derivation of the emulsification and cross-linking method described above and was first reported for micro particles preparation (Wang *et al.*, 2004). The same authors later adapted the method to prepare chitosan nanoparticles loaded with gadolinium, as a strategy for neutron-capture therapy of cancer (Elson *et al.*, 1980). Chitosan is dissolved in the aqueous solution of gadolinium and a small aliquot (1 mL) of this is added to 10 mL of liquid paraffin containing sorbitansesquiolate. The mixture is stirred with a high-speed homogenizer, thus forming an W/O emulsion. In parallel, another W/O emulsion is prepared by adding 1.5 mL NaOH to 10 mL of a similar outer phase. Both emulsions are then mixed using a high-speed homogenizer, leading to droplet coalescence. This results in the solidification of chitosan particles by action of NaOH, which acts as precipitating agent. Afterwards, a further set of washing and centrifugation steps is applied using toluene, ethanol and water (Elson *et al.*, 1980).

2.10.2 Emulsion solvent diffusion

The emulsion solvent diffusion method of preparing chitosan nanoparticles is an adaptation of the original procedure developed to produce Poly (Lactic- co-glycolic acid) PLGA-based nanoparticles (Lamprecht *et al.* 2001). Setting its basis on the partial miscibility of an organic solvent with water. The specific method for preparation of chitosan nanoparticles involves the addition of an organic phase (e.g. methylene chloride and acetone) containing the hydrophobic drug, to an aqueous solution containing chitosan and a stabilizer (e.g. poloxamer and lecithin), under stirring (Rossman, 2003). This leads to the formation of an emulsion which is then subjected to high pressure homogenization. Methylene chloride is subsequently removed under reduced pressure at room temperature. At this stage, acetone diffuses to the aqueous phase, decreasing chitosan solubility and, thus, nanoparticles are formed upon polymer precipitation. An additional amount of water is usually added in order to permit the complete diffusion of acetone. Finally, nanoparticles are isolated by centrifugation.

Notwithstanding, the ability of this method to produce effective vehicles, and it is important to highlight the need for harsh preparation conditions, such as organic solvents and high shear forces, which are absent in several other methods that will be described in subsequent sections.

2.10.3 Reverse micellar method

Ultrafine polymeric nanoparticles with a narrow size range can be prepared with this method. The surfactant is dissolved in an organic solvent to prepare reverse micelles. An aqueous solution of chitosan is added with constant agitation to avoid any turbidity. The aqueous phase is regulated in such a way as to keep the entire mixture in an optically transparent micro emulsion phase. More water should be added if nanoparticles of a larger size are to be
prepared. (Zhang *et al.*,2008) used a reverse micellar method to prepare chitosan nanoparticles. The lower the molar mass of chitosan, the better the control over particle size and size distribution, probably as a result of either a reduction in the viscosity of the internal aqueous phase or an increase in the disentanglement of the polymer chains during the process.

Kumari *et al.*,(2010) prepared Bovine Serum Albumin (BSA)-loaded chitosan nanoparticles using the reverse micellar method. Particles were obtained in the size range of 143 to 428 nm. The FTIR spectrum indicated that BSA was successfully encapsulated into the chitosan nanoparticles. The chitosan concentration and BSA loading played an important role in the release of BSA. Increasing the chitosan solution concentration decreased the release of BSA, both with a BSA loading of 10 % and 20 %, while decreasing the BSA loading accelerated the release of BSA at either a chitosan concentration of 0.1% and 0.2%.

Magnetic chitosan nanoparticles were prepared by a reversed phase suspension method using Span-80 as an emulsifier and glutaraldehyde as cross-linking reagent (Garcia *et al.*,2009). Laccase was immobilized on the chitosan nanoparticles which exhibited an appreciable catalytic capability and had good storage stability and operation stability. The immobilized and free laccase were 140.6 and 31.1 μ M in phosphate buffer (0.1 M, pH 3.0), respectively. The immobilized laccase is a good candidate for the research and development of biosensors based on laccase catalysis.

As compared to other emulsion-based methods, the reverse micellisation method has the advantage of producing ultrafine nanoparticles of around 100 nm or even less, with a narrower size range, in contrast to the larger nano carriers (> 200 nm) usually obtained by

other emulsification techniques. Nevertheless, disadvantages such as the difficult isolation of nanoparticles and the need for larger amounts of solvent, have been mentioned (Yang *et al.*, 2007).

2.10.4 Ionic gelation method

Chitosan nanoparticles can be prepared by the interaction of oppositely charged macromolecules. Tripolyphosphate (TPP) has often been used to prepare chitosan nanoparticles because TPP is nontoxic, multivalent and able to form gels through ionic interactions. The interaction can be controlled by the charge density of TPP and chitosan, which is dependent on the pH of the solution.

Fernandez-Saiz *et al.*, (2009) studied the influence of a number of factors, such as pH, concentration, ratios of components, and method of mixing, on the preparation of chitosan/TPP nanoparticles. (Lin and Wu, 2001) investigated the relationship between free amino groups on the surface and the characteristics of chitosan nanoparticles prepared by the ionic gelation method. These factors were unaffected by TPP concentration in these references.

2.10.5 Desolvation

The method of desolvation is also frequently referred to as simple coacervation or phase separation which involves a macromolecular aggregation brought about by partial desolvation of fully solvated molecules (Gan *et al.*, 2005).

The use of desolvating agents to produce chitosan particles was reported for the first time for the preparation of micron-sized carriers (Matsunaga *et al.*, 1996). But nowadays, this

procedure is frequently applied to the production of chitosan nanoparticles. Substances such as sodium sulfate (Ferguson *et al.*, 2005) and non-solvents miscible with water, like acetone have been proposed as precipitating agents, although the former has been used more frequently (Blasi *et al.*, 2007). The preparation of chitosan nanoparticles by this method is very simple and mild as it involves the drop wise addition of the solvent competing agent of greater hydrophilicity (e.g. sodium sulfate) into a previously formed chitosan solution. As the salt gets in contact with the aqueous environment of chitosan solution, a progressive elimination of salvation water surrounding chitosan occurs as a consequence of the higher affinity of water for the salt.

Eventually, this process leads to the polymer insolubilisation and its consequent precipitation (Janes and Alonso, 2003). This effect is observed because water-salt interactions are more favourable than those occurring between the water and the polymer inducing the partial desolvation of chitosan. This, in turn, leads to increased interactions between chitosan molecules, forming the nano carriers (Javier *et al.*, 2007). It is very frequent to include a stabilizer such as polysorbate 80 in the preparation medium, to stabilize the nanoparticle suspension. A subsequent process of cross-linking, for instance with glutaraldehyde, has been described, in order to harden the nanoparticles (Abdelwahed *et al.*, 2006). Factors such as chitosan molecular weight, chitosan concentration, amount of desolvating agent and stirring rate have been found to strongly affect the final characteristics of nanoparticles. Therefore, it is necessary to undergo an optimisation of these parameters. In addition, a correlation was identified between the amount of sulphate ions needed and chitosan properties, like the molecular weight and the deacetylation degree (Ladeira and Ciminelli, 2004).

2.11 Chitosan Beads

This can be prepared by dissolving chitosan into acetic acid and pumping the obtained viscous solution into a coagulating bath. Metal impregnation results either by adding the metal solution to the viscous solution before coagulation or by putting the beads into a solution containing the metal or finally, by changing the coagulating bath to a metal solution (ionotropic gelation). For example, chitosan-immobilized sodiumsilicate is obtained by changing the coagulating bath to sodium silicate solution. Chitosan zeroviolent iron nanoparticles are obtained reducing Fe(III) with NaBH₄ using chitosan as stabilizer (Tirelli, 2009).

In the case of iron cross-linked chitosan production, the polymer is previously impregnated with ferric nitrate and then cross-linked. Iron impregnated chitosan beads can also be impregnated with As (III) ions to obtain a selective imprinted sorbent for Arsenite to obtain As(III)-impregnated chitosan resin. In this case, the cross-linking step is carried out after loading with As(III) solution and α -Fe₂O₃. Afterwards, the template ions are removed by acid treatment N-Methylglucamine immobilization on cross-linked chitosan beads is achieved, instead, after chitosan bead cross-linking, immobilizing onto the beads the atom transfer radical initiator for the polymerization of glycidyl methacrylate.

2.12 Chitosan Composites

Chitosan is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. (Kumari *et al.*, 2016). Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl

groups, which can serve as the active sites (Wu *et al.*, 2001). Amino groups of chitosan can be cationized, after which they adsorb anionic dyes strongly by electrostatic attraction in the acidic media (Kumari *et al.*, 2016). However, chitosan is very sensitive to pH as it can either form gel or dissolve depending on the pH values (Chiou *et al.*, 2004).

To improve chitosan performance as an adsorbent, cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon diglycidyl ether and isocyanates have been used (Crini *et al.*, 2005). Cross-linking agents do not only stabilize chitosan in acid solutions so that it becomes insoluble but also enhance its mechanical properties (Chiou *et al.*, 2004).

Recently, chitosan composites have been developed to adsorb heavy metals and dyes from wastewater. Different kinds of substances have been used to form composite with chitosan such as montmorillonite (Wang, 2004), polyurethane (Lee, 2009), activated clay (Juang, 2009), bentonite (Tao *et al.*, 2010), kaolinite (Ming *et al.*, 2010), oil palm ash (Hameed *et al.*, 2009) and perlite (Kalyani *et al.*, 2005). Chitosan composites have been proven to have better adsorption capacity and resistance to acidic environment (Wang *et al.*, 2010).

2.13 Zeolites

Bell, in 2001, defined zeolites as microporous crystalline solids with well-defined structures. Generally, they contain silicon, aluminium and oxygen in their framework and metal cations, water and / or other molecules within their pores. Also the commission on new minerals and mineral names stated that "A zeolitic mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedral, each consisting of four oxygen atoms surrounding a metal cation. This framework contains open channels and cages, and as aforementioned, is usually occupied by H₂O molecules and extra-framework cations that are commonly exchangeable.

By the conventional definition, zeolites are microporous aluminosilicates. This definition, according to Ajayi and Adefila (2015) has been modified within the past years and currently isomorphously substituted materials, like for example gallosilicates, titanosilicates or aluminophosphates, are also called zeolites or zeolitic materials. Microporosity (pores with diameters below 2 nm) is an intrinsic feature of all these materials and is caused by channels and cavities within the crystal structures of zeolites. The wide application of zeolites on environmental management is based on its unique properties. Thus zeolites contain cations like Na⁺, K⁺, or NH4⁺ after synthesis. The negative net–charge caused by the trivalent aluminium cations are balanced by the aforementioned cations which are coordinated tetrahedrally by oxygen ions. When solutions containing other metal cations are in contact with zeolite containing sodium ions (Zeolite 4A), the sodium ions can be exchanged with the other ion provided the ions are within the zeolite pore size (molecular sieve).

In another presentation, Ajayi and Adefila (2015) averred that "Zeolites are traditionally known as advanced materials resulting from crystalline silicates and aluminosilicates linked through oxygen atoms, producing a three-dimensional network containing channels and cavities of molecular dimensions. However, some relatively recent discoveries of materials virtually identical to the classical zeolite, but consisting of oxide structures with elements replacing silicon and aluminium from their corresponding columns in the Periodic Table of Elements have stretched the definition. Most researchers now include in their definition of a zeolite virtually all types of these tailorable micro porous oxide structures that have well-

defined pore structures due to a high degree of crystallinity. These oxides are of titanium, gallium, iridium, thallium and phosphates, e.g. AIPOs SAIPOs, GaPOs, etc. The original elements silicon and aluminium can similarly be substituted to extend the formation of zeolites, beyond linking the Columns Three and Four elements, to other contiguous elements, to produce novel advanced materials; the elements can also be replaced with organic functional groups to form organometallic zeolites.

The zeolite history began with the discovery of stilbite by Crönstedt, a Swedish mineralogist in year 1756. Upon heating the zeolite released occluded water, which gave the materials their general name, zeolite, after the Greek words, " $\xi \epsilon_i v$ " (*zeo*), to boil, and " $\lambda_i \vartheta_{0\varsigma}$ " (*lithos*), stone. A representative empirical formula of a zeolite is

$$M_2/nO. Al_2O_3. xSiO_2. yH_2O$$
 (2.1)

where M represents the exchangeable cation of valence n. M is generally a Group I or II ion, although other metal, non-metal and organic cations may also balance the negative charge created by the presence of Al in the structure. The framework may contain cages and channels of discrete size, which are normally occupied by water (Goto *et al.*, 1994).

2.13.1 Properties of zeolites

Zeolites are very stable solids that resist the kind of environmental conditions that challenge many other materials. They have relatively high melting point (over 1000 °C), so they are not affected by high temperature. Zeolite also have resistance for high pressure, oxidized in air and do not have any environmental effects (Medhat, 2015).

2.14 Applications of Zeolites

2.14.1 Catalysis

This is the ability of Zeolites to act as catalysts in chemical reactions taking place in their internal cavities. The reaction catalyzed by hydrogen-exchange zeolites is one of the important reaction in which the framework-bound protons gave rise to a very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerization and fuel synthesis Wei *et al.*, (2011). They often serve as oxidation or reduction catalysts, after metals have been introduced into the framework. Examples are the use of titanium ZSM-5 in the production of caprolactam, and copper zeolites in NOx decomposition.

Zeolites also act as shape-selective catalysts. Moreover, there are many advantages of utilizing zeolites as catalyst and these include; ease of recovery and recycling at low cost, and it is environmentally friendly as fewer by- product are released. Furthermore, attention has been focused on engineering the properties of zeolite catalysts so as to carry out very specific syntheses of high-value chemicals e.g. pharmaceuticals and cosmetics (Helfman, 2005).

2.14.2 Ion exchange

Hydrated cations within the zeolite pores are bound loosely to the zeolite framework, and can readily exchange with other cations when in aqueous media. Applications of this can be seen in water softening devices, and the use of zeolites in detergents and soaps. The largest volume use for zeolites is in detergent formulations where they have replaced phosphates as water-softening agents. They do this by exchanging the sodium in the zeolite for the calcium

and magnesium present in the water. It is possible to remove ion from contaminated water (Doutora, 2013)

2.15 Adsorption

The adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface is termed adsorption. Which in turn creates a film of the adsorbate on the surface of the adsorbent. The molecular species that gets adsorbed on the surface is known as adsorbate and the surface on which adsorption occurs is known as adsorbent. Common examples of adsorbents are clay, silica gel, colloids, metals etc. Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as heterogeneous catalysts, activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increasing storage capacity of carbide-derived carbons and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. (Alan, 2017).

2.16 Types of Adsorption

Depending upon the nature of forces existing between adsorbate molecules and adsorbent, the adsorption can be classified into two types

2.16.1 Physical adsorption (physisorption)

If the force of attraction existing between adsorbate and adsorbent are Vander Waal's forces, the adsorption is called physical adsorption or Vander Waal's adsorption. In physical adsorption, the force of attraction between the adsorbate and adsorbent are very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure. (Dabrowski, 2001).

2.16.2 Chemical adsorption (chemisorption)

If the force of attraction existing between adsorbate and adsorbent are almost same strength as chemical bonds, the adsorption is called chemical adsorption or Langmuir adsorption. In chemisorption the force of attraction is very strong, therefore adsorption cannot be easily reversed. (Dabrowski, 2001).



Plate I: Types of Adsorption

2.17 Adsorption Isotherms

There are a good number of adsorption isotherm studies in literature to study the extent of adsorption of chemical processes. They include: Lagmuir, Freundlich, Temkin, BET, Sips, Redlich-Peterson and Radk-Prausnitz.

2.17.1 Langmuir adsorption isotherm

Langmuir is the simplest type of theoretical isotherms. Langmuir adsorption isotherm describes quantitatively the formation of a monolayer of adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of adsorbate between the solid and liquid phases. The Langmuir adsorption is based on the view that every adsorption site is identical and energetically equivalent (thermodynamically, each site can hold one adsorbate molecule).

(Lee et al., 1995).

The Langmuir isotherm assume that the ability of molecule to bind and adsorbed is independent of whether or not neighboring sites are occupied. This mean, there will be no interactions between adjacent molecules on the surface and immobile adsorption. Also mean, trans-migration of the adsorbate in the plane of the surface is prevented. In this case, the Langmuir isotherm is valid for the dynamic equilibrium adsorption desorption processes on completely homogeneous surfaces with negligible interaction between adsorbed molecules that exhibit the form of Equation 2.2

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{2.2}$$

It is linearly re-written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} Ce + \frac{1}{q_{mb}}$$
(2.3)

Plotting
$$\frac{C_e}{q_e}$$
 against *Ce*

where c_e is the equilibrium concentration in solution, q_e is the amount of adsorbate adsorbed for unit mass of adsorbent q and b are related to standard monolayer adsorption capacity and the Langmuir constant, respectively.

Langmuir model represent one of the first theoretical treatments of non-linear sorption and suggests that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The Langmuir isotherm assumes that adsorption sites on the adsorbent surfaces are occupied by the adsorbate in the solution. Therefore, the Langmuir constant (b) represents the degree of adsorption affinity of the adsorbate. The maximum adsorption capacity (q) associated with complete monolayer cover is typically expressed in (mg/g). High value of b indicates for much stronger affinity of adsorbate adsorbate by (Ferguson *et al.*, 2005), as an essential feature of the Langmuir Isotherm to predict favorability of adsorption which is defined as:

$$R_L = \frac{1}{1 + bC_0}$$
(2.4)

where Co is the reference fluid-phase concentration of adsorbate (mg/l) (initial adsorbate concentration) and b is the Langmuir constant (ml/mg)

Value of R_L indicates the shape of the isotherm accordingly as shown in Table 2.1.

R _L Value	Lagmuir Isotherm type
$0 < R_L < 1$	Favourable
$R_L > 1$	Unfavourable
$R_{L} = 1$	Linear
R= 0	Irreversible

Table 2.3: Type of isotherm according to value of RL

(Diebold, 2003)

2.17.2 Freundlich adsorption isotherms

Freundlich isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. It represents an initial surface adsorption followed by a condensation effect resulting from strong adsorbate-adsorbate interaction. Freundlich isotherm curves in the opposite way of Langmuir isotherm and is exponential in form. The heat of adsorption, in many instances, decreases in magnitude with increasing extent of adsorption. This decline in heat is logarithmic implying that the adsorption sites are distributed exponentially with respect to adsorption energy. This isotherm does not indicate an adsorption limit when coverage is sufficient to fill a monolayer. It is given by Equation 2.5

$$q_e = K_f C e^{1/n} \tag{2.5}$$

The linearized equation is given by:

$$\log q_{e=} -\frac{1}{n} \log C_e + \log K_f \tag{2.6}$$

where K_f is the Freundlich constant related to maximum adsorption capacity (mg/g). It is a

Temperature-dependent constant, n is the Freundlich constant related to surface heterogeneity (dimensionless). It gives an indication of how favourable the adsorption processes (Nethaji, 2012)

With n=1, the equation reduces to the linear form:

$$q_e = k_f \times C_e \tag{2.7}$$

2.17.3 Temkin adsorption isotherm

Temkin Isotherm contains a factor that explicitly takes into the account of adsorbent – adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage (Kabir and Howard, 2007). Its equation is given:

$$q_e = \frac{RT}{b_T} In(K_T Ce) \tag{2.8}$$

The linearized equation is given by:

$$q_e = \frac{RT}{b_T} InCe + \frac{RT}{b_T} InK_T$$
(2.9)

where K_T is the Temkin isotherm equilibrium binding constant (L/g), b_T is the Temkin isotherm constant, R is the universal gas constant (8.314J/mol/K), T= Temperature at 298K and B is the Constant related to heat of sorption (J/mol). Summarized in Table 2.2 are the adsorption isotherm normal equations and their linearized form. (Lee *et al.*, 1995).

Isotherm	Normal Equation	Linear Form	Plot
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m}Ce + \frac{1}{q_m b}$	$\frac{C_e}{q_e} vs. C_e$
Freundlich	$q_e = K_f C e^{1/n}$	$\log q_{e=} \frac{1}{n} \log C_e + \log K_f$	$logq_e$ vs log C_e
Temkin	$q_e = \frac{RT}{b_T} In(K_T Ce)$	$q_e = \frac{RT}{b_T} InCe + \frac{RT}{b_T} InK_T$	q _e vsInC _e
(Diebold, 2003)			

Table 2.4: Adsorption isotherm equations

2.18 Kinetics Model of Adsorption

Adsorption measurements are always carried out when equilibrium is reached which has been reported to be within an hour to a day Yu *et al.* (1999). Under this condition of studies, the extent of adsorption continues to vary with respect to time change and frequently do not reach equilibrium, at least within the time boundaries of the experiment.

2.18.1 Pseudo-first-order kinetics

Lagergren showed that the rate of adsorption of solute on the adsorption is based on the adsorption capacity and follows a pseudo-first-order equation (Kean and Thanou, 2010).

The non-linear form of pseudo-first-order equation is given by Equation 2.10

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.10}$$

Where, qe and qt are the amounts of adsorbate adsorbed g/g at equilibrium time and at any instant of time, t respectively, and $k_1 \text{ min}^{-1}$ is the rate constant of the pseudofirst-order

adsorption operation. The integrated rate law after application of the initial condition of qt= 0 at t = 0, is linearized to Equation 2.11

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2.11}$$

2.18.2 Second order-kinetic model

The second order-kinetic model is shown in Equation 2.12; it is often used for chemical reaction. In kinetics and chemical reaction engineering, but can also be applied for adsorption processes Fan *et al.*,(2012)

$$\frac{1}{c_e} = k_2 t + \frac{1}{c_o} \tag{2.12}$$

where

 c_o is the initial concentration at t = o, c_e is the concentration at time t and k_2 is the second order rate constant.

2.18.3 Pseudo-second-order kinetics

Pseudo-first-order kinetics differs from a true first order equation in two ways: (i) the parameter $k_1(q_e - q_t)$ does not represent the number of available sites, and (ii) the parameter log (qe) is an adjustable parameter and often found not to be equal to the intercept of the plot of log (q_e- q_t)) versus t, whereas in a true first order log q_e should be equal to the intercept. In such cases, applicability of the second order kinetics should be tested with the rate equation given by Equation 2.13

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{2.13}$$

When integrated and linearized will give Equation 2.14

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{2.14}$$

where $h = k_2 q_e^2$

2.18.4 Elovich model

Elovich model is applicable for chemisorption processes (Goto *et al.*, 1994). The equation is often used valid for adsorption surface that is heterogeneous. Equation 2.15

$$q_t = \frac{1}{b}In(ab) + \frac{1}{b}Int \tag{2.15}$$

where a, is the initial adsorption rate (mg/gmin) and b is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). A plot of q_t against *Int* gives a straight line with a slope of $\frac{1}{b}$ and an intercept of $\frac{1}{b}$ In(ab) with correlation coefficients(Kean and Thanou, 2010).

- a. Not quantitative.
- b. Data not reported in the original paper.
- c. Employed concentration lower than the maximum sorption capacity.
- d. Data expressed as mg g^{-1} Mo.
- e. Adopted isotherm not indicated in the original paper.
- f. Data obtained using the Freundlich–Langmuir isotherm.
- g. Data obtained using the Freundlich isotherm.

2.19 Characterization Technique for Chitosan

2.19.1 Fourier Transform Infra-Red (FTIR)

Infra-red (FTIR) radiation is the term used to describe electromagnetic radiation with frequencies and energies somewhat lower than those associated with visible light. A disc is made by grinding 1 mg of the solid with 100-250mg of potassium bromide powder using mortar and pestle. The very fine powder is then put into a circular die and then placed under a mechanical pressure of $1-7 \times 10^8 \text{Nm}^2$ under vacuum. The resulting transparent disc is used to record the spectrum.

FTIR can be used to indicate the nature of the functional groups in a molecule and by comparison with spectra from known compounds, aid the identification of an unknown material (Supraja, 2018).

2.19.2 X-ray diffraction

X-ray Diffraction (XRD) is an advance technique to understand the skeletal structures in semi crystalline polymers like thermoplastics, thermoplastic elastomers and liquid crystalline polymers. Other established methods abound for the determination of molecular structure and crystallinity but in all XRD technique remains the best and accurate analytical method. The diffraction patterns were obtained from 2 to 40 2-theta degree with a scanning rate of 1 min⁻¹. The basal spacing of the silicate layer, *d*, was calculated using Bragg's equation, k = $2d \sin \theta$ (where θ is the diffraction position and k is the wavelength). The scan speed ($2s\theta$ -1) of 0.040 s⁻¹ can be used (Gao *et al.*, 2000).

2.19.3 Scanning Electron Microscopy (SEM)

SEM is a principal technique applied in investigation and explanation of the morphology and microscopic characteristics of solid minerals. (Dudhani and Kosaraju 2010). The external morphology of chitosan-TiO₂ film and Chitosan iron beads can be investigated using Scanning Electron Microscopy (SEM) (Philips, model XL 30CP,USA). The films will be cut and mounted on a brass stubs with double-sided adhesive tape and coated with 50 A^0 of gold vapor with an SCD-040Balzers sputter. The specimen will finally be characterized by SEM using an accelerating voltage of 15 kV, and a 1000× magnification of theoretical specimen size (Supraja, 2018).

2.19.4 Brunauer, Emmett and Teller (BET)

2.19.4.1 Multi-point measurements

The sample data are treated according to the Brunauer, Emmett and Teller (BET) adsorption isotherm equation.

$$\frac{1}{\left[Va\left(\frac{Po}{P}\right)\right]} = \frac{C-1}{Vm.C} * \frac{P}{Po} + \frac{1}{VmC}$$
(2.15)

- *P* = partial vapour pressure of adsorbate gas in equilibrium with the surface at
 77.4 K (b.p. of liquid nitrogen), in pascals,
- P_o = saturated pressure of adsorbate gas, in pascals,
- V_a = volume of gas adsorbed at standard temperature and pressure (STP) (273.15) K and atmospheric pressure (1.013 × 10⁵ Pa)], in millilitres,
- V_m = volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in millilitres,

C = dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

A value of Va is measured at each of not less than 3 values of P/Po. Then the BET value:

$$\frac{1}{Va(\frac{P_0}{P}-1)}\tag{2.16}$$

is plotted against P/P_o according to equation (2.15). This plot should yield a straight line usually in the approximate relative pressure range 0.05 to 0.3. The data are considered acceptable if the correlation coefficient, *r*, of the linear regression is not less than 0.9975; that is, r^2 is not less than 0.995. From the resulting linear plot, the slope, which is equal to $(C - 1)/V_mC$, and the intercept, which is equal to $1/V_mC$, are evaluated by linear regression analysis. From these values, V_m is calculated as 1/(slope + intercept), while *C* is calculated as (slope/intercept) + 1. From the value of V_m so determined, the specific surface area, *S*, in $m^2 \cdot g^{-1}$, is calculated by the equation:

N = Avogadro constant (6.022 × 10²³ mol⁻¹),

A = effective cross-sectional area of one adsorbate molecule, in square metres $(0.162 \text{ nm}^2 \text{ for nitrogen and } 0.195 \text{ nm}^2 \text{ for krypton}),$

M =mass of test powder, in grams,

22400 = volume occupied by 1 mole of the adsorbate gas at STP allowing for minor departures from the ideal, in millilitres.

A minimum of 3 data points is required. Additional measurements may be carried out, especially when non-linearity is obtained at a P/Po value close to 0.3. Because non-linearity

is often obtained at a P/Po value below 0.05, values in this region are not recommended. The test for linearity, the treatment of the data, and the calculation of the specific surface area of the sample are described above (Supraja, 2018)

2.19.4.2 Single point measurement

Normally, at least 3 measurements of Va each at different values of P/Po are required for the determination of specific surface area by the dynamic flow gas adsorption technique or by volumetric gas adsorption. However, under certain circumstances described below, it may be acceptable to determine the specific surface area of a powder from a single value of Va measured at a single value of P/Po such as 0.300 (corresponding to 0.300 mole of nitrogen or 0.001038 mole fraction of krypton), using the following equation for calculating Vm:

$$S = \frac{VmNa}{M*22400}$$
(2.17)

The specific surface area is then calculated from the value of V_m by equation (2.16) given above. The single-point method may be employed directly for a series of powder samples of a given material for which the material constant *C* is much greater than unity. These circumstances may be verified by comparing values of specific surface area determined by the single-point method with that determined by the multiple-point method for the series of powder samples. Close similarity between the single-point values and multiple-point values suggests that 1/C approaches zero.

The single-point method may be employed indirectly for a series of very similar powder samples of a given material for which the material constant C is not infinite but may be assumed to be invariant. Under these circumstances, the error associated with the single-point

method can be reduced or eliminated by using the multi-point method to evaluate *C* for one of the samples of the series from the BET plot, from which *C* is calculated as (1 + slope/intercept). Then V_m is calculated from the single value of V_a measured at a single value of P/P_o by the equation:

$$Vm = Va(1 - \frac{P}{Po}) \tag{2.18}$$

The specific surface area is calculated from V_m by Equation (2.18) (Allison *et al.*, 2000).

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

3.1 Materials-Chemicals and Equipment

This chapter gives an insight of the methods, starting materials, reagents and equipment used in this research work.

3.1.1 Materials and chemicals

The major starting material used in this research work include commercial chitosan, zeolite

- Y, Sodium hydroxide (NaOH), Acetic Acid and Heavy Metals (Copper Sulphate (CuSO₄)

and Arsenic) of analytical grades.

Table 3.1 summarizes the properties of some of the chemicals used and the list of equipment,

materials used are also presented in Table 3.2

	Table 3.1: List of materials and reagents used			
	Materials	Sources	Usage	
1	Sodium Hydroxide (NaOH)	Federal .University of Technology Minna (FUTMinna) Chemical laboratory.	Used to prepare a solution of 1M of NaOH solution for proper beads formation.	
2	Neutral detergent	F.U.T Minna Chemical lab.	For washing reagents.	
3	Copper Sulphate (CuSO ₄)	F.U.T Minna Chemical lab.	Heavy metal adsorbate	
4	Arsenic(III)Oxide As_2O_3	F.U.T Minna Chemical lab.	Heavy metal adsorbate	
5	Commercial Chitosan	CZY Delgado China	Used as the base substance for the beads formation	
6	Zeolite Y	F.U.T Chemical lab	Used with the chitosan for composite formation.	

	Equipment	Sources	Usage
1	A Batch Rector (Water	F.U.T Chemical lab.	Used for Adsorption
2	A Magnetic Stirrer	F.U.T Chemical lab.	Used to obtain a uniform mixture during various stages of the experiment
3	Glass wares (beakers, conical flask, measuring cylinders)	F.U.T Chemical lab.	For mixing, reacting and measuring.
5	Storage Devices (air tight containers)	Panlack Chemicals minna	To preserve the adsorbent for subsequent use.
6	Syringe pump	Panlack Chemicals minna	Used for gradual dropping of mixture into NaOH solution for beads formation.
7	Electronicweighing balance	F.U.T Chemical lab.	To measure samples in grams
8	Sieve 2.36 µm metal mics. ASTM)	F.U.T. Fishery Lab.	Used to obtain particle size of grinded croaker fish scales
9	Digital P ^H meter	F.U.T Chemical lab.	To observe the change in P ^H level with respect to neutrality
10	Filter Paper (Whatman 11cm)	Panlac Chemicals	For collection of filtrate after washing of sample.
11	FTIR Machine	NARICT Zaria FTIR-8400s Fourier Transform Infrared Spectrophotometer (Shimadzu)	Used to Characterize adsorbent produced to determine its functional group.
12	ZETASIZER	F.U.T	Used for particle size analysis

Table 3.2: List of Equipment and Apparatus

1 4010 0120	. List of Equipment and Ap	pulutus	
13	BET Machine	Federal University Technology Minna STEP-B Quantachrome Nova Win Version 11.03 Shimadzu,Model 6000	For determination of surface area of the samples
14	X – rayDiffraction (XRD) Machine.	South Africa	Use to analyze adsorbent Crystallinity
15	SEM Machine	South Africa	Used for Morphology analysis.
16	AtomicAdsorption Spectrometer	Multi – User Laboratory Ahmadu Bello University, MY15150001 machine	To determine the concentration in ppm of heavy metals adsorbed.

Table 3.2a: List of Equipment and Apparatus

Table 3.3 Properties of the Commercial Chitosan Used (Batch No. 20170220)

S/No	Test item	Test Standard	Test result
1	Color/state	white	White
2	Mesh size	120 mesh size	120 mesh size
3	Moisture content	<10%	6.3%
4	Ash content	<1%	0.54%
5	Viscosity	50 – 100 (mpa.s)	85(mpa.s)
6	Degree of Deacetylation	>90%	90.3%
7	Heavy metals	<10ppm	1ppm
8	Total plate count	<1000cfu/g	<10cfu/g
9	Impurities	None	None

3.2 Methodology

3.2.1 Reagent preparation

Reagents like Acetic acid, Sodium Hydroxide, Arsenic Oxide, Copper Sulphate Pentahydrate solution of various concentrations were prepared by dissolving calculated quantity of these chemicals of analytical grade into de – ionized water of which metal ions of desired concentrations were freshly prepared from the stock solution.

3.3 Preparation of Chitosan Beads

2g of chitosan powder was dissolved in 50ml of 5 % (v/v) acetic acid solution and heated to a temperature of 90°C with simultaneous stirring at 200 rpm for 2hrs until complete dissolution of the chitosan was achieved. (Mohammad Taghi *et al.*, 2016)

The above mixture of chitosan and glacial acetic acid solution (Jelly) was filled into a 5ml syringe pump and precipitated by the drop wise addition into a 1M NaOH solution. This was actually carried out in a water bath by exerting equal pressure at distance of approximately 3cm. The beads formed were left for 45 - 60 mins for proper formation of the beads.

The beads formed were washed with distilled water until neutralization occurs using a buffer solution of P^{H} 7.0 as reference. Wet beads were sieved, dried at atmospheric condition for 48hours, weighed then packaged for further studies. (Mohammad Taghi *et al.*, 2016)

3.4 Preparation of Chitosan – Zeolite Beads (CS/Z)

In this procedure, 0.55grams of chitosan and 3.76grams of zeolite Y (silica to alumina ration of 1:5) nanoparticles in a ratio of 1:7 from the complex composite design, samples of each

of the chitosan and zeolite were based on optimized measurements using complex composite design as proposed by (Auta *et al*; 2017).

3.5 Structural Analysis of Chitosan Beads and Chitosan – Zeolite Composite Beads The structural surface morphology, surface area and functional composition of the synthesized chitosan Beads, Chitosan – Zeolite Beads samples were studied using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and the Fourier Transform Infrared Spectroscopy (FTIR) and Brunnauer Emmette Teller (BET) respectively.

3.5.1 Determination of crystallinity using X –ray diffraction (XRD)

Room temperature low angle X-ray diffraction (XRD) pattern of the of the samples of chitosan beads and chitosan - zeolites composite beads were studied using X-ray powder diffractometer using a Ni – filtered Cu K α X – ray radiation source. 1g of each sample were air dried properly, homogenized, and placed on the sample holder of the machine for scanning. The average bulk compositions were determined.

The samples were analyzed using the reflection-transmission spinner stage with the Theta-Theta settings. Two-Theta starting position was 0.00483 and ends at 75.96483 with a twotheta step of 0.026 at 3.57 seconds per step. Tube current was 40 mA and the tension was 45 VA. Fixed Divergent Slit size of 1^0 was used and the goniometer radius was 240 mm.

The intensity of diffracted X-rays was continuously noted as the sample and detector rotate through their respective angles.

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{3.1}$$

where D is the particle size diameter, β is the full width at half maximum, λ is the wavelength of X-ray (0.1541 nm), θ is the diffraction angle and *K* is the Scherrer constant (0.94).

3.5.2 Determination of surface morphology using scanning electron microscopy (SEM)

The surface morphology was studied using an electron microscope Philip XL40 to carry out this experiment and it was carried out under a vacuum condition and at 5 bar pressure. The samples were mounted over sample holder (stubs) aided by double sided tape. Bio Rad coating systems were used to further coat the sample with gold and this was carried out at 10⁻¹ mbar with 30mA of current flow or 75 °. The samples were then placed into SEM instrument for scanning. Tungsten filament was utilized as electron source and SEM micrograph was recorded with 10 Kv resolution to obtain 1000 X, and 2000 X enlargement. As this characterization was to verify the surface morphology I

images of the samples, surfaces were recorded at different areas and magnifications.

3.5.3 Determination of functional groups using fourier transform infrared

spectroscopy (FTIR)

FTIR characterization of chitosan was performed with a Nicolet Magna 550 FT-IR instrument. Chitosan samples were prepared in the forms of thin film. For the preparation, 2% w/v chitosan was dissolved in 2% acetic acid solution, poured on a petri dish, and finally dried at 60 °C for 16 hours under vacuum. Was prepared to maintain equal sample thickness

all through. The spectra of the chitosan sample (in the forms of thin film) were obtained with a frequency range of 4000–400 cm⁻¹ at 4 cm⁻¹ resolutions and the major vibrations were identified associated with the main chemical groups.

3.5.4 Determination of surface area, pore volume, pore size using brunauer, emmett teller (BET)

The BET was carried out by nitrogen adsorption – desorption method using nitrogen temperature (-196 °C) with an autosorb BET apparatus, Micrometrics ASAP 2020, surface area and porosity analyzer. The analysis procedure was automated and operated with static volumetric techniques. The samples were first degassed at 200 °C for 2hours before each measurement was recorded. These were carried out to determine the surface area and porosity of the adsorbent after production.

3.6 Preparation of Copper II Stock Solution

Copper II Sulfate Pentahydrate (CuSO_{4.}5H₂O) was used as the raw source for Copper II stock solution. All the various solutions were prepared with analytical reagents and distilled water. 4.637 g of 99% CuSO_{4.}5H₂O was dissolved in distilled water of 1.0 L volumetric flask up to the mark to obtain 1000 ppm (mg/L) of Cu stock solution. All synthesized samples various concentrations of Cu II were then prepared from the above stock solution by appropriate dilutions. And the concentration of copper being determined by UV spectrophotometer. For example, to obtain 0.5pp of Cu II from CuSO_{4.}5H₂O:

 $\frac{X}{Molecular weight of the whole compound} = predicted experimental conc.$ = 0.5ppm

Where,

X is the actual concentration to be prepared, Molecular weight of compound as provided by the manufacturer = 249.86

Making X subject the desired concentration is obtained.

3.7 Preparation of Arsenic Stock Solution

Arsenic Trioxide (As₂.O₃) was used as the raw source for Arsenic stock solution. All the various solutions were prepared with analytical reagents and distilled water. 1.320 g of 99% As₂.O₃ was dissolved in distilled water of 1.0 L volumetric flask up to the mark to obtain 1000 ppm (mg/L) of As stock solution. All synthesized samples various concentrations were then prepared from the above stock solution by appropriate dilutions. And the concentration of Arsenic being determined by UV spectrophotometer i.e

3.8 Design of Adsorption Experiments Using Chitosan and Chitosan Beads

The Response Surface Methodology (RSM) was applied using Design Expert 7.0.0 program design. The experimental design as a function of the selected process variables was carried out using Central Composite Design (CCD). In order to obtain the required data, the range of values of each variable was determined. The mass of chitosan and zeolite were chosen for the independent variables. For variables (n = 4), n_t is the number of centre points = 6 and two levels (low (-) and high (+)), the total number of experiments was 30 determined by the expression: $2^n + 2n + n_t$. The percentage removal was selected as the response for the combination of the independent variables.

The results were analyzed by applying the response plot. For RSM, the most commonly used second –order polynomial equation developed to fit the experimental data can be written as:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x^2 + \sum \sum \beta_{ij} x_{ij} x_j + \varepsilon$$
(3.6)

where y is the response (yield); β_0 is the intercept coefficient, β_i is the linear terms, β_{ii} is the squared terms and β_{ij} is the interaction terms and x_i and x_j are the uncoded independent variable (Ghadge *et al.*,2006).

Variables Adsorbent Initial metal Activation Activation dosage (g) concentration time (min) temperature $(^{\circ}C)$ (mg/L)Low level (-) 40 0.5 0.5 30 High level (+) 1.5 1.5 50 80

 Table 3.5: Experimental design matrix using RSM for Copper and Arsenic removal onto chitosan beads and Chitosan zeolite

3.9 Procedure for the Adsorption Studies on Chitosan and Chitosan – Zeolite

Beads

Batch technique was employed in evaluating the rate and equilibrium data because of its simplicity using Central Composite Design. Equilibrium Isotherms were obtained by studying the adsorption process at different initial concentration, Time, Temperature and adsorbent dosage. The Batch adsorption study was carried based on the following procedures:

- 1. Adsorbents were measured and weighed based on required measurement as indicated by design expert 7.0.
- 2. Similar procedure was also done for the adsorbate and dissolved in distill waster.

- 3. Both the adsorbent and adsorbate contained in a conical flask were both placed on the water bath
- 4. Setting the water bath to the specified temperature as stipulated by design expert 7.0 and set to 200rpm
- 5. Then at each stipulated time, ranging from 40 80min, syringe was used to suck out a portion of the adsorbate and poured into a sample bottle for further analysis.

The effect of temperature at 40, 50 and 60 °C, in order to evaluate the adsorption thermodynamics parameters. Effects of adsorbent dosage and initial concentration were also studied with similar range at 0.5, 1.0 and 1.5 g respectively. Also the effect of time was also studied within a range of 40, 60, and 60mins respectively. The adsorbate was removed by filtration through Whatmann filter paper. The residual concentration of Cu and As were determined by UV spectrophotometer.

The experiments were performed and the amount of Cu and As ions adsorbed in milligram per litre was determined by using the following mass balance equation

$$q_t = \frac{(C_{0-C_e})}{m} \mathbf{V}$$
(3.4)

where, Co and C_e are Cu and As concentration (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in g rams. The percentage removal of Cu and As ions was calculated from the following equation:

$$\% \text{Removal} = \frac{(c_{o-c_e})}{c_o} \times 100$$
(3.5)

CHAPTER FOUR

- 4.0 RESULTS AND DISCUSSION
- 4.1 Characterization of the Produced Adsorbent (Chitosan and Chitosan-Zeolite beads)
- 4.1.1 Analysis of the fourier transformed infrared spectroscopy (FT-IR) obtained for chitosan and chitosan zeolite beads.

FTIR analysis of Chitosan beads and Chitosan- Zeolite beads are depicted in the Figure 4.1 and 4.2 respectively.



Figure 4.1: FT-IR Result for the obtained Chitosan Beads



Figure 4.2: FT-IR Result for the obtained Chitosan- Zeolite Beads

Figure 4.1, from Chitosan beads peak at 1040cm^{-1} and 1150 cm^{-1} correspond to N–H bending of the secondary amide II band of –CONH– whereas, the amide I band is generally observed at 1643.41 cm⁻¹. In the present case (figure 4.1), the amide 1 band is not found. Further bands that are observed in the region of 1380–1460 cm-1 are attributed to the symmetric and asymmetric bending vibrations of the methyl groups. Li *et al.*, (1998) also found that the peak at 1415 cm-1 indicates the C–H bending vibrations of –CH₂. A small peak around 2931.52 cm⁻¹ relates to –CH₂, and –CH₃ functional groups. The C–O stretching vibrations of the structure are observed at 1041.60 cm-1. The peak near 3410 cm⁻¹ is usually attributed to intermolecular –H bands. This result is in agreement with Choi *et al.*, (2007) who observed similar characteristic peaks for chitosan from fish scale at 2940 cm⁻¹ (–CH₃, –CH₂), 1655 (C=O stretch vibration of secondary amide I band), 1555 cm⁻¹ (N–H bending vibration of amide I I band), 1570 cm⁻¹ (N–H bending vibration of primary amides) and 1070 cm⁻¹ (C–O stretching. Figure 4.2 shows bands for Chitosan- Zeolite beads The spectra was observed to have a band located at 3425.69 cm⁻¹which indicates the stretching vibration of aliphatic O-H, which are more evident in the Chitosan- Zeolite spectrum (Lima *et al.*, 2004). Absorption peak at 2924.18 and 2345.52 cm⁻¹ is from C-H vibration of -CH₃. Absorption band at 1643.41 cm⁻¹ represents the stretching vibration of the carbonyl group, C=O from acetamide (-NHCOCH₃). Other characteristic absorptions for Chitosan- Zeolite beads are at 1319.35and 1388.78 cm⁻¹ indicating the bending vibration of –NH and stretching vibration of –CN from acetamide group, respectively. Absorption peak at 1018.45 and 1141.90 cm⁻¹ is attributed to the Aliphatic C-O stretching (Kumari *et al.*, 2016).

4.1.2 X- ray diffraction (XRD) analysis

The X-ray powder pattern of the chitosan-zeolite and Chitosan-bead are shown in Figure 4.3



Figure 4.3: XRD Diffractograph of (a) Chitosan-Zeolite (b) Chitosan Beads

From the Figure 4.3, the XRD patterns of Zeolite composites show similar characteristic peaks and broad band at $2\Theta^{\circ} = 76.84.78.80$, 81.12 and 84.34 representing a highly crystalline structure. These peaks occurred at diffraction angle which depict a chitosan polymorph which is referred to as 'tendor' hydrated polymorph (Ngahet al., 2011). This occurred as a result of strong intra- and intermolecular interactions characterized by hydrogen bonds formed between amino, hydroxyl, amide, and other functional groups present in the chitosan molecule as evidenced in FTIR result. The disappearance of the broad band observed after the major peaks indicates that the zeolitization of the mineral fraction of the parent composite was complete. Thus, suggesting the destruction of hydrogen bonding between the amino and the hydroxyl group in chitosan and decrease in basal spacing after cross-linking. The Debye-Scherrer equation (Equation 4.1) was applied to the XRD broad peak to obtain crystallite sizes as presented in Figure 4.3. The result shows that the Chitosan-Zeolite and Chitosan beads are nanopolycrystalline, with a crystal size of 24 and 114 nm. The mean crystallite size of Chitosan-Zeolite and Chitosan beads were obtained as41.64 and 74.45 nm which are characteristic of crystalline material.
4.1.3 Scanning electron microscopy (SEM) analysis

The SEM images of chitosan-zeolite and chitosan-beads are shown in Figure 4.4





According to Figure 4.4(a), the SEM image has homogenous, smooth flaky surface and evenly distributed in the composite. The micrographs revealed that the shape are of uniform size with cavities (abundant pores) which improves adsorption sites, whereas, image shown

in Figure 4.4(b) depict that the surface was relatively rough, irregular in shapes and presence of agglomerate particles (Xu *et al.*, 2003). Comparing Figure 4.4(a) and (b), result shows that the modification alters the crystal structure of zeolite but the gap and pore on the surface suggest that the chitosan cover the surface of zeolite. In similar manner, at high magnification (Figure 4.4c), the chitosan-zeolite coagulate to form non-uniform porous dome like shape with dry scale layer. Moreover, chitosan-bead (Figure 4.4d) revealed a smooth coiled-like shape with tube head (protrude grooves) with an observation of patchy section. Based on this result, modifying the chitosan into beads has significantly reduced the amount of pore surface earlier observed in Figure 4.4(c). Hence, modifying chitosan into beads greatly affect the potential adsorption capacity of the chitosan with zeolite (Wei *et al.*, 2011). It is noteworthy to mention that the modification changes the topography (surface) of the raw material and not crystallinity.

Samples	Surface area (m²/g)	Pore volume (cc/g)	Pore size (nm)
Chitosan- Zeolite beads	691.10	0.274	6.591
Chitosan beads	376.40	0.134	6.522

4.1.4 Brunauer emmet teller (BET) surface area analysis

Table 4.1. DET and last a seconda for Chitagen and Chitagen. Zaslita has de

Table 4.1 are values of surface area, pore volume and pore size analysis by BET for Chitosan and Chitosan- Zeolite beads. The Chitosan beads have surface area of 376.40 m²/g, pore volume of 0.134 cm²/g and pore size of 6.522 nm. The surface area, pore volume and pore size of the chitosan Chitosan – zeolite were 691.10 m²/g, 0.274 cm²/g and 6.591 nm

respectively. The increased in the BET surface area of Chitosan- Zeolite beads maybe attributed to the incorporation of more functional group. The increased in surface area, pore size and pore volume of the produced Chitosan- Zeolite bead composite which is also obvious in the SEM presented in figure 4.4 as the pore space is revealed in the scan maybe what is responsible for the high percentage removal of Copper and Arsenic.

4.2 Design of Experiment using Response Surface Methodology

4.2.1 Responses obtained from the experiment

The correlation between the experimental process variables and the removal efficiency of both Copper and Arsenic were evaluated using the ANOVA modeling technique on both Chitosan beads and Chitosan Zeolite beads. Second order polynomial regression equation fitted between the response removal efficiency and the process variables: Adsorbent dosage (A), Initial metals concentration (B), Adsorption temperature (C) and Adsorption time (D) as shown on Table 4.3 and 4.4 respectively.

Independent Variable	Low	High
Adsorbent dosage (g)	0.5	1.5
Initial Metal Conc. (mg/L)	0.5	1.5
Temperature (°C)	30	50
Time (mins)	40	80

 Table 4.2: Experimental Design for the Optimization of Adsorption Process executed by the Response Surface Methodology (RSM).

Cop	per and Ars	senic removal (mu cintosa	in Deaus Usin	g Design E	xpert 7.0.	
RUNS	A (g)	B (mg/L)	$C(^{0}C)$	D (min)	% Cu	% As	
1	0.50	0.50	30.00	40.00	90.34	88.90	
2	1.50	0.50	30.00	40.00	92.33	90.89	
3	0.50	1.50	30.00	40.00	84.44	83.89	
4	1.50	1.50	30.00	40.00	87.89	82.67	
5	0.50	0.50	50.00	40.00	92.67	90.56	
6	1.50	0.50	50.00	40.00	91.16	91.88	
7	0.50	1.50	50.00	40.00	91.22	84.89	
8	1.50	1.50	50.00	40.00	84.56	86.11	
9	0.50	0.50	30.00	80.00	92.56	80.67	
10	1.50	0.50	30.00	80.00	96.10	83.22	
11	0.50	1.50	30.00	80.00	93.22	80.44	
12	1.50	1.50	30.00	80.00	86.67	82.78	
13	0.50	0.50	50.00	80.00	98.03	84.56	
14	1.50	0.50	50.00	80.00	97.67	96.22	
15	0.50	1.50	50.00	80.00	95.61	84.67	
16	1.50	1.50	50.00	80.00	88.02	91.40	
17	0.50	1.00	40.00	60.00	94.34	93.24	
18	1.50	1.00	40.00	60.00	91.56	93.56	
19	1.00	0.50	40.00	60.00	92.56	88.90	
20	1.00	1.50	40.00	60.00	82.70	89.05	
21	1.00	1.00	30.00	60.00	89.89	89.40	
22	1.00	1.00	50.00	60.00	92.35	90.04	
23	1.00	1.00	40.00	40.00	90.87	92.00	
24	1.00	1.00	40.00	80.00	91.66	89.33	
25	1.00	1.00	40.00	60.00	92.01	89.56	
26	1.00	1.00	40.00	60.00	91.33	92.01	
27	1.00	1.00	40.00	60.00	91.08	90.00	
28	1.00	1.00	40.00	60.00	90.01	91.00	
29	1.00	1.00	40.00	60.00	88.99	88.90	
30	1.00	1.00	40.00	60.00	91.01	90.20	

Table 4.3: Experimental Design with the Corresponding Response using RSM for Copper and Arsenic removal onto chitosan beads Using Design Expert 7.0.

DING	A (-)	D (D (min)	0/ C	0/ 1 -
RUNS	A (g)	B (mg/L)		D (min)	% Cu	% As
1	0.50	0.50	30.00	40.00	91.87	90.34
2	1.50	0.50	30.00	40.00	95.33	92.33
3	0.50	1.50	30.00	40.00	89.55	89.44
4	1.50	1.50	30.00	40.00	89.45	87.89
5	0.50	0.50	50.00	40.00	94.67	92.67
6	1.50	0.50	50.00	40.00	93.16	91.16
7	0.50	1.50	50.00	40.00	93.90	94.22
8	1.50	1.50	50.00	40.00	90.58	84.56
9	0.50	0.50	30.00	80.00	94.00	92.56
10	1.50	0.50	30.00	80.00	97.20	96.10
11	0.50	1.50	30.00	80.00	95.32	93.22
12	1.50	1.50	30.00	80.00	88.88	86.67
13	0.50	0.50	50.00	80.00	99.78	97.03
14	1.50	0.50	50.00	80.00	98.00	99.10
15	0.50	1.50	50.00	80.00	93.02	95.61
16	1.50	1.50	50.00	80.00	87.02	88.02
17	0.50	1.00	40.00	60.00	95.34	94.34
18	1.50	1.00	40.00	60.00	92.66	91.56
19	1.00	0.50	40.00	60.00	90.70	92.56
20	1.00	1.50	40.00	60.00	82.89	82.70
21	1.00	1.00	30.00	60.00	94.89	89.89
22	1.00	1.00	50.00	60.00	94.35	92.35
23	1.00	1.00	40.00	40.00	91.87	90.87
24	1.00	1.00	40.00	80.00	94.66	91.66
25	1.00	1.00	40.00	60.00	92.00	92.01
26	1.00	1.00	40.00	60.00	92.56	91.33
27	1.00	1.00	40.00	60.00	91.98	91.08
28	1.00	1.00	40.00	60.00	91.00	90.01
29	1.00	1.00	40.00	60.00	90.89	88.99
30	1.00	1.00	40.00	60.00	91.88	91.01

Table 4.4: Experimental design matrix using RSM for Copper and Arsenic removal on chitosan- Zeolite beads

Table 4.2 and 4.3 shows the design matrix consisting of types of runs, coded and actual factors as randomized by the software and respective responses obtained from the experiment. The six centre points, run 25- 30 were conducted to determine the experimental error and the reproducibility of the data. From the results obtained, it could be observed that the highest percentage removal of copper and Arsenic on Chitosan beads were 98.03 and 96.22 % while the percentage removal using Chitosan- Zeolite beads were 99.78 and 99.10

%. The highest removal efficiency on both adsorbent (Copper and Arsenic) on Chitosan-Zeolite beads could be as a result of the processes employed; using Zeolite to modify Chitosan because of its good stability in acids solutions and the supports for high temperature which may also result to high adsorption surface area and active sites present in the structure of the adsorbent. In comparison, recent studies by Agata *et al.* (2017) on Zeolite modified by Chitosan as an adsorbent for environmental applications shows that the removal efficiency of 100 % for Copper was obtained.

4.2.2 Development of regression model equation

The development of a polynomial regression equation for analysis of correlation between Chitosan beads and Chitosan- Zeolite beads and its ability to remove both Copper and Arsenic was done. Correlation between the response surface and factors were developed using the ANOVA of the Design Expert 7.0 software as shown on Table 4.4 and 4.5

Variable	Copper removal	Arsenic removal
Standard deviation	1.17	1.77
Coefficient of variation (%)	1.95	2.01
R- Squared (R ²)	0.9726	0.9627
R ² - Adjusted	0.9512	0.9414
Adeq. Precision	11.388	11.219
Mean	91.09	88.36

 Table 4.5: Statistical parameters obtained from the analysis of variance (ANOVA) on

 Chitosan heads

	Leonte beads	
Variable	Copper removal	As removal
Standard deviation	1.16	1.58
Coefficient of variation (%)	1.25	1.73
R- Squared (R ²)	0.9904	0.9868
R ² - Adjusted	0.9748	0.9657
Adeq. Precision	19.073	11.881
Mean	92.78	91.38

 Table 4.6: Statistical parameters obtained from the analysis of variance on Chitosan-Zeolite beads

The accuracy of the model developed can be understood by the value of R^2 , adjusted R^2 and standard deviation. R² indicates the ratio between sum of the squares (SSR) with total sum of the square (SST) and it describes up to what extent perfectly the model estimated experimental data points. Correlation coefficient and standard deviation were used to evaluate the fitness of the models developed. The closer the R² value to unity and the smaller the standard deviation, the better the model in predicting the response Alam et al., (2009). Table 4.4 shows that the quadratic model percentage removal for Copper and Arsenic on Chitosan beads. The result shows a relatively small standard deviation of 1.17 and relatively R^2 value of 0.9726 in reasonable agreement with adjusted R^2 (0.9512) for Copper and standard deviation of 1.77 which was relatively small, R^2 value of 0.9627 with adjusted R^2 (0.9414) for Arsenic on chitosan beads. Table 4.5 also shows that quadratic model for Copper and Arsenic removal efficiency on Chitosan- Zeolite beads have relatively small standard deviations of 1.16 and 1.58; relatively high R^2 values of 0.9904 and 0.9868 in reasonable agreement with adjusted R^2 (0.9748 and 0.9657). The result implies that the quadratic model for both Copper and Arsenic removal on Chitosan and Chitosan- Zeolite beads were not aliased and can be used to describe excellently the relationship between response on removal efficiency and the interacting variables. Determination of Correlation of Variance (CV) value is essential as it indicates the ratio between standard error of estimate with the mean value of the observed response as percentage. It measures the reproducibility of the model. If the value is less than 10% the model used can be considered reproducible. It was found that the CV values obtained for the removal of percentages of Copper and Arsenic were 1.95 and 2.10 on Chitosan beads and 1.25 and 1.73 on Chitosan-Zeolite beads respectively showing reproducibility of the models (Sarra *et al.*, 2016). The R² values can be attributed to the four factors (A- Adsorbent dosage, B- Initial metal concentration, C- Activation temperature and D- Activation time) considered. Therefore, the quadratic models were selected as suggested by the software and the response surface model equations for X and Y (Chitosan and Chitosan-Zeolite beads) in their actual values is

$$0.71*D^2$$
 (4.2)

$$X_{\%}As = +91.04 + 1.49 * A - 1.66* B + 2.08* C - 1.03* D - 0.53* A * B + 0.95* A * C$$

+1.25* A * D - 0.14* B * C+1.21* B * D +1.42* C * D +1.59* A² - 2.83* B² - 2.09 * C² - 1.14 * D² (4.3)

 $Y_{\%} Cu = +91.72 - 1.07* A - 2.67* B + 0.22* C + 1.19* D - 0.95* A * B - 0.55* A * C - 0.85* A * D - 0.12* B * C - 1.07* B * D - 0.48* C * D + 2.27* A^2 - 4.94* B^2 + 2.89* C^2 + 1.53* D^2$ (4.4)

$$Y_{\%} As = +90.57 - 1.22 * A - 2.31 * B + 0.90 * C + 1.47 * D - 1.96 * A * B - 0.88 * A * C + 0.14 * A * D - 0.21 * B * C - 0.68 * B * D + 0.54 * C * D + 2.54 * A^2 - 2.78 * B^2 + 0.71 * C^2 + 0.86 * D^2$$

$$(4.5)$$

These equations (4.2- 4.5) reveals how the individual variables or double interactions affected Copper and Arsenic removal efficiency from aqueous solution on Chitosan and Chitosan beads as adsorbent. Negative coefficient values indicate that individual or double interaction factors negatively affect Copper and Arsenic adsorption (i.e., removal percentage decreases) whereas positive coefficient values indicate that factors increases the percentage removal (Aravind *et al.*, 2015).

4.2.3 Analysis of variance (ANOVA) of Chitosan and Chitosan – Zeolite Beads

4.2.3.1 Analysis of variance (ANOVA) on Chitosan beads for Copper and Arsenic removal

The ANOVA was used to further emphasize the adequacy of the models and their significance. The mean squares in the ANOVA for the surface response quadratic models were obtained by dividing the sum of the squares of each of variation sources, the model and the error variance by the respective degrees of freedom. The ANOVA suggests that the equation and the actual relationship between the response and the significant variables

represented by the equation were adequate. The larger the value of F and the smaller the value of p, the more significant is the corresponding coefficient term (Kalavathy *et al.*,2009).

Source	Sum of square	Degree of freedom	Mean square	F- Value	Prob> F
Model	320.39	14	22.88	7.27	0.0002
A-Dosage	15.07	1	15.07	4.79	0.0449
B- Conc.	133.88	1	133.88	42.54	< 0.0001
C-Temp.	17.70	1	17.70	5.62	0.0315
D-Time	64.45	1	64.45	20.48	0.0004
AB	27.59	1	27.59	8.77	0.0097
AC	21.51	1	21.51	6.83	0.0195
AD	4.23	1	4.23	1.35	0.2643
BC	0.064	1	0.064	0.020	0.8887
BD	0.38	1	0.38	0.12	0.7347
CD	2.38	1	2.38	0.76	0.3983
A^2	14.87	1	14.87	4.72	0.0462
\mathbf{B}^2	22.16	1	22.16	7.04	0.0181
C^2	0.83	1	0.83	0.26	0.6152
D^2	1.31	1	1.31	0.42	0.5288
Residual	47.21	15	3.15	-	-
Lack of fit	41.46	10	4.15	3.61	0.0847
Pure error	5.74	5	1.15	-	-

 Table 4.7: ANOVA response surface cubic model on Copper removal for Chitosan Bead

Table 4.8: ANOVA response surface cubic model on Arsenic removal for Chitosan bead

	Sum of square	Degree freedom	of	Mean square	F- Value	Prob> F
Model	422.45	14		30.18	9.58	< 0.0001
A-Dosage	40.23	1		40.23	12.77	0.0028
B- Conc.	49.67	1		49.67	15.77	0.0012
C-Temp.	78.00	1		78.00	24.77	0.0002
D-Time	19.01	1		19.01	6.04	0.0267
AB	4.46	1		4.46	1.42	0.2524
AC	14.57	1		14.57	4.63	0.0482
AD	24.93	1		24.93	7.91	0.0131
BC	0.32	1		0.32	0.10	0.7556
BD	23.26	1		23.26	7.38	0.0159
CD	32.06	1		32.06	10.18	0.0061
A^2	6.56	1		6.56	2.09	0.1687
\mathbf{B}^2	20.76	1		20.76	6.59	0.0214
\mathbf{C}^2	11.27	1		0.83	3.58	0.0780
D^2	3.37	1		3.37	1.07	0.3173
Residual	47.24	15		3.15	-	-
Lack of fit	41.22	10		4.12	3.42	0.0933
Pure error	6.02	5		1.20	-	-

The value of prob>F lower than 0.05, indicates that the model may be considered to be statistically significant. For the removal of Copper on Chitosan beads, the ANOVA results (Table 4.7) indicated the model F-value of 7.27 which implied that it was significant and had only a 0.02% chance that its magnitude could occur due to noise (induced variation under normal operating conditions by uncontrollable factors). As expected, non-significant lack of fit was obtained with lack of fit F-value of 3.61 implying its non-significance relative to the pure error and the chances that 8.47 % of its value also occurred due to noise. As shown in Table 4.7, model terms A, B, C, D, AB, AC, A², B² were found significant. The ANOVA results for Table 4.8 for the removal of Arsenic on Chitosan beads also indicates the model F-value of 9.58 which implied that it was significant and had only a 0.01% chance that its magnitude could occur due to noise (induced variation under normal operating conditions by uncontrollable factors). As expected, non-significant lack of fit was obtained with lack of fit F-value of 3.42 implying its non-significance relative to the pure error and the chances that 9.33 % of its value also occurred due to noise. As also shown in Table 4.8, model terms A, B, C, D, AC, AD, BD, CD, B² were found significant. The Model Equation (4.3 and 4.4) reduces to Equations 4.7 and 4.8 after eliminating the insignificant coefficients: X_% Cu = + 90.65 - 0.9* A -2.7 * B +0.99* C +1.89* D -1.31* A * B -1.16* A * C

$$+2.40^{*}A^{2}-2.92^{*}B^{2}$$
 (4.6)

$$X_{\%} As = +91.04 + 1.49 * A - 1.66* B + 2.08* C - 1.03* D + 0.95* A * C + 1.25* A * D$$

+1.21* B * D +1.42* C * D - 2.83* B² (4.7)

The data were also analyzed to check the correlation between the experimental and predicted percentage removal, as shown on Table 4.9. The experimental values were the result obtained, while the predicted values were obtained by calculation from the quadratic equation. It is shown in Figure 5.1 that the data points on the plot are distributed near to the straight line, indicating a good relationship between the experimental and predicted values of the response. The result also suggests that the selected quadratic model was adequate in predicting the response variables for the experimental data.

	С	Arsenic ren	noval (%)			
Runs	Actual	Predicted	Residual	Actual	Predicted	Residual
1	90.34	89.33	1.01	88.90	89.85	0.95
2	92.33	93.48	1.15	90.89	89.49	1.40
3	84.44	86.96	2.50	83.89	85.45	1.56
4	87.89	85.83	2.06	82.67	82.98	0.31
5	92.67	92.99	0.32	90.56	89.55	1.01
6	91.16	92.50	1.34	91.88	93.01	1.13
7	91.22	90.34	0.88	84.89	84.59	0.30
8	84.56	84.60	0.038	86.11	85.94	0.17
9	92.56	93.68	1.12	80.67	80.05	0.62
10	96.10	95.77	0.33	83.22	84.69	1.47
11	93.22	90.67	2.55	80.44	80.48	0.039
12	86.67	87.52	0.84	82.78	83.00	0.22
13	98.03	98.88	0.85	84.56	85.42	0.86
14	97.67	96.33	1.34	96.22	93.87	2.35
15	95.61	95.62	0.012	84.67	85.28	0.61
16	88.02	87.82	0.20	91.40	91.62	0.22
17	94.34	93.96	0.38	93.24	91.14	2.10
18	91.56	92.13	0.57	93.56	94.13	0.57
19	92.56	90.45	2.11	88.90	89.87	0.97
20	82.70	84.99	2.29	89.05	86.55	2.50
21	89.89	90.22	0.33	89.40	86.87	2.53
22	92.35	92.20	0.15	90.04	91.04	1.00
23	90.87	89.46	1.41	92.00	90.93	1.07
24	91.66	93.25	1.59	89.33	88.87	0.46
25	92.01	90.65	1.36	89.56	91.04	1.48
26	91.33	90.65	0.68	92.01	91.04	0.97
27	91.08	90.65	0.43	90.00	91.04	1.04
28	90.01	90.65	0.64	91.00	91.04	0.042
29	88.99	90.65	1.66	88.90	91.04	2.14
30	91.01	90.65	0.36	90.20	91.04	0.84

Table 4.9: Actual- predicted values and residual for Chitosan Bead responses.



Figure 4.5: Actual – Predicted Value Plot on Percentage Adsorption of (a) Copper



Figure 4.6: Actual – Predicted Value Plot on Percentage Adsorption of

Arsenic on Chitosan Beads

4.2.3.2 Analysis of variance (ANOVA) on chitosan-zeolite beads for copper and arsenic removal

The statistical significance of the model equation was performed with F-Test ANOVA, and the results obtained were shown on Table 4.10 and 4.11 for the percentage removal of Copper and Arsenic on Chitosan-Zeolite beads.

	Zeolite							
Source	Sum of square	Degree of freedom	Mean square	F- Value	Prob> F			
Model	325.17	15	23.23	17.20	< 0.0001			
A-Dosage	20.42	1	20.42	15.12	0.0015			
B- Conc.	128.53	1	128.53	95.18	< 0.0001			
C-Temp.	0.88	1	0.88	0.65	0.4310			
D-Time	25.68	1	25.68	19.02	0.0006			
AB	14.50	1	14.50	10.73	0.0051			
AC	4.76	1	4.76	3.53	0.0800			
AD	11.48	1	11.48	8.50	0.0107			
BC	0.22	1	0.22	0.17	0.6900			
BD	18.47	1	18.47	13.68	0.0021			
CD	3.70	1	3.70	2.74	0.1188			
A^2	13.35	1	13.35	9.89	0.0067			
\mathbf{B}^2	63.10	1	63.10	46.73	< 0.0001			
C^2	21.64	1	21.64	16.02	0.0012			
D^2	6.10	1	6.10	4.52	0.0505			
Residual	20.26	15	1.35	-	-			
Lack of fit	18.17	10	1.82	4.36	0.0589			
Pure error	2.08	5	0.42	-	-			

 Table 4.10 ANOVA Response Surface Cubic Model on Copper Removal for Chitosan-Zeolite

				CIIIIOS			
Source	Sum	of	Degree	of	Mean square	F- Value	Prob> F
	square		freedom				
Model	303.95		15		21.71	8.69	< 0.0001
A-Dosage	26.99		1		26.99	10.81	0.0050
B- Conc.	95.77		1		95.77	38.35	< 0.0001
C-Temp.	14.72		1		14.72	5.90	0.0282
D-Time	38.98		1		38.98	15.61	0.0013
AB	61.78		1		61.78	24.74	0.0002
AC	12.46		1		12.46	4.99	0.0411
AD	0.30		1		0.30	0.12	0.7326
BC	0.74		1		0.74	0.30	0.05943
BD	7.40		1		7.40	2.96	0.1057
CD	4.62		1		4.62	1.85	0.1937
A^2	16.76		1		16.76	6.71	0.0205
\mathbf{B}^2	19.97		1		19.97	8.00	0.0127
C^2	1.32		1		1.32	0.53	0.4785
D^2	1.91		1		1.91	0.76	0.3956
Residual	37.46		15		2.50	-	-
Lack of fit	37.71		10		3.17	2.76	0.1370
Pure error	5.74		5		1.15	-	-

Table 4.11: ANOVA Response Surface Cubic Model on Arsenic Removal for Chitosan-Zeolite

Table 4.10 shows that response surface quadratic model on percentage removal of Copper on Chitosan-Zeolite beads having F-value of 17.20 which implied that it was significant and had only a 0.01% chance that its magnitude could occur due to noise (induced variation under normal operating conditions by uncontrollable factors). Non-significant lack of fit was obtained with lack of fit F-value of 4.36 implying that its non-significance relative to the pure error and the chances that 5.89 % of its value also occurred due to noise. Values of Prob> F less than 0.05 indicates that the model terms are significant and the only significant model terms in this case were A, B, D, AB, AD, BD, A², B², C². Table 4.10 shows that response surface quadratic model on percentage removal of Arsenic on Chitosan- Zeolite beads has Fvalue of 8.68 which implied that it was significant and had only a 0.01% chance that its magnitude could occur due to noise (induced variation under normal operating conditions by uncontrollable factors). As expected, non-significant lack of fit was obtained with lack of fit F-value of 2.76 implying that its non-significance relative to the pure error and the chances that 13.70 % of its value also occurred due to noise. Values of Prob> F less than 0.05 indicates that the model terms of A, B, C, D, AB, AC, A^2 , B^2 are significant. Therefore, removing the insignificant model terms, the quadratic models for the responses for the percentage removal of Copper and Arsenic on Chitosan- Zeolite beads becomes

$$Y_{\text{Cu}} = +91.72 - 1.07* \text{ A} - 2.67* \text{ B} + 1.19* \text{ D} - 0.95* \text{ A} * \text{ B} - 0.85* \text{ A} * \text{ D} - 1.07* \text{ B} * \text{ D}$$

+2.27* A² - 4.94* B² +2.89* C² (4.8)

$$Y_{\text{\%}As} = +90.57 - 1.22 * A - 2.31 * B + 0.90 * C + 1.47 * D - 1.96 * A * B - 0.88 * A * C + 2.54 * A^2 - 2.78 * B^2$$
(4.9)

The residual of the response surface models presented on Table 4.12 shows that the highestlowest error (residual) for Copper percentage removal response is 0.0097- 1.74 % and that of percentage Arsenic removal is 0.00041- 2.79 %. This signifies the quality of the model in terms of predicting the responses. The plots of actual versus predicted values of response percentage removal in Figure 4.6, shows a very minimal divergence of points from the diagonal indicating that these response surface model equations for Copper and Arsenic removal on Chitosan- Zeolite beads can be used to adequately represent the interaction of the four variable.

	C	opper remova	Arsenic rem	oval (%)		
Runs	Actual	Predicted	Residual	Actual	Predicted	Residual
1	91.87	91.79	0.083	90.34	90.00	0.34
2	95.33	94.35	0.98	92.33	92.97	0.64
3	89.55	90.37	1.18	89.44	91.11	1.67
4	89.45	89.48	0.033	87.89	86.22	1.67
5	94.67	94.52	0.15	92.67	92.93	0.26
6	93.16	94.90	1.74	91.16	92.73	1.21
7	93.90	92.99	0.91	94.22	93.17	1.05
8	90.58	89.56	1.02	84.56	84.76	0.20
9	94.00	98.98	0.98	92.56	92.95	0.39
10	97.20	98.15	0.95	96.10	96.47	0.37
11	95.32	93.63	1.69	93.22	91.34	1.88
12	88.88	88.99	0.11	86.67	87.00	0.33
13	99.78	99.79	0.0097	97.03	98.03	1.00
14	98.00	96.78	1.22	99.10	98.02	1.08
15	93.02	93.96	0.94	95.61	95.56	0.052
16	87.02	87.15	0.13	88.02	87.69	0.33
17	95.34	95.06	0.28	94.34	94.34	0.00041
18	92.66	92.93	0.27	91.56	91.89	0.33
19	90.70	89.46	1.24	92.56	90.10	2.46
20	82.89	84.12	1.23	82.70	85.49	2.79
21	94.89	94.39	0.50	89.89	90.38	0.49
22	94.35	94.84	0.49	92.35	92.19	0.16
23	91.87	92.06	0.19	90.87	89.96	0.91
24	94.66	94.45	0.21	91.66	92.20	1.24
25	92.00	91.72	0.28	92.01	90.57	1.44
26	92.56	91.72	0.84	91.33	90.57	0.76
27	91.98	91.72	0.26	91.08	90.57	0.51
28	91.00	91.72	0.72	90.01	90.57	0.56
29	90.89	91.72	0.83	88.99	90.57	1.58
30	91.88	91.72	0.16	91.01	90.57	0.44

 Table 4.12: Actual- Predicted Values and Residual for Chitosan- Zeolite Beads Responses.

 Conner removal (%)



Figure 4.7: Actual – Predicted Value Plot on Percentage Adsorption of (a) Copper



(b)

Figure 4.8: Actual – Predicted Value Plot on Percentage Adsorption of Arsenic on

Chitosan- Zeolites Beads

4.2.4 Response surface plots

4.2.4.1 Interaction effects of Copper removal parameters on Chitosan beads

The interaction effects of adsorbent dosage, initial metal concentration, temperature and time parameters for Copper removal catalyst on chitosan beads as shown in Figure 4.7 (a-f)



Figure 4.9: 3D Surface Plots for Effects of Copper Adsorption Parameters on Chitosan Beads

The effect of initial concentration (A) and adsorbent dosage (B) is given in Figure 4.9a. The plot indicates that both parameters have significant effect on Copper removal with the linear (A, B) and interaction AB terms having a marked effect (p-<0.05) as seen on Table 4.6. The resultant effect of both parameters on copper removal may be attributed to the enhanced surface area and the availability of more active binding sites in adsorbing the solute. The concentration of Copper ensued increasing of the mass transfer driving force and the rate of Copper passing the bulk solution to the particle surface. At a concentration of 0.5 mg/L and adsorbent dosage of 0.5 g, the maximum percentage removal of copper was 98.03 %. The sloppy nature of the 3D plot as a function of adsorbent dosage (A) and time (C) depicted in Figure 4.9b, shows that the two terms have significant effect on Copper removal with the linear (A, C) and interaction AC term having a marked effect (p<0.05) as seen on Table 4.6 The Copper percentage removal increased from 82.7-98.03 % as the temperature increased and remained approximately same with lower adsorbent dosage. Figure 4.7c represents the 3D plot for time (D) as a function of adsorbent dosage (A) for Copper removal. According to the plot, the two terms have significant effect on Copper removal; however adsorbent dosage has a much higher effect, this behaviour is attributed to the availability of more active site and surface area which is largely determined by adsorbent dosage. An adsorbent dosage of 0.5 mg/L is observed to give a Copper removal of over 98 % at a time of 80 min. The surface plot for the interaction of temperature (C) and initial concentration (B) on the synthesised Chitosan beads used in the removal of Copper is displayed in Figure 4.9d. The plot shows that both terms significantly influenced Copper removal with the linear (C, B) having a marked effect on the removal. This trend could be as a result of initial concentration due to the saturation of metal binding sites of the adsorbent and at maximum temperature (50 ⁰C), maximum removal of Copper was favoured. The relationship between time (D) and initial concentration (B) is illustrated in the 3D plot of Figure 4.9e. The curvature nature of the plot suggests that a significant individual interaction exits between the two terms. It shows that the combination of low initial concentration and high adsorption time favours maximum Copper removal. Figure 4.9f represents the 3D plot for time (D) as a function of temperature (C) for Copper removal. According to the plot, the two terms have significant individual effect on Copper removal; however adsorption time has a much higher effect. An increased in temperature (30-50 °C) and increased in time (40-80 °C) result to an increased in the maximum removal of Copper.

4.2.4.2 Interaction effects of Arsenic removal parameters on Chitosan beads

The interaction effects of adsorbent dosage, initial metal concentration, temperature and time parameters for Copper removal catalyst on chitosan beads as shown in Figure 4.10 (a-f)





(a)







(**d**)



16 Au

(e)



(**f**)

Figure 4.10: 3D Surface lots for Effects of Arsenic Adsorption Parameters on

Chitosan Beads

The effect of initial concentration (A) and adsorbent dosage (B) is given in Figure 4.10a. The plot indicates that both parameters have significant effect on Arsenic removal with the linear (A, B) terms having a marked effect (p-<0.05) as seen on Table 4.7. The resultant effect of both parameters on copper removal may be attributed to the enhanced surface area and the availability of more active binding sites in adsorbing the solute. At lower concentration of Arsenic and higher adsorbent dosage, the removal of Arsenic was maximum (96.22 %). The sloppy nature of the 3D plot as a function of adsorbent dosage (A) and time (C) depicted in Figure 4.10b, shows that the two terms have significant effect on Arsenic removal with the linear (A, C) and interaction AC term having a marked effect (p < 0.05) with temperature having the highest effect base on their F- values as seen on Table 4.7. The Percentage removal of Arsenic increased from 82.67-96.22 % as the adsorbent dosage increased and remained approximately same with decreased initial concentration due to the binding sites of the adsorbent. Figure 4.10c represents the 3D plot for time (D) as a function of adsorbent dosage (A) for Arsenic removal. According to the plot, the two terms have significant effect on Arsenic removal; however adsorbent dosage has a much higher effect, this behaviour is attributed to the availability of more active site and surface area which is largely determined by adsorbent dosage. An adsorbent dosage of 1.5 mg/L is observed to give an Arsenic removal of over 96.22 % at a time of 80 min. The surface plot for the interaction of temperature (C) and initial concentration (B) on the synthesised Chitosan beads used in the removal of Copper is displayed on Figure 4.10d. The plot shows that both terms significantly influenced Copper removal with the linear (C, B) having a marked effect on the removal. This trend could be as a result of initial concentration which is due to the saturation of metal binding sites of the adsorbent. The relationship between time (D) and initial concentration (B) is illustrated in the 3D plot of Figure 4.10e. The curvature nature of the plot suggests that a significant interaction exits between the two terms and based on their F-value, initial concentration has the highest effect on the percentage removal. It shows that the combination of lower initial concentration (0.5 mg/L) and higher adsorption time (80 min) favours maximum Arsenic removal. Figure 4.10f represents the 3D plot for time (D) as a function of temperature (C) for Copper removal. According to the plot, the two terms have significant interaction effect on Arsenic removal; however adsorption temperature has a much higher effect. An increased in temperature (30-50 °C) and increased in time (40-80 °C) result to an increased in the percentage removal.

4.2.4.3 Interaction effects of copper removal parameters on chitosan-zeolite beads

The interaction effects of adsorbent dosage, initial metal concentration, temperature and time parameters for Copper removal catalyst on chitosan beads as shown in Figure 4.11 (a-f)



Figure 4.11: 3D Surface plots for effects of Copper adsorption parameters on Chitosan-Zeolite Beads

The effect of initial concentration (A) and adsorbent dosage (B) is given in Figure 4.11a. The plot indicates that both parameters have significant effect on Copper removal with the linear (A, B) and interaction AB terms having a marked effect (p-<0.05) as seen on Table 4.9. The resultant effect of both parameters on copper removal by the Chitosan-Zeolite bead may be attributed to the enhanced surface area and the availability of more active binding sites in adsorbing the solute. At lower concentration of Copper and higher adsorbent dosage, the removal of Arsenic was maximum (99.78 %) which may also be as a result of the two adsorbent being combined together as composite. The nature of the 3D plot as a function of adsorbent dosage (A) and time (C) depicted in Figure 4.11b, shows that the two terms have significant effect both as individual and as combined effect on Copper removal by the Chitosan-Zeolite beads with the linear (A, C) and interaction AC term having a marked effect (p<0.05) with adsorbent dosage having the highest effect base on their F- values (15.12) as seen on Table 4.9. The Percentage removal of Copper increased as the temperature is increased and decreased as the adsorbent dosage is increased which maybe as a result of blockage on the active site of the adsorbent. Figure 4.11c represents the 3D plot for time (D) as a function of adsorbent dosage (A) for Copper removal. According to the plot, the two terms combined have insignificant effect on Copper removal but have an individual significant effect with time showing a higher. This behaviour could be attributed to the fact that; the longer the adsorbent stayed in the adsorbate the better the rate of adsorption and the better the active site of the adsorbent to adsorbed the Copper n the aqueous solution. The surface plot for the interaction of temperature (C) and initial concentration (B) on the synthesised Chitosan-Zeolite beads used in the removal of Copper is displayed on Figure 4.11d. The plot shows that both terms significantly influenced Copper removal with the linear (C, B) and interaction BC having a marked effect (p < 0.05) on the removal. This trend could be as a result of initial concentration which is due to the saturation of metal binding sites of the adsorbent. Increase in temperature at lower concentration gives a better Copper removal. The relationship between time (D) and initial concentration (B) is illustrated in the 3D plot of Figure 4.11e. The sloppy nature of the plot suggests that a significant interaction exits between the two terms and based on their F-value, initial concentration has the highest effect on the percentage removal. It shows that at of lower initial concentration (0.5 mg/L) and higher adsorption time (80 min) maximum Copper removal is favored. This maybe as a result of the fact that adsorption takes place faster at a lower concentration due to more active sites on the adsorbent. Figure 4.11f represents the 3D plot for time (D) as a function of temperature (C) for Copper removal. According to the plot, the two terms have significant interaction effect on Copper removal; however adsorption time has a much higher effect. At maximum temperature (50 0 C) and maximum time (80 min); the percentage removal of Copper on Chitosan-Zeolite beads became maximal (99.78 %).

4.3.4.4 Interaction effects of Arsenic removal parameters on Chitosan-Zeolite beads

The interaction effects of adsorbent dosage, initial metal concentration, temperature and time parameters for Copper removal catalyst on chitosan beads as shown in Figure 4.12 (a-f)



Figure 4.12: 3D Surface Plots for Effects of Arsenic Adsorption Parameters on

Chitosan-Zeolite Beads

The effect of initial concentration (A) and adsorbent dosage (B) is given in Figure 4.12a. The plot indicates that both parameters have significant effect on Arsenic removal with the linear (A, B) and interaction AB terms having a marked effect (p-<0.05) as seen on Table 4.10. The resultant effect of both parameters on Arsenic removal by Chitosan-Zeolite beads may be attributed to the enhanced surface area and the availability of more active binding sites in adsorbing the solute which result to faster adsorption at low concentration of the Arsenic metal. At a concentration of 0.5 mg/L and adsorbent dosage of 1.5 g, the maximum percentage removal of Arsenic was 99.10 %. The sloppy nature of the 3D plot as a function of adsorbent dosage (A) and time (C) depicted in Figure 4.12b, shows that the two terms have significant effect on Arsenic removal with the linear (A, C) and interaction AC term having a marked effect (p<0.05) as seen on Table 4.10 The Arsenic percentage removal increased from as the temperature is increased and remained approximately same with high adsorbent dosage. Figure 4.12c represents the 3D plot for time (D) as a function of adsorbent dosage (A) for Arsenic removal on Chitosan- Zeolite beads. According to the plot, the two terms have significant effect on Arsenic removal; however adsorption time has a much higher effect, this behaviour is attributed to the longer time the adsorbent is left in the adsorbate and availability of more active site and surface area which is largely determined by adsorbent dosage. The surface plot for the interaction of temperature (C) and initial concentration (B) on the synthesised Chitosan beads used in the removal of Arsenic is displayed in Figure 4.12d. The plot shows that both terms significantly influenced Arsenic removal with the linear (C, B) having a marked effect on the removal with initial metal concentration having a higher effect (F-value= 38.35). This trend could be as a result saturation of the metal binding sites of the adsorbent. Figure 4.12f represents the 3D plot for time (D) as a function of temperature (C) for Arsenic removal. According to the plot, the two terms have significant individual effect on Copper removal; however adsorption time has a much higher effect. An increased in temperature (30-50 0 C) and increased in time (40-80 0 C) result to an increased in the maximum removal of Arsenic. The longer the time the adsorbent stayed in adsorbate at a maximum temperature; the better the adsorption of Arsenic metal in the aqueous solution.

4.3 Effect of Contact Time on Adsorption of Copper and Arsenic unto Chitosan-Zeolite Beads

The importance of this experiment was to determine the adsorption time required to reach the equilibrium between the solid phase (Chitosan- Zeolite beads) and liquid phase (aqueous solution). Figures 4.13 and 4.14 shows that the adsorption capacity uptake increases with time and after some time, it reaches a constant value where no more metal ion can be removed from the solution.









(c)

Figure 4.13: Effect of contact time on the adsorption of Copper on Chitosan-Zeolite beads at (a) 30 °C, (b) 40 °C and (c) 50 °C. (rpm= 140, V= 100 mL, W= 0.5 g, PH= 7).







(c)

Figure 4.14: Effect of contact time on the adsorption of Arsenic on Chitosan-Zeolite beads at (a) 30 °C, (b) 40 °C and (c) 50 °C. (rpm= 140, V= 100 mL, W= 0.5 g, PH= 7).

At this point, the amount of metal ions being adsorbed by the adsorbent was in a state of dynamic equilibrium with the amount of metal ions desorbed from the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time. The amount of metal ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under these particular conditions. Figures 4.13(a), (b) and (c) results showed that the adsorption of Copper at different concentrations 0.5, 1.0 and 1.5 mg/L at various temperatures (30, 40 and 50 °C) on Chitosan- Zeolite beads increases with time up to 80min for initial concentration of 0.5 and 1.0 mg/L and then it becomes almost constant at the end of the experiment while at 1.5 mg/L took 90 min before equilibrium was established. Figures 4.14(a), (b) and (c)results for Arsenic adsorption on Chitosan-Zeolite beads also showed that it took 80min before equilibrium was established for initial concentration of 0.5 mg/L while for 1.0 and 1.5 mg/L it took 90 min for equilibrium to be established. The fast uptake observed at the initial stages maybe as a result of abundant active sites on the surface of the adsorbent available for binding to the Copper and Arsenic in solution which becomes saturated as the time progresses and increase in temperature also increases the rate of adsorption (Akpomie et al., 2013; Sdiri et al., 2016).

4.3.2 Effect of initial concentration on adsorption of Copper and Arsenic unto Chitosan-Zeolite beads

The initial metals concentration effect on the Chitosan-Zeolite adsorption capacity is an adsorption process that is useful and its usually measured when equilibrium position is established between the metals to be removed and the adsorbent; that is, the point at which the amount of metals adsorbed on the adsorbent is in a state of dynamic equilibrium with the

amount of metals desorbing from the adsorbent. The effect of initial concentration is shown in Figure 4.13 and 4.14 respectively.



Figure 4.15: Effect of initial concentration on Copper adsorption onto Chitosan-Zeolite beads at (a) 30 °C, (b) 40 °C and (c) 50 °C (rpm= 140, V= 100 mg/L, W= 0.5 g, PH= 7).


(a)



(b)



(c)

Figure 4.16: Effect of Initial Concentration on Arsenic Adsorption onto Chitosan-Zeolite beads at (a) 30 0 C, (b) 40 0 C and (c) 50 0 C (rpm= 140, V= 100 mL, W= 0.5 g, PH=7).

Different initial concentrations of 0.5, 1.0 and 1.5 mg/L for Copper and Arsenic were used to study the effect of initial concentration adsorption on Chitosan-Zeolite beads. The results on effect of initial concentration on adsorption of Copper and Arsenic unto Chitosan-Zeolite beads at different temperatures are presented in Figures 4.15-4.16. Results revealed that at initial Copper concentration of 0.5 and 1.0 mg/L using Chitosan-Zeolite beads as adsorbent, equilibrium condition was attained at 80 min while at 1.5 mg/L concentration it took 90 min before equilibrium was established. The attainment of equilibrium on Arsenic removal was at 80mins for initial concentrations of 0.5 mg/L while at 1.0 and 1.5 mg/L it took 80 minutes to attained equilibrium, respectively; at 30, 40 and 50 °C. At lower metals (Copper and Arsenic) concentration, the adsorption capacity was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of metals became higher, the adsorption capacity decreased since the available sites for adsorption became less due to saturation of adsorption sites (SenthilKumar et al., 2010). The result also shows that at low concentrations of the metals, equilibrium position was achieved faster while it took longer time for higher initial metals concentrations to attain equilibrium and this could be attributed to the fact that more vacant sites were present on the Chitosan- Zeolite beads with less number of molecules of the adsorbate to occupy and so, the limited available molecules were speedily adsorbed (Chen et al., 2005).

4.3.3 Effect of pH on adsorption of copper and arsenic unto chitosan-zeolite beads

The percentage removal of Copper and Arsenic on Chitosan-Zeolite beads were studied by pre-selected ranges of pH values from 2-12. The results have been depicted in Figure 4.17.



Figure 4.17: Effect of pH on the Adsorption of Copper and Arsenic onto Chitosan-Zeolite Beads (V= 0.5 mg/L, W= 0.5 g, rpm= 140 rpm, t= 90 min)

The result in Figure 4.17 revealed a sharp decrease in the percentage removal of Copper and Arsenic when the pH value of the solutions changes from 2- 12. The maximum adsorption of both Copper and Arsenic were obtained at pH 2. This result may be attributed to the hydrogen ions available to protonate the amine groups (-NH₂) on the adsorbent to form – NH_3^+ in the acidic solution which causes an increase in the number of available binding sites and surface area on the adsorbent surface for the adsorption of the metals. The $-NH_3^+$ groups formed due to protonation increases the electrostatic repulsion between the metals and the surface of the Chitosan- Zeolite beads causing a decrease in the adsorption capacity of the adsorbent composite. Also decrease in percentage removal of the metals at higher pH may also be due to the formation of soluble hydroxyl complexes (Medhat, 2015).

4.3.4 Effect of adsorbent dosage on adsorption of copper and arsenic unto chitosanzeolite beads The percentage removal of Copper and Arsenicon Chitosan-Zeolite beads were studied, the dosage was varied from 0.1-1 and the results have been depicted in Figure 4.18.



Figure 4.18: Effect of pH on the Adsorption of Copper and Arsenic onto Chitosan-Zeolite Beads (V= 0.5 mg/L, rpm= 140, W= 0.5 g, t= 90 min)

Figure 4.16 shows the effect of adsorbent dosage on the percentage removed metals (Copper and Arsenic) at equilibrium conditions. It was observed for both metals unto Chitosan-Zeolite beads that the amount of metals adsorbed varied with varying adsorbent dosage. An increase in the adsorbent dosage from 0.1 to 0.5 g resulted in a rapid increase in the uptake of Copper and Arsenic. However, further increase in the adsorbents dosage from 0.6 -1 g, did not result in a sufficient increase in the adsorption capacity. This may be due to overlapping of adsorption site as a result of overcrowding of adsorbent particles (T.Shi *et al.*, 2016). The increase in the percentage adsorption of metals is related to the adsorption sites on the Chitosan-Zeolite beads. At lower adsorption dosage, the metals compete for adsorption at limiting adsorption sites. However, as the amount of Chitosan- Zeolite beads is increased, the availability of adsorption sites promotes adsorption resulting in a greater percentage removal of the metals (Copper and Arsenic). This may also be attributed to the availability of more and more binding sites for complexation of the metals (Pahlavanzadeh *et al.*, 2012).

4.4 Isotherm Study

Adsorption isotherm studies give information about the distribution of adsorbate between the liquid phase and the solid phase when adsorption process reaches equilibrium. The equilibrium characteristics of this adsorption study were described through Langmuir, Freundlich and Temkin equations. The models parameters which were obtained from the plots of equilibrium adsorption against their corresponding concentration are presented on Table 4.12.

Copper		Arsenic					
Isotherms	Parameters	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Langmuir	Q _m (mg/g)	167.233	189.810	201.342	136.143	157.615	186.242
	$K_L (L/g)$	0.178	0.211	0.428	0.031	0.069	0.045
	\mathbb{R}^2	0.981	0.998	0.998	0.937	0.945	0.981
Freundlich	$K_{\rm F}$	71.071	82.391	86.261	24.311	29.150	45.912
	1/n	0.180	0.184	0.223	0.505	0.510	0.611
	\mathbb{R}^2	0.783	0.709	0.727	0.872	0.825	0.894
Temkin	A _T (L/mg)	63.133	94.563	96.241	71.852	87.189	96.241
	b _T (KJ/mol)	0.416	0.816	0.887	0.171	0.238	0.284
	\mathbb{R}^2	0.887	0.831	0.845	0.757	0.922	0.966

Table 4.12: Langmuir, Freundlich and Temkin Isotherm Models unto Chitosan-Zeolite Beads at Various Temperatures

The three isotherms under studies give an insight of the adsorption of Copper and Arsenic on Chitosan- Zeolite beads but not without some level of variance of their fitness. The best fit

of isotherm was selected based on the highest correlation coefficient (R^2) value (closest to unity) which described the fitness of the isotherm to the experimental data. Assessment of the models fitness revealed that Langmuir model was the best fit for adsorption of Copper and Arsenic on Chitosan- Zeolite beads as seen by their larger values of R^2 (>0.90) and was closely followed by the Temkin and Freundlich isotherm model. The affinity for adsorption was consistently increasing as the temperature increased as revealed by Langmuir constant K_L. The Langmuir monolayer adsorption capacities of Copper and Arsenic were estimated at 167.233 - 201.342 mg/g and 136.143 - 186.242 mg/g at different temperatures on the adsorbent (Table 4.12). However, the monolayer adsorption capacity of Copper was higher on the adsorbents than Arsenic. This was attributed to easier sorption of smaller molecular sized Copper as compared with Arsenic. Moreover, the high value of K_L has been related to specifically adsorbed metal at high energy surfaces with low dissociation constants while the low value of K_L appears to be related to adsorption at low energy surfaces with high dissociation constants (Mabrouk and Mourad, 2010). The results of essential characteristics of Langmuir isotherm expressed in dimensionless separation factor R_L, 0.000313- 0.102 and 0.00372- 0.0362 value range calculated for all concentrations (0.5, 1.0 and 1.5 mg/L) at various temperatures revealed that the entire adsorption processes were favourable because their values were in the range of 0 < RL < 1 which also indicates that the metals preferred to remain bound to the Chitosan- Zeolite beads (Bhattacharyya and Gupta, 2006). The Freundlich isotherm model gives information on surface heterogeneity of Copper and Arsenic adsorption process and the exponential distribution of active sites and their energies. The parameter 1/n gives information on adsorption intensity or surface heterogeneity with values between 0 and 1 becoming more heterogeneous as the value gets closer to zero. The results obtained showed that the adsorption surface of the Chitosan –Zeolite beads was heterogeneous in nature from 1/n values calculated for the two adsorbate (Copper and Arsenic) adsorption which were between 0.180- 0.223 and 0.505- 0.611 while the homogeneous behavior of Copper and Arsenic adsorption process was informed by Langmuir isotherm model. The applicability of Temkin isotherm model shows the increase of coverage due to adsorbate- adsorbent interactions which leads to decrease in heat of adsorption of all molecules in the layer; and this adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy which may be dependent strongly on density and distribution of functional group on the metals and the adsorbent surface (Auta and Hameed, 2011).

4.5 Adsorption Kinetics Study

The pseudo- first and second order parameters generated from the plots for adsorption of Copper and Arsenic on Chitosan- Zeolite beads are presented on Table 4.13- 4.15. The correlation coefficients (R^2) values and comparison of experimental and theoretical adsorption capacity q_e were used to predict the fitness of the kinetic models to the adsorption systems.

Note: The kinetic studies were carried out at different temperature in order to ascertain the optimum condition the will give best result in terms of highest percentage removal of the heavy metals.

]	Pseudo- f	Pseudo- second order				
	initial conc. (mg/L)	q _e exp (mg/g)	q <mark>ecal</mark> (mg/g)	k ₁ (min ⁻¹)	R ²	qecal (mg/g)	K2 (min ⁻¹)	R ²
Copper	0.5	0.495	0.0294	0.00921	0.607	0.567	0.0125	0.999
	1.0	0.956	0.122	0.00207	0.661	1.222	0.00986	0.999
	1.5	1.489	0.175	0.0276	0.851	1.601	0.00442	0.998
Arsenic	0.5	0.488	0.0301	0.0161	0.619	0.555	0.0221	0.966
	1.0	0.934	0.0935	0.00230	0.862	1.220	0.00488	0.997
	1.5	1.487	0.236	0.0299	0.859	1.456	0.00203	0.998

 Table 4.13: Pseudo- First and Second Order Kinetics for Copper and Arsenic Adsorption on Chitosan-Zeolite Beads at 30 °C

Table 4.14: Pseudo- First and Second Order Kinetics for Copper and ArsenicAdsorption on Chitosan- Zeolite Beads at 40 °C

		Pseudo- first order				Pseudo- second order			
Metals	Initial conc. (mg/L)	q _e exp (mg/g)	q <mark>ecal</mark> (mg/g)	k1 (min ⁻¹)	R ²	q _e cal (mg/g)	K2 (min ⁻¹)	R ²	
Copper	0.5	0.495	0.0251	0.0115	0.483	0.467	0.0136	0.999	
	1.0	0.956	0.0593	0.00230	0.514	1.0221	0.00701	0.999	
	1.5	1.489	0.158	0.0207	0.847	1.677	0.00480	0.999	
Arsenic	0.5	0.488	0.0258	0.0161	0.834	0.601	0.0601	0.996	
	1.0	0.934	0.0574	0.00921	0.857	0.989	0.00343	0.998	
	1.5	1.487	0.230	0.0299	0.910	1.701	0.00223	0.998	

]	Pseudo- f	irst order	Pseudo- second order			
Metals	Pb ²⁺ conc. (mg/L)	q _e exp (mg/g)	q _e cal (mg/g)	k ₁ (min ⁻¹)	R ²	q _e cal (mg/g)	K2 (min ⁻¹)	-R ²
Copper	0.5	0.0203	0.0138	0.0392	0.525	0.522	0.0174	0.999
	1.0	0.0593	0.000	0.0345	0.673	0.999	0.0101	0.999
	1.5	0.167	0.0276	0.0368	0.838	1.409	0.00354	0.999
Arsenic	0.5	0.488	0.0179	0.0161	0.830	0.611	0.0311	0.997
	1.0	0.934	0.0540	0.0511	0.938	1.209	0.00747	0.998
	1.5	1.487	0.219	0.0322	0.939	1.781	0.00832	0.998

Table 4.15: Pseudo- First and Second Order Kinetics for Copper and ArsenicAdsorption on Chitosan- Zeolite Beads at 50 °C

The results of the two kinetic models (Pseudo first order and Pseudo – second order kinetics) tested to show which best describe the adsorption process but pseudo-second-order model gave the best adsorption of Copper and Arsenic on Chitosan- Zeolite beads as can be seen from the small value of the model's rate adsorption constant when compared with the adsorption constant values for first order. From the results also, pseudo second- order kinetic model gave $R^2 > 0.90$ for all concentrations. The values of the rate constants decreased with increase in initial concentration of the two metals. The qe values calculated from the linear plot of the pseudo-second-order kinetic model were also found to be in agreement with experimental qe values (Table 4.13 - 4.15) but for pseudo first- order there were deviations which may be due to the actual process not being in conformity with the order of reaction. Since pseudo-second-order kinetic model fitted best with this system than the pseudofirst-order kinetic model, coupled with the high agreement between its calculated and experimental qe values it can be suggested that the adsorption was controlled by physio

sorption (Hammed *et al.*, 2009; Ketcha and Bougo, 2010). This process involves valence forces through exchange of electrons between adsorbate and adsorbent. Also the decrease in rate constant K_2 as the initial concentration of Copper and Arsenic increases reveals the fact that it is faster for the adsorption process on Chitosan – Zeolite beads to reach equilibrium at lower initial concentration (Nanganoa *et al.*, 2014).

4.6 Thermodynamic Adsorption Study

Thermodynamic parameters for adsorption of Copper and Arsenic on Chitosan-Zeolite were undertaken at various temperatures of 30, 40 and 50 0 C. This was done to determine the spontaneity of the adsorption process as shown on Table 4.16

 Table 4.16: Thermodynamics Parameters of Chitosan- Zeolite Beads on Copper and Arsenic Adsorption at Different Concentrations

Metals	Initial conc. (mg/L)	∆H (kJ/mol)	∆S (J/Kmol)		∆G (kJ/mol)		R ²
				30 °C	40 °C	50 °C	
Copper	0.5	0.00649	1.0996	-0.339	-0.350	-0.361	0.860
	1.0	0.00571 b	1.131	-0.348	-0.360	-0.371	0.798
	1.5	0.00406	1.398	-0.431	-0.444	-0,459	0.920
Arsenic	0.5	0.00712	0.484	-0.153	-0.159	-0.163	0.994
	1.0	0.00657	0.115	-0.0414	-0.0426	-0.0437	0.798
	1.5	0.00735	0.240	-0.0800	-0.0825	-0.0849	0.873

The results on Table 4.16 shows that all values obtained for ΔG are negative, indicating the spontaneity of the process and the great affinity of Copper and Arsenic on the adsorbent used. The positive ΔH indicate that the process is endothermic and chemical in nature. The increase in adsorption with temperature is associated with the raising of the diffusion rate of molecules of adsorbate, with a higher quantity of molecules with sufficient energy to undergo interaction with active surface sites, or even with the dilation of the internal structure of the adsorbent materials (Dogan *et al.*, 2004). The positive values of ΔS indicate an increase in the level of disorder of the species adsorbed, possibly associated with the changes in the configuration of the adsorbate molecules and of the surface of the adsorbent materials

(Lian et al., 2009).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

From the work carried out on the chitosan and chitosan – zeolite composite beads for the removal of Copper and Arsenic from aqueous solution, the following conclusions can be drawn:

IR spectrum analysis suggested the different functional groups which are present in the Chitosan and Chitosan- Zeolite beads to be -CONH-, $-CH_2$ and $-CH_3$, C-O, stretching N-H bending, $-NHC00CH_3$ and -NH bending. The BET shows the surface area of the Chitosan and Chitosan- Zeolite beads to be 376.40 and 691.10 m2/g respectively.

The optimal conditions obtained for Copper removal on Chitosan beads and Chitosan-Zeolite beads were 0.5 g, 0.5 M, 50 0 C and 80 min which translated to 98.03 and 99.78 % removal and conditions obtained for Arsenic removal on Chitosan and Chitosan-Zeolite beads were 0.5 g, 1.5 M, 50 0 C and 80 min which also resulted in 96.22 and 99.10 % removal respectively.

The combined effect of adsorbent dosage and temperature and the combined effect of temperature and time from the four parameters studied for Chitosan beads were found to have the greatest impact on Copper and Arsenic removal while the combined effect of initial concentration and time and that of adsorbent dosage and initial concentration were also found to have high impact on both Copper and Arsenic removal based on their F- values.

Batch adsorption studies on Chitosan-Zeolite beads for Copper and Arsenic removal showed effects on the variables adsorbent dosage, equilibrium time (90 min), initial metals

concentration, pH and temperature. The results provide a good indication of the different operating conditions that would be required for efficient removal of Copper and Arsenic from aqueous solution.

The isotherm parameters obtained from models revealed that Langmuir was the best isotherm that best described the adsorption process. The Copper and Arsenic adsorption process on Chitosan- Zeolite beads kinetics data were best modeled by pseudo second order kinetics. The thermodynamic constants, ΔG , ΔH and ΔS of the adsorption process showed that adsorption of the both metal on the adsorbent were endothermic, spontaneous and is built on the principle of physical adsorption which is caused by van der waals forces a relatively weak bond.

5.2 **Recommendations**

Based on the extent of this work, the following recommendations and suggestions were made:

- 1. The adsorption column study for the process should be considered for further research.
- Proper equipment (i.e centrifuge) for the preservation of chitosan and the chitosan zeolite composite beads to retain its moisture content after its synthesis to avoid it shrinkage should be made readily available to enhance sound result.

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APPENDICES

Appendix I

Preparatory stages of the synthesized chitosan beads, chitosan – zeolite beads, and adsorption studies stages.



Plate II: Jelly Mixture of Chitosan nanoparticles and 5% Acetic Acid Solution



Plate III: Drop wise Addition of Jelly Mixture of Chitosan nanoparticles and 5% Acetic Acid Solution into 1M solution of NaOH



Plate IV: Wet Synthesized chitosan Beads Undergoing Atmospheric Drying



Plate V: Dried and Finished Synthesized Chitosan Beads



Plate VI: Synthesized Chitosan – Zeolite Beads Composite



PLATE VII: Chitosan and Chitosan – Zeolite Beads Separately Immersed into the Simulated Waste water ready for Adsorption Process



PLATE VIII: Chitosan and Chitosan – Zeolite Beads Separately Immersed into the

Simulated Waste Water After Adsorption Process

Appendix II

REPRESENTATION OF LANGMUIR ISOTHERM PLOTS FOR COPPER AND ARSENIC USING CHITOSAN – ZEOLITE AT DIFFERENT TEMPERATURES.



Appendix IIA Isotherm for Copper Removal at 30°C



Appendix IIB Isotherm for Arsenic Removal at 30°C



Appendix IIC Isotherm for Copper Removal at 40^oC



Appendix IID Isotherm for Arsenic Removal at $40^{\rm 0}{\rm C}$



Appendix IIE Isotherm for Copper Removal at 50°C



Appendix IIF Isotherm for Arsenic Removal at 50°C

REPRESENTATION OF FREUDLICH ISOTHERM PLOTS FOR COPPER AND ARSENIC USING CHITOSAN – ZEOLITE AT DIFFERENT TEMPERATURES.



Appendix IIIA Isotherm for Copper Removal at 30°C



Appendix IIIB Isotherm for Arsenic Removal at 30°C



Appendix IIIC Isotherm for Copper Removal at 40°C



Appendix IIID Isotherm for Arsenic Removal at 40°C



Appendix IIIE Isotherm for Copper Removal at 50°C



Appendix IIIF Isotherm for Arsenic Removal at 50°C

REPRESENTATION OF TEMKIN ISOTHERM PLOTS FOR COPPER AND ARSENIC USING CHITOSAN – ZEOLITE AT DIFFERENT TEMPERATURES.



Appendix IVA Isotherm for Copper Removal at 30°C



Appendix IVB Isotherm for Arsenic Removal at 30°C


Appendix IVC Isotherm for Copper Removal at 40°C



Appendix IVD Isotherm for Arsenic Removal at 40°C



Appendix IVE Isotherm for Copper Removal at 50°C



Appendix IVF Isotherm for Arsenic Removal at 50°C

REPRESENT OF KINETICS FOR PSEUDO FIRST ORDER REACTION FOR COPPER AND ARSENIC AT DIFFERENT TEMPERATURES.



Appendix VA Copper Removal at 30°C



Appendix VB Arsenic Removal at 30°C



Appendix VC Copper Removal at 40°C



Appendix VD Arsenic Removal at 40°C



Appendix VE Copper Removal at 50°C



Appendix VF Arsenic Removal at 50°C

Appendix VI

REPRESENT OF KINETICS FOR PSEUDO SECOND ORDER REACTION FOR COPPER AND ARSENIC AT DIFFERENT TEMPERATURES.



Appendix VIA Copper Removal at 30°C



Appendix VIB Arsenic Removal at 30°C



Appendix VIC Copper Removal at 40°C



Appendix VID Arsenic Removal at 40°C



Appendix VIE Copper Removal at 50°C



Appendix VIF Arsenic Removal at 50°C

Appendix VII

REPRESENTATION OF THERMODYNAMICS PLOTS FOR COPPER AND

ARSENIC



Appendix VIIA Copper Removal



Appendix VIIB Arsenic Removal