



REMEDIATION OF ACID MINE DRAINAGE USING PRAWN SHELLS

BY

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DECLARATION

I, **Tshikovhi Fhatuwani Precious** hereby declare that the research dissertation for the Degree of Masters of Science in Environmental Science is submitted at the University of the Witwatersrand, Johannesburg, South Africa. I clearly state that this research dissertation has not been submitted previously for a degree at this or any other institution, moreover, I swear that this is my own work in design and execution and as thus, all reference materials and resources used has been duly acknowledged.

A handwritten signature in black ink, appearing to read 'P. Tshikovhi', is enclosed within a rectangular box.

(Signature of candidate)

This 28th day of May 2018, Johannesburg

DEDICATION

To my father Albert Tshikovhi, mom Avhatakali Joyce Nekhofhe, my husband Humbulani Mafune and my daughter Zwothe Zwavhudi Mafune, I love you.

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TABLE OF CONTENTS

DEDICATION	ii
ACKNOWLEDGEMENTS.....	iii
LIST OF FIGURES	x
LIST OF TABLES	xii
ACRONYMS AND ABBREVIATIONS.....	xiii
ABSTRACT	xiv
CHAPTER 1	1
INTRODUCTION	1
1.1 Background information	1
1.2 Wastewater remediation methods	3
1.3 Motivation	4
1.4 Breakdown of dissertation chapters	5
CHAPTER 2	7
LITERATURE REVIEW	7
2.1 Acid mine drainage and its inorganic minerals	7
2.2 History of Uranium	8
2.3 Applications of uranium	9

2.4	Cradle and fate of uranium in the environment.....	10
2.5	Chemistry and speciation of uranium in aquatic environment	11
2.6	Effects of uranium on human health	12
2.7	Regulations on uranium	12
2.8	Water remediation techniques	13
2.8.1	Neutralization	13
2.8.2	Bioremediation	14
2.8.3	Photo-catalysis	14
2.8.4	Adsorption	14
2.8.4.1	Previous uranium adsorption in aquatic environments	15
2.9	Prawn shells structure	16
2.10	Previous adsorption studies using chitin polymer	16
2.11	Inductively coupled plasma-optical emission spectroscopy (ICP-OES)	
	17	
2.12	Principle of BET	18
2.13	Principle of Fourier Transform infrared (FTIR)	18
2.14	Principle of Thermogravimetric Analysis (TGA)	19
CHAPTER 3		20
AIMS AND OBJECTIVES OF THE STUDY		20

3.1	Main aim	20
3.2	Specific objectives	20
3.3	Research questions	20
CHAPTER 4		22
MATERIALS AND METHODS		22
4.1	Collection and treatment of prawn shells	22
4.2	Reagents.....	22
4.3	Characterization	22
4.4	Batch adsorption Studies	23
4.4.1	Effect of pH.....	23
4.4.2	Effect of shaking time	23
4.4.3	Effect of adsorbent dosage	23
4.4.4	Effect of concentration	24
4.4.5	Effect of temperature	24
4.4.6	Effect of competing anions.....	24
4.4.7	Effect of competing metal ions	24
4.4.8	Desorption studies	25
4.4.9	Preparation of solutions	25

4.4.10	Data processing	25
4.4.11	Removal efficiency.....	26
4.4.12	Adsorption capacity	26
4.4.13	Normalized standard deviation	26
4.5	Adsorption Data Modelling.....	26
4.5.1	Kinetic modelling	26
4.5.2	Isotherm modelling.....	27
4.5.3	Langmuir isotherm	27
4.5.4	Freundlich isotherm	27
4.5.5	Dubinin–Radushkevich (D–R) models.....	28
4.5.6	Thermodynamic modelling	28
4.6	Geochemical Modelling	29
CHAPTER 5		30
RESULTS AND DISCUSSIONS		30
5.1	Characterization.....	30
5.1.1	Fourier transform-infrared (FT-IR) spectroscopy of prawn shells	30
5.1.2	Thermogravimetric analysis	31
5.1.3	BET	32

5.2	Batch studies.....	33
5.2.1	Effect of pH.....	33
5.2.2	Effect of adsorbent dosage	34
5.2.3	Effect of time	35
5.2.4	Kinetic studies	36
5.2.5	Effect of concentration	38
5.2.6	Isotherm modelling.....	40
5.2.7	Effect of temperatures	44
5.2.8	Thermodynamic modelling	45
5.2.9	Effect of competing anions.....	45
5.2.10	Effect of existing cations.....	48
5.3	Desorption studies.....	49
CHAPTER 6		50
CONCLUSIONS AND RECOMMENDATIONS		50
6.1	Conclusion	50
6.2	Recommendations	51
REFERENCES.....		52
APPENDICES		71

Appendix A1.....71

LIST OF FIGURES

CHAPTER 2

Figure 2.1: The chemical structure of chitin monomers	16
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CHAPTER 5

Figure 5.1: FTIR spectrum of (a) unused prawn shells and (b) prawn shells after batch adsorption	30
Figure 5.2: TGA of unused of prawn shells.....	32
Figure 5.3: Percentage removal of uranium using prawn shells at different pH ranges. Conditions: 10 mg L ⁻¹ uranium, room temperature, at 24 h and 150 rpm.....	33
Figure 5.4: Effect of adsorbent dosage of 10 mg L ⁻¹ uranium using prawn shells as the adsorbent varied from 50 mg to 1000 mg at pH 3 over 24 h.	34
Figure 5.5: Effect of adsorbent dose and contact time on 10 mg L ⁻¹ U adsorption capacity at T=25°C. Percentage removal of uranium as a function of shaking time and adsorbent dosage. Conditions: 10 mg L ⁻¹ uranium, pH 3 and room temperature.....	35
Figure 5.6: (a) The kinetic studies of prawn shells for pseudo first-order (b) The kinetic studies of prawn shells for pseudo second-order	37
Figure 5.7: Percentage removal of uranium as a function of adsorbate concentration. Conditions: 1000 mg of prawn shells at pH 3 over at T =25°C and 150 rpm	39
Figure 5.8: (a) Langmuir isotherm models for uranium adsorption (b) Freundlich isotherm model for uranium adsorption (c) Dubinin-Radushkevich isotherm model for uranium adsorption.....	42

Figure 5.9: Variation in adsorption capacity of uranium(VI) by prawn shells as a function of temperature. Conditions: 15 mg L ⁻¹ uranium, 1000 mg of prawn shells at pH 3 over at T =25°C and 150 rpm.....	44
Figure 5.10: The relationship between Ln KD and 1/T	45
Figure 5.11: Variation on the effect of competing anions on the adsorption of uranium. Conditions: 15 mg L ⁻¹ uranium, 1000 mg of prawn shells at pH 3, T =25°C and 150 rpm.	46
Figure 5.12: Adsorption efficiency of uranium in a multi-metal solution. Conditions: 15 mg L ⁻¹ uranium, 1000 mg of prawn shells at pH 3, T =25°C and 150 rpm	49

LIST OF TABLES

CHAPTER 5

Table 5.1: Properties of prawn shells from BET analysis.....	32
Table 5.2: The kinetic parameters of uranium adsorption onto prawn shells	38
Table 5.3: The parameters of the uranium adsorption isotherm models.....	44
Table 5.4: Desorption of uranium from prawn shells.	49

ACRONYMS AND ABBREVIATIONS

AMD	Acid mine drainage
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
D-R	Dubinin–Radushkevich
FTIR	Fourier transform-infrared
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
PHREEQC	pH Redox Equilibrium computer code
SA	South Africa
TDS	Total dissolved solid
TGA	Thermogravimetric analysis
U	Uranium
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
<i>Sd</i>	standard deviation

ABSTRACT

Acid mine drainage (AMD) is a serious global problem, particularly focusing on the Witwatersrand Basin, where most abandoned gold mines constituting mine waste containing pyritic rocks exist and leach sulfuric acid into surrounding waters as effluent containing trace elements like Fe, Co, Cu, Ni, Mg, Zn, Ca and U. Using currently available treatment technologies, it would be costly to remediate the approximately 3,000 miles of streams affected by AMD in Johannesburg hence probing a need for further research and new technology development. Therefore, this research explored the possibility of using prawn shells which contain a deacetylated form of chitin with a buffer capacity for use as a polluted mine water adsorbent. The effect of adsorption parameters such as contact time, adsorbent dosage, initial pH, initial uranium ion concentration, competing anions and competing cations were investigated. An optimum adsorption of uranium(VI) of 92% was achieved using 1000 mg adsorbent dosage achieved optimum removal efficiency at pH 3, room temperature and 15 mg L⁻¹ after 6 h equilibration time. The kinetics, isotherms followed pseudo second-order and the Freundlich models. The thermodynamic parameters for the adsorption of uranium onto prawn shells showed that the process proceeded in an exothermic nature, that is, adsorption capacity of uranium decreased with an increase in temperature. The desorption studies performed using HNO₃ as an eluent gave efficiency of 19 ± 0.01% for 0.5 mg L⁻¹, 37 ± 0.09% for 1 mg L⁻¹ and NaHCO₃ desorption capacity of 77.0 ± 0.01% for 0.5 mg L⁻¹, 93.2 ± 0.05% for 1 mg L⁻¹ and 99.7 ± 0.02% for 2 mg L⁻¹, respectively. Consequently, NaHCO₃ was found to be a good reagent for the desorption of uranium. The adsorption capacity was observed to be 0.17 mg g⁻¹. At high concentrations the competing species showed an insignificant effect as uranium adsorption reached 97%. In all the experimental conditions, the speciation of uranium was determined using the PHREEQC geochemical modelling code. For instance, negatively charged U-carbonate complexes (e.g. UO₂(CO₃)₂²⁻) were predicted, explaining the potency of NaHCO₃ as a desorbent for uranium. In the presence of competing ions, the speciation of uranium did not change significantly and hence the maintenance of elevated

adsorption. Overall, the results of the study demonstrated that prawn shells are effective for the recovery of UO_2^{2+} ions, making them ideal for potential application for the remediation of uranium in liquid waste.

Keywords:

Uranium;

Adsorption;

Prawn shells;

Acid mine drainage;

Modelling

CHAPTER 1

INTRODUCTION

1.1 Background information

Gold mining in the Witwatersrand basin started in 1886 (Werdmuller, 1986) and it was extracted using mercury amalgamation method. However, according to Naicker *et al.* (2003), “as mining operations became deeper, autoxidized ore containing pyrite (FeS_2) was encountered and interfered with the extraction”. Then, this method was replaced by the process of gold extraction which is called MacArthur-Forrest and it entails extraction of silver and gold ores by dissolving them in a dilute solution of sodium cyanide or potassium cyanide (Naicker *et al.*, 2003). This method involves the extraction of conglomerates to the surface for further processing. The conglomerates mined in Witwatersrand Basin consist of approximately (70-90%) quartz pebbles and (10-30 %) phyllosilicates, containing sericite, $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ (Feather and Koen, 1975). Mineral ores that were extracted from underground reserves were taken to the surface, where it was crushed until it turn out to be fine sand, which was then exposed to a film of mercury spread on copper plates (Naicker *et al.*, 2003). During gold extraction processes tailing were formed. There are different types of tailings, namely slims, sandy slims, and clay slims. These tailings were channelled to the disposal slims dumps.

According to Tutu *et al.* (2008), “The cyanidation gold extraction method is relatively selective for silver and gold”. This consequently led to the remaining of other minerals in the tailings. Furthermore, these minerals mostly iron sulphide minerals (pyrite) become exposed and react with water and oxygen result in the formation of sulphuric acid and iron hydroxides producing acidic runoff (acid mine drainage) (Singer and Stumm, 1970).

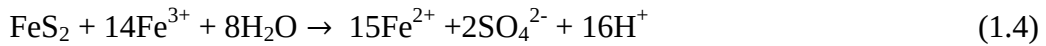
The chemistry of acid mine drainage (AMD) can be illustrated by oxidation reaction of pyrites, which results in the production of ferrous ions followed by ferric ions. Pyrite oxidation reaction is the highest contributor to the formation of acid mine drainage (AMD). An oxidation of FeS_2 leads to the generation of a very acidic drainage that has high total dissolved solids (TDS) and elevated concentration of $\text{Fe}^{2/3+}$, SO_4^{2-} , and H^+ protons as expressed by equation 1.1 and 1.2 AMD equations can be expressed as follows (Singer and Stumm, 1970):



The release of Fe^{3+} is usually accompanied by precipitation from the solution following the formation of iron hydroxide. This process occurs with the release of acidity (H^+):



Further, Fe^{3+} becomes an oxidant, which oxidises pyrite in a self-perpetuating chemical reaction:



Several studies have reported the occurrence and impacts of AMD in Witwatersrand Basin (Tutu *et al.*, 2008; Durand, 2012; Naicker *et al.*, 2003; Marsden, 1986; Werdmuller, 1986; Akcil and Koldas, 2006). Furthermore pollution problems caused by gold extraction process on the Witwatersrand basin in Johannesburg area have been investigated (Durand, 2012). It was concluded that mine dumps are the major source of pollution particularly older sand dumps and this consequently lead to the increasing of total dissolved solids load in the Vaal River which is the main water supply to Johannesburg. It is projected that most of the societies are surrounded by the catchments (DWAF, 2004). Furthermore, Vaal barrage catchment is also characterized by enormous number of gold and coal mines. These mines consequently lead to the pollution of water in the Vaal River. (DWAF, 2004). According to Jones *et al.* (1988), “erosion of

dump material into water courses also contributed to pollution because of rain water which had percolated through the dumps, creating polluted ground water plumes beneath the dumps which were emerging at surface in streams”.

AMD effects lead to deterioration of water quality, rendering such water in those ecosystems unsuitable to be used by communities relying on them for their various domestic purposes (Zhang, 2011). These effects also provide favourable conditions for outbreak of chronic waterborne diseases which in turn pose a serious health risks such as cancer to communities residing near these polluted ecosystems. Moreover, AMD is also associated with deterioration of various aquatic ecosystems such as lakes, rivers and wetlands. These consequently results in scarcity of clean freshwater which is a fundamental element for most organisms (Zhang, 2011). Therefore, this study was designed with the aim of exploring the feasibility of using prawn shells as an effective adsorbent for removal of uranium from acid mine drainage. The ultimate intended use of this application is bulk remediation of AMD in situ e.g. in shallow groundwater systems where a reactive barrier consisting of these adsorbents can be constructed across the flow path of the water.

1.2 Wastewater remediation methods

As indicated earlier, AMD is well-known to have deleterious effects on the environment as cited by a number of studies (Habashi, 1992; Garbarino *et al.*, 1995; Horsfall and Spiff, 1999; Peplow, 1999; Akcil and Koldas, 2006; Coetzee and Winde, 2006; Tutu *et al.*, 2008). Several approaches have been used both at large scale and small scale levels to remediate AMD. Among these there are methods such as phytoremediation (Karathanasis and Johnson, 2003; Mendez and Maier, 2008), wetlands (Smith, 1997; Sheoran and Sheoran, 2006), neutralization (Kalin *et al.*, 2006; Akcil and Koldas, 2006), chemical precipitation (Matthew *et al.*, 2002; Wei *et al.*, 2005), reverse osmosis (Vaclav and Gulikova, 2005), sulphate reduction (Kaksonen and Puhakkai, 2007; Sanchez-Andrea *et al.*, 2014) and adsorption (Motsi *et al.*, 2009; Zhang, 2011). Adsorption, by far presents many opportunities for improvement compared to others as an extensive diversity

of resources can be used, including: clays, zeolites, iron oxides, nanomaterials, agricultural waste, biomass, chitin-based substances and polymers among others.

The chitosan biopolymer has been used for a variety of applications such as bioconversion for the production and conservation of food from microbial worsening, cleansing of water, creation of biodegradable and repossession of waste material from food processing discards (Shahidi and Synowiecki, 1991). Moreover, chitin was reported to yield variety of fatty acids, hydrogen and acetate during the fermentation process (Vera *et al.*, 2001), hence confirming that it a sustainable substrate that can be used for sulfate-reducing bacteria. It has also been revealed that chitin is a good physical sorbent for trace elements such as copper, iron, zinc, arsenic, chromium and manganese from effluent (Franco *et al.*, 2004; Hawke *et al.*, 1991; Mcafee *et al.*, 2007; Vijayaraghavan *et al.*, 2005). Daubert and Brennan (2007), reported that chitin can also be used to clean AMD effluent.

In this study, prawn shells were used as adsorbents for treating polluted mine water. According to Harkness *et al.*, (2003), prawn shells are made of chitin which has a deacetylated form with a chemical formula $C_8H_{13}NO_5$. It also contains 6–7% nitrogen which is essentially the constituent in prawn shells (Abudulkarim *et al.*, 2013). Further, prawn shells also consist of amino acids ($R-CH(NH_2)COOH$) (Gulgun *et al.*, 2008).

The presence of these functional groups i.e. nitrogen-based make prawn shells to be attractive adsorbents for the removal of metals as it is well known that these groups tend to interact strongly with a variety of metals e.g. Cu, Co, Zn, Fe and U. Further, prawn shells also contain calcium carbonate ($CaCO_3$) and calcium phosphate ($CaPO_4$) which can provide a buffering capacity, thus potentially increasing the alkalinity of treated waters (Daubert and Brennan, 2007).

1.3 Motivation

In this study, prawn shells were extracted from waste food collected from selected Ocean Basket Restaurants around Johannesburg. Therefore they are readily

available, cost effective, and their use to treat AMD is yet to be explored in South Africa. This study aimed to assess the ability of prawn shells to serve as cheap adsorbents for AMD remediation. This study, as hinted earlier, acted as a pre-study platform for a wider intention to apply this type of seafood waste to reactive barriers for large scale water clean-up.

1.4 Breakdown of dissertation chapters

This dissertation is comprised of five (5) chapters that are categorically organised to explain different aspects of the study. A brief explanation of the contents of each chapter is given below.

Chapter 1: Introduction to the study

In this chapter, a specific summary of the potential threats that were caused by elevated levels of trace elements which consequently led to pollution of water is presented. It also emphasized on the significance of prawn shells as a good adsorbent for treating polluted mine water.

Chapter 2: Literature related to this study

This chapter highlights a literature related to the chemistry and speciation of uranium in aquatic environment. The advantages and disadvantages of uranium in mine polluted water remediation techniques are discussed. The chapter concludes by discussion on the data modelling of uranium.

Chapter 3: Research aims, objectives and questions

In this chapter, the aims and objectives governing the focus of the study were outlined. The main objective/aim was supported by specific objectives. The questions to be answered by this study were also explained in detail.

Chapter 4: Research methodology

This chapter highlights significant evidence concerning the materials and methods used to accomplish the research aims and objectives as highlighted in chapter 3. Furthermore, the chapter also stipulates the chemicals, research tools, research

laboratory and mathematical methods performed in order to interpret and explain the results and discussions as hinted in chapter 5.

Chapter 5: Results and discussions

In this chapter, results obtained from the experimental study were duly discussed. This was also supported by documented studies from a number of scientific sources.

Chapter 6: Conclusion and Recommendations

This chapter summarizes the outcomes of the entire study on the basis of the results and discussions that were given in chapter 5 and infer future recommendations as it pertains to the identified research gaps.

References

In this section, materials used to support claims of this study were duly acknowledged.

CHAPTER 2

LITERATURE REVIEW

This chapter seeks to give a detailed literature review on acid mine drainage and its inorganic minerals, industrial applications and the geochemistry of uranium. It also highlighted the depollution chemistry and mechanisms.

2.1 Acid mine drainage and its inorganic minerals

Acid mine drainage (AMD) refers to acidic water containing pyrite and sulphide waste minerals that are oxidised in the presence of water, air and microorganisms at mine site (Name and Sherindan 2014). Acid mine drainage from abandoned mines pollutes both groundwater and surface water (Gaikwad and Gupta, 2008). Other sources of acidic wastewater are metal plating, ore processing, basic steel and metal alloy, leather tanning, petrochemicals, and fertilizer industries (El-Wakil *et al.*, 2014, Al-Omair, 2005). AMD is a major environmental concern all over the globe (Gaikwad and Gupta, 2008).

The AMD contains minerals consisting of trace elements such as mercury (Hg), iron (Fe), lead (Pb), copper (Cu), cobalt (Co), manganese (Mn), aluminium (Al), zinc (Zn), arsenic (As), nickel (Ni), and uranium (U) (Balakrishnan *et al.*, 2010; Gitari *et al.*, 2011; Motsi, 2010; Correa, 2010). Heavy metals or transition metals are generally defined as periodic table elements consisting of the d-block subshell orbital (Zayat and Smith, 2006). These heavy metals are toxic (Machida *et al.*, 2004), non-biodegradable (Mishra, 2014.) and bio-accumulative (Balakrishnan *et al.*, 2010; Horsfall and Spiff, 2005; Tavengwa, 2013). In the presence of oxygen, water and acidophilic chemotrophic bacteria such as *Gallionella ferruginea* (Johnson and Hallberg, 2005), These heavy metals get oxidized (Michalková *et al.*, 2013). During high rainfall, the oxidized heavy metals are eroded into aquatic environments where they can easily be accessed and harm human beings and other aquatic organisms (Gaikwad and Gupta, 2008).

The elevated amounts of these metals can cause adverse effects on human organs such as kidney, liver, and reproductive system (Zayat and Smith, 2006). The following specific human diseases have been linked to the corresponding heavy metals; gastrointestinal disturbances and bone anomalies - copper and zinc, lung cancer – chromium (Nomanbhay and Palanisamy, 2005), kidney failure - uranium (Bakatula *et al.*, 2015) and central nervous system malfunctions, hepatitis and nephritic syndrome – lead (El-Wakil *et al.*, 2014). Uranium is even more dangerous because it is a radioactive inorganic toxicant. In human, uranium has also been associated with DNA changes (Tavengwa, 2013). Thus, uranium is an hazardous inorganic environmental pollutant of major concern (Cheng *et al.*, 2004).

The transportation of acid mine drainage minerals are influenced by various environmental factors. The important factors that influence transportation, distribution or mobility of AMD heavy metals such as uranium into water systems are namely; type of water system (aquifer or surface water) (Catalano *et al.*, 2016), pH (Giammar, 2001), ligands type and concentrations (Cheng *et al.*, 2004), other natural ions (Wazne *et al.*, 2003), mineral availability (Planer-friedrich, 2008), microbial activity (Fox *et al.*, 2006), temperature conditions (Horsfall and Spiff, 2005) and redox potential (Gronowski, 2013) of the acid mine drainage environment.

In the aquifer (groundwater) and in alkaline pH medium where calcium carbonate ligand is present, uranium(IV) mobility is also associated to the formation of uranyl-carbonate complexes, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{CaUO}_2(\text{CO}_3)_2^0$ (Fox *et al.*, 2006).

2.2 History of Uranium

According to literature (Munter, 2013), radionuclides have always existed on earth since the origin of planet earth. Uranium is one such radionuclide, it has atomic number 92 and it occurs naturally in living and non-living systems such as rocks, oceans and microorganisms (Bagherifam *et al.*, 2010). The use of this actinide heavy metal (Gronowski, 2013) for metal and dyes manufacturing started

before the year 1879 (Brugge and Goble, 2002). Henceforth, it is not surprising that the first uranium caused lung cancer was reported during 19th century in Schneeberg (Germany) and in Joachimsthal (Czechoslovakia) (Saccomanno *et al.*, 1988). In fact, biological activity of uranium in dogs and rabbits was first reported in 1824 (Hodge, 1973).

Currently, uranium is mostly introduced to the environment by anthropogenic activities. In present day, significant amounts of uranium are found at gold mining fields such as the one in Witwatersrand basin (Bakatula *et al.*, 2015) and in seawater (Mehta *et al.*, 2015; Giammar, 2001). These human operations are namely; nuclear industry, lignite burning in power stations, mineralisation process, application of agricultural fertilizers and mining (Khalili *et al.*, 2013).

The mining of uranium for nuclear purposes began around 1940. Uranium mining in United State of America (USA) and Australia started in late 1940s (Samet *et al.*, 2010). Around 1950s most uranium mines were opened in Australia, but few others have already been in use from the times of World War 2 (Mudd, 2011). Uranium capturing methods in seawater were first invented in 1960 (Mehta *et al.*, 2015). Initially uranium was mined as part of painting ingredient. However, the first *in situ* leach method for extracting uranium by chemical agents dates back to 1975 (Tavengwa, 2013). This method has been used in countries such as USA, Australia, China, Russia, Ukraine, Bulgaria, Czech Republic and Germany (Arnold *et al.*, 2011). A significant decline in uranium demand occurred during 1980s (Tutu *et al.*, 2009). In the year 2004, uranium demand and pricing suddenly increased again (Gronowski, 2013). If the present uranium usage for electricity continues, it is projected that the current uranium content in mines and seawater can last for the next 80 - 250 years.

2.3 Applications of uranium

There are four most common uranium ores, namely; uraninite (UO₂), pitchblende (U₃O₈), davidite [(Fe, Ce, U)₂(Ti, Fe, V, Cr)₅O₁₂] (Waseem *et al.*, 2015) and brannerite (UO₃Ti₂O₄) (Naicker *et al.*, 2003). These ores of uranium are mostly mined for use in nuclear fuel and weapon developing industries (Giammar, 2001;

Krestou and Panias, 2004). Uranium is used in military (Wazne *et al.*, 2003) as part of ammunition (Bagherifam *et al.*, 2010). Some institutions use uranium as part of nuclear technology and agricultural uranium-phosphate fertilizers (Sprynskyy *et al.*, 2011). There is reports that uranium can be used as a catalyst or staining pigment (WHO, 2012). The demand for uranium is projected to raise in the near future, primarily for electrical or nuclear power generation (Mehta *et al.*, 2015). Uranyl acetate was also used for nucleic acid staining (Zobel and Beer, 1961).

2.4 Cradle and fate of uranium in the environment

Uranium contaminate both soil and groundwater (Fox *et al.*, 2006). All three most common natural uranium radionuclides; ^{234}U , ^{235}U and ^{238}U decay by both alpha and gamma (WHO, 2012). ^{238}U makes largest percentage (99.27%) of the uranium isotopes (Waseem *et al.*, 2015). Owing to human activities, ^{233}U and ^{236}U are now reported to be available in reasonable amounts (Giammar, 2001).

The significant amounts of uranium in the environment are associated to improper management of nuclear energy and gold mining tailing wastes (Bagherifam *et al.*, 2010; Bakatula *et al.*, 2015). The inorganic uranium from the waste sites is distributed along the surrounding environment as part of surface water and groundwater (Kaghazchi, 2008).

The main promoter of soil contamination by uranium is soil perturbation by groundwater forming an aquifer. In general solution pH, uranium speciation, microbes (e.g. bacteria) (Pollmann *et al.*, 2006) and the complexing ligands availability determine water and soil contamination or mobility of radioactive uranium (Chisholm-Brause *et al.*, 2001). Uranium composing groundwater can slowly penetrate soil and accumulate at the site within an aquifer. The uranium that accumulates within the soil aquifer is massively pushed along the surface gradient as a result of saturation caused by high rainfall. The fate of both uranium contaminated surface water and groundwater is in the water streams, rivers, dams, boreholes and consequently human kind. ^{238}U isotope with half-life of 4.5×10^9 years is the most abundant in water (Waseem *et al.*, 2015).

The uranium contaminated water from the catchments can be accessed, contacted and possibly ingested into human body. Once uranium is in the human body, it can cause a variety of organismic malfunctioning of biological processes (Waseem *et al.*, 2015). These physiological failures may cause severe health impacts depending on the uranium concentration ingested (or contacted), exposure time and physiological functioning of the anatomical human part affected (Rajendra, 2011). For instance, uranium can easily form stable non-diffusible complexes such as uranium – albumin uranyl and diffusible hydrogen carbonate complex ($\text{UO}_2\text{HCO}_3^+$) because uranium has high affinity to number of chemical groups such as phosphate, carboxyl, and hydroxyl and nucleotides (WHO, 2012; Troyer *et al.*, 2016).

2.5 Chemistry and speciation of uranium in aquatic environment

Uranium naturally exists in a number of oxidation states which includes +2, +3, +4, +5 and +6, of that, +6 state is the most common (WHO, 2012), followed by the +4 oxidation states (Arnold *et al.*, 2011). As reported in literature; uranium mostly exists as a hexavalent linear uranyl ion, UO_2^{2+} of oxidation state +6 (Fox *et al.*, 2006). As acidic conditions become more dilute, uranium retain its +6 oxidation state but hydrolyses to exist as mononuclear $\text{UO}_2(\text{OH})^+$, dimers $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and trimers (Bakatula *et al.*, 2015; Planer-friedrich, 2008). In reducing condition, uranium is usually found in a less soluble tetravalent (+4) oxidation state (Gronowski, 2013). Generally, the distribution of uranium and its oxidation state is dependent on pH (Tavengwa, 2013).

There are at least 100 uranium identified minerals (Waseem *et al.*, 2015). Uranium movement, complex formation, concentrations and speciation in water depend on the solution pH, surrounding temperatures, complexing ligands availability and sorption of uranium species onto mineral surfaces (Bakatula *et al.*, 2015; Planer-Friedrich, 2008; Cheng *et al.*, 2004). These factors distinguishably facilitate the migration of uranium in the aquatic environment. For instance, the high uranium binding affinity for different ligands enables the formation of calcium uranyl carbonate complexes ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ (aq) and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) in alkaline medium (Fox *et al.*, 2006; Gronowski, 2013), linear UO_2^{2+} or hydrolysed

$\text{UO}^2(\text{OH})^+$ or $\text{UO}_2)_2(\text{OH})_2^{2+}$ in acidic medium (Bakatula *et al.*, 2015) and uranyl hemicarbonate at pH near neutral (Wazne *et al.*, 2003).

Availability of phosphate (Cheng *et al.*, 2004), sulphates (Bakatula *et al.*, 2015) and carbonates (Fox *et al.*, 2006) ligands also determine uranium mobility and binding behaviour in water. Study (Mehta *et al.*, 2015) showed that the predominant uranium-phosphate reactions in subsurface sediments is the autunite-type U(VI) phosphates.

2.6 Effects of uranium on human health

Heavy metals can be detrimental to human health even at low concentrations (Lukman *et al.*, 2013). Uranium is a well-recognised harmful heavy metal to human health. Diseases caused by uranium are kidney failure and DNA mutations (Tavengwa, 2013). Sometimes the use of uranium explosive can result in long term DNA damage to human population. The type of uranium biological harm depends on factors such as the source of uranium contaminated environment, the concentrations of uranium present, the human immune system and the types of organic molecular complexing with uranium (Wan *et al.*, 2006).

Uranium can cause defects such as lung cancer (Samet *et al.*, 2010), DNA alteration (Zobel and Beer, 1961) and renal malfunctions (Bakatula *et al.*, 2015).

2.7 Regulations on uranium

Most governments have put laws that require industries to treat heavy metal water before their release into the environment (Akpomie *et al.*, 2015; Gitari *et al.*, 2011; Zayat and Smith, 2006). In 1958, the Nuclear Energy Agency was established in order to facilitate peaceful nuclear energy use, advancing economic nuclear technology and provide legal environmental assessment inputs towards nuclear energy management (Wang, 2016). The earlier laws meant to reduce uranium health impacts to miners was enacted in 1971, this law limited the human exposure to radon – 222 daughter gas from uranium rocks to working levels not exceeding 4 months in a year (Saccomanno *et al.*, 1988). In USA, according to Environmental Protection Agency Environmental (EPA) legal requirements, 30

$\mu\text{g L}^{-1}$ has been set as the maximum permissible concentration of uranium in water (Munter, 2013).

2.8 Water remediation techniques

The removal of toxic chemical species such as uranium from aquatic systems is a prime environmental concern (El-Wakil *et al.*, 2014). Water treatments methods can either be passive or active (Gitari *et al.*, 2011; Johnson and Hallberg, 2005). Active treatment includes use of sodium carbonate or lime in the area affected by AMD while an example passive treatment is the construction of wetlands for trapping AMD minerals (Yadav *et al.*, 2016).

Some common water remediation techniques are neutralization or liming (Balintova *et al.*, 2012), chemical precipitation (El-Wakil *et al.*, 2014), bioremediation or biosorption (Odokuma and Akponah, 2010), permeable reactive barriers (PRBs) (Daubert *et al.*, 2006), membrane separation (Sprynskyy *et al.*, 2011), photo-catalysis (Doll and Frimmel, 2005) and adsorption (Zayat and Smith, 2006). Among this processes, adsorption is the most important water remediation technique for heavy metal uptake (Mahmoud, 2013). Adsorption is advantageous because it is highly efficiency, inexpensive and allows regeneration of adsorbent through desorption processes (El-Wakil *et al.*, 2014). Some of these common water remediation methods are briefly discussed below:

2.8.1 Neutralization

Neutralization or liming process refer to treatment of acid mine drainage effluents by basic agents such as, sodium hydroxide, ammonia or limestone (Michalková *et al.*, 2013). The addition of these reagents promotes acid-base reactions that lead to increased pH of AMD. However, the addition of lime (CaO) and NaOH to AMD cause gradual precipitation of radioactive waste and iron species that form a layer that coat and prevent the AMD from further pH increases. Therefore, the disadvantage of liming for uranium removal is that, it can effectively improve the solution pH to certain levels for a particular period and it also introduces radioactive aluminum or iron secondary wastes in the form of sludge precipitates (Kim *et al.*, 2016; Nomanbhay and Palanisamy, 2005).

2.8.2 Bioremediation

Bioremediation or bio-sorption is a water remediation technology that uses microbes and plants such as bacteria, algal, fungal biomass and biopolymers to either detoxify or transform hazardous substances (Igwe *et al.*, 2005). During AMD bioremediation, the microorganisms are exploited to reduce heavy metals in acidic water and thereby forming metal sulphide precipitation (Michalková *et al.*, 2013). Some microorganisms can utilize phosphate to reduce uranium(VI) to uranium(IV) (Cheng *et al.*, 2004; Wang, 2016).

Biological species that have been used over time for uranium adsorption includes *Rhizopus arrhizus* biomass (Tsezos, 1984). Bioremediation can occur through bioaccumulation of heavy metals inside the microbial cells and the rate of the bioaccumulation depends on concentration of biomass and heavy metals as well as temperature and pH (Odokuma and Akponah, 2010).

2.8.3 Photo-catalysis

Photocatalysis (photo-catalysis) in water remediation refers to the degradation of water pollutants using sunlight. During photocatalysis water treatment technique, persistent compounds are transformed, deactivated and finally minimized (Doll and Frimmel, 2005). The agents used in photocatalysis are usually titanium dioxide (TiO₂) and zinc sulphide (ZnS) (Zhong *et al.*, 2007). Most advanced oxidation processes use TiO₂ for photochemical degradation of organic water pollutants (Sirés and Brillas, 2012). Photocatalysis is extensively used to degrade persistent organic pollutants such as phenols, pharmaceuticals and organic dyes (Tijani *et al.*, 2014). Since trace elements such as uranium are non-degradable, photocatalysis is not effectively applicable for inorganic pollutants from AMD (Bailey *et al.*, 1999).

2.8.4 Adsorption

Adsorption refers to the deposition of a substance (adsorbate) from liquid phase onto the surface of the solid phase (adsorbent) (Correa, 2010). This method is the

widely used as an alternative convenient water treatment method for heavy metal in comparison to the other water treatment methods (Zayat and Smith, 2006).

The wide use of adsorption in wastewater is associated with the ease of operation, cost-efficiency and the availability of indefinite adsorbents to choose from (Balakrishnan *et al.*, 2010). Sorption depends on the target metals initial concentration and temperature (Odokuma and Akponah, 2010), nature of the adsorbent (Correa, 2010), pH (Planer-Friedrich, 2008), and competing species (Antoniadis *et al.*, 2007).

2.8.4.1 Previous uranium adsorption in aquatic environments

Researchers have developed several adsorbents for uranium removal from wastewater (Cheng *et al.*, 2004; Sprynskyy *et al.*, 2011.) Activated carbon is commonly used for uranium adsorption (Zayat and Smith, 2006), for examples activated carbon was used in a study (Mehta *et al.*, 2015) to remove uranium and its recorded adsorption capacity was 3.4 g U kg^{-1} .

Activated carbon has been a widely commended adsorbent in depollution science, however, its cost factor and preparation demands limit its application. In that regard, several adsorption alternatives have been developed to replace activated carbon. Some alternative adsorbents that showed commendable uranium adsorption includes natural clinoptilolite zeolite (Krestou and Panias, 2004) and ion-imprinted polymers (IIPs) (Tavengwa *et al.*, 2014). However, these adsorbents have disadvantages that include at least one of the following; high cost, ineffective at low uranium concentrations, low adsorption capacity selectivity in the presence of competing species and non-reusability (Mahmoudl, 2013; Planer-Friedrich, 2008). Therefore, the developments of cheap adsorbents for removal of heavy metals such as uranium remains a course for research (Bakatula, 2011).

Literature (Bangerifam *et al.*, 2010) recommends use of polyfunctional adsorbents for uranium binding because of the diversity of uranium speciation. Therefore, the selected adsorbent for uranium adsorption must be both cheap and polyfunctionalised. Subsequently, the cheap and readily available prawn shells

characterised by a multifunctional polymer consisting of organic amine and hydroxyl groups (Daubert *et al.*, 2006;) are among the material for consideration in uranium adsorption.

2.9 Prawn shells structure

Prawn shells can be basically described as the exoskeletal chitin material similar to that of crab shells. The crab shell are mainly made of biopolymers know as chitin (Daubert *et al.*, 2006). The chemical formulae of chitin can be denoted by the following combination: $C_8H_{13}NO_5$. The chemical formation of chitin is well suited for metal ion uptake due to the presence of carboxylic, hydroxyl and lactone group which pose strong affinity for metal ions (Nomanbhay and Palanisamy, 2005). The chemical structure of chitin monomers connected by a β -1,4-linkage (Daubert *et al.*, 2006) is shown in Fig. 2.1.

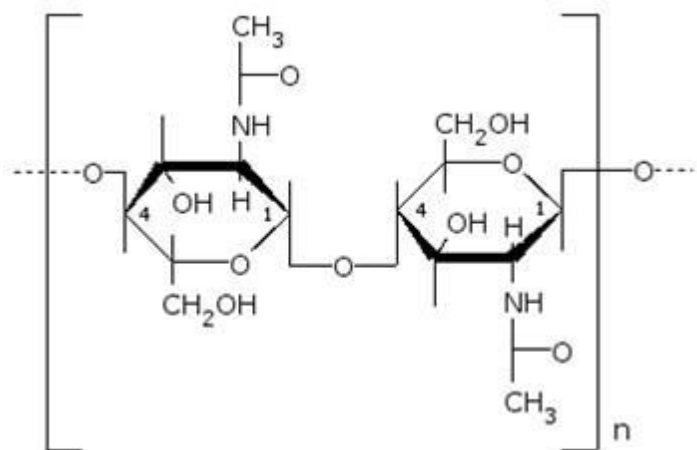


Figure 2.1: The chemical structure of chitin monomers

2.10 Previous adsorption studies using chitin polymer

According to literature, after cellulose, chitin is the second most naturally occurring polymer (Brugnerotto *et al.*, 2001; Kumirska *et al.*, 2010). The principal derivative of chitin is derived by deacetylation of chitin to yield what is known as chitosan (Brugnerotto *et al.*, 2001). Chitosan/graphene oxide composite and

glycine modified cross-linked chitosan resin have been used previously to adsorb gold (III), palladium and platinum (II) (Liu *et al.*, 2012; Ramesh *et al.*, 2008).

2.11 Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Inductively coupled plasma – optical emission spectroscopy instruments have been in the market since 1974 (Olesik, 1999). ICP–OES is an analytical technique widely used for multi-element analysis of inorganic metals present in environmental, agricultural, biological, clinical and food samples. The samples are analysed in liquid form. For solid samples, the organic fraction is first destroyed by digestion methods which may use suitable combinations of acid reagent and instruments such as microwave (Gouveia *et al.*, 2001). The common oxidant agents used for organic analytes digestion for ICP-OES analysis of solid samples are hydrochloric acid (HCl), nitric acid (HNO₃) and hydrofluoric acid (HF) (Wheal *et al.*, 2011). The most common pre-concentration technique for reducing matrix effect in samples to be analysed by ICP-OES is solid phase extraction (SPE) (Faraji *et al.*, 2010).

When samples are prepared, ICP-OES principles for analysis is as described: sample solutions are sucked into the instrument through peristaltic movement. The sample is then converted into vapour by a nebulizer. The remaining liquid is excreted through a tube into waste bottle. The aerosol part of the sample is carried through the spray chamber for combination with argon carrier gas inside the torch before irradiation by radiofrequency temperatures of about 7000–1000 K. The gas helps to heat the sample without vaporisation. The heated sample attains atomic and ionic state of high energy. When the atoms come to lower energy state, they release light (discrete photons) which is characteristic of the elements contained in the sample solution (Hou and Jones, 2000).

Since different atoms of different elements release discrete light at different wavelength, in ICP-OES the light is directed to a sensor or photodetectors that can help amplify and identify the elements according to wavelength and concentrations of the elements composing the sample. One of the detectors used

in ICP-OES is the charge coupled detector/device (CCD) (Barnard *et al.*, 1993). The ICP-OES is connected to personal computer which provides virtual information about the sample properties. The sample wavelength is related to the elements contained in the sample whereas the amount of photons released is related to the concentration of the elements whose emitted photons corresponds to the wavelength that showed the presence of a given elements.

2.12 Principle of BET

Brunauer-Emmett-Teller (BET) is an analytical technique used to determine the pore volume, pore size and surface area (Munonde *et al.*, 2017) of materials using gas adsorption-desorption model to multi-layer (Zhu *et al.*, 2012). During BET analysis, a sufficient amount of sample is degassed in nitrogen (N₂) at suitable constant temperatures. After degassing and performing BET adsorption, the BET data is solved by plotting it on the plot of $1/[v(p/p_o)^{-1}]$ versus p/p_o (Tavengwa, 2013). The BET specific surface areas can then be evaluated from isothermal adsorption of nitrogen using equation 2.1:

$$\frac{\frac{p}{p_o}}{v\left(1-\frac{p}{p_o}\right)} = \frac{1}{v\left(\frac{p}{p_o}-1\right)} = \frac{1}{v_m c} + \frac{c-1}{v_m} \cdot \frac{p}{p_o} \quad (2.1)$$

Where, p and p_o are adsorbate pressure and adsorbate vapour pressure, respectively. V refers to adsorbed volume (v_m) in monomolecular layer volume and c is a quantity related to heats of adsorption and liquefaction.

2.13 Principle of Fourier Transform infrared (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a non-destructive analytical technique that relies on excitation of molecules by photons which cause them to give vibrations that offers essential information about the physicochemical properties the molecular structure (Chen *et al.*, 2015). Most FTIR studies are conducted with the region of 400 to 4000 cm⁻¹ wavelength. The vibrations at molecular level can be stretching, bending, twisting and rotating. The advantage of using FTIR for structural elucidation is that it can analyse organic, inorganic, crystals aqueous, and lipids solutions without additional use of molecular probes

(Haris and Chapman, 1992). The FTIR spectroscopy has been used previously to gain insight molecular level understanding of chitin (Kumirska *et al.*, 2010), which is basic structural component of prawn shells and other crustaceans .

2.14 Principle of Thermogravimetric Analysis (TGA)

During thermogravimetric analysis, a constant temperature raise is used to gradually heat solid material while purging using constant rate of inert air (nitrogen) and constant temperature increments (Zhu *et al.*, 2012). The mass difference is calculated throughout the subjection of the material to heat increments. When the sample shows mass loss, such mass loss is related to various chemical species known to desorb at particular temperature ranges under thermogravimetric analysis. Loss of different functional groups is shown by either inflections at different temperature ranges or very deep mass loss inflections on the TGA curves.

CHAPTER 3

AIMS AND OBJECTIVES OF THE STUDY

This chapter gave a full description of the aims and objectives that were governing the study and steering it to the required directions and goals.

3.1 Main aim

This study aimed at assessing the efficiency of prawn shells in removing uranium from synthetic acid mine drainage.

3.2 Specific objectives

To achieve the outlined aim, the following specific objectives were set as milestones:

- To assess the adsorption capability of prawn shells in batch systems under varying conditions e.g. pH, concentration, amount of adsorbent, temperature and presence of other ions.
- To assess the effect of competing trace elements and oxyanions on uranium removal from liquid waste.
- To model analysis onto the resulting data of the above objectives so as to establish the optimal conditions for the application of the prawn shells.

3.3 Research questions

To fulfil the aims and objectives of this study, the following research questions were outlined:

- What is the adsorption capability of prawn shells in batch systems under varying conditions e.g. pH, concentration, amount of adsorbent, temperature and presence of other ions?

- Does the occurrence of cations and oxyanions affect adsorption of uranium from liquid waste using prawn shells?
- From mathematical models, what are the optimal conditions for the application of the prawn shells?

CHAPTER 4

MATERIALS AND METHODS

This chapter seeks to present various methods and materials applied for data generation, analysis and interpretation.

4.1 Collection and treatment of prawn shells

Prawns shells were collected from waste food at Ocean Basket Restaurants, then they were washed with distilled water in order to take out meat residues and other contaminants then dried out in the oven at 40°C to constant weight. The prawn Shells were then crushed in the form of small flakes using pistil and mortar.

4.2 Reagents

Throughout the study, a standard solution of uranium ions with 1000 mg L⁻¹ was prepared from uranyl salt (UO₂(NO₃)₂•6H₂O). A multi-component solution with 15 mg L⁻¹ of metals from MgSO₄(s), CaCO₃(s) and Na₂HPO₃(s) was also prepared. The pH adjustment to the desired values (2, 3, 4, 5, 8, 9 and 11) was achieved using 0.01 mol L⁻¹ sodium hydroxide (NaOH) pellets and 10% (v/v) nitric acid (HNO₃). HNO₃ and deionised water were used to prepare a cleaning solution for all sample vials, volumetric flasks, centrifuge tubes, and other glassware. Distilled water was collected from Millipore-Q water system.

4.3 Characterization

The surface area of the adsorbent was measured using the Brunauer-Emmet-Teller (BET). Functional groups within prawn shells were examined using FTIR. The pH measurements were done using Mettler Toledo - Five Easy FE20. The thermogravimetric analyses were achieved using the model Perkin Elmer TGA 6000. All samples were mechanically agitated using Model spomp8 from Lab design while WiseCube fuzzy control system was used for temperature effect analysis.

4.4 Batch adsorption Studies

Batch adsorption experiments involved both single and multi-elements solutions. Standard solutions of Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Fe^{3+} , Ca^{2+} , Mg^{2+} and U^{6+} were prepared. Each metal ion uptake by the adsorbent was determined by weighing 1000 mg amount of the adsorbent and mixing it with 15 mg L^{-1} of the standard solution of the uranium at an acidic pH, and room temperatures. A 15 mL aliquot containing uranium was shaken for 24 h. Thereafter, the supernatant was extracted for metal ion adsorption analysis.

4.4.1 Effect of pH

To study the effect of pH, 250 mg, 500 mg and 1000 mg of prawn shells were added into a series of centrifuge tubes containing 15 mg L^{-1} of standard metal concentration of uranium in 15 mL varied at pH values (2-11). The pH adjustments were made by adding dilute solutions of NaOH and HNO_3 . The centrifuge tubes were shaken at 150 rpm for at room temperature for 24 h. Thereafter, the mixture was centrifuged and the solids and supernatants were separated. The suspensions were filtered using a filter paper.

4.4.2 Effect of shaking time

The effect of shaking time on the removal of uranium was assessed by adding 1000 mg of the adsorbent in a series of centrifuge tubes containing 15 mL of standard metal concentration of U (15 mg L^{-1}) at pH 3. The centrifuge tubes were shaken at 150 rpm at time intervals ranging from 5 s to 24 h. Separation and analysis were done as described in section 4.4.1.

4.4.3 Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of uranium was determined by adding 50, 100, 250, 500 and 1000 mg of an adsorbent in a series of centrifuge tubes containing 15 mL of standard metal concentration of uranium at pH 3. The

centrifuge tubes were shaken at 150 rpm for 24 h at room temperature. Separation and analysis were done as described in section 4.4.1.

4.4.4 Effect of concentration

The effect of concentration was analyzed by varying concentration of 1, 5, 10, 15 and 20 mg L⁻¹ of the uranium concentration at pH 3. The mass of the adsorbent was 1000 mg. The centrifuge tubes were shaken at 150 rpm for 6 h. Separation and analysis were done as described in section 4.4.1.

4.4.5 Effect of temperature

The effects of temperature were evaluated at 25, 30, 35 and 40°C using 15 mg L⁻¹ of uranium concentration at pH 3. The mass of the adsorbent was 1000 mg. The centrifuge tubes shaken at 150 rpm for 6 h. The centrifuge tubes were shaken at 150 rpm at 6 h. Separation and analysis were done as described in section 4.4.1.

4.4.6 Effect of competing anions

The effect of competing anions was prepared using MgSO₄(s), CaCO₃(s) and Na₂HPO₃(s) at 15 mg L⁻¹ of uranium at pH 3 and 298 K. The mass of the adsorbent was 1000 mg. The centrifuge tubes shaken at 150 rpm for 6 h. The centrifuge tubes were shaken at 150 rpm for 6 h. Separation and analysis were done as described in section 4.4.1.

4.4.7 Effect of competing metal ions

The effects of competing ions were investigated by adding a multicomponent solution consisting of 15 mg L⁻¹ of each U, Cu, Zn, Fe, Ca, Mg, Ni, and Co with 15 mg L⁻¹ of U at pH 3 and 298 K. The mass of the adsorbent was 1000 mg. Two different solutions of Na₂SO₄ were separately prepared in different centrifuge tubes at different concentrations of 100 mg L⁻¹ and 200 mg L⁻¹ at pH 3 and were separately mixed with competing metal species. The centrifuge tubes were shaken at 150 rpm for 6 h. PHREEQC was used to check uranyl ion speciation. Separation and analysis were done as described in section 4.4.1.

4.4.8 Desorption studies

Desorption studies performed using 0.5, and 1 mg L⁻¹ HNO₃ and 0.5, 1 and 2 mg L⁻¹ NaHCO₃. Different solutions were prepared in different flasks according to the designed concentration and desorption conducted separately using the two solutions. The process of adsorption of uranium was undertaken. Then, prawn shells were dried, then was re-suspended in 1 mL of distilled water and was shaken for 10 min at 25°C. Then, 1000 mg of prawn shells were added for treatment with distilled water for uranium desorption from the prawn shells then was shaken for 1 h, and the suspensions were filtered using filter paper for analysis by ICP-OES. Equation (4.1) was used to determine the recovered percentage of uranium. HNO₃ and NaHCO₃ solutions were used as desorbing solutions.

$$Recovered\% = \frac{U_{adsorbed} - U_{desorbed} (mg\ g^{-1})}{U_{adsorbed} (mg\ g^{-1})} \times 100 \quad (4.1)$$

4.4.9 Preparation of solutions

The stock solution of uranium was used to prepare all the required experimental solutions. The anions solutions were prepared by dissolving necessary quantities of the anions from their equivalent salts, of MgSO₄ (-SO₄²⁻), CaCO₃ (-CO₃²⁻), and NaHPO₄ (-PO₄³⁻) (analytical grade). The solutions of cationic metals were prepared by dissolving necessary quantities of the cationic salts, namely; U, Cu, Zn, Fe, Ca, Mg, Ni, and Co. The two solutions of Na₂SO₄ with 100 and 200 mg L⁻¹ were prepared in two 250 mL volumetric flasks.

4.4.10 Data processing

Microsoft Excel was used for data capturing and processing. The results were reported as mean value.

4.4.11 Removal efficiency

The adsorption efficiency was calculated using equation 4.2:

$$\text{Percentage removal (\%)} = \frac{C_i - C_t}{C_i} \times 100 \quad (4.2)$$

Where; C_i (mg L^{-1}) is the initial concentration of uranium ions and C_t (mg L^{-1}) represents the remaining concentration of uranium existing in solution at time (t), respectively.

4.4.12 Adsorption capacity

The amount of uranium adsorption capacity was calculated using equation 4.3:

$$\text{Adsorption capacity (} q_e \text{)} = \left(\frac{C_i - C_e}{m} \right) \times v \quad (4.3)$$

Where , q_e (mg g^{-1}) represents the adsorption capacity of uranium concentration, C_i and C_e represent uranium ions concentrations initially and at equilibrium respectively, V (L) is the volume of the solution and m (g) is the mass of the adsorbent.

4.4.13 Normalized standard deviation

Errors were less than 5% therefore no error bars were shown out through all graphs.

4.5 Adsorption Data Modelling

4.5.1 Kinetic modelling

Kinetic studies were explored using pseudo first-order for physio-sorption and pseudo second-order for chemisorption corresponding equations 4.4 and 4.5 respectively:

$$\log(q_e - qt) = \log q_e - \frac{k_1}{2.303} t \quad (4.4)$$

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (45)$$

Where k_1 (min^{-1}) represent the rate constant of pseudo first-order and can be obtained from the slope of the plot of $\log (q_e - q_t)$ vs t (min), k_2 (g mg min^{-1}) is the rate constant of pseudo second-order and can be determined by the intercept of the plot of t/q_t v/s time (min).

4.5.2 Isotherm modelling

To understand the adsorption isotherms, the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were used as reported in documented studies (Langmuir, 1918; Freundlich, 1909 and Dubinin *et al.*, 1947).

4.5.3 Langmuir isotherm

Langmuir model was expressed in equation 4.6:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (4.6)$$

Where q_{ml} (mg g^{-1}) and b (L g^{-1}) refer to adsorption capacity and energy respectively and saturated sorption equilibrium constant, respectively. C_e is concentration of adsorbate at equilibrium (mg g^{-1}). R_L is the separation factor as expressed from equation 4.7:

$$R_L = \left(\frac{1}{1 + b C_i} \right) \quad (4.7)$$

4.5.4 Freundlich isotherm

The Freundlich isotherm was expressed from equation 4.8:

$$\log q_e = n \log C_e + \log k_f \quad (4.8)$$

Where, K_F and n are Freundlich adsorption constant and sorption intensity constant, respectively. This can be determined from the intercept and the slope.

4.5.5 Dubinin–Radushkevich (D–R) models

The Dubinin–Radushkevich (D–R) isotherm was used to determine the mechanisms of adsorption (chemisorption or physisorption) as expressed from equation 4.9:

$$\ln q_e = q_{m3} - K\varepsilon^2 \quad (4.9)$$

Where K is the adsorption energy constant, q_{m3} is the theoretical saturation capacity and (ε) represents the Polanyi potential as expressed from equation 4.10:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (4.10)$$

Where R represent the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T refers to the absolute temperature in Kelvin and (E_a) is the activation energy of adsorption process as expressed from equation 4.11:

$$E_a = 1/(-2K)^{-1/2} \quad (4.11)$$

4.5.6 Thermodynamic modelling

Thermodynamic mechanisms as function of temperature were determined using Gibbs model. ΔG° represents Gibbs free energy change, (ΔS°) is the entropy change and (ΔH°) refers to enthalpy change as expressed in equation 4.12 and 4.13 (Gaiward *et al.*, 2008):

$$\Delta G = -RT \ln \left(\frac{q_e}{C_e} \right) \quad (4.12)$$

$$\ln K_D \text{ or } \ln (q_e / C_e) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4.13)$$

where; R is the universal gas constant ($\text{kJ mol}^{-1} \text{ K}^{-1}$) (Singh *et al.*, 2014), T represents the temperature in Kelvin (Fox *et al.*, 2006) and K_D represents the equilibrium constant ($\text{m}^3 \text{ mol}^{-1}$) (Zhong *et al.*, 2007).

4.6 Geochemical Modelling

PHREEQC (Parkhurst and Appelo, 1999) was used to obtain the uranium speciation. It is also capable of doing mobility, complex formation probability, saturation index and chemical reaction pathways (Parkhurst and Appelo, 1999).

CHAPTER 5

RESULTS AND DISCUSSIONS

This chapter presents the results obtained from the experimental studies and infer detailed discussions with the use of documented studies. Conditions that are suitable for the removal of uranium will also be pointed out.

5.1 Characterization

5.1.1 Fourier transform-infrared (FT-IR) spectroscopy of prawn shells

The infrared spectra of unused and used prawn shells are shown in Figure 5.1.

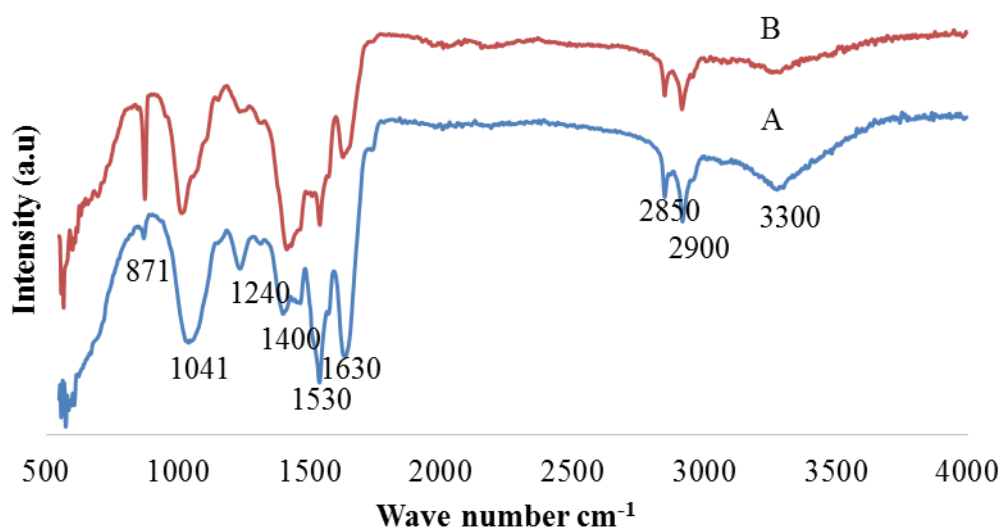


Figure 5.1: FTIR spectrum of (a) unused prawn shells and (b) prawn shells after batch adsorption.

As shown in Fig. 5.1, the characteristic peaks of unused prawn shells are: The peak of PO_4^{3-} at 871 cm^{-1} and 1041 cm^{-1} (Agullo *et al.*, 2004; Bachmaf *et al.*, 2008). The stretching vibrations at 1240 cm^{-1} corresponds to secondary and primary $-\text{OH}$ groups. The stretching vibrations of $\text{C}=\text{O}$ at 1400 cm^{-1} , deformed C-

H group at 1530 cm^{-1} , the asymmetric and symmetric peaks of $-\text{CH}_2$ at 2850 and 2900 cm^{-1} were also observed, and it is an indication of the carbonate component of the prawn shells, respectively (Beaney *et al.*, 2005). Furthermore, the loaded prawn shells spectra showed; a new peak at 1530 cm^{-1} can also be linked to a U-phosphate bond formation. The enhanced adsorption band at 1630 cm^{-1} is attributed to adsorption of uranium to the glycosidic bond comprising β -D-glucose unit (Wang, 2016) and CO_3^{2-} (Bachmaf *et al.*, 2008; Ismail and Yim, 2015) of the exoskeleton of crustaceans such as prawn shells (Chandumpai *et al.*, 2004). The $-\text{OH}$ group around 3300 cm^{-1} was partially suppressed due to hydroxyl-uranyl complex formations and remained unchanged.

5.1.2 Thermogravimetric analysis

TGA was used to further assess the structural composition of prawn shells; the results are as shown in Figure 5.2.

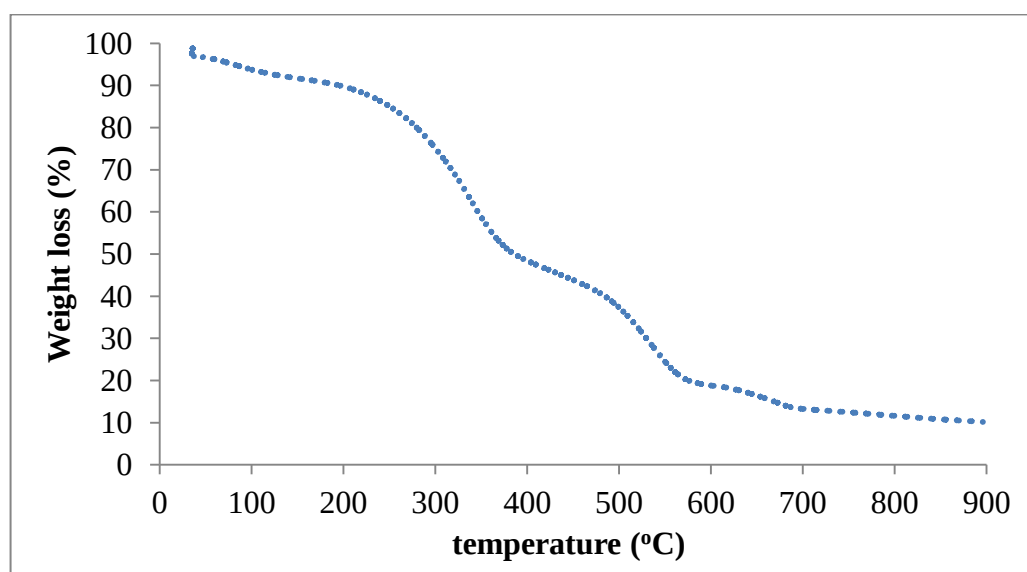


Figure 5.2: TGA of unused prawn shells.

As shown in Fig. 5.2, the thermal decomposition of prawn shells identified four stages of mass degradation at temperature ranges between $49\text{--}110^\circ\text{C}$, $220\text{--}365^\circ\text{C}$, $390\text{--}574^\circ\text{C}$, and $614\text{--}698^\circ\text{C}$, which may be linked to a slight water evaporation, loss of labile oxygen functional groups constituting chitosan (Ali *et al.*, 2011), and degradation of organic material such as H_3COCHN and pyrolysis of carbon

skeleton (Sun *et al.*, 2011). Similar studies have shown a possibility of a four stages of weight loss during solid mass degradation by TGA (Zhang, 2011). An example of chitosan containing adsorbent that gave four reflections during TGA is Chitosan-g-PAN copolymer (Shanmugapriya *et al.*, 2013). The decomposition of similar material containing chitosan gave similar degradation of various organic groups and carbon skeleton at temperatures corresponding to those of this study (Microcapsules *et al.*, 2011). The presence of the abundant stages representing different functional groups implies that the prawn shells present a variety of active sites that can possibly trap varied uranium species.

5.1.3 BET

The surface area and porosity studies of BET are shown in Table 5.1.

Table 5.1: Properties of prawn shells from BET analysis

Parameter/property	Values	units
BET Surface Area	0.8202	m ² g ⁻¹
Slope at STP	4.8466	g cm ⁻³
Y-Intercept at STP	0.4611	g cm ⁻³
C	11.5102	
Qm at STP	0.1884	cm ³ g ⁻¹
Correlation Coefficient	0.9543	
BJH Adsorption cumulative volume of pores	0.006950	cm ³ g ⁻¹

The prawn shells gave a small BET surface area of 0.8202 m² g⁻¹ and the BJH volume of pores equalling 0.006950 cm³ g⁻¹ indicates that the prawn shells are not a characteristic of an excessively porous material. This is consistent with the finding by similar studies that reported that biomass adsorbents such as biochar are nano-porous composites (Inyang and Dickenson, 2015). Therefore, the adsorption of uranium by prawn shells exclusively depends on the functional groups identified in the FTIR and TGA results.

5.2 Batch studies

5.2.1 Effect of pH

The effect of pH on the removal of uranium from wastewater is shown in Figure 5.3.

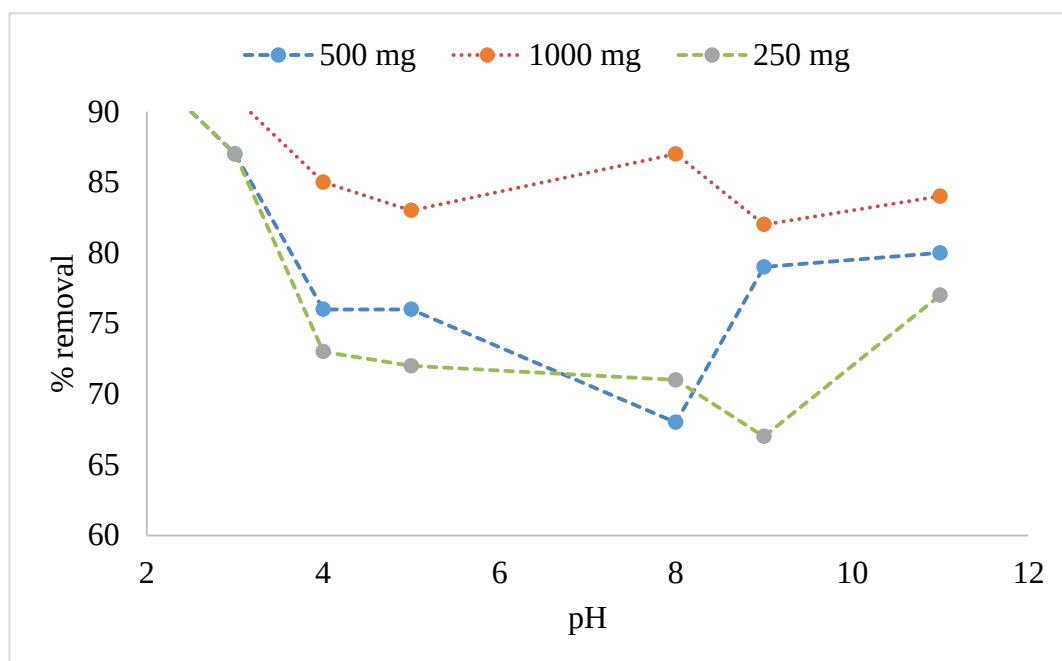


Figure 5.3: Percentage removal of uranium using prawn shells at different pH ranges. Conditions: 10 mg L⁻¹ uranium, room temperature, at 24h and 150 rpm.

As depicted by Fig. 5.3, the adsorption of uranium using prawn shells as an adsorbent is high at lower pH range, which is between pH 2 and 3. Motawie *et al.*, (2014), showed that adsorption of uranium using chitosan was high at pH 3. As the pH increases above 3 to 5 the adsorption % decreases. In alkaline pH 8, 9 and 11 the adsorption % of uranium using prawn shells is similar to the uranium removal percentage observed in pH 4 to 5. Previous studies have shown that chitosan can also adsorb trace elements such as Arsenic (Benavente, 2008) and Zinc (Jaafarzadeh *et al.*, 2015) at optimum pH between 2 and 3. Uranium can exist at pH 2 to 3 as UO₂²⁺ (Krestou and Panias, 2004; Smith, 2010; Kumar *et al.*, 2011). According to these results, the suitable pH range for use in batch and column studies for uranium removal from polluted water is between pH 2 and 3.

5.2.2 Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of uranium from wastewater is shown in Figure 5.4.

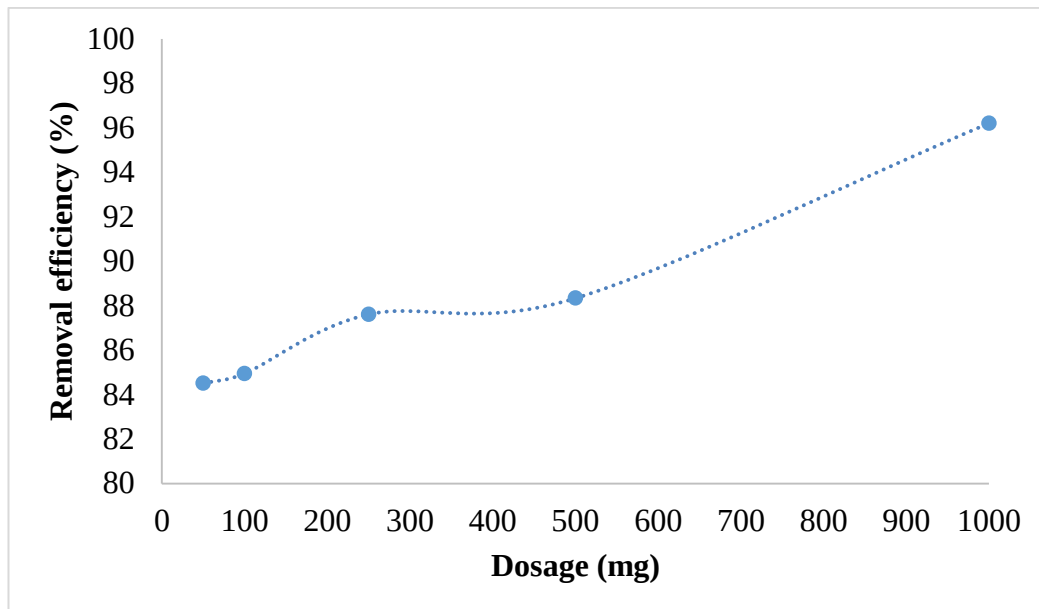


Figure 5.4: Effect of adsorbent dosage (conditions: 10 mg L⁻¹ uranium and pH 3 over 24 h).

The adsorption of uranium was done by considering constant time, pH and concentration. Prawn shells doses were varied from 50 mg to 1000 mg. As showed by Fig. 5.4 below, the increase in adsorbent doses positively affect the adsorption percentage. The maximum removal percentage was 96.21% for uranium at a dose of 1000 mg. Several studies showed that removal of heavy metals such as uranium (Annaduzzaman, 2015; Muzzarelli, 2011; Suc and Ly, 2011), Lead (Asandel *et al.*, 2009) and Arsenic (Benavente, 2008; Liu *et al.*, 2011; Robin, 2006) increases with chitosan dosage. Furthermore, Annaduzzaman reported “that the removal percentage of uranium using chitosan was 100% in both doses of 80 g/l and 90 g/l (Annaduzzaman, 2015). According to these results, the removal percentage is directly related to the number of available sites and they agree with other findings in literature (Souundarrajjan *et al.*, 2012). Moreover, low values adsorbent dose also indicate an increase in removal percentage of uranium. This shows that prawn shells have potential removal of uranium from contaminated water. The initial pH of the removal efficiency of uranium was 3.01

and the sample exhibit final pH of 7.09. This shows that removal percentage of uranium increases with pH. The increase of the final pH can be caused by rapture of internal hydrogen bonds caused by swelling of chitosan and amino groups in prawn shells (Argullo *et al.*, 2004). Therefore, according to this results dose of 1000 mg in 24 h was considered for uranium removal because there was a significance difference between 500 mg to 1000 mg and p-value was less than 0.05.

5.2.3 Effect of time

The effect of shaking time and adsorbent dosage on the removal of uranium using prawn shells is shown in Figure 5.5.

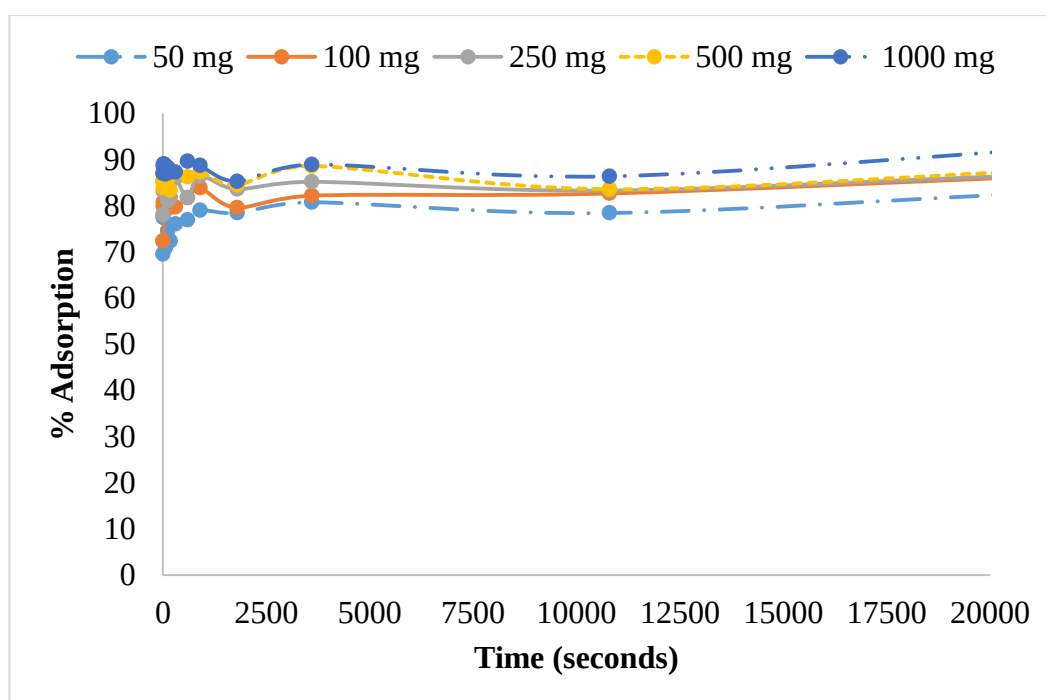


Figure 5.5: Percentage removal of uranium as a function of shaking time and adsorbent dosage. Conditions: 10 mg L⁻¹ uranium, pH 3 and room temperature.

As shown in Fig. 5.5, the sorption of 10 mg L⁻¹ uranium(VI) aqueous solution as a function of adsorbent dose (from 50 mg-1000 mg) and contact time (from 5 s to 6 h) on prawn shells was studied under a constant pH of 3 as reflected in Fig. 5.5. Generally, the results revealed that increasing adsorbent dose and contact time increases adsorption efficiency up to a certain limit. The optimum uranium(VI) removal efficiency of 92% was achieved using 1000 mg prawn shells after 6 h.

There was no significant effect in removal efficiency after 6 h. This may imply that (1) after 6 h, all active sites in the 1000 mg prawn shells are occupied by uranium atoms, and/or (2) the prawn shells dosages below 1000 mg present fewer active sites on the adsorbent surface for interaction with uranium cations available in the aqueous solution. Therefore, the prawn shells mass of 1000 mg and equilibrium time of 6 h were used for subsequent analysis of other batch studies parameters such as concentration and temperature. Study by Ayndin and Aksoy (2009), reported that 700 mg prawn shells achieved 90% removal efficiency under similar batch conditions. However, Annaduzaman (2015), reported 100% removal efficiency of uranium using 8000 and 9000 mg prawn shells after 6 h under the same pH 3 conditions.

5.2.4 Kinetic studies

The kinetics parameters of pseudo first and second order kinetics were shown in Figure 5.6.

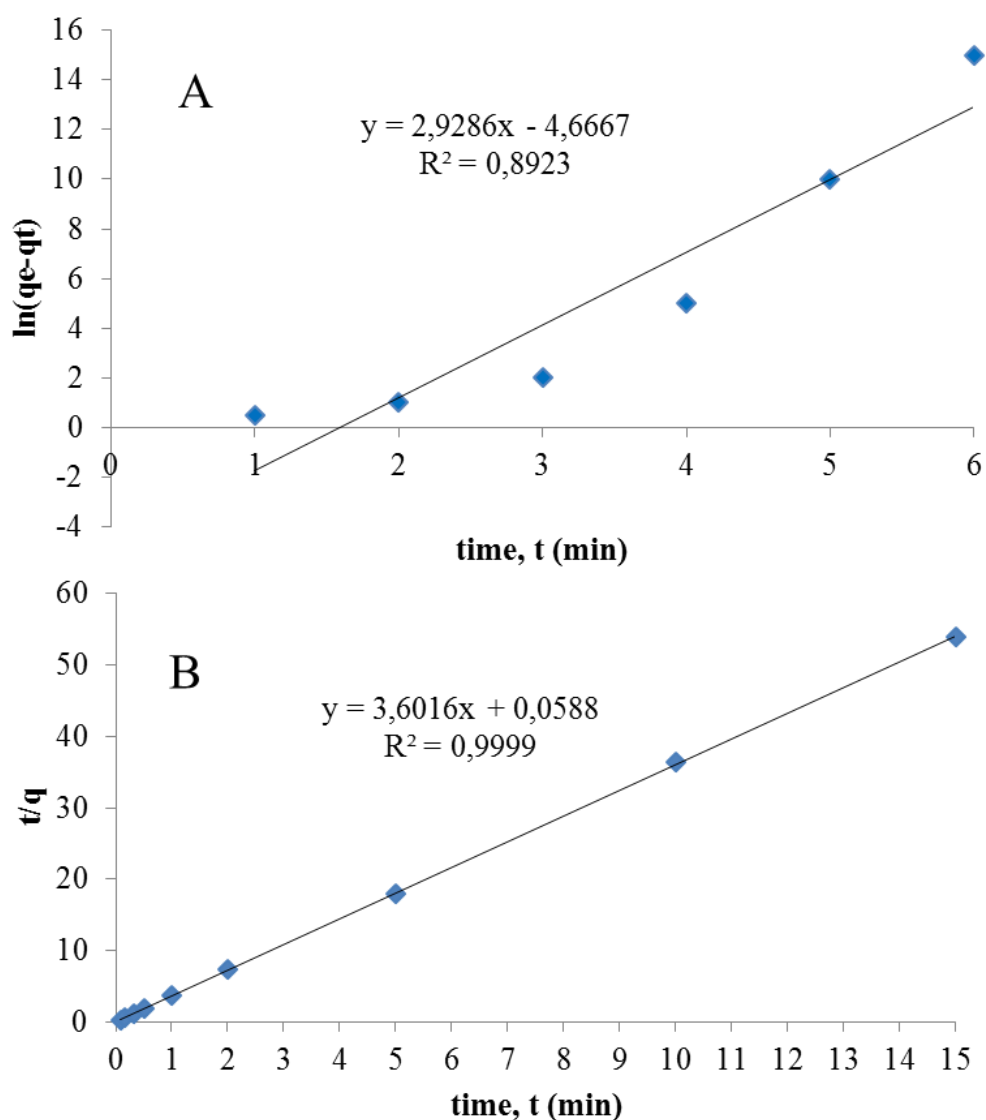


Figure 5.6: (a) Kinetic studies of prawn shells for the pseudo first-order (b) kinetic studies of prawn shells for the pseudo second-order.

Generally, the pseudo-first-order and pseudo second-order kinetic models were used to investigate the kinetic properties of the adsorption mechanisms accompanying uranium(VI) onto crustacean shells. The reliability of the kinetic model was determined on the basis of coefficient of determination (R^2). The pseudo-first-order and pseudo second-order models were used via the linearized Equation 5.1 and 5.2 respectively, (Wazne *et al.*, 2003):

$$\ln(q_e - q) = \ln q_e - \frac{k_1 t}{2.303} \quad (5.1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5.2)$$

Where q_e , (mg g^{-1}) is the adsorption capacity at equilibrium and q_t (mg g^{-1}) is the uranium adsorption capacity at time t (min), respectively. The k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constant of pseudo first-order and pseudo second-order respectively. For, pseudo-first-order, the straight-line plot of $\ln(q_e - q_t)$ versus t was used to calculate q_e and k_1 while for pseudo second-order a linearized plot of t/q versus t was utilized to calculate the value of q_e^2 and k_2 .

The calculated kinetic parameters are recorded in (Table 5.2). According to the recorded results, the kinetic model of best fit is pseudo second-order because it gave higher coefficient of determination ($R^2 = 0.99$) (Fig. 5.6: b) in contrast to pseudo first-order model that gave lower coefficient of determination ($R^2 = 0.89$) (Fig. 5.6: a). Furthermore, the calculated adsorption capacity of uranium for pseudo second-order ($q_m = 2.8 \text{ mg g}^{-1}$) is closer to the actual equilibrium adsorption capacity of 2.7 mg g^{-1} as opposed to the 10.01 mg g^{-1} calculated for pseudo first-order. This implies that the rate determining mechanism of uranium removal was chemically controlled. Similar dependence of uranium adsorption on pseudo second-order was reported in previous uranium adsorption studies (Wazne *et al.*, 2003, Bakatula *et al.*, 2015). Kinetics parameters are shown in Table 5.2.

Table 5.2: Kinetic parameters of uranium adsorption onto prawn shells

Pseudo first-order			Pseudo second-order		
k_1	q_{m1}	R^2	k_2	q_{m2}	R^2
min^{-1}	mg g^{-1}		$\text{g mg}^{-1} \text{min}^{-1}$	mg g^{-1}	
6.74	10.01	0.89	0.14	0.28	0.99

5.2.5 Effect of concentration

The effect of adsorbate concentration on the removal of uranium is shown in Figure 5.7.

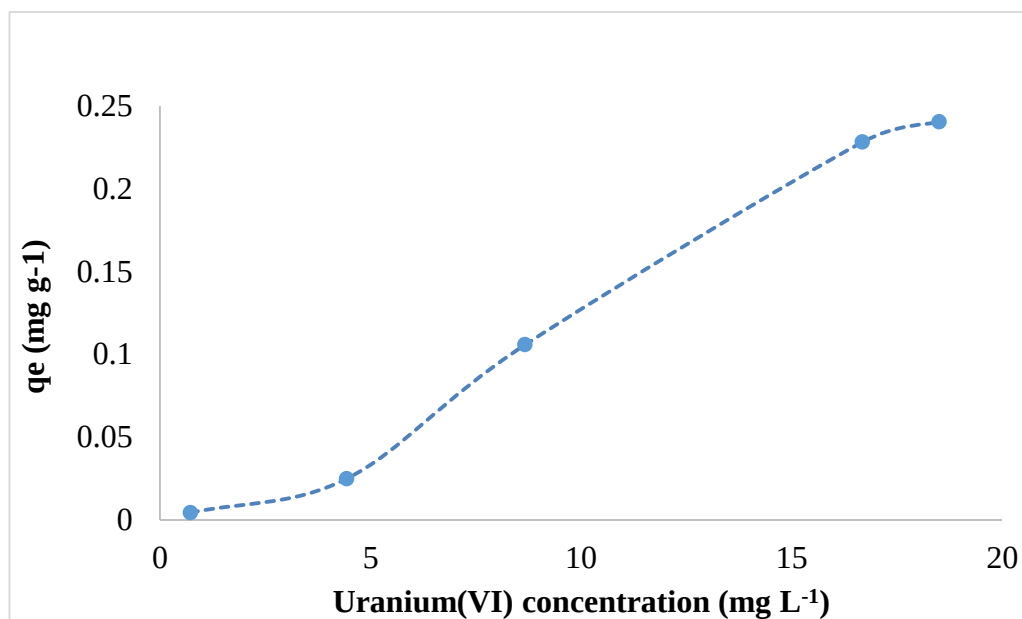


Figure 5.7: Percentage removal of uranium as a function of adsorbate concentration. Conditions: 1000 mg of prawn shells at pH 3 over at T =25°C and 150 rpm.

The effect of the initial uranium(VI) concentration on the adsorption capacity of prawn shells is shown in Fig. 5.7. The initial concentrations were varied from 1 to 20 mg L⁻¹, at pH 3, 25°C and 1000 mg prawn shells. The outcomes showed that the adsorption capacity increased with an increase in the initial uranium concentration until reaching a plateau at $q_e = 0,228 \text{ mg g}^{-1}$ and $C_e = 16,68 \text{ mg L}^{-1}$ uranium concentration. After the maximum adsorption capacity is reached at the plateau, there is no further increase observed in the adsorption capacity. This can be explained as follows, in the presence of low uranium concentrations, there is higher number of vacant active site on the prawn shells surface presented to sufficient capture uranium(VI) (Singh, 2014). As the initial uranium(VI) concentration increases, most active sites of the prawn shells are occupied by adsorbate and therefore resulting in a stagnant adsorption capacity once all active sites are occupied. These results corroborate the findings by Bakatula *et al.* (2015) that suggested that the adsorption capacity of heavy metals increases with increasing initial concentrations. The study conducted by Annaduzzaman (2015) also reported that uranium adsorption capacity increases with increasing initial

concentration when using chitosan until the percentage removal of 93.28% is reached.

5.2.6 Isotherm modelling

Adsorption data from Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) models is shown in Figure 5.8.

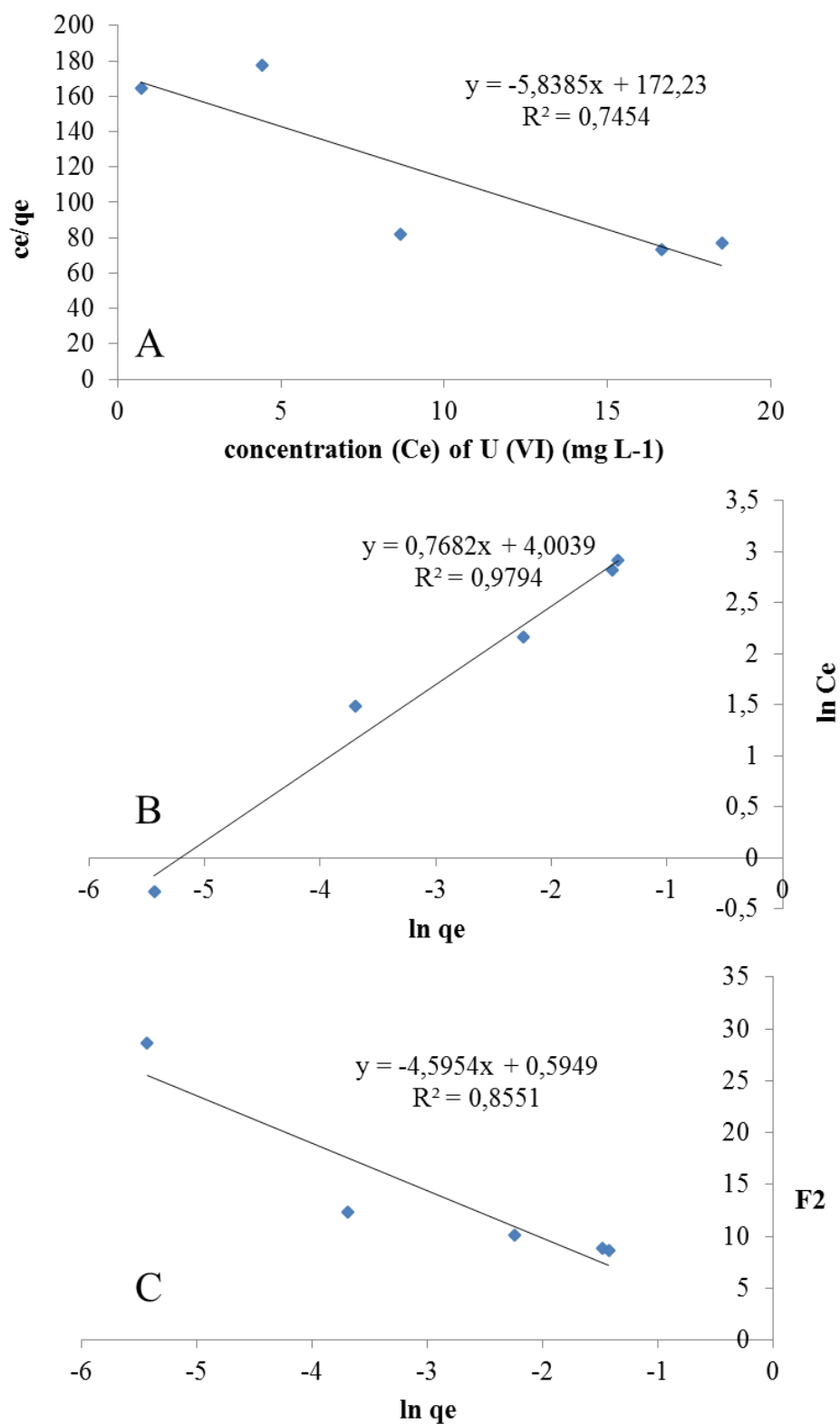


Figure 5.8 (a): Langmuir isotherm models for uranium adsorption (b) Freundlich isotherm model for uranium adsorption (c) Dubinin-Radushkevich isotherm model for uranium adsorption.

The adsorption mechanisms taking place at the adsorbent-adsorbate interface is controlled by adsorbent surface properties and the nature of the adsorbent. The insight understanding of these adsorption mechanisms can be understood by fitting the adsorption data to the commonly used isotherm models; the Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) models. The equilibrium model is considered as best fit if the correlation coefficient (R^2) is higher or closer to one (1), and the difference between q_m and q_{cal} is smaller or closer to zero (0).

The assumption of Langmuir model is that the adsorption proceeds through a homogenous surface with finite active sites of same energy (Akpomie *et al.*, 2015). The Langmuir model was applied using Equation 5.3 (Horsfall and Spiff, 2005):

$$q = q_{m1} \frac{b.C_e}{b.C_e + 1} \quad (5.3)$$

The corresponding values of Langmuir parameters; R^2 and q_m were 0.75 and 0.17 mg g⁻¹, respectively (Fig. 5.8: a) and (Table 5.3). These values therefore suggests that Langmuir model do not best fit the data of uranium adsorption mechanism onto prawn shell mechanisms.

The Freundlich model assumes that the adsorption mechanism occurs heterogeneously on active sites characterized by varied exponential energies. The Freundlich was applied using Equation 5.4 (Horsfall and Spiff, 2005):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5.4)$$

where K_F (mg g⁻¹) is the Freundlich constant and n is the and heterogeneity energy factor. The calculated Freundlich parameters were $K_F = 64.81$, $n = 1.30$ (Table 5.3) and $R^2 = 0.98$ (Fig. 5.8: b). The value of $R^2 > 0.9$ and $n > 1$ implies that a heterogeneous mechanism compatible to Freundlich model was favourable at the experimental conditions.

Similar studies showed that uranium(VI) adsorption best fitted the Freundlich models when using; crystalline tin oxide nanoparticles (Nilchi and Screening, 2017) wood powder and wheat straw powder (Bagherifam *et al.*, 2010). However, other studies of uranium adsorption using adsorbents such as; diglycolamide

functionalized multi-walled carbon nanotubes (Chen *et al.*, 2016), graphene oxide-activated carbon felt composite (Chen *et al.*, 2016), Orange peel (Wazne *et al.*, 2003) and amidoximated polyacrylonitrile-encapsulated macroporous beads (Singh *et al.*, 2014) showed that Langmuir can be favoured in comparison to Freundlich. In some studies both Freundlich and Langmuir can be favoured, and the nature of the adsorption can therefore be concluded as physisorption or chemisorption on the basis of D-R isotherm model as it was the case when palm-shell-based adsorbent was used to adsorb uranium and the results favoured both Langmuir and Freundlich.

The Dubinin–Radushkevich (D-R) isotherm is widely used to determine the nature of the adsorption mechanism as either physisorption or chemisorption. The D-R isotherm model was applied using the linearized Equation 5.5 and 5.6 (Akpomie *et al.*, 2015) and 5.7 (Nekhunguni *et al.*, 2017):

$$\ln q_e = \ln q_m + \beta \varepsilon^2 \quad (5.5)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (5.6)$$

$$E_s = \frac{1}{\sqrt{-2\beta}} \quad (5.7)$$

Where q_m (mg g⁻¹), β (mol² kJ⁻²) and ε represent the optimum adsorption capacity constant, sorption energy constant and Polanyi constant, respectively. The Polanyi constant (ε) can be expressed by Equation (5.6). The adsorption energy (E_s in equation (5.7) in the range, $E_s < 8$ kJ mol⁻¹, $8 \leq E_s \leq 16$ kJ mol⁻¹ and $E_s > 40$ kJ mol⁻¹ implies that the process continues by the physical nature, ion exchange and chemisorption, respectively. However, the calculated value of $E_s = 0.33$ kJ.mol⁻¹ (Table 5. 3) cannot be conclusively relied upon because R^2 for D-R model is 0.86 (Fig. 5.8: c) which is far less than the commonly acceptable $R^2 = 0.99$ as compared to both Langmuir and Freundlich. Consequently, it can be deduced that the D–R model did not best fit the experimental data of uranium(VI) adsorption onto prawn shells. Adsorption isotherm parameters are shown in **Table 5.3**.

Table 5.3: The parameters of the uranium adsorption isotherm models

Langmuir				Freundlich			D-R	
R_2	b	q_m	R_L	R^2	K_F	N	R^2	E_s
		mg g^{-1}	L mg^{-1}		mg g^{-1}			kJ.mol^{-1}
0.75	0.03	0.17	0.61	0.98	64.81	1.30	0.86	0.33

5.2.7 Effect of temperatures

The results of the temperature effect on adsorption of uranium are shown in **Figure 5.9**.

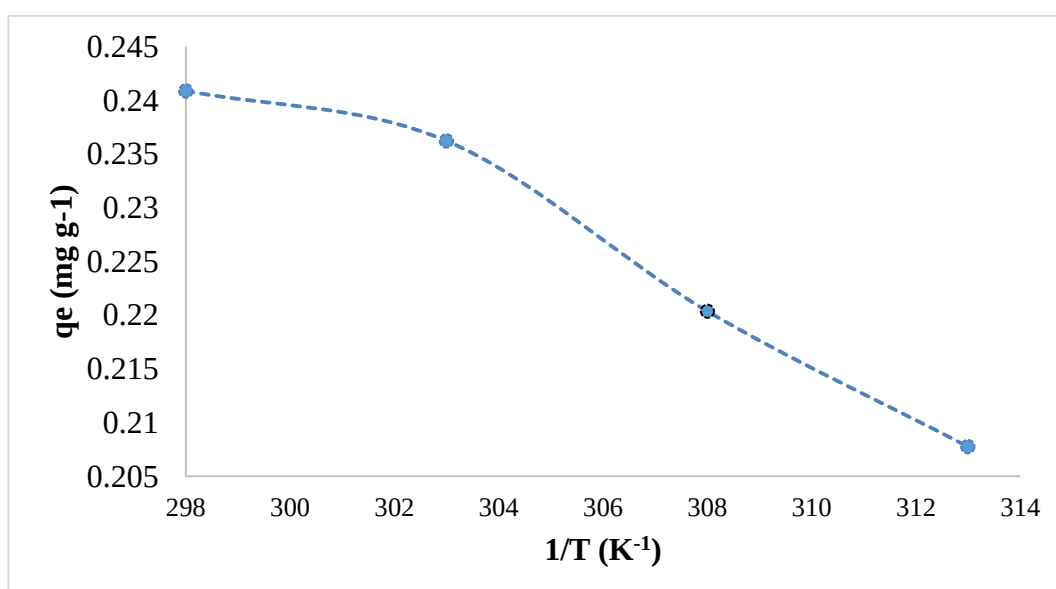


Figure 5.9: Variation in adsorption capacity of uranium(VI) by prawn shells as a function of temperature. Conditions: 15 mg L⁻¹ uranium, 1000 mg of prawn shells at pH 3 over at T=25°C and 150 rpm.

The effect of temperature on adsorption capacity of uranium can be used to elucidate the thermodynamic mechanisms involved at equilibrium conditions. Basically, the adsorption capacity of uranium decreased with an increase in temperature. Therefore, uranium adsorption by prawn shells is favourable at ambient temperatures. The highest adsorption capacity of uranium adsorption was achieved at temperatures of 25°C. Similar findings were reported for adsorption of uranium using chitosan (Motawie *et al*, 2014).

5.2.8 Thermodynamic modelling

The thermodynamics parameters for the adsorption of uranium onto prawn shells are shown in **Figure 5.10**.

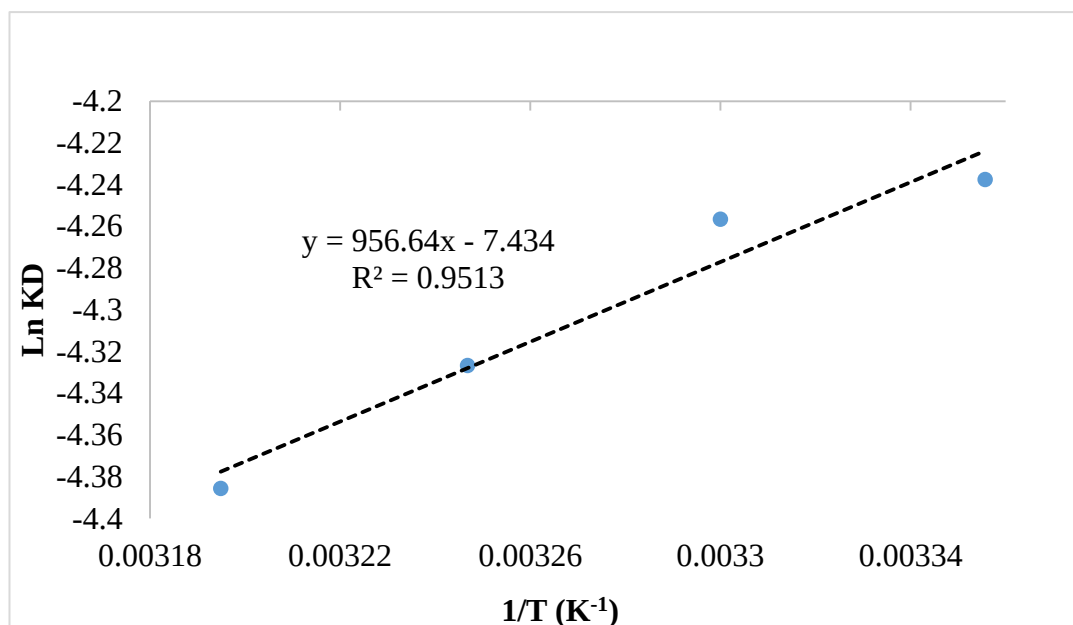


Figure 5.10: The relationship between Ln KD and 1/T

The enthalpy change was $-7.95 \text{ kJ mol}^{-1}$, meaning the adsorption proceeded in an exothermic nature (Ayndin and Aksoy, 2009). The entropy change (ΔS^0) was found to be $-61.806 \text{ kJ mol}^{-1}$. The negative (ΔS^0) indicates that the adsorption process occurred in an orderly mode. The orderly adsorption may be attributed to the decrease in the degree of freedom of the absorbed species (Zhong *et al.*, 2007; Sari and Tuzen, 2008).

5.2.9 Effect of competing anions

Variation on the effect of competing anions on the adsorption of uranium is shown in Figure 5.11.

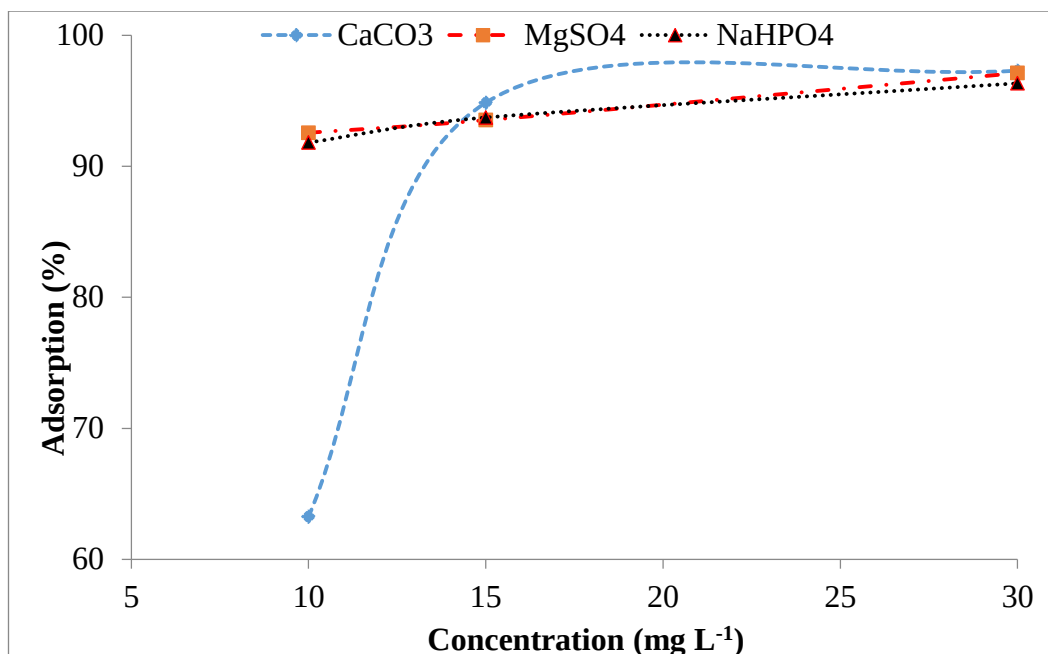


Figure 5.11: Variation on the effect of competing anions on the adsorption of uranium. Conditions: 15 mg L⁻¹ uranium, 1000 mg of prawn shells at pH 3, T =25°C and 150 rpm.

A study by Planer-Friedrich (2008) has shown that various anions such as sulphate, carbonate, and phosphate can affect the adsorption of uranium(VI). The effect of anions such CO_3^{2-} , SO_4^{2-} and HPO_4^- on the adsorption of 15 mg L⁻¹ uranium was investigated and the results are shown in Fig. 5.11. The input script and output script modelled using PHREEQC are shown in (Appendix A1). Generally, the PHREEQC output showed that the possibly dominant species formed are $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2$, UO_2CO_3 , $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2$, $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, U_3O_8 , $\text{U}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, and UO_2 . The adsorption of uranium(VI) using CO_3^{2-} was lower at 10 mg L⁻¹ and progressed to an optimum of 97% as CO_3^{2-} increased. From phreeqc studies, it can be suggested that the species, $\text{NaHCO}_3\text{:Na}_2\text{CO}_3\text{:}2\text{H}_2\text{O}$ with k value of -0.80 is likely to form as opposed to $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ with k value of -16.29 or UO_2CO_3 with K value of -14.45 (low K value means the species is unlikely to form). This implies that as more concentration of carbonate is added, the carbonates are attached significantly to

the alkali cation (H proton) to form $\text{NaHCO}_3\cdot\text{Na}_2\text{CO}_3\cdot 2\text{H}_2\text{O}$ and thereby leaving more uranium in solution to attach to the amine and oxygen groups of the prawn chitosan structures. The high content of uranium moving freely in water is indicated by the uranium content $K = 20.53$ for U_3O_8 and $K = 0.10$ for UO_2 and their respective negative SI (saturation index) of -12.45 and -6.74 which means that these species are actively mobile within the solution. The high K value equalling 5.40 for the neutral to basic species $\text{UO}_2(\text{OH})_2\cdot\text{H}_2\text{O}$ also suggests that this species is likely to form and thereby decreasing the adsorption by repelling the negatively charged active sites of the prawn shells. The adsorption of uranium increased from 92% with increasing concentrations of SO_4^{2-} and HPO_4^- until a maximum adsorption of 97% was achieved for both adsorbent. The results showed that all the anions improved adsorption efficiency of uranium to 97% when 30 mg L^{-1} concentrations was used. There was no significant difference for adsorption efficiency under the influence of 30 mg L^{-1} of all anions used. The study by Bakatula and co-researchers (2015) showed that the use of CO_3^{2-} and SO_4^{2-} yield a contrasting decrease in adsorption capacity when using ammonium-modified Zeolite as an adsorbent (Bakatula *et al.*, 2015). This observation of different influence on adsorption of the same cation by same competing anions can be attributed to the total composition of competing species solution and the nature of the adsorbent (type of active sites groups and amount of the charge).

It is expected that phosphate containing anions bind strongly to uranium, however, in this case the addition of HPO_4^- to compete for uranium binding showed insignificant results and this may be due to the low probability for the formation of $\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2$ ($K = -47.93$) and $\text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2$ ($K = -47.41$) characterised by high radius shown by negative $\log \text{IAP}$ and low ionic strength shown by saturation index approaching zero (approaching equilibrium). Although the same can be said about $\text{U}(\text{OH})_2\text{SO}_4$, only one form of uranyl phosphate is likely to form and thereby increases the chances of uranium binding to other species other than sulphates. The order of affinity for uranium on the basis of the solution studies is therefore, $\text{CaCO}_3^{2-} > \text{SO}_4^{2-} \geq \text{HPO}_4^-$. This results are consistent with the desorption studies.

5.2.10 Effect of existing cations

The effects of existing cations on the adsorption of uranium by prawn shells is shown in Figure 5.12.

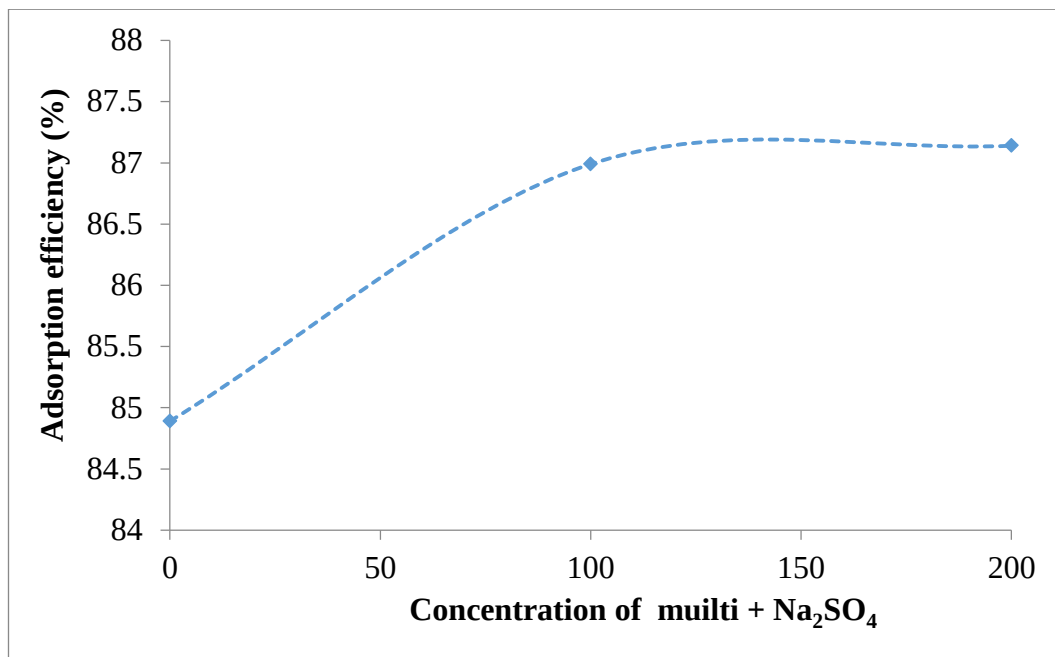


Figure 5.12: Adsorption efficiency of uranium in a multi-metal solution. Conditions: 15 mg L⁻¹ uranium, 1000 mg of prawn shells at pH 3, T =25°C and 150 rpm.

The presence of other species such as phosphates and iron oxides are reported to affect the adsorption of uranium (Wang, 2016). Fig. 5.12, depicts the results obtained for uranium adsorption using a multi-metal solution composing a constant concentration of 15 mg L⁻¹ for each of the following cationic metal elements; U, Cu, Zn, Fe, Ca, Mg, Ni, and Co while the concentration of Na₂SO₄ was varied from 0 to 200 mg L⁻¹. The addition of Na₂SO₄ increased the uranium adsorption efficiency from 85% in multi-metal solution with Na₂SO₄ to 86.9% and 87.14% in the presence of 100 mg L⁻¹ Na₂SO₄ and at 200 mg L⁻¹ Na₂SO₄, respectively (Jnr, 2005). Therefore, the maximum adsorption efficiency was recorded to have been achieved when 100 mg L⁻¹ of Na₂SO₄ was reached.

5.3 Desorption studies

Desorption studies aid to reveal the adsorption nature and recyclability of the adsorbent (Balakrishnan *et al.*, 2010). Equally, desorption of the toxic uranium(VI) from adsorbents surfaces is an important aspect for water remediation (Souundarrajan *et al.*, 2012). The higher the probability of unloading uranium from the already loaded adsorbent is important since it enable the adsorbent reusability and deductions as to whether the adsorption occurred by physisorption or chemisorption (Bagherifam *et al.*, 2010). Table 5.4, shows the results corresponding dislodging of uranium(VI) sorbed onto prawn shells performed using 0.5, and 1 mg L⁻¹ HNO₃ and 0.5, 1, 2 mg L⁻¹ NaHCO₃. The desorption studies performed using HNO₃ as an eluent gave 19±0.01% for 0.5 mg L⁻¹, 37±0.09% for 1 mg L⁻¹ and NaHCO₃ yield adsorption capacity of 77.0±0.01% for 0.5 mg L⁻¹, 93.2±0.05% for 1 mg L⁻¹ and 99.7±0.02% for 2 mg L⁻¹, respectively. The higher desorption percentage observed for NaHCO₃ implies that NaHCO₃ is well suited for uranium desorption from prawn shells than HNO₃. An almost complete dislodging of uranium from prawn shell surfaces was achieved using 2 mg L⁻¹ of NaHCO₃. Therefore, a concentration of 2 mg L⁻¹ of NaHCO₃ was taken as the most effective and optimum desorption concentration.

Table 5.4: Desorption of uranium from prawn shells.

Concentration (mg L ⁻¹)	Desorption by HNO ₃ (%)	Desorption by NaHCO ₃ (%)
0.5	19±0.01	77.0±0.01
1.0	37±0.09	93.2±0.05
2.0	Not test	99.7±0.02

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

The principal aim of this research project was to evaluate the feasibility of using prawn shells as an effective and novel adsorbent for the removal of uranium ions from acid mine drainage. To fulfil the goals of this study, this project was guided by a number of research objectives and they entail characterisation of the prawn shells and prawn shells loaded with uranium; optimisation of the adsorption conditions; degeneration of the adsorbents and performing the mathematical models so as to point out the mechanisms thereof. This study successfully achieved the designed research objectives and dully responded to the questions. From the experimental studies, it was discovered that adsorption of uranium was influenced by various parameters such as initial pH, absorbent dosage, contact time, initial uranium ions concentration, effect of anions and effect of cations. Batch experiments revealed that the optimum adsorption of uranium was 92% at 100 mg dose, pH 3, room temperature and 15 mg L⁻¹ after 6 h equilibration time. The kinetics, isotherms and thermodynamics followed pseudo second-order hence confirming chemisorption, Freundlich thus confirming a multi-site adsorption and exothermic reaction as indicated by Gibbs model. Furthermore, it was observed that the adsorption capacity of uranium decreased with an increase in temperature. The adsorption of uranium was also observed to be independent of existing ions (anionic and cationic species). From the obtained findings, it can be concluded that this ground-breaking study can be used to remove uranium from acid mine drainage.

6.2 Recommendations

This study only focused on the batch experiment, as such, it can be recommended that:

- It is imperative for a study to also do column studies so as to ensure a continuous system that can be deployed to an industry.
- In this study, synthetic samples were used for optimisation experiments and real samples were not used. Thus, there is a need for the adsorbent to be tested in real samples.
- The study recommends further development of the materials into reactor beads or sachets to use them as adsorbents for uranium for less polluted water.
- From this study, it can also be recommended that the classification, beneficiation and uranium recovery for generated bio-waste be considered in future research.
- The comparison of the efficacy of prawn shells against other adsorbents used for the removal of uranium as reported in literature using real samples can also be explored.

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APPENDICES

Appendix A1

Phreeqc input and output scripts for uranium and competing anions

Reading data base.

```
SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
PHASES
EXCHANGE_MASTER_SPECIES
EXCHANGE_SPECIES
SURFACE_MASTER_SPECIES
SURFACE_SPECIES
RATES
END
```

Reading input data for simulation 1.

DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.3.3-
10424\database\wateq4f.dat

```
TITLE test1
SOLUTION 1 Acidic
units  mg/L
pH  3.0
pe  4.0
temp 25.0
U    15
```

Ca 15
Mg 15
Na 15
S(6) 15
P 15
O(0) 30
C(4) 15
END

TITLE

test1

Beginning of initial solution calculations.

Initial solution 1. Acidic

-----Solution composition-----

Elements	Molality	Moles
C(4)	2.459e-04	2.459e-04
Ca	3.743e-04	3.743e-04
Mg	6.171e-04	6.171e-04
Na	6.526e-04	6.526e-04
O(0)	1.875e-03	1.875e-03
P	4.843e-04	4.843e-04
S(6)	1.562e-04	1.562e-04
U	6.303e-05	6.303e-05

-----Description of solution-----

pH = 3.000
 pe = 4.000
 Activity of water = 1.000
 Ionic strength = 3.357e-03
 Mass of water (kg) = 1.000e+00
 Total alkalinity (eq/kg) = -9.441e-04
 Total CO2 (mol/kg) = 2.459e-04
 Temperature (°C) = 25.00
 Electrical balance (eq) = 2.909e-03
 Percent error, 100*(Cat-|An|)/(Cat+|An|) = 66.14
 Iterations = 10
 Total H = 1.110143e+02
 Total O = 5.551127e+01

-----Redox couples-----

Redox couple	pe	Eh (volts)
O(-2)/O(0)	17.7631	1.0508

-----Distribution of species-----

Species	Molality	Log Activity	Log Molality	Log Activity	mole V	Gamma	cm ³ /mol
H+	1.060e-03	1.000e-03	-2.975	-3.000	-0.025	0.00	
OH-	1.067e-11	1.001e-11	-10.972	-11.000	-0.028	(0)	
H2O	5.551e+01	9.999e-01	1.744	-0.000	0.000	18.07	
C(4)	2.459e-04						

CO2	2.457e-04	2.459e-04	-3.610	-3.609	0.000	(0)
HCO3-	1.163e-07	1.094e-07	-6.934	-6.961	-0.027	(0)
MgHCO3+	6.410e-10	6.018e-10	-9.193	-9.221	-0.027	(0)
CaHCO3+	4.238e-10	3.987e-10	-9.373	-9.399	-0.027	(0)
NaHCO3	3.765e-11	3.768e-11	-10.424	-10.424	0.000	(0)
UO2CO3	4.554e-13	4.558e-13	-12.342	-12.341	0.000	(0)
CO3-2	6.565e-15	5.129e-15	-14.183	-14.290	-0.107	(0)
CaCO3	2.454e-15	2.456e-15	-14.610	-14.610	0.000	(0)
MgCO3	2.300e-15	2.302e-15	-14.638	-14.638	0.000	(0)
NaCO3-	6.224e-17	5.851e-17	-16.206	-16.233	-0.027	(0)
UO2(CO3)2-2	7.055e-20	5.481e-20	-19.151	-19.261	-0.110	(0)
UO2(CO3)3-4	3.293e-29	1.199e-29	-28.482	-28.921	-0.439	(0)
U(CO3)4-4	0.000e+00	0.000e+00	-42.462	-42.901	-0.439	(0)
UO2(CO3)3-5	0.000e+00	0.000e+00	-44.946	-45.631	-0.685	(0)
(UO2)3(CO3)6-6	0.000e+00	0.000e+00	-53.796	-54.783	-0.987	(0)
U(CO3)5-6	0.000e+00	0.000e+00	-55.104	-56.091	-0.987	(0)
Ca	3.743e-04					
Ca+2	3.660e-04	2.858e-04	-3.437	-3.544	-0.107	(0)
CaSO4	5.716e-06	5.721e-06	-5.243	-5.243	0.000	(0)
CaH2PO4+	2.563e-06	2.409e-06	-5.591	-5.618	-0.027	(0)
CaHSO4+	3.570e-08	3.351e-08	-7.447	-7.475	-0.027	(0)
CaHPO4	3.203e-09	3.205e-09	-8.494	-8.494	0.000	(0)
CaHCO3+	4.238e-10	3.987e-10	-9.373	-9.399	-0.027	(0)
CaOH+	5.042e-14	4.743e-14	-13.297	-13.324	-0.027	(0)
CaPO4-	8.067e-15	7.584e-15	-14.093	-14.120	-0.027	(0)
CaCO3	2.454e-15	2.456e-15	-14.610	-14.610	0.000	(0)
H(0)	1.415e-17					
H2	7.074e-18	7.079e-18	-17.150	-17.150	0.000	(0)
Mg	6.171e-04					
Mg+2	6.006e-04	4.702e-04	-3.221	-3.328	-0.106	(0)
MgSO4	1.105e-05	1.106e-05	-4.957	-4.956	0.000	(0)
MgH2PO4+	5.369e-06	5.048e-06	-5.270	-5.297	-0.027	(0)

MgHPO4	7.124e-09	7.130e-09	-8.147	-8.147	0.000	(0)
MgHCO3+	6.410e-10	6.018e-10	-9.193	-9.221	-0.027	(0)
MgOH+	1.814e-12	1.707e-12	-11.741	-11.768	-0.026	(0)
MgPO4-	1.790e-14	1.683e-14	-13.747	-13.774	-0.027	(0)
MgCO3	2.300e-15	2.302e-15	-14.638	-14.638	0.000	(0)
Na	6.526e-04					
Na+	6.522e-04	6.126e-04	-3.186	-3.213	-0.027	(0)
NaSO4-	3.276e-07	3.080e-07	-6.485	-6.511	-0.027	(0)
NaHCO3	3.765e-11	3.768e-11	-10.424	-10.424	0.000	(0)
NaHPO4-	2.599e-11	2.443e-11	-10.585	-10.612	-0.027	(0)
NaCO3-	6.224e-17	5.851e-17	-16.206	-16.233	-0.027	(0)
O(0)	1.875e-03					
O2	9.376e-04	9.384e-04	-3.028	-3.028	0.000	(0)
P	4.843e-04					
H2PO4-	3.504e-04	3.295e-04	-3.455	-3.482	-0.027	(0)
UO2(HPO4)2-2	6.295e-05	4.890e-05	-4.201	-4.311	-0.110	(0)
MgH2PO4+	5.369e-06	5.048e-06	-5.270	-5.297	-0.027	(0)
CaH2PO4+	2.563e-06	2.409e-06	-5.591	-5.618	-0.027	(0)
UO2HPO4	3.113e-08	3.115e-08	-7.507	-7.506	0.000	(0)
HPO4-2	2.623e-08	2.046e-08	-7.581	-7.689	-0.108	(0)
UO2H2PO4+	1.517e-08	1.424e-08	-7.819	-7.846	-0.027	(0)
MgHPO4	7.124e-09	7.130e-09	-8.147	-8.147	0.000	(0)
CaHPO4	3.203e-09	3.205e-09	-8.494	-8.494	0.000	(0)
UO2(H2PO4)2	4.246e-10	4.249e-10	-9.372	-9.372	0.000	(0)
UO2(H2PO4)3-	3.059e-11	2.872e-11	-10.514	-10.542	-0.027	(0)
NaHPO4-	2.599e-11	2.443e-11	-10.585	-10.612	-0.027	(0)
UO2H3PO4+2	1.608e-11	1.249e-11	-10.794	-10.903	-0.110	(0)
UO2PO4-	1.002e-11	9.408e-12	-10.999	-11.026	-0.027	(0)
MgPO4-	1.790e-14	1.683e-14	-13.747	-13.774	-0.027	(0)
CaPO4-	8.067e-15	7.584e-15	-14.093	-14.120	-0.027	(0)
PO4-3	1.613e-17	9.222e-18	-16.792	-17.035	-0.243	(0)
S(6)	1.562e-04					

SO4-2	1.287e-04	1.003e-04	-3.891	-3.999	-0.108	(0)
MgSO4	1.105e-05	1.106e-05	-4.957	-4.956	0.000	(0)
HSO4-	1.038e-05	9.753e-06	-4.984	-5.011	-0.027	(0)
CaSO4	5.716e-06	5.721e-06	-5.243	-5.243	0.000	(0)
NaSO4-	3.276e-07	3.080e-07	-6.485	-6.511	-0.027	(0)
CaHSO4+	3.570e-08	3.351e-08	-7.447	-7.475	-0.027	(0)
UO2SO4	2.949e-09	2.952e-09	-8.530	-8.530	0.000	(0)
UO2(SO4)2-2	3.725e-12	2.894e-12	-11.429	-11.539	-0.110	(0)
USO4+2	1.122e-16	8.712e-17	-15.950	-16.060	-0.110	(0)
U(SO4)2	7.264e-17	7.269e-17	-16.139	-16.139	0.000	(0)
U(3)	6.450e-32					
U+3	6.450e-32	3.654e-32	-31.190	-31.437	-0.247	(0)
U(4)	5.431e-15					
U(OH)3+	2.825e-15	2.653e-15	-14.549	-14.576	-0.027	(0)
U(OH)2+2	1.579e-15	1.227e-15	-14.802	-14.911	-0.110	(0)
U(OH)4	7.249e-16	7.255e-16	-15.140	-15.139	0.000	(0)
UOH+3	1.163e-16	6.588e-17	-15.934	-16.181	-0.247	(0)
USO4+2	1.122e-16	8.712e-17	-15.950	-16.060	-0.110	(0)
U(SO4)2	7.264e-17	7.269e-17	-16.139	-16.139	0.000	(0)
U+4	6.273e-19	2.284e-19	-18.203	-18.641	-0.439	(0)
U(CO3)4-4	0.000e+00	0.000e+00	-42.462	-42.901	-0.439	(0)
U(CO3)5-6	0.000e+00	0.000e+00	-55.104	-56.091	-0.987	(0)
U6(OH)15+9	0.000e+00	0.000e+00	-81.827	-84.048	-2.221	(0)
U(5)	6.857e-11					
UO2+	6.857e-11	6.437e-11	-10.164	-10.191	-0.027	(0)
UO2(CO3)3-5	0.000e+00	0.000e+00	-44.946	-45.631	-0.685	(0)
U(6)	6.303e-05					
UO2(HPO4)2-2	6.295e-05	4.890e-05	-4.201	-4.311	-0.110	(0)
UO2HPO4	3.113e-08	3.115e-08	-7.507	-7.506	0.000	(0)
UO2+2	2.682e-08	2.083e-08	-7.572	-7.681	-0.110	(0)
UO2H2PO4+	1.517e-08	1.424e-08	-7.819	-7.846	-0.027	(0)
UO2SO4	2.949e-09	2.952e-09	-8.530	-8.530	0.000	(0)

UO ₂ (H ₂ PO ₄) ₂	4.246e-10	4.249e-10	-9.372	-9.372	0.000	(0)
UO ₂ OH ⁺	1.400e-10	1.314e-10	-9.854	-9.881	-0.027	(0)
UO ₂ (H ₂ PO ₄) ₃ ⁻	3.059e-11	2.872e-11	-10.514	-10.542	-0.027	(0)
UO ₂ H ₃ PO ₄ +2	1.608e-11	1.249e-11	-10.794	-10.903	-0.110	(0)
UO ₂ PO ₄ ⁻	1.002e-11	9.408e-12	-10.999	-11.026	-0.027	(0)
UO ₂ (SO ₄) ₂ -2	3.725e-12	2.894e-12	-11.429	-11.539	-0.110	(0)
UO ₂ CO ₃	4.554e-13	4.558e-13	-12.342	-12.341	0.000	(0)
(UO ₂) ₂ OH+3	1.528e-15	8.657e-16	-14.816	-15.063	-0.247	(0)
(UO ₂) ₂ (OH) ₂ +2	1.340e-15	1.041e-15	-14.873	-14.983	-0.110	(0)
UO ₂ (OH) ₃ ⁻	1.400e-18	1.314e-18	-17.854	-17.881	-0.027	(0)
UO ₂ (CO ₃) ₂ -2	7.055e-20	5.481e-20	-19.151	-19.261	-0.110	(0)
(UO ₂) ₃ (OH) ₄ +2	1.464e-23	1.138e-23	-22.834	-22.944	-0.110	(0)
(UO ₂) ₃ (OH) ₅ ⁺	2.712e-24	2.546e-24	-23.567	-23.594	-0.027	(0)
UO ₂ (CO ₃) ₃ -4	3.293e-29	1.199e-29	-28.482	-28.921	-0.439	(0)
UO ₂ (OH) ₄ -2	2.681e-29	2.082e-29	-28.572	-28.681	-0.110	(0)
(UO ₂) ₄ (OH) ₇ ⁺	2.523e-32	2.369e-32	-31.598	-31.625	-0.027	(0)
(UO ₂) ₃ (OH) ₇ ⁻	9.623e-34	9.034e-34	-33.017	-33.044	-0.027	(0)
(UO ₂) ₃ (CO ₃) ₆ -6	0.000e+00	0.000e+00	-53.796	-54.783	-0.987	(0)

-----Saturation indices-----

Phase	SI**	log IAP	log K(298 K, 1 atm)
-------	------	---------	---------------------

(UO ₂) ₃ (PO ₄) ₂ :4w	-19.71	-57.11	-37.40 (UO ₂) ₃ (PO ₄) ₂ :4H ₂ O
---	--------	--------	---

Anhydrite	-3.18	-7.54	-4.36 CaSO ₄
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Aragonite	-9.50	-17.83	-8.34 CaCO ₃
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Artinite	-24.55	-14.95	9.60 MgCO ₃ :Mg(OH) ₂ :3H ₂ O
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Autunite	-9.05	-52.98	-43.93 Ca(UO ₂) ₂ (PO ₄) ₂
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B-UO ₂ (OH) ₂	-7.23	-1.68	5.54 UO ₂ (OH) ₂
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Brucite	-14.17	2.67	16.84 Mg(OH) ₂
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Calcite	-9.35	-17.83	-8.48 CaCO ₃
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CO ₂ (g)	-2.14	-3.61	-1.47 CO ₂
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Dolomite	-18.36	-35.45	-17.09	CaMg(CO ₃) ₂
Dolomite(d)	-18.91	-35.45	-16.54	CaMg(CO ₃) ₂
Epsomite	-5.19	-7.33	-2.14	MgSO ₄ ·7H ₂ O
Gummite	-12.08	-1.68	10.40	UO ₃
Gypsum	-2.96	-7.54	-4.58	CaSO ₄ ·2H ₂ O
H-Autunite	-7.50	-55.43	-47.93	H ₂ (UO ₂) ₂ (PO ₄) ₂
H ₂ (g)	-14.00	-17.15	-3.15	H ₂
H ₂ O(g)	-1.51	-0.00	1.51	H ₂ O
Huntite	-40.72	-70.69	-29.97	CaMg ₃ (CO ₃) ₄
Hydromagnesite	-59.04	-67.80	-8.76	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O
Hydroxyapatite	-25.37	-28.79	-3.42	Ca ₅ (PO ₄) ₃ OH
Magnesite	-9.59	-17.62	-8.03	MgCO ₃
Mirabilite	-9.31	-10.42	-1.11	Na ₂ SO ₄ ·10H ₂ O
Na-Autunite	-8.45	-55.86	-47.41	Na ₂ (UO ₂) ₂ (PO ₄) ₂
Na ₄ UO ₂ (CO ₃) ₃	-47.11	-63.40	-16.29	Na ₄ UO ₂ (CO ₃) ₃
Nahcolite	-9.63	-10.17	-0.55	NaHCO ₃
Natron	-19.40	-20.72	-1.31	Na ₂ CO ₃ ·10H ₂ O
Nesquehonite	-12.00	-17.62	-5.62	MgCO ₃ ·3H ₂ O
Ningyoite	-2.35	-56.26	-53.91	CaU(PO ₄) ₂ ·2H ₂ O
O ₂ (g)	-0.14	-3.03	-2.89	O ₂
Portlandite	-20.34	2.46	22.80	Ca(OH) ₂
Rutherfordine	-7.52	-21.97	-14.45	UO ₂ CO ₃
Saleeite	-9.11	-52.76	-43.65	Mg(UO ₂) ₂ (PO ₄) ₂
Schoepite	-7.09	-1.68	5.40	UO ₂ (OH) ₂ ·H ₂ O
Thenardite	-10.25	-10.42	-0.18	Na ₂ SO ₄
Thermonatrite	-20.84	-20.72	0.13	Na ₂ CO ₃ ·H ₂ O
Trona	-30.09	-30.89	-0.80	NaHCO ₃ :Na ₂ CO ₃ :2H ₂ O
U(HPO ₄) ₂ ·4H ₂ O	-3.41	-58.71	-55.30	U(HPO ₄) ₂ ·4H ₂ O
U(OH) ₂ SO ₄	-13.44	-16.64	-3.20	U(OH) ₂ SO ₄
U ₃ O ₈ (c)	-12.45	8.08	20.53	U ₃ O ₈
U ₄ O ₉ (c)	-9.18	-12.57	-3.38	U ₄ O ₉
UO ₂ (a)	-6.74	-6.64	0.10	UO ₂

UO2HPO4:4H2O -3.52 -15.37 -11.85 UO2HPO4:4H2O
UO3(gamma) -9.40 -1.68 7.72 UO3
Uraninite(c) -1.84 -6.64 -4.80 UO2

**For a gas, $SI = \log_{10}(\text{fugacity})$. Fugacity = pressure * phi / 1 atm.
For ideal gases, phi = 1.

End of simulation.

Reading input data for simulation 2.

End of Run after 0.09 Seconds.