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Adsorption Of Arsenic, Chromium, And Uranium From Saline Water On Clinoptilolite And The Treatment Of The Spent Regenerant By Duffusion Dialysis

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ADSORPTION OF ARSENIC, CHROMIUM AND URANIUM FROM SALINE WATER ON
CLINOPTILOLITE AND THE TREATMENT OF THE SPENT REGENERANTS BY
DUFFUSION DIALYSIS

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Dedication

I dedicate this thesis to the Almighty God, The King of the Universe and the uncreated creator.
To my Parents; Tanimola Ishola Azeez & Tanimola Aduke Nimotallai idera.
To Late Sheik Abdul Salam Akoshile and Late Alabi.
To my Late Grandmothers; Humuani iya ile oba , Molounu-wuraola, Abike akoshile and Raliat.

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by

MUTIU OLAITAN TANIMOLA, BSc.

THESIS

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The University of Texas at El Paso
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for the Degree of

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.....TO ALMIGHTY GOD IS THE GLORY!!!!

Abstract

Among various water purification and recycling technologies, adsorption is a fast, inexpensive and universal method. The development of low-cost adsorbents has led to the rapid growth of research interests in this field. The objective of this present study is the optimization of process parameters in adsorption of arsenic, chromium and uranium ions. The adsorption behavior of natural zeolite (clinoptilolite) has been studied in order to determine its applicability in treating water containing arsenic, chromium and uranium. The multiple adsorption of arsenic As (V), trivalent chromium Cr (III)] and uranium (VI) on natural zeolite (clinoptilolite) in single component and multiple component systems has been studied. The optimum conditions for the treatment process were investigated by observing the influence of pH, time, adsorbate concentration, the presence of competing ions and the effect of sodium chloride (NaCl) on metal ions adsorption by natural zeolite. The adsorption of arsenic, chromium and uranium by clinoptilolite was studied under batch and column experiments. The adsorption of the metals was evaluated using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The data were interpreted with an adsorption model, in which a linear relationship was employed to express the equilibrium relationship using Langmuir and Freundlich models. According to the equilibrium studies, the adsorption selectivity sequence in both single and multiple systems can be given as $Cr > U > As$. The Freundlich equation was the most suitable adsorption model for the adsorption equilibrium data with R^2 values of 0.96, 0.96, and 0.95 for As, Cr, and U respectively. The adsorption studies showed low affinity by clinoptilolite for the removal of Arsenic (37.2%) compared to both chromium (88.6%) and uranium (87.5%) at initial maximum concentration of 1000 ($\mu\text{g/L}$) in the multiple component adsorption system. The presence of sodium chloride increased the adsorption rates of the clinoptilolite. In the single component adsorption the maximum percent adsorption of As, Cr and U were 38.3%, 87.8% and, 85.2% respectively and in the binary metal mixtures the maximum percent adsorptions of As, Cr and U were 34.8%, 87.3%, and 82.6 % respectively at an initial concentration of 1000 $\mu\text{g/L}$. This was no significant

difference when the metals were in a single component system or in a binary mixture. The breakthrough curve analysis was determined using the experimental data obtained from the continuous adsorption column experiment.

The chromium and uranium had a break-through time of 25 h and 21 h, respectively, while arsenic had an instant breakthrough from the zeolite. Regeneration of the zeolite was carried out with hydrochloric acid to reduce the sludge produced and for economic benefits. The spent acid was recovered with an anion-exchange membrane by diffusion dialysis. The result obtained indicates high performance of the diffusion dialysis with 77% HCl recovery, 94% chromium ion rejection and 71.7% uranium rejection. The anion-exchange membrane by diffusion dialysis was not effective in the rejection of arsenic. It has 0% rejection, which is an indication of a negative charged arsenic complex formed.

Clinoptilolite natural zeolite proved to be a good adsorbent for removing chromium and uranium but not arsenic. Diffusion dialysis with an anion-exchange membrane effectively recovers acid from the spent regenerant waste stream.

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Chapter 1: Introduction

The extremely fast growth of the world population in the last century, in addition to the industrial revolution, resulted in a considerable rise in both fresh water consumption and wastewater production. Fresh water demand has already exceeded supply in many places, and currently special treatment is often required in order to obtain drinking water of high quality as well as to produce an environmentally acceptable effluent (Shoumkova A, 2011). Wastewaters obtained from processes of many industries contain pollutants (inorganic cations, anions, oils, organic matter, etc.) that have a toxic effect on the ecosystem. It is necessary to treat the metal-contaminated wastewater prior to discharge into the environment, and the removal of these pollutants requires economically justifiable and efficient technologies and techniques (Wang S and Peng Y, 2010). Metals and their derivatives are potential pollutants that could be particularly problematic due to their stability and mobility. Several conventional techniques for treating metal-contaminated waste streams include electro-chemical precipitation, ion exchange, reverse osmosis, and adsorption; most of these techniques are not suitable for large-scale wastewater treatment, especially in developing countries (Gupta and Babu, 2006); the choice of method is based jointly on the concentration of heavy metals in the solution and the cost of treatment (Richardson and Harker, 2002). Among these, reverse osmosis, ion exchange, electro-dialysis and electrolysis are costly technologies with \$10 to \$450 per million liter cost for treated water. The cost of treated water by adsorption varies from 10 to 200 US\$ per million liters. Adsorption is a popular method for the removal of heavy metals from the wastewater (Omer et al., 2003; Heping et al., 2006). Adsorption is a fast, inexpensive and widely applicable technique (Ali et al, 2005). It is a versatile and effective method for removing heavy metals, particularly when it is combined with an appropriate regeneration step. Regeneration reduces the problem of sludge disposal and renders the system economically viable, especially when the adsorbents used are also of low cost. Adsorption is used in a variety of important industrial applications, and now it is increasingly used on a large scale as an economical and efficient separation technique for

metal ion removal from wastewater (Zvinowanda *et al.*, 2009), particularly when natural materials that are available in large quantities or certain waste products from industrial or agricultural activities may have potential as an inexpensive sorbent (Bailey *et al.*, 1999). Many researchers have studied the removal of heavy metals from aqueous solution using different adsorbents like nut shells (Agarwal *et al.*, 2006), soya cake (Daneshvar N. *et al.*, 2009), feed stock such as sawdust (Sumathi and Nandu, 2005), rubber tires (Hamadi *et al.*, 2001) activated sludge(Xie, B.; Kang, K. S., 2003), fly ash (Alinnor I.J, 2007; Meng and Dermatas, 2003) wheat bran, (Nameni M. *et al*, 2008), dead biomass, blast furnace slag, clay, tree bark, tea leaves, natural zeolite (Erdem,E. *et al*, 2004), activated carbon (Guo *et al.*, 2003) and rice husk (Nhapi, I., *et al*, 2011). Natural zeolites in wastewater treatment are very effective in comparison with other methods, because regeneration and reuse of the zeolite is possible. Likewise, the reuse of the obtained concentrate metal ions after regeneration of the zeolite is possible. The efficiency of removing metal ions from waste waters by zeolite depends on many factors, such as initial concentration of metal ions in wastewater, the pH, and the amount of water to be treated.

Chapter 2: Thesis Overview

The goal of this research is to quantify the selective adsorption by zeolite in removing contaminants (arsenic, chromium and uranium) in water. One part of the work focuses on the uptake kinetics of arsenic, chromium and uranium by zeolite in a batch method to evaluate the adsorption of an individual metal in solution, and selective adsorption of multiple metals in solution. The optimum conditions for the treatment process were investigated by observing the influence of pH, time, adsorbent dose, adsorbate concentration, the presence of competing ions, and the effect of sodium chloride (NaCl) on adsorption by natural zeolite in both batch and column experiments. Different molarities of sodium chloride were introduced to see the effect of salt on the adsorptive capacity of zeolite, and particularly to test the effectiveness of zeolite in the removal of these metals in saline water. The equilibrium data were interpreted with an adsorption model to express the equilibrium relationship using the Langmuir and Freundlich isotherms. The best fit was indicated.

Another part focuses on the column adsorption process; a solution containing salts of these metals was passed through beds of zeolite (clinoptilolite) at a constant flow rate to evaluate the adsorption capacity, bed exhaustion time, volume treated and the breakthrough curve of each metal. These effluent samples were evaluated by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Experimental parameters were varied to have an understanding of the conditions and processes required for maximum utilization of the adsorptive capacity of the clinoptilolite.

Regeneration of clinoptilolite after it has reached exhaustion was carried out by treatment of the clinoptilolite with a regenerant solution of a known normality of hydrochloric acid or sodium hydroxide. The concentrations of the metals removed from the beds were measured by ICP OES while the normality of the acid or the base was measured by titration. The spent regenerant (HCl) was recovered by diffusion dialysis with an anion-exchange membrane. The amount of acid

recovered was expressed as a percentage of the amount of acid in the starting regenerant solution. The percentage of metals passing through the membrane was also evaluated.

Chapter 3: Literature Review

3. 1. Heavy Metals

A metal is classified as a heavy metal when its density is five times that of water. The most commonly found toxic heavy metals are arsenic, lead, mercury, cadmium, iron and aluminum. Others include antimony, copper, manganese, nickel, uranium, vanadium, chromium, cobalt and zinc. Wastewaters containing heavy metals are produced from many industrial manufacturing processes. Such industries include metal finishing, automotive, aerospace, printed circuit board manufacturing, semiconductor manufacturing, washing of electroplated metal parts, textile dyes and steel, to name a few. As a result of improper treatment of wastewater prior to discharge, many dissolved metals have found their way in harmful concentrations into groundwater, which is a significant source for potable drinking water. Although certain heavy metals (in small quantities) are essential for a healthy life, large amounts of any of them may cause poisoning. The presence of heavy metals in the environment is of major concern because of their toxicity, which is a threat to human life and the environment (Igwe JC *et al*, 2006). It is important that they are removed from the wastewater before discharging to water bodies. The metals of interest for this research are arsenic, chromium and uranium. Conventional methods for removing dissolved heavy metal ions are chemical precipitation, ion exchange, chemical oxidation or reduction, filtration, electrochemical treatment, application of membrane technology, evaporation recovery and biological treatment (Chaudhari S, Tare V, 2008). These methods employed in removing heavy metals have their advantages and limitations (Fu F, Wang Q, 2011). The adsorption process is considered better than other methods because of convenience, easy operation and simplicity of design. Thus, this process has wider applicability in water pollution control. A good adsorbent is necessary to achieve faster kinetics for the effective removal of pollutants. A fundamentally important

characteristic of good adsorbents is their high porosity and consequent larger surface area with more specific adsorption sites (Bhatnagar A, Minocha A K, 2006).

3.2. Arsenic

Arsenic is a metalloid that occurs naturally, and it is a component of more than 345 minerals. Arsenic is a ubiquitous element. Its toxicity, movement and accumulation in water and living organism usually depend on the form in which the element is present. The wastewater from industries such as metallurgy, mining, chemical plants, production and use of pesticides and leather tanning contain arsenic. Arsenic is a major problem in groundwater in Bangladesh and other places in the world. Well water contaminated by natural sources has been reported as the cause of arsenic toxicity around the world. Arsenic gained much attention since the recognition in 1990s of its large occurrence in well-water in Bangladesh (WHO, 2001). The WHO guideline for arsenic in drinking water is 10 µg/L. On January 22, 2001, the Final Arsenic Rule was published in the Federal Register that revised the MCL level for Arsenic to 10 µg/L (U.S EPA, 2001). In March 2001, the effective date of the rule was extended to provide time for the National Academy of Science to review new studies on the health effect and for the National Drinking water Advisory Council to review the economic issues associated with the standard. After these reviews, U.S EPA finalized the arsenic MCL level at 0.01 mg/L (10 µg/L) in January 2002. The U.S EPA revised the rule text on March 25, 2003, for further clarification of the original rule to affirm that the public health standard for arsenic in drinking water established in January 2001 is 10 parts per billion (ppb) and that any monitoring result greater than 0.010 mg/L is a violation of the January 2001 arsenic standard. The final rule required all community and non-transient, non-community water systems to comply with the rule by 2006. Similarly, in Canada the current guideline is 25 µg/L, but re-evaluation is going on to reduce the level to 5 µg/L when improved treatment technologies are developed. The World health

organization has also reviewed the arsenic concentration and established a provisional guideline at 10 µg/L after establishing that arsenic is carcinogenic. These regulations reviews are necessary because of the toxic effect of arsenic in lower concentrations than it was previously assumed.

3.2.1. Arsenic Occurrence and Chemistry

Arsenic is a metalloid meaning it can assume the properties of both metals and non-metals. It has an atomic weight of 75 amu. Arsenic is the 20th most abundant element found in the earth's crust at a concentration of 2-5 ppm. It's often found with mineral-ores, metals (copper, gold, zinc) and other geo-thermal sources like the geysers of Yellowstone and hot springs. The picture on the left is a mine and the one on the right is near the outlet of a hot spring (Gooch and Whitfield, 1888).



Figure 1. Arsenic in the Earth Crust Picture.

(Source: http://www.civil.umaine.edu/macrae/what_is_arsenic.htm).

Arsenic occurs in the environment with oxidation states, i.e. +3, +5, -3 and 0. It occurs in natural waters in both organic and inorganic forms. However inorganic forms such as arsenite [(As(III) with a +3 valence] and arsenate [As(V) with a +5 valence] are predominant in natural waters. The arsenite is more mobile (Schnoor, J. L., 1996) and toxic due to its thiol-reactivity (Knowles and Benson, 1983) than the arsenate. The actual valence state and chemical forms of inorganic arsenic are dependent on the oxidation-reduction conditions and pH of the water and the

presence of complex ions (Xu, Y.; Nakajima, T.; Ohki, A.J., 2002, Schnoor, J. L., 1996). In surface water (oxidizing conditions), arsenate predominates while in ground water (anoxic condition), arsenite becomes stable. Under more oxidizing conditions, arsenite converts to arsenate (Kelly B. Payne and Tarek M. Abdel-Fattah, 2005). Dissolved arsenite and arsenate compounds tend to have an overall negative charge, and at near neutral pH, the predominant forms are H_2AsO_4^- and HAsO_4^- for arsenate, and uncharged H_3AsO_3 for arsenite (Figure 2). Arsenic can be in organic forms like monomethylarsonic acid, dimethylarsinic acid, trimethylarsine-oxide tetramethyl-diarsine, arsenobetaine, arsenocholine to name a few. The arsenic forms of major concern in drinking water are the soluble inorganic arsenious acid, As(III) and the arsenic acid, As(V). Figures (2, 3, and 4) are structural diagrams of arsenic in these forms. The bonds between oxygen and hydrogen are an assumption.

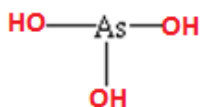


Figure 2a. Structural Diagram of Arsenious Acid

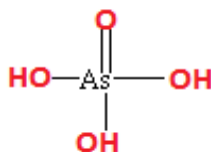


Figure 2b. Structural Diagram of Arsenic Acid

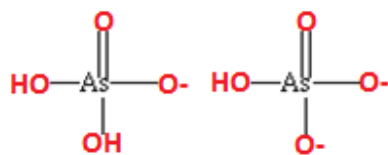


Figure 2c. Structural Diagram of H_2AsO_4^- and HAsO_4^{2-} .

Arsenic acid tends to lose its protons as the pH increases. The arsenic acid As(V) occurs majorly in the form of univalent H_2AsO_4^- between pH 2.3 and pH 6.8, while divalent HAsO_4^{2-} (Figure 4) dominates between pH 6.8 and pH 11.6. At neutral pH, arsenic acid co-exists as both univalent and divalent forms. The trivalent form (AsO_4^{3-}) dominates at the highest pH values while the neutral form (H_3AsO_4) dominates at the lowest (acidic) pH (Figure 3). This negative charge at the neutral pH (H_2AsO_4^- and HAsO_4^{2-}) explains why As (V) is attracted to positive charge surface sites of soil particles and thus their lower mobility in ground water. Domenico, P. et al (1998) has reported the electrostatic attraction of arsenic on iron hydroxide. This attraction continues until the binding sites of the soil are saturated with As(V). The neutral form, H_3AsO_4 travels freely with the water and binds less with the soil particles. Arsenite compounds are reported to be 4-10 times more soluble than arsenate compound (Griffin and Shimps, 1978). The behavior of arsenate in soil is analogous to that of phosphate, because of their chemical similarities. They both form insoluble precipitates with iron, calcium and aluminum. The presence of iron in soil is very effective in controlling arsenate movement in soil. The adsorption of arsenate in soil by aluminum and iron oxide showed maximum adsorption at a pH 3 before gradual decrease at increased pH an adsorption mechanism called inner sphere complexation (Hingston et al, 1971; Anderson et al., 1976), which is the same mechanism controlling the adsorption of phosphate by oxide surfaces (Hingston et al, 1971; Anderson et al 1976; Anderson and Malotky, 1979). Arsenate adsorption in soil by kaolinite and montmorillonite gave maximum adsorption at pH 5 (Griffin and Shimps, 1978 ;). The scenario is different with arsenious acid, which remains un-charged at acidic and neutral pH until the pH rises above 9 where the arsenite ion acquires a negative charge. This explains the reason why As (III) is not

attracted to positive charged (aluminum, iron, zinc). Both pH and the redox are important in assessing the fate of arsenic in soil and water.

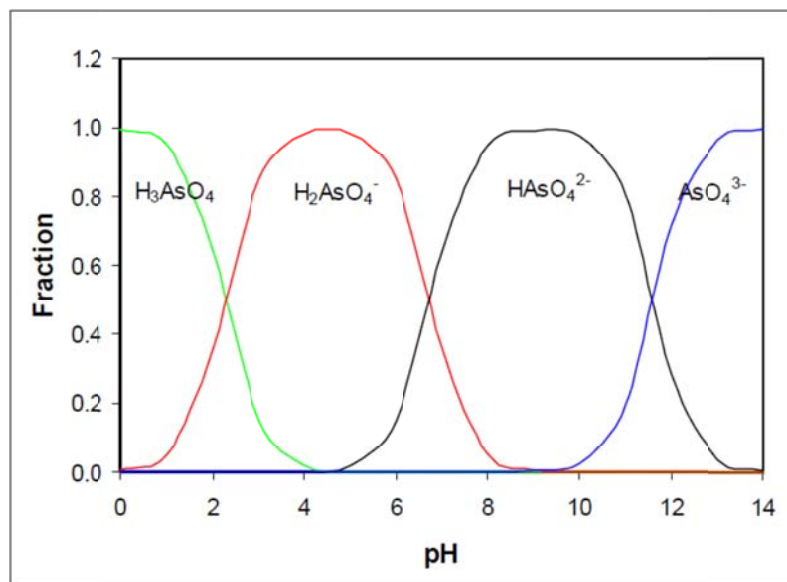


Figure 3. Arsenic Speciation in Water.

http://www.epa.gov/nrmrl/wswrd/dw/arsenic/pubs/6_modified_epa_as_course_ix.pdf.

3.2.2 Health Effect OF Arsenic Exposure

Groundwater is one of the major sources of human exposure to inorganic arsenic. High concentrations of arsenic in drinking water have been reported from several regions of the world (Battacharya P et al, 1997; Battacharya et al., 2002, Naidu R. et al., 2006). Arsenic contamination has been documented in different places like west Bengal India Bangladesh Nepal, Mexico (Cebrian M.E. et al., 1983; Armjenta, M.A., et al., 1995; Rodriguez R. et al., 2004), China (Liafang W. et al., 1994; Lou Z.D., et al., 1997), Ghana (Smedley, P. 1996) Chile (Borgoño, J. M., et al. 1972, Borgoño, J. M., et al. 1977), Argentina (Smedley, P.L., et al., 2002; Smedley, P.L., et al., 2005; Bunschuh J., 2004; Cebrian M.E., et al., Battacharya P et al, 1997; Battacharya P et al., 2005) Taiwan (Lu, F.J. et al, 1990; Chen, S.L. et al., 1994), Canada (Grantham, D.A. et al., 1977), United States and other places around the world. Arsenic

concentrations above the MCL imposed by US EPA, has been reported within the United States such as; California, Nevada, Alaska, Arizona, Indiana, Missouri, Washington, New Hampshire, Idaho, Ohio and Wisconsin (Welch, A.H., et al, 1998; Welch, A.A. et al 2000; Moncure G., et al., 1992, Sclootmann J.L., et al., 1992, Frost, F. et al., 1993, McArthur, J.M. et al., 2001, ATSDR, 2007). The case in the United States is not as critical as that of Nepal, India or Bangladesh where it resulted into mass poisoning of the population. The crises in Bangladesh and India testify to the devastating chronic effect of arsenic poisoning. In 1983, traces of arsenic skin diseases were noticed in West Bengal, India (Clarke, T., 2002) while Bangladesh Department of Public Health Engineering identified the first arsenic-affected person in 1993. In 1997 the contamination of arsenic made headline around the world (DCH trust, 2002). It was estimated that 20-60 million of the 125 million population were at risk of exposure to arsenic in their drinking water (McArthur, J. M. et al, 2001; Harvard University, 2000, Ngai T.K., 2002) and about 7 million people were at risk in neighboring west Bengal (Murcott S., 2002). Recent results from different research groups that tested tube wells around this region show a well-documented arsenic contamination above the 10 µg/L WHO guideline (NRCS, 2000; Halsey, P.M., 2000; NRCS, 2000). The source of contamination in Nepal and Bangladesh was agreed to be natural processes and not anthropogenic and two hypotheses were proposed to describe the source and release mechanism of arsenic in this region; the pyrite oxidation hypothesis (Dipankar et al, 1996) and the iron oxy-hydroxide reduction (Bridge, T., Husain, M., 2000). Research carried out by Harvey et al (2001) and recent studies believe that oxidation theory is not acceptable but support the hypothesis of oxy-hydroxide reduction (Harvey et al, Husain, M., 2000; Nickson, R., et al., 1998; Hemond, H., Fechner-Levy, E., 2000). The symptoms of arsenic poisoning can be classified into acute and chronic symptoms. The acute symptoms are seen immediately after exposure to high concentration of arsenic while the chronic is often hidden; it occurs gradually over time and develops after a long term exposure to a low concentration of arsenic. Acute symptoms are muscle pain, violent vomiting weakness, nausea, abdominal pain, diarrhea, red rashes on the skin, intense thirst, numbness in hand and feet, drowsiness, confusion,

paranoid delusions, hallucination, seizure, coma and death (Saha, J.C., et al., 1999). Acute poisoning has mortality rate of 50-75%, and death usually occurs within 48 hours (Ngai T.K., 2001). Survivors of acute arsenic poisoning suffer damaged peripheral nervous system (Saranko, C.J. et al., 1998). The behavior of arsenic (III) and As (V) has been reported to differ in acute poisoning, As (III) affect proper body function while As(V) interferes with the energy production thus As(III) is more acutely toxic than As(V) (Saranko C.J. et al., 1998).

The primary routes of arsenic entry into the body of human are through ingestion and inhalation. Meat, fish and poultry accounts for 80% of dietary arsenic intake. The average dietary intake of arsenic by adult in United States is estimated as 40 µg/day (ATSDR).

Chronic exposure to arsenic can cause major health effect in human. Long term exposure causes dermal, vascular and cancer effects (NRC, 2001). Dermal effects are noticeable skin changes such as keratosis (Tseng et al., 1968; Centeno et al. 2002) and hyper pigmentation (Yoshida et al., 2004; Guha, 2003) as shown in Figure 4, the post effect of these is a possibility of cancer occurrence. Cancer is usually observed after more than ten years of chronic exposure to arsenic (Halsey, Patricia M., 2000). US EPA has classified inorganic arsenic as a Group-A carcinogen (US EPA, 2000). Victims of chronic arsenic exposure have been reported to suffer from skin cancer (Rossman et al., 2004, Luster and Simeonova, 2004), Bladder cancer in Figure 5 (Steinmaus et al., 2003, Morales et al., 2000) and lung cancer (Hopenhayne_Rich et al., 1998; Chen, C. L., et al., 2004; Chui, H.F., et al., 2004; Xia Y., et al., 2004), neuropathy (Tsai, S.Y., et al, 2003) pain, hypertension (Rahman M., et al., 1999) weakness, atrophy (Mukherjee, S. C. et al., 2003; Guha Mazumder, D. N., 2003). Others effect such as reproductive (Chakraborti, D., et al., 2003; Chattopadhyay, S., et al, 2002; Hopenhayne, C. et al., 2003; Hopenhayne, C. et al., 2003), cardio vascular disease (Lee, M.Y., et al., 2002), ischemic heart disease (Tseng, C.H., et al., 2003), carotid atherosclerosis (Wang, C. H., et al., 2002), respiratory (Guha Mazumder, D. N., 200; Milton, A.H., et al., 2002; Milton, A.H., et al., 2003), hormonal (Bodwell., J.E., 2004), diabetes mellitus-type two (Tseng C. H., et al., 2000, Tseng C. H., et al., 2002).

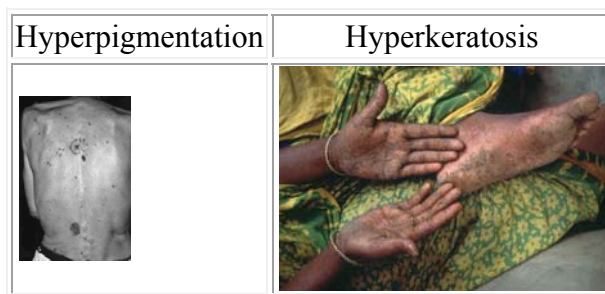


Figure 4. Hyper-Pigmentation and Hyperkeratosis.



Figure 5. Skin Cancer and Blackfoot.

Sources; (<http://www.atsdr.cdc.gov/csem/csem.asp?csem=1&po=11>)
(<http://www.cram.com/flashcards/glycolysis-2060508>).

Exposure to arsenic causes cardiovascular and peripheral vascular diseases (e.g Blackfoot disease). Black foot diseases patients are reported to have higher death rate. In Bangladesh, higher incidences of spontaneous abortions, stillbirths and pre-term births have been associated with arsenic in drinking water (Ahmad et al., 2001). The amount of arsenic required to cause adverse health effects depends on the chemical and physical form of the ingested arsenic. The toxic effects of arsenic exposure actually depend on how much arsenic a person is exposed, how long the person is exposed the form of the arsenic and the sensitivity of the individual.

3.2.3 Uses of Arsenic

As(III) has been reported to be used as a chemotherapeutic agent to treat leukemia and other forms of cancer (Nriagu, J.O., 2002, Miller et al., 2002; Hu et al., 2005). Arsenic is found in some

Asian traditional medicine (Garvey et al., 2001, Chan 1994) and in some naturopathic or homeopathic remedies (Kerr and Saryan, 1986). Arsenic was long used as paints and dye pigments, becoming one of the earliest recognized chemical occupational hazards (Azcue, J.M., Nriagu, J.O., 1994). Arsphenamin (Salvarsan) was the first effective medicine for syphilis until replaced by antibiotics after World War II (Rossman 2007). Arsenic compound, Chlorovinyl dichloroarsine also called lewisite was also used as a chemical warfare agent. Arsenic is also useful in pesticides and other industrial processes.

3.3 Chromium

Chromium is one of the heavy metals of major concern in water and waste water treatment (karthikeyan et al., 2005) and it's ranked as one of the top 16th toxic pollutants due to its tetratogenic and carcinogenic nature (Torresdey, et al., 2000). It accumulates into the food and affects human physiology causing severe health problems (Mohanty, M., and Patra, H.K., 2011). It can find its way into the environment through different means such as; industrial (electroplating, leather tanning, and textile industries) (Gao et al., 2007), Environmental (cement dust, contaminated land fill, asbestos lining erosion) and occupational sources (textile, welding, tattooing, paint, antifreeze, cement, paint pigments). The enforceable EPA maximum contamination level of total chromium in drinking water is 0.1mg/L (EPA, 2007).

In 1997, according to the Toxic Release Inventory, the estimated releases of chromium was 111,384 pounds to water, 3391 pounds to air, 30,862,235 pounds to soil and from large processing facilities which amount to 0.3%, 2.2% and 94.1% respectively of total environmental release (ATSDR 2000). Chromium finds its way into the human body through inhalation, ingestion and dermal absorption. The mean dietary intake of chromium from food is 60 µg/day. The maximum contamination level of Cr(III) permitted in waste water is 5mg/L. Chromium is commonly found in two stable states in the environment as Cr(III) and Cr(VI). The Cr(III) is a cation and forms stable complexes with negatively charged compounds while C(VI) is soluble in water and forms strong divalent anionic oxidants. Due to its anionic nature Cr(VI) is not retained

on negatively charged soil particle, but the Cr(III) are retained on the negatively charged soil particles. Trivalent chromium, Cr(III) is less toxic than Cr(VI), but its disposal is of great concern, because it can be oxidized to Cr(VI) in the environment, which may pose a serious health risks (Jinhua Li, et al., 2012; Shanker A.K., 2005). Therefore, the removal of chromium in any of the forms is necessary. Many different methods have been used to remove chromium in water. Some of these includes chemical precipitation, ion exchange (Sahu S.K. et al., 2009), membrane process (Pagana, A.E. et al., 2009), liquid extraction, electro-dialysis (Verma et al., 2006), reduction (Zeng zhi-xiang et al., 2009) and electro coagulation (Zaroua, Z. et al., 2009). The adsorption method is one of the preferred methods for a large scale removal of metal ion from wastewater because of its efficiency and low cost (Li et al., 2007; Zvinowanda et al., 2009). Regeneration reduces the problem of sludge disposal and renders the process cost efficient (Zvinowanda, C. et al., 2009). Different natural adsorbent have been used to investigate the adsorption of chromium. Several types of crystalline clay minerals such as zeolite are very good adsorbent and readily available (Mark, 1998; Mier et al., 2001; Inglezakis, 2004; Meshko et al., 2006). Bradl (2004) observed the adsorption of Cr(VI) by soil phases with hydroxyl group such as those present in and Montmorillonite. Khan et al. (1995) also reported that hydroxylated surfaces of oxides of Al, Ca, Mg and Si acquire charge when present in aqueous solution through amphoteric dislocation. The hexavalent form of chromium, Cr(VI), present as either dichromate($\text{Cr}_2\text{O}_7^{2-}$) or chromate (CrO_4^{2-}), is toxic, carcinogenic and mutagenic. It is very mobile in soil and water. It is a strong oxidant capable of being adsorbed by the skin (I.B., Singh and D.R. Singh, 2002). These forms are distributed in solution depending on the pH. When the pH is less than 2, Cr^{3+} is the predominant species and at pH 4, the species are Cr^{3+} and $\text{Cr}(\text{OH})$.

3.4 Uranium

Uranium is the chemical element with atomic number 92. Natural uranium is a mixture of three isotopes, ^{238}U (99.276%), ^{235}U (0.718%) and ^{234}U (0.004%). Uranium is naturally occurring,

ubiquitous, lithophilic metal found in various chemical forms in the environment (Gindler, J.E., 1973). It can be easily oxidized; thus, in nature uranium mainly occurs in oxidized forms. . At 200- 400 °C, uranium powder may self-ignite in the presence of CO₂ and N₂.

Uranium exists in five oxidation states +2, +3, +4, +5, and +6. The +4 and +6 states are the stable forms. The tetravalent uranium is the fairly stable and forms hydroxide, hydrated fluoride and phosphates of low solubility. The most stable of uranium is the hexavalent and mostly occur in the form of U₃O₈. Based on the radiological risks by the radiation of uranium isotopes and chemical risks from heavy metals, the health effects of uranium can be divided into carcinogenic and non-carcinogenic effects. The toxic nature of uranium (VI) ions, even at trace levels, has been a public health problem for many years. Exposure to uranium causes renal and respiratory effect and cancer, which is attributed to radiation (Ballou, J.E. et al., 1986, Dockery, D.W., et al, 1993, Dungworth, D.L. et al, 1989). Latest research has shown that large radiation doses can initiate and promote carcinogenesis and interfere with reproduction and development (Morris, K.J. et al., 1990, Sanders, C.L., 1986, UNSCEAR, 1988). Acute high level of exposure also causes kidney failure (Zhao, S., 1990).

Nephritis is the primarily chemically induced effect of uranium in humans. USEPA has classified uranium as a confirmed human carcinogen and suggested that zero tolerance is the only safe acceptable limit. They prescribed that maximum contaminant level goal (MCLG) for uranium as zero in 1991. In addition, the US EPA finalized a realistic regulation of 20 µg/L as the maximum contaminant level (USEPA, 2000). The WHO recommended 15 µg/L as the maximum uranium level in drinking water (WHO, 2008). Though stringent environmental regulation exists against the release of uranium contaminated solution into the environment, effluents from nuclear and many other conventional industries are found to have significant quantity of uranium. For this reason, uranium removal from waste water is of great importance (Yusan, 2008). Different methods have been used for cleaning solutions contaminated with uranium such as co-precipitation, ion exchange, membrane based separation and sorption on various surfaces (Baeza, A. et al, 2006; A., Krestou et al., 2004; Chellam S., Clifford D.A., 2002; K. L., Lin, et al., 2002).

Membrane methods have also been applied in some nuclear centers around the world (Zakrzewska, 2006). In acidic solution, uranium exist as U(VI). In neutral or basic pH, it normally exists as neutral or anionic species forming complexes with anionic ligands such as OH⁻ and CO₃²⁻. Thus in neutral pH ranges, ion exchange is less effective for the removal of uranium.

3.5 Heavy Metal Removal In Water

Several methods have been used by researchers to remove heavy metals from drinking water. The methods include; ion exchange, coagulation/flocculation, reverse osmosis, nanofiltration, adsorption technique, limestone to mention a few. The primary methods for removing arsenic from drinking waters in the developed world include;

3.5.1 Ion Exchange

This is one of the effective methods of removing heavy metals in water, and the ion-exchange materials can be easily recovered and reused by regeneration (I-H, Lee et al., 2006; Clifford, 1999). Different types of exchange materials that are natural or synthetic resin are used in wastewater treatment. These materials can be categorized based on their functional groups as anion-exchange resins and cation-exchange resins (Dorfner, 1991). Ion exchange can also be used to remove heavy metal from the sludge using a cation-exchange by shifting the dynamic equilibrium of $M(OH)^2 \rightleftharpoons M^{2+} + 2OH$, according to Le Chatelier principles. Lee et al., (2006) conducted an experimental study to remove heavy metal from sludge using both IRC-718 and Amberlite IR-20. The problems with ion exchange are chromatography peaking, fouling by organic substance in water, and rich brine sludge produced from regeneration process.

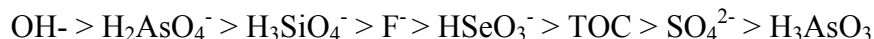
3.5.2 Coagulation/ Filtration

Wastewater treatment by coagulation has been applied traditionally to reduce turbidity, by removing non-settling or slow settling colloidal particles from water (Yuassa A., 1998; Mijalova, P., et al., 1996). The coagulation process promotes aggregation of the suspended solids to form

flocs, which can be removed by sedimentation or filtration. Arsenic or other toxic metals can be removed through coagulation treatment by adding alum or ferric chloride through adsorption and occlusion mechanism (Chararntarayak, L. et al., 1999). Several researchers have investigated the use of FeCl_3 and alum to remove arsenic from water (Hering, J.G., et al., 1996; Hering, J.G., et al., 1997; Edwards, M., 1994; Chen, R.C., et al., 1994). Chen, R.C et al. (1994) also examined the enhanced removal of arsenic by cationic polymers. The ferric salt and alum are used to form flocs that sorbs and co-precipitate dissolve arsenic (Chang et al., 1994; Fields et al., 2000a) which are filtered out. The ferric salts are more effective on weight basis (Sorg, 1993; Sorg and Logsdon, 1978) and are more widely used than aluminum salts. The precipitate $[\text{Al}(\text{OH})_3]$ or $[\text{Fe}(\text{OH})_3]$ is removed by either granular media filtration (GMF) or membrane microfiltration. If GFM is used, a flocculation step has to be included to enhance floc production. This extra step is not needed in membrane microfiltration. Disposal of sludge is important, but sludge (Al and Fe residue) from this process is not classified as hazardous.

3.5.3 Activated Alumina

Activated Alumina (AA) can be used as a sorbent for arsenic (Wang et al., 2000) and is prepared by partially dehydrating $\text{Al}(\text{OH})_3$ at high temperatures. Activated alumina has been used to remove arsenic and chromium in water. Nasri et al., (2003), investigated the use of activated alumina and rice husk for the removal of chromium (VI) from synthetic solution and the effect of operating parameter. Tony, Sarvinder Singh and K.K., Pant (2003) investigated the equilibrium kinetics and thermodynamics for adsorption of As(III) on activated alumina. AA sorbs arsenate more completely than arsenite. The selectivity sequence for AA is (Clifford, 1999)



After bed exhaustion, regeneration of the activated alumina with NaOH followed by a sulfuric acid wash is done. This limits the number of times the media can be cycled, and the regeneration

produces metal-rich waste. Better long-term performance of regenerated media and pre-treatment is needed to prevent media clogging.

3.5.4 Lime Softening and Iron Removal

It is well known that lime softening will remove substances from water other than hardness. Lime softening is effective for arsenic removal. Arsenic removal increases at higher pH during lime softening (Sorg and Logsdon, 1978) particularly when $\text{Mg}(\text{OH})_2$ forms at pH greater than 10.8. The arsenic uptake is believed to be a combination of sorption, co-precipitation, and occlusion on the calcium and magnesium solids (McNeill and Edwards, 1997b). McNeill and Edwards (1997a; 1997b) proved that aluminum and iron precipitation can be optimized for arsenic removal at low cost (McNeill and Edwards, 1997a). High pH and the generation of large volume waste are disadvantages of the system.

3.5.5 Membrane Processes

Membranes emerged as a viable means of water purification since 1960 with the development of high synthetic membranes, and due to increase scarcity in fresh water, exploration began using membrane for water desalination. Membrane processing can be considered as the most energy saving and environmental friendly method for heavy metals removal from water. Most membranes (MF, UF, NF and RO) are synthetic organic polymers. Microfiltration and ultra-filtration membranes are often made from the same materials but with different pore sizes (Pinnau et al., 2000). Membrane processes such as reverse osmosis, nano-filtration, electrodialysis, Donnan dialysis and liquid membrane have been supported by a number of researches (Korus, 199; Zhang, 2002). Zaki (2002) separated uranium from aqueous solution by electrodialysis.

3.5.6 Electrodialysis (ED)

Electrodialysis with ion exchange membrane represents one of the most important membrane methods (Sadrzadeh, 2007) and it has successfully performed over the last decade mainly in the production of potable water from brackish or sea water, and regeneration of ion exchange resin and production of ultrapure water, demineralization and de-acidification in food, purification of radioactive wastewater in nuclear power plants and recovery of water and valuable metals from industrial effluents (Konstantinos, 2008). Continuous electro deionization (CEDI) is a hybrid separation of electrodialysis and ion exchange, but it operates continuously and no regeneration of ion resin is required (A. Zaheri et al., 2010). Woo Lee, (2007) observed that CEDI has the advantage of the conductivity in the resin-filled dilute cell increased more than two orders of magnitude. Mohammadi et al., (2004) observed that the performance of electrodialysis depends on parameters such as feed, flow rates, cell design, current density and perm-selectivity of the membrane.

3.5.7 Reverse Osmosis and Nanofiltration (NF)

Reverse osmosis is commonly used to reduce dissolve matter from water. Reverse osmosis has been researched to remove several metals As, Cr, Al, Cu, Zn, silver, iron and lead (Dvorak, 2008) to mention a few. Mousavi, S., et al., (2009) has researched the removal of chromium (VI) from aqueous solution by reverse osmosis. M.D. Fayed Ahmad, (2012) researched the removal of arsenic (V) and As(III) by reverse osmosis and concluded that both forms of arsenic were efficiently removed. The influence of trans-membrane pressure and feed concentration on permeate flux, water recovery, permeate concentration and salt rejection was investigated in reverse osmosis operation for metal removal (Mousavi S.A., et al, 2009).

Nano-filtration membranes remove different valence ions and different molecular weight organic molecules in water depending on the membrane charge and the pore size. NF is useful for water purification biochemical substance separation, waste water reclamation and water softening (Ji et al., 2011). Fouling is a major problem in membrane operation.

Problems with Membrane operation; Fouling occurs either on the surface of a membrane or within its pores, and it causes a decrease in flux. The four types of fouling common to membranes are: bio-fouling, scaling, organic and colloidal (Amjad Z., 1993). The presence of suspended solids, scale, microbes, hydrogen sulfide, iron and manganese, and organics limits membrane life, so pre-treatment is often necessary. Reverse osmosis and nano-filtration are expensive, generate waste brine and consume large volume of water.

3.6 Adsorption

Adsorption of arsenic onto metal oxide or metal hydroxide surfaces has been well known for many years. Early studies focused on the use of activated alumina ($\gamma\text{-Al}_2\text{O}_3$) primarily as a selective adsorbent for As and F (Sorg and Logsdon, 1978) (Clifford and Lin, 1991; Xu et al., 1988). Wide varieties of adsorbents have been used in recent years. Al and Fe (III)-based sorbents tend to work best at pH at or below 7, whereas many groundwater have pH greater than 7. A pH adjustment is therefore likely to be an important factor in technology selection. The initially lowering and subsequent raising of the pH (to avoid corrosion of plumbing) increase costs, complexity, and require handling of hazardous acid.

3.7 Zeolite

Zeolites (Figure 5) are naturally occurring alumino-silicates that belongs to the class of minerals called “tectosilicates”. They possess endless three dimensional crystal structures, which make them hard and insoluble in water and enable them to exchange their ions with other preferable ions in solution. Natural zeolites are low cost alumino-silicates, with a cage-like structure (Figure 6) suitable for ion exchange due to isomorphic placement of Al^{3+} with Si^{4+} in the structure that results into a deficiency of positive charge in the frame work. This deficiency is balanced by exchangeable cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} . These cations are arranged with defined number of water molecules located on specific sites in framework channels (Peric, J., M. Trgo, and V.V. Mevidovic, 2004). The process by which zeolites exchange their ion is

heterogeneous, while the zeolite structure remains practically unchanged (Joshi, A. and M. Chaudhuri, 1996; Obradovic S., et al., 2006). Zeolite structure consists of framework silicates of interlocking tetrahedrons of SiO_4 (Figure 8) and AlO_4 in a (Si+Al)/O ratio 1: 2. The aluminosilicate structure is negatively charged and attracts positive ions onto the surface of the zeolite. Zeolite has large spaces in its structure, which is interconnected to form long wide channels and allows space for cations. These channels allow easy movement of the residing ions and molecules in and out of the structure. One of the main characteristics of a zeolite is its ability to absorb and lose water with no damage to their crystal structure. Zeolite has low specific gravity because of these large channels (Zeng, Y., et al., 2010). In recent years, natural zeolite have been intensively investigated because of their effectiveness in removing trace quantities of different ions from aqueous solution and because of their ability to undergo the phenomenon called ion exchange (Misaelides, P., et al 1994; Shanableh, A. and A. Kharabsheh, 1996). The mineralogy composition of zeolite is complex, and a combination of different methods such as classical chemical analysis – gravimetric method, Atomic Absorption Spectrometry or X-ray Fluorescence Spectrometry are used to determine the chemical composition of zeolite. Natural zeolite are divided into seven main groups based on their structure or morphology, physical appearance, types of binding, free pore volume and the type of exchangeable cations in its structure. The removal efficiency of a zeolite is a function of factors such as pH of the system, metal hydroxide formation, previous modification of the zeolite and the volume of water to be purified. Zeolite can be modified to suit removal of some metal ions in solution.



Figure 6. Photograph of Zeolite Particles

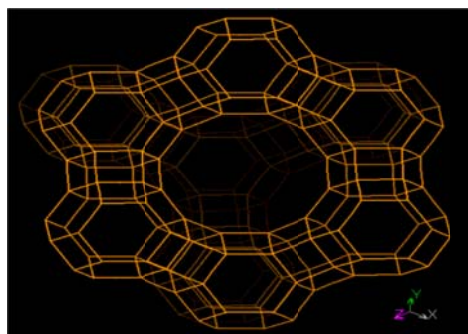


Figure 7. Picture of Zeolite Structure.

(Source for Figure 6 and Figure 7: Karmen Margeta, et al., 2013 Natural Zeolites in Water Treatment – How Effective is Their Use).

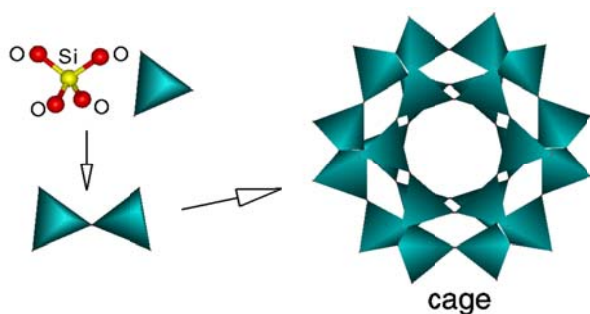


Figure 8. SiO_4 Tetrahedron Showing the Group of Formations into Larger Zeolite Structures.

(Source: Karmen Margeta, et al., 2013 Natural Zeolites in Water Treatment – How Effective is Their Use).

3.8 Clinoptilolite

Clinoptilolite is one of the most used natural zeolite and is of the formula $(\text{Na},\text{K})_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$. Clinoptilolite has exchangeable cations of Na^+ , K^+ , Ca^{2+} and Mg^{2+} throughout its channels. The structure of clinoptilolite is sheet-like, and it differs from heulandites in its potassium and silica enrichment. The sheets are connected by a few bonds, and channels are formed throughout the crystal. The size of these channels controls the size of the ions or molecules that can pass through them. Therefore, clinoptilolite can act as a chemical

sieve, allowing the passage of some ions while blocking others. The selectivity of a sorbent depends on the ionic radius, cation charge, structure, distribution of active centers, and temperature (Sprynskyy, M., et al., 2007). Clinoptilolites observed at different places (USA, Croatia, Serbia, Australia, China, Turkey, Cuba, Ecuador, Ukraine, Argentina and Brazil) consist of SiO_2 (65 wt%), Al_2O_3 (12 wt%) , Fe_2O_3 , Na_2O , K_2O , CaO , and MgO .

Chapter 4: Adsorption

4.1. Surface Adsorption Background

Adsorption is the adhesion of chemical substance (adsorbate) onto the surface of a solid (adsorbent). It is the binding of molecules or particles to a surface. The molecules are adsorbed from bulk phase onto the adsorbing phase through a homogenous surface (Figure 9). The binding is usually weak and reversible, so regeneration is an advantage. The widely used industrial adsorbents in water treatment are carbon, silica gel and alumina, because they have large surface area per unit weight. The adsorption process is mostly used by various researchers for heavy metals removal (R., Ahmed et al., 2006; D.F., Aloko and E.A., Afolabi, 2007; D.F., Aloko and E.A., Afolabi, 2006; C. C. Chen and Y. C. Chung, 2006, N. Amin, et al, 2006). The adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by a sorbent (K., Steeve, et al., 1998).

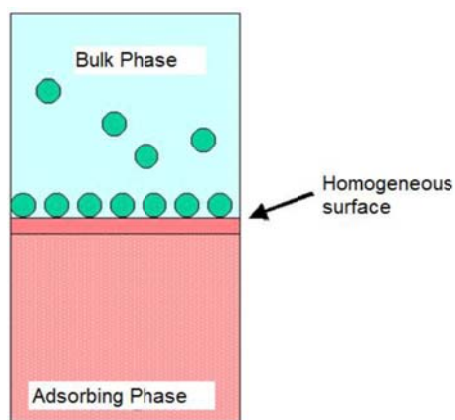


Figure 9. Mechanism of Adsorption.

Source

(<http://mimoza.marmara.edu.tr/~zehra.can/ENVE401/3.%20Adsorption%20Equilibria.pdf>)

4.2. Adsorption – The Process

Adsorption has been used for centuries; it was thought to be first conceived in ancient times, and the first results were documented in the late 1700's. Adsorption was used at the time to test the ability of charcoals and clays to uptake gases. In 1814 Saussure, concluded that all types of

gases can be taken up by porous media such as asbestos, cork and sea-foam. By the early 1900's, the Freundlich equation was developed. Although, the Freundlich empirical equation was firstly proposed by Boedocker van Bemmelen, it is known in literature as Freundlich, because Freundlich assigned great importance to it and popularized its use (C., Boedecker, J Landw, 1985). Other equations were also developed, this include Langmuir, Euckena and Polanyi. The Langmuir equation was originally developed for monolayer. In 1911, the phenomenon of capillary condensation was developed by Zsigmondy. This phenomenon was described by the Kelvin equation for cylindrical pores, with pore width 2-50nm (J., Oscik, et al., 1982). In 1914 Eucken –Polanyi theory includes the adsorption potential, potential theory and the characteristic adsorption curve that are adsorption temperature independent (A. Eucken, et al, 1914; M. Polanyi, Verh. Deutsch, 1914; M. Polanyi, Verh. Deutsch, 1916). Langmuir in 1918 derived the first clear concept of monolayer adsorption, formed on energetically homogeneous solid surfaces. This concept of Langmuir applied to physic-sorption (I. Langmuir, J., 1461). Langmuir understood that surface catalysis is usually preceded by chemisorption, and he interpreted the kinetics of surface reaction in terms of his monolayer equation. In 1932, Langmuir was awarded the Nobel Prize in chemistry for his discoveries, researches and contributions to surface chemistry (K.J. Laidler, 1993). Branauer, Emmet, and Teller (BET, 1938) proposed the multilayer isotherm, BET uses the same assumption as Langmuir. The principal assumption of the BET is that the Langmuir equation applies to every adsorption layer. The BET was originated for a definite model of adsorption Layer (Brunauer P.H., et al, 1938), and next, it was extended to the finite numbers of layers (Brunauer, L.S., et al, 1940; S. Brunauer, et al, 1945). The BET theory made the first attempt to create a universal gas theory of physical adsorption (K.S.W. Sing, 1996).

4.3 Isotherm Model

There are other isotherm models, but Langmuir and Freundlich are considered to be the most commonly used ones especially for monolayer and noncompetitive adsorption processes. The isotherms describes the competence and capability of the adsorbent used.

4.3.1 Adsorption Equilibrium

Adsorption equilibrium is an important stage in adsorption process and for equilibrium to be reached, the following steps are necessary: (1) film diffusion – this is the transport of adsorbate through a surface layer to the outer surface of the adsorbent (ii) pore diffusion – this is the diffusion of adsorbate through the pores of the adsorbent, and (iii) adsorption of the adsorbate on the inner planes bounding pore and capillary spaces. The equilibrium reached in adsorption is illustrated by plotting the amount of solute (metals in this case) adsorbed per unit weight of the adsorbent, q_e , against the concentration of the solute still remaining in the solution, C_e . This relationship develops into an adsorption isotherm.

4.3.2 Adsorption Isotherm

Adsorption isotherm is a graph showing the relationship between the amount adsorbed by a unit weight of an adsorbent (e.g. Zeolite) and the equilibrium concentration (C_e). By equilibration of several different known quantities of adsorbent with a solution of known concentration of adsorbate, one can generated a plot that can be described by an equation that relates the amount adsorbed onto the solid and the equilibrium concentration of the solution at a given temperature. The plot shows the distribution of adsorbable solute between the liquid and solid phases at various equilibrium (C., Ng, et al., 2002). The three well-known isotherms are (i) Freundlich (ii) Langmuir, and (iii) BET adsorption isotherm (K., Steve, et al., 1998). There are two traditional approaches to quantitatively express the adsorption from solution process. "Freundlich isotherm" technique and the Langmuir isotherms

4.3.3 Freundlich Isotherm

The Freundlich isotherm is an empirical model, where q_e is the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_f and n are parameters that depend on the adsorbate and adsorbent.

$$q_e = K_f C_e^{1/n} \quad (1)$$

The equation can be changed to linear form and the temperature dependent constants K_f and $1/n$ can be found.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

Since Equation (8) is in the form of a straight line it is possible to evaluate the two constants based on the values of the slope and intercept of a suitable plot (Figure 10).

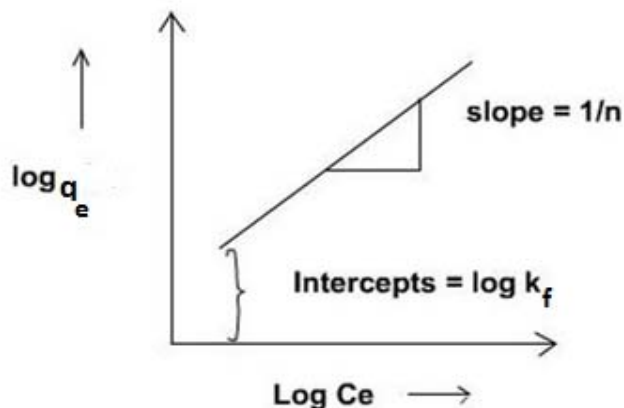


Figure 10. Freundlich Isotherm.

Source: (www.amrita.vlab.co.in/?sub=2&brch=190&sim=606&cnt=1)

The value of n is from the slope and substitute to solve for K_f

From the plot of $\log q_e$ vs. $\log C_e$, the Freundlich constants can be determined. K_f and n are Freundlich constants. The K_f is the adsorption capacity and n is the adsorption intensity, which

indicates the degree of non-linearity between solution concentration and adsorption. If $n=1$, the adsorption is linear; If $n < 1$, the adsorption is a chemical process; If, $n > 1$, the adsorption is physical process. The situation $n > 1$ is the most common and could be due to surface site distribution or any other factors causing a decrease in adsorbent-adsorbate interaction with increase in surface density (B.E, Reed and R., Matsumoto, 1993). The values of n between 1 and 10 represent the physical adsorption of metal ions on the adsorbent (G., Mackay et al., 1980; A., Ozer et al., 2006). A second common approach to data analysis is based on the work of Langmuir. Equation 3 illustrates the "Langmuir isotherm".

4.3.4 Langmuir Isotherm

The Langmuir isotherm assumes a uniform surface. It is represented by

$$q_e = \frac{q_m k_a C_e}{1 + k_a C_e} \quad (3)$$

The reciprocal of each side gives the linear form of the equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_a} \quad (4)$$

The graph of C_e/q_e against C_e can be plotted (Figure 11). The isotherm constants are the monolayer sorption capacity q_m and the K_a which can be calculated from the slope and the intercept of the plot.

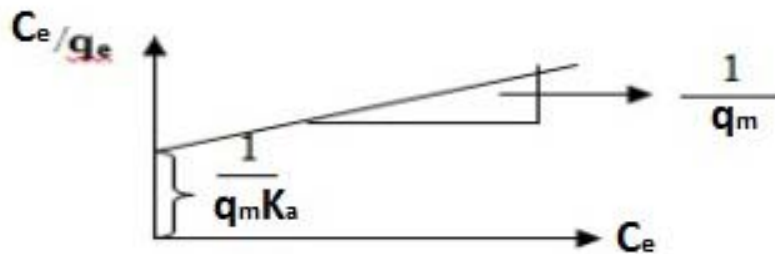


Figure 11. Langmuir Isotherm Plot.

Source

(<http://mimoza.marmara.edu.tr/~zehra.can/ENVE401/3.%20Adsorption%20Equilibria.pdf>)

The Freundlich equation (*Equation 2*) predicts that relative adsorption will increase indefinitely with the concentration in a logarithm trend, but the Langmuir equation (*Equation 4*) the relative adsorption will approach a finite limit as concentration increases. The difference in the prediction of concentration dependence is evidence that the Langmuir treatment is more realistic than the Freundlich model. This seems reasonable since there are actually a finite number of adsorption sites per gram of solid. When the adsorption surface is exhausted, corresponding to the maximum value of q_e , further increasing the solute concentration will have no effect on the amount of solute adsorbed.

4.4 Adsorption Procedure

Two standard procedures are usually applied to remove contaminants from water using adsorption viz;

- (i) Batch and
- (ii) Column procedures.

4.4.1 Batch Process

Adsorption studies were conducted by the batch and the column technique with synthetic solution of wastewater that contains arsenic chromium and uranium. The batch experiments to determine the adsorption isotherms of the metal ions (As, Cr and U) onto the zeolite adsorbent were done in 125-mL high density polyethylene plastic bottles. The bottles, air tight with a known mass of adsorbate, adsorbent concentration and constant volume, were placed on a shaker at a constant revolution per minute, allowing sufficient time for adsorption equilibrium. The experiments were conducted at room temperature in duplicates and the average values were used for further calculation and graphs. The pH of the solution was measured. The effects of various parameters on adsorption process were observed by varying the pH, adsorbent concentration and the normality of NaCl. The solution volume was kept constant. The amount of metal adsorbed per unit mass is calculated. The C_o and C_e are initial and equilibrium concentration ($\mu\text{g/L}$) respectively. The mass of the adsorbent is m (g) and V is the volume of solution (mL). Percent metal ion removal is calculated by the equation. The percentage of metal ion adsorbed is calculated by equation 5.

$$\% \text{Metal adsorptin} = 100 * \frac{(C_o - C_e)}{C_o} \quad (5)$$

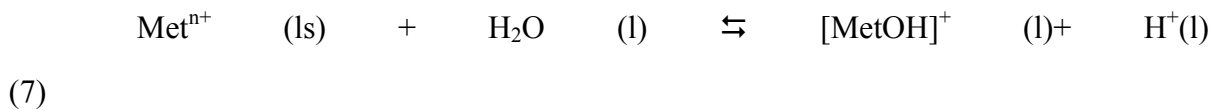
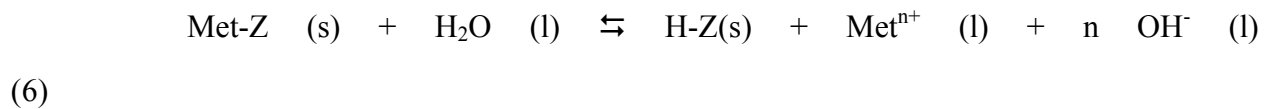
4.4.2 Column Process

The column process is used for the removal of metal ion in solution. Several parameters affect the cation adsorption by zeolite, such factors are mainly temperature, pH, the flow rate, the initial ion concentration, the presence of other competing ions in the solution, characteristics of the heavy metal being removed and solid-specific factors (particle size, surface dust, impurities in the zeolite sample). Results of test in the column operation are presented by breakthrough curves (Vukojević Medvidović N, *et al.*, 2006; Vukojević Medvidović N, *et al* 2007). One of the important properties of natural zeolite is regeneration and their re-use. Recent studies of

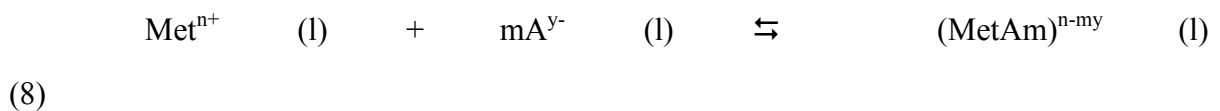
desorption efficiency of metal ions and regeneration of natural zeolite - clinoptilolite indicate that the process is reversible in most cases [Katsou E. *et al*, (2011).

4.5 Ion Exchange, Adsorption and Hydrolysis

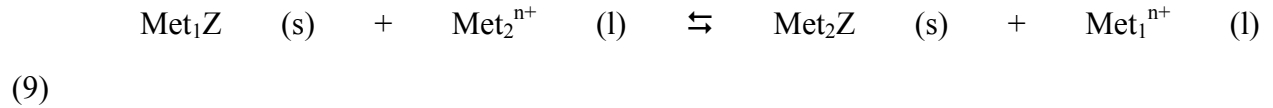
The processes of ion exchange and adsorption on natural zeolite occur concurrently with hydrolysis in aqueous solutions. The hydrolysis process is a reaction that follows the process of ion exchange (Caputo D, Pepe F., 2007). A good understanding of the hydrolysis of zeolite is of great importance to explaining the properties of zeolite. A sudden increase in the pH is usually noticed at beginning of the hydrolysis process. Where n - The charge number of exchangeable cations., Met – exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), Z – zeolite. The equation can be described as follows;



The OH^- ions cause an increase in the pH value of the system, reaction with and metallic ions happens simultaneously (Misaelides, P., 2011). The OH^- ions adsorb onto the surface of zeolite particles. Anions on the zeolite surface form stable complexes with exchangeable cations, depending on the stability constant (Fu, F., Wang, Q., 2011)



The hydrolyzed cations in the zeolite channel connected by weak electrostatic bonds to the basic aluminum-silicate structure are very mobile and able to exchange with the cations from the solution. The exchange of ions is preceded by the adsorption of ions from the solution to the surface of zeolite particles. A balance is achieved within the zeolite–solution system by a reversible reaction.



Met_1Z and Met_2Z - concentrations of exchangeable cations in zeolite (Z)

Met_2^{n+} and Met_1^{n+} - concentrations of exchangeable cations in the solution

The process of diffusion in zeolite-aqueous solution can be divided into several phases as illustrated in Figure 12: (I) Diffusion in solution, (II) Diffusion through the film of stagnant solution at the surface of the particle, (III) Diffusion in pores, and (IV) Ion exchange.

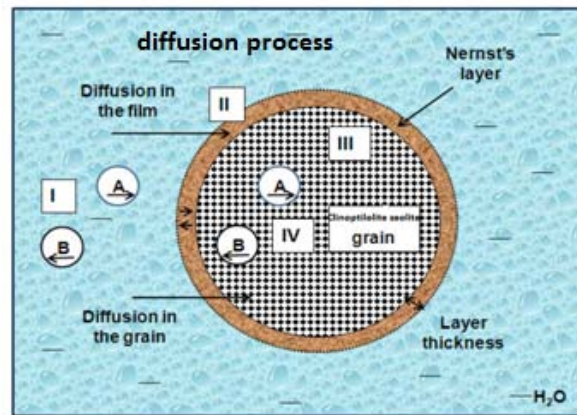


Figure 12. Diffusion Processes of Zeolite System in Aqueous Solution

(Source: Karmen Margeta, et al., 2013 Natural Zeolites in Water Treatment – How Effective is Their Use).

Chapter 5: Diffusion Dialysis

5.1 Background

Mineral acids are utilized for many industrial applications which include cleaning, activating, anodizing and pickling of raw metal stock and finished parts. For example mineral acid baths are employed for the removal of surface oxides from metal parts after initial forming and manufacturing steps, after cleaning and prior to painting and plating operations. During use, an excessive concentration of metal ions can limit the performance of the pickling bath. Present methods for maintaining acceptable metal concentration include make up of a completely fresh acid bath and treatment or offsite disposal of the dumped solution. These disposal methods generate wastes that cause health and environmental problems. Due to their wide use, industry is recognizing the economic and environmental benefits of extending the life of mineral acid pickling baths. There are technologies currently available that can offer these benefits. Two of these technologies are diffusion dialysis and acid sorption.

5.2. Diffusion Dialysis Theory

Diffusion is a process in which a solute moves from an area of high concentration to an area of low concentration wherein the concentration gradient of the system is the driving force for mass transfer. Solutes can be separated from each other by the differences in their diffusivity. Dialysis is a phenomenon in which a solute in solution permeates through a diaphragm. The membrane acts as a diaphragm through which a solute at a high concentration will diffuse into a similar solvent containing lower concentrations of that solute.

Diffusion Dialysis is a membrane separation technology that solely depends on concentration gradient between a dilute solution (de-ionized water) and a concentrated solution (contaminated acid) to effect transport of ions. This technology employs a technique in which the two solutions are physically separated by an anion permeable and ion selective membrane. The membrane acts as the barrier that retards diffusion of the metal ions and allows permeation of the acid. The movement of ion movement across the membrane occurs as a result of high concentration

difference between the solute (acid) and the solvent (D.I. water). The anion permeable membrane exhibits a strong affinity for acid absorption and low affinity for cations. Thus negatively charged ions migrate freely through the membrane while movement of the positively charged metal ions is retarded.

In order to maintain charge equilibrium as required by the law of electro-neutrality, either anions need to exchange through the membrane at an equal rate in both directions, or each anion that diffuses must be accompanied by an associated cation (Figure 15). Due to the extremely small physical size of the hydrogen ion, it is easy for it to move through the perm-selective membrane in conjunction with an anion such as chloride, fluoride, nitrate, phosphate, or sulfate. A typical diffusion dialysis system is comprised of a stack of membranes separated by solution compartments. The membranes are usually prepared from copolymers of 4-vinylpyridine and divinylbenzene. It is customary in diffusion dialysis to feed the metal-contaminated acid stream into the bottom of the membrane stack and de-ionized water into the top of the stack. The acid solution flows upward across one side of the membrane, and the water flows downward across the opposite side of the membrane. A countercurrent flow arrangement (Figure 14) ensures the most effective concentration gradient throughout the entire membrane stack. Acid feed and de-ionized water head tanks are physically located above the membrane stack to allow head pressure from the height difference to push the fluid through the membrane stack. The flow rate devices (measuring pumps or control valves) which promote optimum flow rate of the exiting streams and optimize ion migration process are typically placed on the lines exiting the stack. The two streams exiting the process are referred to as diffusate, the acid rich and metal-depleted solution, and dialysate (the depleted acid and metal-rich solution). Figure 13 schematically illustrates a typical diffusion dialysis system. Because the exclusion of cations from the anion-exchange membrane is not complete, some leakage of metal ions through the membrane does occur. The rate of metal leakage and the rate of acid recovery are functions of solution-membrane contact time. Given the fixed membrane area in a dialysis stack, the recovery equilibrium is controlled by the solution flow rates. Slower solution flow rates will maximize the percent of acid that is

recovered and cause a higher leakage rate. Faster solution flow rates will maximize the throughput volumes and minimize the metal leakage at the expense of recovery efficiency. Therefore, a balance is sought which maximizes the percent recovery of acid and minimizes the percent leakage of metal ions.

5.3 Process Considerations

The performance of a diffusion dialysis system is influenced by several variables that include acid and metal concentrations, solution flow rates, and osmosis within the membrane stack. The efficiency of acid recovery and metal rejection largely depends on the concentrations of acid and metals. A feed solution with high acid concentration will typically give better percent acid recovery in the diffusate when compared to one with low acid concentration. This is due to the greater concentration gradient across the membrane. Conversely, a high concentration of metal in the feed acid tends to allow greater leakage of metal into the diffusate. Varying the ratio of flow rates allows the system to achieve different results. Operation of the system with the diffusate flow rate higher than the dialysate flow rate results in recovery of acid at a lower concentration and higher metal rejection. Operation with the diffusate flow rate lower than the dialysate flow rate results in higher acid concentration and lower metal rejection. This characteristic of the diffusion dialysis process allows flexibility to tailor the process to various applications. Because of the small membrane area and large solution lines in the laboratory diffusion dialysis system, a period of 24 to 36 hours was required to reach equilibrium after initial startup. This is necessitated by the slow nature of the concentration gradient driven process and the corresponding long residence time requirement of the solution in the membrane stack. Periodic sampling (once every 8 to 12 hours during start-up) and analysis of the diffusate and dialysate is necessary to monitor performance and detect the equilibrium point. Sampling and analysis frequency can be reduced once the process has reached equilibrium. Actual operation of a diffusion dialysis system is relatively simple and does not require much operator intervention.

Main requirements for proper operation are maintaining constant diffusate and dialysate flows and recording the volume of waste acid and de-ionized water fed to the system. It is very easy to study a diffusion dialysis system prior to observing one in operation and assume that the volume of feed acid fed to the system equals the volume of dialysate produced, or that the de-ionized water volume fed to the system equals the volume of diffusate produced. This, in fact, is a misconception. The reason for this discrepancy is osmotic transport of water through the membrane. The concentration gradient causes acid to diffuse through the membrane into the deionized water. The same gradient causes osmosis, water transport through the membrane into the acid. The effect of osmosis, in this case, is that the feed acid stream becomes diluted. The effect of osmosis can be minimized by adjustment of the diffusate and dialysate flow rates. However, in addition to flow rates, acid and metal concentrations play a role in osmosis. A mass balance on the process may indicate that the system is recovering 96% of the acid feed. However, due to osmosis, the acid recovered in the diffusate will not be 96% of the original feed acid concentration.



Figure 13. Diffusion Dialysis

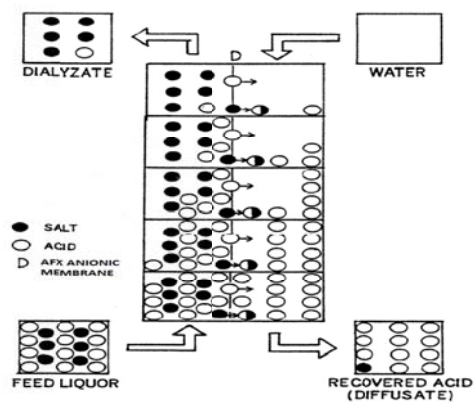


Figure 14. Diffusion Dialysis Operation

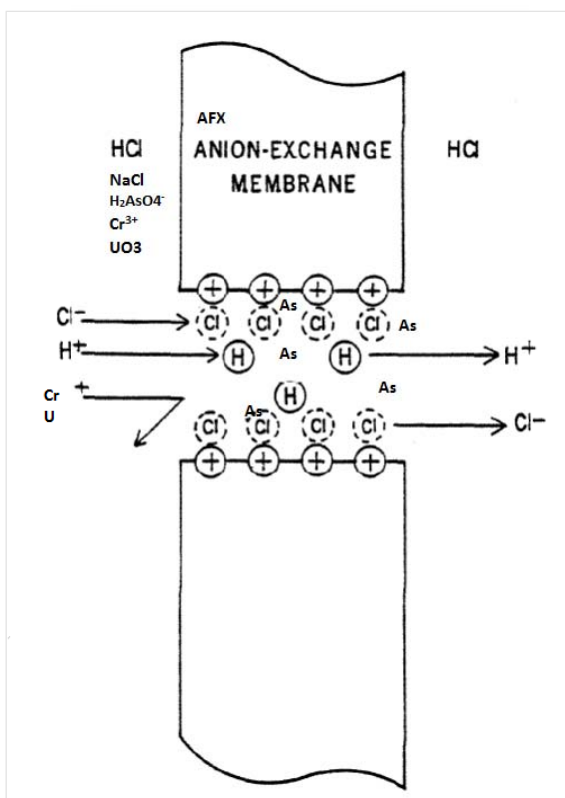


Figure 15. Mechanism of HCl Transport through Anion-Exchange Membrane.

Sources for (Figure 14) and (Figure 15): Dhuru P and Steven J. P., Recovery and recycling of spent acid in the metals processing industry <http://www.brownandcaldwell.com>.

5.4 Process Operation

Several physical variables affect the operation and performance of a diffusion dialysis system. These variables are acid and metal concentrations, solution flow rates, and osmosis within the membrane stack. Acid and metal concentrations in the feed acid greatly affect the efficiency of acid recovery and metal rejection.

5.5 Performance Evaluation

The system performance of a diffusion dialysis performance is calculated from the recorded flow rates and concentrations of the feed acid, diffusate, and dialysate streams. The two main performance indicators are the percent acid recovery in the dialysate and the percent metal rejection in the diffusate. Percent acid recovery is determined using mathematical Equation 10. Percent metal rejection is determined using mathematical equation below.

$$\% \text{ Acid recovery} = \frac{100 \times (F_{\text{diff}} \times C_{\text{acid diff}})}{[(F_{\text{diff}} \times C_{\text{acid diff}}) + (F_{\text{dial}} \times C_{\text{acid dial}})]} \quad (10)$$

Where,

F_{diff} = Diffusate flow rate

$C_{\text{Acid diff}}$ = Diffusate acid concentration

F_{dial} = Dialysate flow rate

$C_{\text{Acid dial}}$ = Dialysate acid concentration

$$\% \text{ Ion Rejection} = \frac{100 \times (F_{\text{dial}} \times C_{\text{Metdial}})}{[(F_{\text{diff}} \times C_{\text{Met diff}}) + (F_{\text{dial}} \times C_{\text{Met dial}})]} \quad (11)$$

Where,

F_{dial} = Dialysate flow rate

$C_{\text{Met dial}}$ = Dialysate metal concentration

F_{diff} = Diffusate flow rate

$C_{\text{Met diff}}$ = Diffusate metal concentration

Chapter 6: Materials and Methods

6.1 Chemicals

- Reagent :
- As^{5+} 100ug/mL in H_2O from High Purity Standards
- 2% HNO_3 Chromium from High Purity Standards
- Uranium Oxide (+6) UO_3 in 3% nitric acid 1000ppm Ricca Chemical Company
- Hydrochloric acid
- Sodium Hydroxide

6.2 Materials

- Shaker
- pH Meter
- Conductivity Meter
- Clinoptilolite beds
- AFX membrane
- Magnetic stirrer and hot plate
- Stop watch
- Mesh
- 125-mL high density polyethylene plastic bottles
- Clamps and Monkey bars
- PVC adsorption column, tubing
- Pipette
- Burette
- Phenolphthalein pillows
- Beakers, plastic bottles, volumetric flask, graduated cylinder, Erlenmeyer flask
- Water Tanks

- Color Markers, Tape and Labels

6.3 Methods

The stock solution of chromium with concentration of 500 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$ was prepared by adding a known volume of reagents to de-ionized water in a volumetric flask and filling up to the mark with de-ionized water. This solution was then diluted to obtain standard solutions containing different concentrations of metals. Hydrochloric acid and/or sodium hydroxide solutions were used throughout experiments to adjust the pH of the solution.

6.4. Zeolite-Clinoptilolite

The properties and characteristic of the clinoptilolite were extracted from the work done by Camacho et al (2010) on clinoptilolite from the same source.

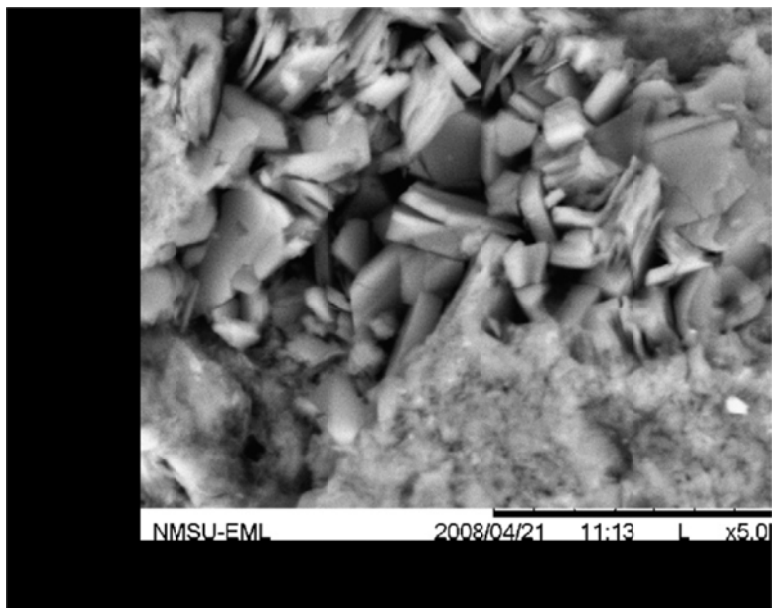


Figure 16. SEM Image of the Natural Clinoptilolite (Magnification = 5.0 K, ScaleBar = 20 μm).

Source: (L.M. Camacho et al. / Journal of Hazardous Materials 175 (2010) 393–398)

Table 1. Pore Properties of Clinoptilolite.

BET surface area (m ² /g)	18
Langmuir surface area (m ² /g)	118
BJH pore volume (cm ³ /g)	0.065
H-K maximum pore volume (cm ³ /g)	0.027
BJH average pore size (Å)	166
H-K median pore size (Å)	95

6.5 Batch Experiments

In this thesis, batch experiments were performed with different dosages (50, 100, 250, 500 and 1000µg/L) of heavy metals and weighed amounts of clinoptilolite (typically 1 g) with the optimum contact period of 48 h and constant pH of 6.5. Batch adsorption equilibrium study was carried out at room temperature (average is about 25°C) using 100 mL composite wastewater with 0.2M NaCl with above mentioned dosages in separate bottles. The bottles were shaken in a rotary shaker (Figure 17) at 100 rpm for an average contact period of about 48 h and the equilibrium concentration of the samples were analyzed for arsenic, chromium and uranium concentration using the ICP-OES. Different models were used to analyze the data in order to establish the most appropriate adsorption model.



Figure 17. The Shaker

6.6 Variation of pH with Time

6.6.1 Variation of pH of Arsenic Solution with Time

A batch of stock solution containing 500 $\mu\text{g/L}$ of arsenic was prepared from a calibration standard solution As^{5+} 1000 $\mu\text{g/L}$ in H_2O from High Purity Standard Company. Three samples of 110 ml containing 100 $\mu\text{g/L}$ of arsenic were prepared from the stock solution and adjusted with 0.10M NaOH or 0.1M HCl solution to pH 7.0. A 10-mL sample of each of the solutions was taken out to test if the initial concentration is true. The 100 ml of solution left in the bottles was then mixed with 1 g of clinoptilolite zeolite in 125 mL high density polyethylene plastic bottles. The bottles were tightly closed and placed in an automatic shaker at constant temperature (25°C) and agitation speed (100 rpm). A standard pH meter was used during the batch adsorption experiments to monitor the changes in the pH of the solutions every half hour during the first hours and then with increased time interval.

6.6.2 Variation of pH of Arsenic Solution with Time plus NaCl

Arsenic+NaCl- Samples with two replicates were prepared with the same concentration (100 µg/L), but a known molar concentration of NaCl was added to simulate brackish water. Other parameters such as temperature (25°C) and agitation speed (100 rpm) remained constant. A standard pH meter was used during the batch adsorption experiments to monitor the changes in the pH of the solutions every half an hour during the first hours and then with increased time interval.

6.6.3 Variation of pH of Chromium Solution with Time

Three samples of 110 ml containing 100 µg/L of Chromium were prepared from the stock solution and adjusted with 0.10M NaOH or 0.1M HCl solution to pH 7.0. A 10-mL sample of each of the solutions was taken out to test if the initial concentration is true. One gram of clinoptilolite zeolite was added to the 100 mL of chromium solution in 125 mL high density polyethylene plastic bottles. The bottles were tightly closed and placed in an automatic shaker (model lab-line Orbit No. 359) at constant temperature (25 °C) and agitation speed (100 rpm). A standard pH meter was used during the batch adsorption experiments to monitor the changes in the pH of the solutions every half an hour during the first hours and then with increased time interval.

6.6.4 Variation of pH of Chromium Solution with Time plus NaCl

Chromium was added with sodium chloride samples with two replicates prepared with the same concentration 100 µg/L, but a known molar solution of NaCl was added to simulate brackish water. Other parameters such as temperature (25°C) and agitation speed (100 rpm) remained constant. A standard pH meter was used during the batch adsorption experiments to monitor the changes in the pH of the solutions every half an hour during the first hours and then with

increased time interval.

6.6.5 Variation of pH of Uranium Solution with Time

Three samples (110 mL each) containing 100 µg/L of uranium were prepared from the stock solution and adjusted with 0.10M NaOH or 0.1M HCl solution to pH 7.0. A 10-mL quantity of each of the sample solutions was taken out to test if the initial concentration is true. The 100 mL of solution left in the bottles was then mixed with 1 g of clinoptilolite zeolite in 125 mL high density polyethylene plastic bottles. The bottles were tightly closed and placed in an automatic shaker at constant temperature (25°C) and agitation speed (100 rpm). A standard pH meter was used during the batch adsorption experiments to monitor the changes in the pH of the solutions every half an hour during the first hours and then with increased time interval.

6.6.6 Variation of pH of Uranium Solution with Time plus NaCl

Other samples with two replicates were prepared with the same concentration 100 µg/L, but a known molar solution of NaCl was added to simulate brackish water. Other parameters such as constant temperature (25°C) and agitation speed (100 rpm) for 60 h remained the same. A standard pH meter was used during the batch adsorption experiments to monitor the changes in the pH of the solutions every half an hour during the first hours and then with increased time interval.

6.6.7 Variation of pH of Metals Solution with Time

Methodology: Three samples of 110 mL containing 100 µg/L of all the three metals (As+Cr+U) were prepared from the stock solution and adjusted with 0.10M NaOH or 0.1M HCl solution to pH 7.0. A 10-mL sample of each of the solutions was taken out to test if the initial concentration is true. The 100 mL solution left in the bottles was then mixed with 1 g of clinoptilolite in 125 mL high density polyethylene plastic bottles. The bottles were tightly closed and placed in an

automatic shaker (model lab-line Orbit No. 359) at constant temperature (25°C) and agitation speed (100 rpm).

A standard pH meter was used during the batch adsorption experiments to monitor the changes in the pH of the solutions every half an hour during the first hours and then with increased time interval.

6.6.8 Variation of pH of Metals Solution with Time plus NaCl

Samples with two replicates were prepared with the same concentration 100 µg/L, but a known molar solution of NaCl was added to simulate brackish water. Other parameters such as constant temperature (25°C) and agitation speed (100 rpm) remained the same. A standard pH meter was used during the batch adsorption experiments to monitor the changes in the pH of the solutions every half an hour during the first hours and then with increased time interval. The pH meter must be calibrated before use. Calibration solutions are prepared with pH buffer tablets.

6.7 Variation of pH of metals Solution with Adsorption

Methodology: Three samples of 110 ml containing 100 µg/L of all the three metals (As+Cr+U) were prepared from the stock solution and adjusted with 0.10M NaOH or 0.1M HCl solution to pH 3, 5, 7 and 9. A 10-mL sample of each of the solutions was taken out to test if the initial concentration is true. The 100 ml solution left in the bottles was then mixed with 1 g of clinoptilolite zeolite in 125-mL high density polyethylene plastic bottles. The bottles were tightly closed and placed in an automatic shaker at constant temperature (25°C) and agitation speed (100 rpm) for 50 h.

6.7.1 Variation of pH of Metals Solution with Adsorption plus NaCl

Other samples with two replicates were prepared with the same concentration (100 µg/L) of all three metals, but a known molar solution of NaCl was added to simulate brackish water. Other parameters such as temperature (25°C) and agitation speed (100 rpm) remained constant. The samples were removed from the shaker after 50 h and analyzed using the ICP-OES.

6.7.2 Variation of NaCl Molarity with Adsorption

Two replicates samples were prepared with the metals concentration (100 µg/L) and sodium chloride of different molarities (0.5M, 1M, and 2M) to simulate brackish water. Other parameters such as temperature (25°C), time and agitation speed (100 rpm) remained constant. The samples were removed from the shaker after 50 h and analyzed using the ICP-OES.

6.8. Column Experiments

Column experiment was performed to establish the breakthrough curve, breakthrough time and exhaustion time. Most importantly, to measure and compare the difference in adsorption capacity between the batch and the column experiment. A break through curve is a curve showing the relative adsorption of an adsorbate in a coulumn with time. The breakthrough point on the curve is the point in operation where the column is in equilibrium with the influent water. The exhaustion is the point where all the capacity of the adsorbent is fully utilized. At this point, the effluent concentration equals the influent concentration.

6.8.1. Adsorption in Column with Clinoptilolite

Before starting a run, the bed was rinsed by pumping de-ionized water upwards through the column. This preparation was intended to get the bed wet and to remove all bubbles in the column. The bed of clinoptilolite was kept submerged throughout the runs to avoid air

entrapment in the beds. The column test was carried out as half-column bed fill and full-column bed fill with clinoptilolite natural zeolite bed mass of 17.64 g and 35.48 g respectively. Composite wastewater (As+Cr+U) concentration of 500 $\mu\text{g/L}$ with 0.2M NaCl was pumped continuously through a column of height 32 cm and internal diameter (I.D.) 1.1 cm by a peristaltic pump with a flow rate of 1.32 mL/min. The column bed depth is 15 cm to 30 cm at half column to full column respectively. The setup of the column study is shown in Figure 24. For practical reason the water passed through the column in an upward flow to achieve more uniform contact with the zeolite and eliminate any bubbles within the bed. The effluent samples were collected at various time intervals. Starting with small time intervals and gradually increasing the time until a total run time of 50 hours was attained. The pH and the conductivity of the effluent were also recorded and analyzed for arsenic, chromium and uranium concentration by ICP OES. All breakthrough curves were plotted taking into account the cation concentration in the outlet samples as a function of the running time (C/C_0 versus t). From the results of analysis a set of breakthrough curves was developed, and breakthrough times were obtained.

6.8.2 Analysis of Column Data

The amount of metal adsorbed by the zeolite was obtained by finding the area under the breakthrough curve up to the break through point and multiplied with the flow rate. The uptake capacity (q , mg/g) of the zeolite was calculated as the ratio of the mass of metal treated (mg) to the mass of zeolite used (g).

Mass of metal ions adsorbed (mg) is the product of concentration C_e (mg/ml), flow rate mL/min and time (min).

The q mg/g is the ratio of the mass of metal ions adsorbed (mg) to the mass of zeolite (g).

6.8.3 Regeneration with Hydrochloric Acid

After the bed exhaustion, a de-sorption experiment was carried out using 0.1N HCl. The column was first rinsed with de-ionized water for couple of hours to remove the solutions in the column. Hydrochloric acid (500 mL) flowed upward through the column at the same flow rate for adsorption test. The pH and the conductivity of the effluent were also recorded. Samples from the column were collected at regular intervals, and the samples were analyzed for arsenic, chromium and uranium concentration by ICP OES.



Figure 18. Column Experiment

6.9 Acid Recovery-Diffusion Dialysis

The experiment was set up as shown below. The membrane used was an AFX anion-exchange membrane and the pump is a Masterflex C/L dual-channel variable-speed tubing pump, 1 to 6 rpm, which allows the pumping of both the feed and the water at the same rate. The diffusion dialysis (DD) stack has five membranes, each of area 200 cm^2 (0.02 m^2). Solutions flowed through compartments 10 cm wide, 20 cm long and 0.075 cm thick formed by rubber perimeter gaskets and plastic netting in the cavity. The spent acid from the zeolite regeneration is the feed solution for the diffusion dialysis. The de-ionized water and feed solutions were kept in 2-L tanks. Prior to the experiments, the membranes were conditioned for one day with DI water

circulating through the stack to keep the membrane wet and remove any bubbles in the stack. The de-ionized water was boiled (to remove dissolved gases) and allowed to cool to room temperature. The dual channel pump was connected to the two chambers. Waste acid flowed countercurrent to the de-ionized water stream in the membrane stack. This permits the acid concentration in the recovered acid stream to approach the concentration in the waste acid and the acid concentration in the depleted acid stream to approach zero. Samples were collected at some point in time, and the pH and conductivity were measured. Samples of the diffusate and the dialysate were titrated against 0.2M NaOH to determine the acid concentration in these two effluent streams. The remaining sample volumes were later analyzed with the ICP OES to determine the amount of metal ions present in the two effluent streams. The approach to steady state for titration values provided the indication of when to stop the experiment. The data and the result were analyzed with equations (12 and 13) to determine the percentage of acid recovery, the percentage of metal rejection and the performance of the diffusion dialysis.

$$\% \text{ Acid Recovery} = \frac{100 \times C_f}{C_i} \quad (12)$$

C_i = Initial Concentration of Acid

C_f = Final Concentration of Acid

$$\% \text{ Metal Rejection} = \frac{100 \times (C_{mf})}{C_{mi}} \quad (13)$$

C_{mi} = Initial Concentration of Metal

C_{mf} = Final Concentration of Metal

6.9.1 Performance Data

Data collected in diffusion dialysis experiments include the measured flow rates for the product streams from the diffusion dialysis units and the chemical compositions of the spent acid, recovered acid, and depleted acid. Calculated results included the flow rates for the spent acid and de-ionized water entering the membrane stacks and the percent acid recoveries and metals rejections for each of the sets of samples taken. The values for the flow of spent acid and de-ionized water were calculated based on an acid and volume balance around the membrane stack. The acid recoveries and metal rejections were calculated based on the chemical analyses of the two product streams and the measured flow rates of the two product streams from Equations (10 and 11). Each specific acid recovery was calculated by dividing the mass flow rate of the acid anion in the recovered acid stream by the sum of the mass flow rate of the acid anion in the recovered and depleted acid streams. On the other hand, the metal rejections were calculated by dividing the mass flow rate of the metal in the depleted acid stream by the sum of the mass flow rate of the metal in both product streams.

Chapter 7: Result and Discussion

7.1 Change of pH of Arsenic Solution with Time

Measurement of pH with adsorption time was conducted to observe the pH variation during adsorption and to determine the minimum time required for obtaining adsorption equilibrium. Figure 19 displays the experimental data for a solution with initial pH values of 7.0. The overall trends of pH variation with time for these two sets of experiments for solutions containing arsenic only (XA) and arsenic with NaCl (XB) are almost the same. During the first 2 hours, the pH of XA and XB decreased from 7 to 6.61 and 6.2 respectively then increased slowly. After the initial decrease, the pH of the two solutions increased steadily for the next 48 hours before it stabilizes. This is an indication of the minimum hours requires before bed exhaustion.

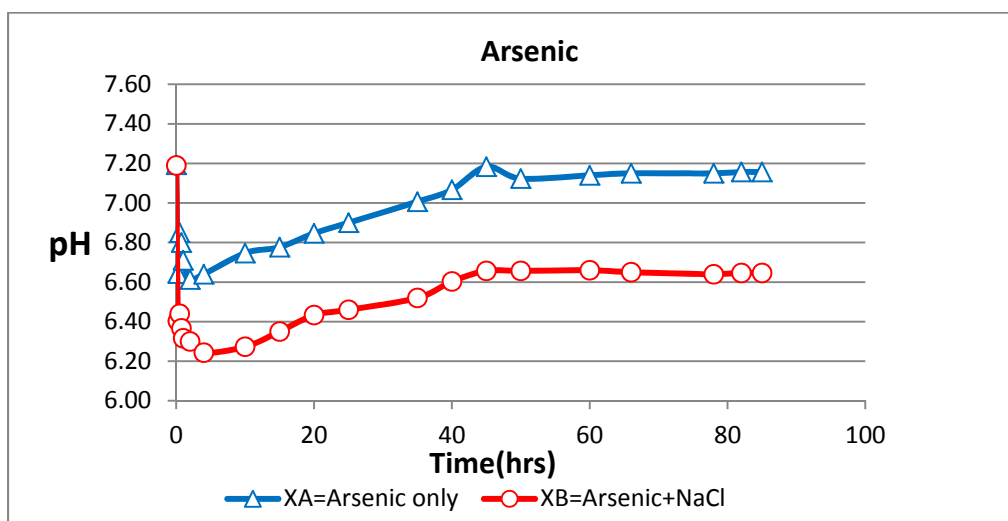


Figure 19. Variation of Arsenic Ion Solution pH with Adsorption Time on Natural Clinoptilolite at 25 °C and Initial Concentration of 100 µg/L with NaCl added and without NaCl.

7.2 Change of pH of Chromium Solution with Time

Measurement of pH with adsorption time was conducted to observe the pH variation during adsorption and to determine the minimum time required for obtaining adsorption equilibrium. Figure 20 displays the experimental data for a solution with initial pH values of 7.0. The overall trends of pH variation with time for these two sets of experiments at chromium only (YA) and chromium with NaCl (XB) are almost the same. During the first 2 h, the pH of YA and YB decreased from 7 to 6.91 and 6.63 respectively then increased slowly. After the initial 4 h, the pH of the two solutions increased steadily for the next 48 h before it stabilizes.

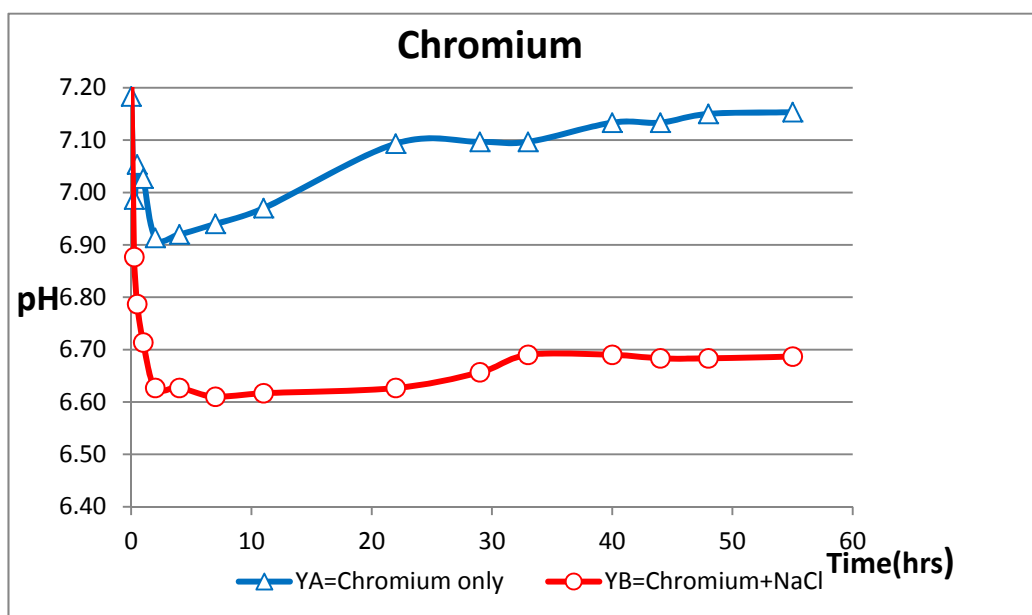


Figure 20. Variation of Chromium Ion Solution pH with Adsorption Time on Natural Clinoptilolite

at 25 °C and Initial Concentration of 100 µg/L with NaCl added and without NaCl.

7.3 Change of pH of Uranium Solution with Time

Figure 21 Discussion - An experiment was conducted to observe the pH variation during adsorption and to determine the minimum time required for obtaining adsorption equilibrium. Figure 21 displays the experimental data for a solution with initial pH values of 7.0. The overall trends of pH variation with time for these two sets of experiments with uranium only (ZA), and uranium with NaCl (ZB) are almost the same as those observed for arsenic and chromium. During the first two hours the pH of ZA and ZB decreased from 7 to 6.9 and 6.52 respectively then increased slowly. The change in the pH during the first 5 h of the adsorption process is a result of neutralization reaction, adsorption and/or ion-exchange reactions between the uranium and the zeolite. Camacho *et al* observed similar phenomena when removing uranium from groundwater by natural clinoptilolite zeolite:

After the initial 5 h, the pH of the two solutions increased steadily for the next 40 h before it stabilizes. This is an indication of uranium removal by physical adsorption and ion-exchange.

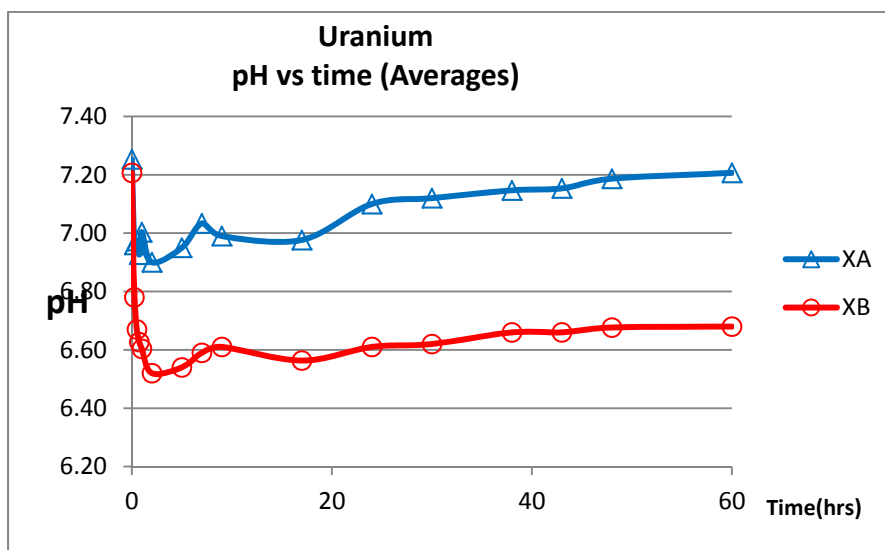


Figure 21. Variation of Uranium Ion Solution pH with Adsorption Time on Natural Clinoptilolite at 25 °C and Initial Concentration of 100 µg/L with NaCl added and without NaCl.

7.4 Change of pH of Metal Ions Solution with Time

Measurement of the variation of pH with adsorption time was conducted to observe the pH variation during adsorption and to determine the minimum time required for obtaining adsorption equilibrium. Figure 22 displays the experimental data for a solution with initial pH values of 7.0. The overall trends of pH variation with time for these two sets of experiments all the three metals only (MA) and Metals with NaCl (MB) are almost the same as previously observed with the separate solutions of these metals. During the first two hours the pH of MA and MB decreased from 7 to 6.99 and 6.83 respectively then increased slowly. After the initial 3 h, the pH of the two solutions increased steadily for the next 20 h before it stabilizes. This is an indication of metal removal by physical adsorption and ion-exchange. It was also observed that the XA, uranium solution without NaCl returns to the initial pH 7 before stabilizing, but the XB, arsenic solution with NaCl, did not return to initial pH before stabilizing.

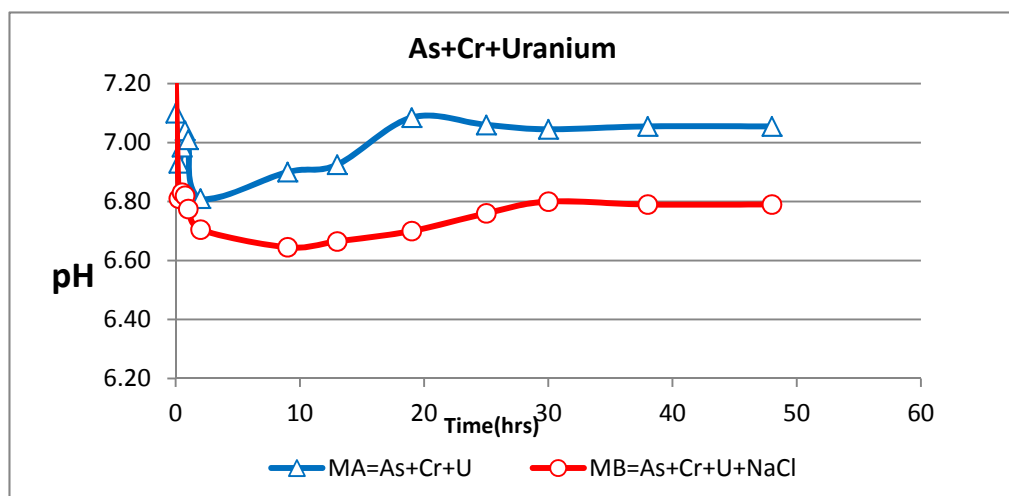


Figure 22. Change of pH of the Solution (all the three metals) with Time

7.5 Discussion (pH vs Time)

The graph of pH with time for the three metals follows the same pattern. This is an indication that the three metals undergo similar sorption reaction. The pH dropped at the initial stage and increased rapidly until it stabilized. Camacho *et al.*, (2010) observed similar phenomena when removing uranium from groundwater by natural clinoptilolite zeolite. Filippidis and Kantiranis, (2007) observed the same phenomena by adding Ca-rich clinoptilolite zeolite into an acidic water stream and a basic water stream. The increase in pH from the first 2 h of the adsorption process is a result of neutralization reaction, and this is due to the amphoteric nature of the zeolite (Camacho *et al.*, 2010) After 4 hours there was a noticeable increase in pH. The created OH^- in (Equation 11) during the hydrolysis process is the reason for the increase in pH value of the system. This is also an indication of initial rapid adsorption due to the availability of positively charged surface of adsorbent for the metal ions in solution. Increase in the concentration of OH^- ions at the beginning of hydrolysis causes OH^- ions to adsorb onto the surface of zeolite particles, which in turn causes opening of the surface layer of zeolite particles. The metal ion and OH^- form complexes at the surface of the zeolite.

After the hydrolysis reaction, ion exchange begins and this was noticed at about 24 hours. The late slow increase in the pH after this is due to electrostatic hindrance and repulsive force caused by the already adsorbed negative charged ions in solution. It can be seen that the total time required for the pH to stabilize is 48 hours. The average pH reached to stability for the three metals at 6.8 (with no sodium chloride added) and 7.1 when sodium chloride was added.

7.6 Change in Concentration of Metals Solution with pH

It is evident that pH plays an important role in the adsorption of the three metals. The graph shows that the final concentration is lower than the initial concentrations of the metal ions. This indicates that the removal of the three metal ions in solution occur at different pH from 3 to 9.

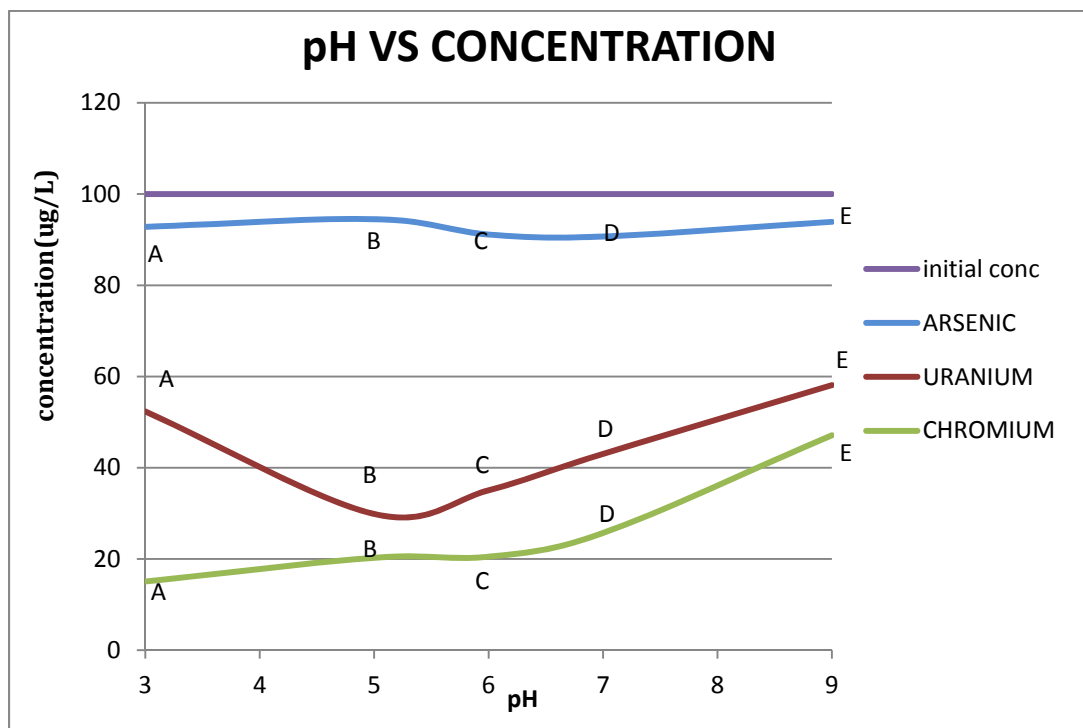


Figure 23. Change in Concentration of Metals Solution with pH

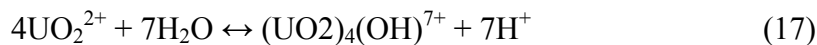
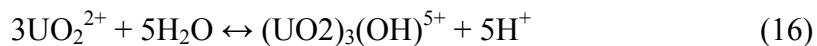
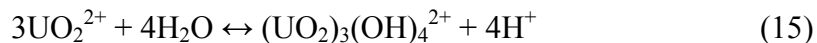
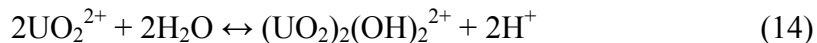
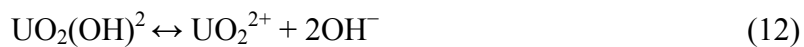
7.7 Discussion-pH with Concentration

Arsenic; as observed from the graph (Figure 23), the clinoptilolite is not effective in removing arsenic from the solution. The maximum uptake of arsenic ion occurs at pH 6. Both pH and the redox are important in assessing the fate of arsenic in water. According to Figure 2, arsenic acid As(V) occurs majorly in the form of univalent H_2AsO_4^- between pH 2.3 and pH 6.8, HAsO_4^{2-}

dominates between pH 6.8 and pH 11.6. The trivalent form (AsO_4^{3-}) dominates at the highest pH values, while the neutral form (H_3AsO_4) dominates at the lowest (acidic) pH. At the pH of 6, the species adsorb as the univalent H_2AsO_4^- , which is attracted to positive charge surface sites of the clinoptilolite. Camacho, et al., observed the familiar result when removing arsenic from groundwater by MnO_2 modified natural clinoptilolite zeolite.

Uranium; The adsorption of uranium by clinoptilolite increased with increased pH from 3 to 5.5, then decreased gradually as the pH of the solution increased. The minimum adsorption of uranium occurred at 9 while the maximum adsorption occurs at 5.5. Camacho *et al.*, (2010) observed similar phenomena when removing uranium from groundwater by natural clinoptilolite zeolite. This behavior can be explained by the speciation of uranium at different pH in water. The presence of hydrolysis products of uranium (VI) such as mononuclear and polynuclear uranium affect adsorption (Baes, C. F. et al., 1976).

The uranyl (UO_2^{2+}) ion dominates at lower pH ($\text{pH} < 3$) while its mononuclear hydrolysis product, $\text{UO}_2(\text{OH})^+$, is the dominant species at pH 3 (Equation 13). At pH from 3 to 5 the polynuclear products $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, and $(\text{UO}_2)_3(\text{OH})^{5+}$ are present and adsorbed according to Equations (14, 15, and 16). At pH 5, these species can be readily adsorbed by the clinoptilolite then gradual decrease in adsorption at pH higher than 6 due to the absence of these polynuclear species (P. Misaelides et al., 1995).



The chromium ion is the most adsorbed of the three ions. The adsorption decrease as the pH of the solution increases. The adsorption increased from acidic medium to pH 6, and it decreased as the pH increased. Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the adsorbent. Hence, metal sorption is critically linked with pH. Not only do different metals show different pH optima for their sorption, but the optimum pH may also vary from one kind of adsorbent to another.

7.8 Effect of Sodium Chloride

The diagram below shows that the molarity of sodium chloride affects the adsorption of metal ion in solution. The molarity increased from 0.05 M to 0.2 M, and the concentration of adsorbed metal ion increased in the same trend. It was observed that the NaCl added has an effect on the structure or adsorption capacity of the zeolite. The Na^+ ion is the most weakly bound ion in clinoptilolite and was exchanged with the cations in solution. The sodium chloride adsorbed on the zeolite surface forms oxi-hydroxides, which then form stable complexes with the anions in solution. The NaCl must have created an adsorption layer on the zeolite surface and changed the surface charge on zeolite. Further effect of adding sodium chloride was investigated and described in Figures 25, 26, and 27. Chromium is most adsorbed compared to arsenic and uranium while the addition of NaCl increased the adsorption capacity of zeolite by 29 % in arsenic 65 % in chromium and 77 % in uranium.

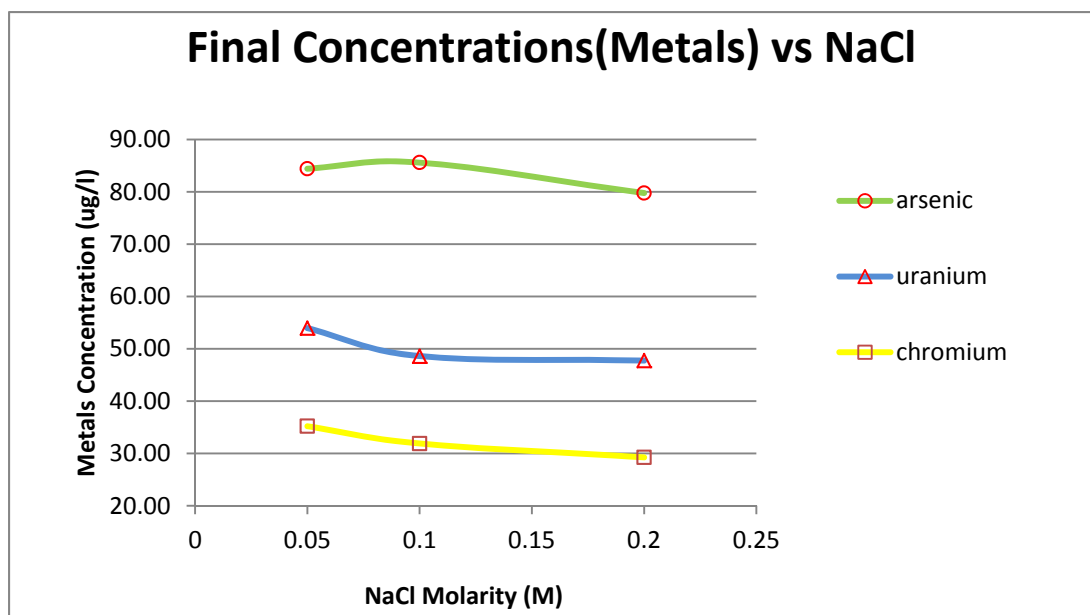


Figure 24. Effect of Sodium Chloride on Adsorption

7.8.1 All Metals are in Solution with Zeolite + NaCl (RED)

Figures 25-26 Discussion-It is observed that chromium is the most adsorbed. Irrespective of the influence of NaCl, the selective adsorption is $Cr > U > As$. The chromium is most adsorbed, while the arsenic is less adsorbed. There is less adsorption of uranium when the metals are together. The adsorption studies showed low affinity by clinoptilolite for the removal of Arsenic (37.19%) compared to both chromium (88.62%) and uranium (87.47%) at initial maximum concentration of 1000 ($\mu\text{g/L}$) in the multiple component adsorption system.

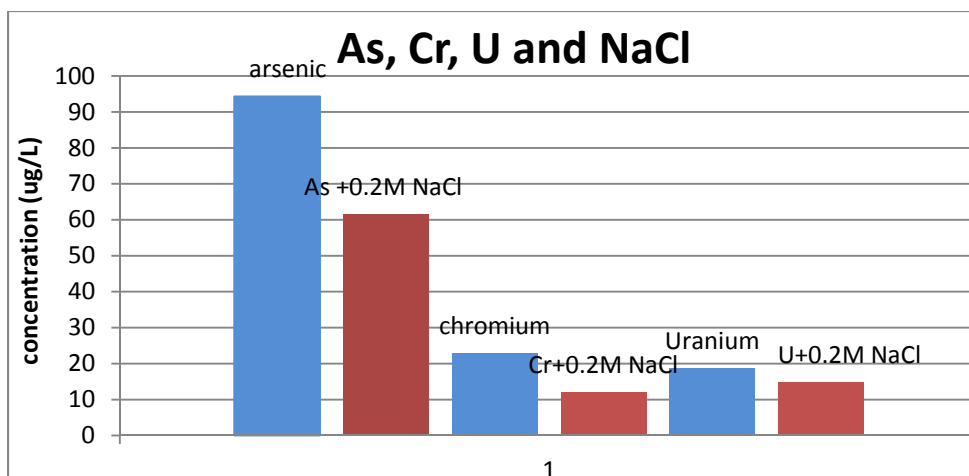


Figure 25. The effect of NaCl (0.2M) on adsorption of Individual Metals by clinoptilolite.

The above diagram shows experiments with individual metal ions (blue) and individual metal ions plus NaCl.

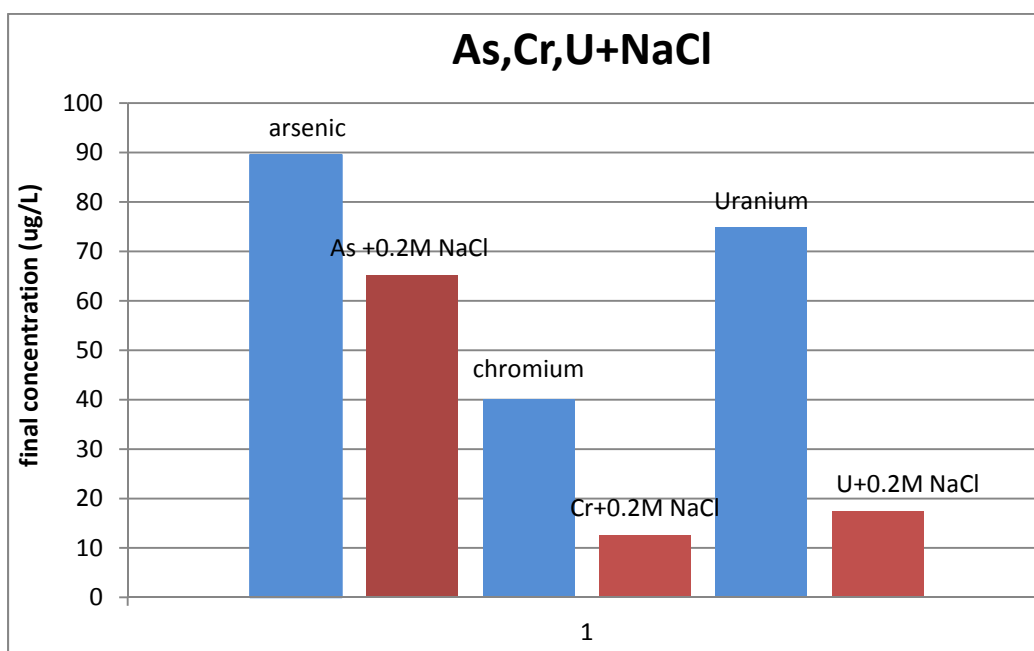


Figure 26. The Effect of NaCl (0.2M) on Adsorption of Composite Metals by Clinoptilolite.

The above diagram shows experiments with the three metal ions (blue) and three metal ions plus 0.2M NaCl (RED)

7.8.2 Adsorption Isotherm Result

The results of the Freundlich and Langmuir models are shown in Figures (27, 28, and 29) for arsenic, chromium, and uranium respectively. The Freundlich equation was the most suitable adsorption model for the adsorption equilibrium data with R^2 values of 0.96, 0.96, and 0.95 for As, Cr, and U respectively. The adsorption studies showed that natural clinoptilolite is ineffective for the removal of Arsenic (37.2%) compared to both chromium (88.6%) and uranium (87.5%) at initial maximum concentration of 1000 ($\mu\text{g/L}$) in the multiple component adsorption system.

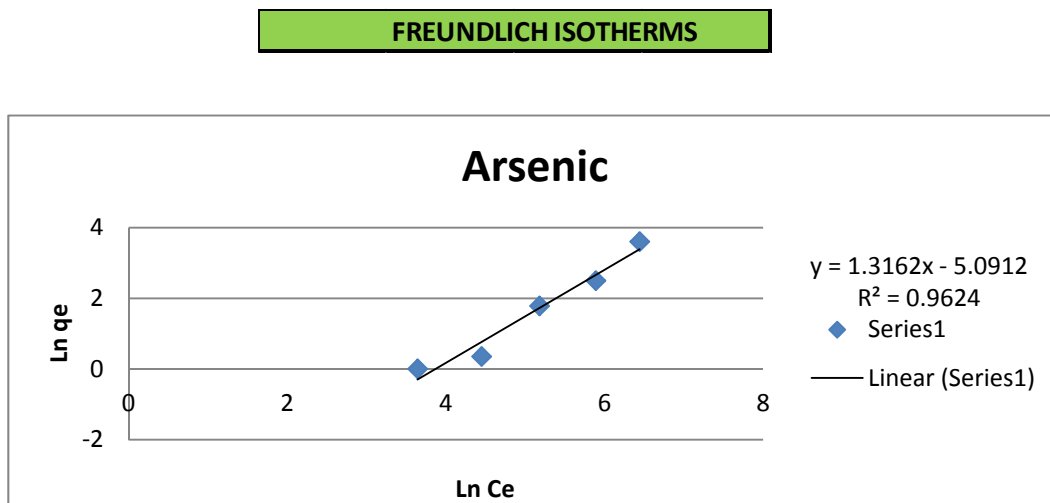


Figure 27. Arsenic Freundlich Isotherm.

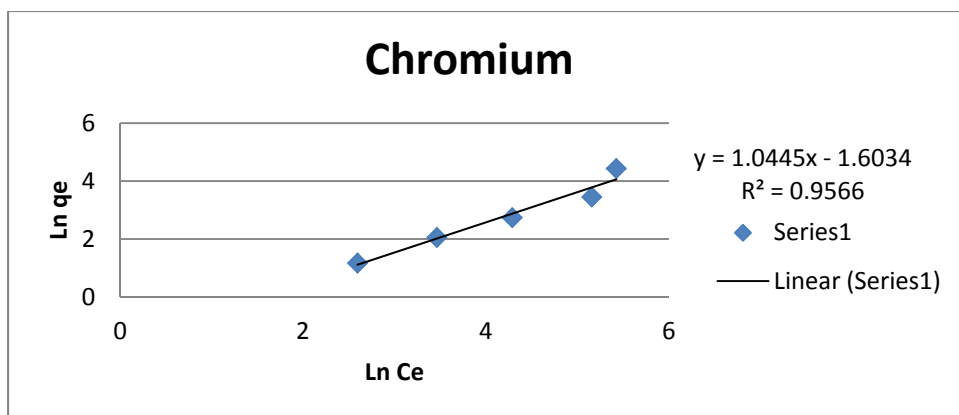


Figure 28. Chromium Freundlich Isotherm

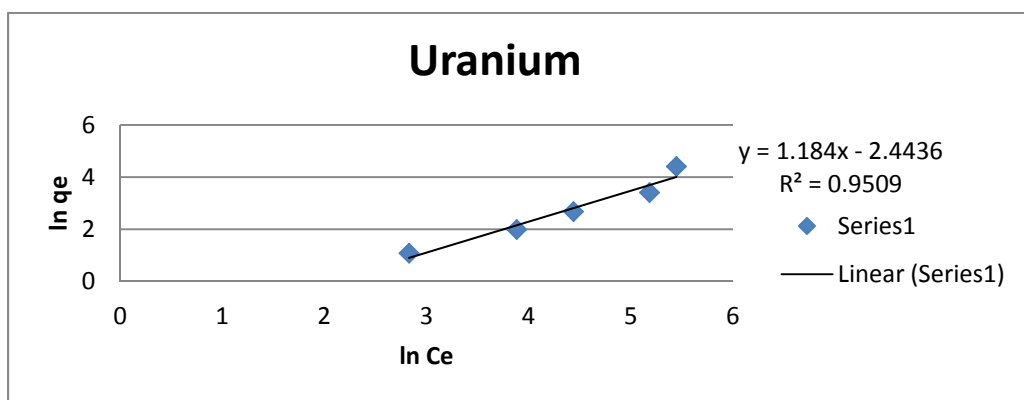


Figure 29. Uranium Freundlich Isotherm.

LANGMUIR ISOTHERMS

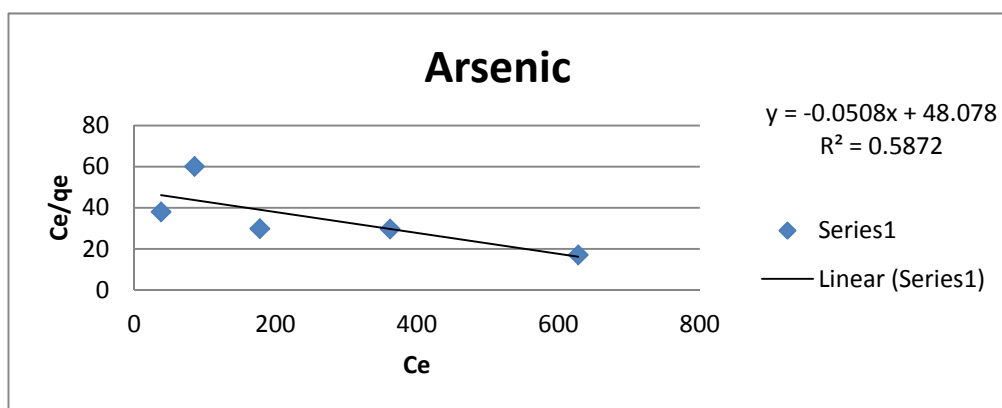


Figure 30. Arsenic Langmuir Isotherm.

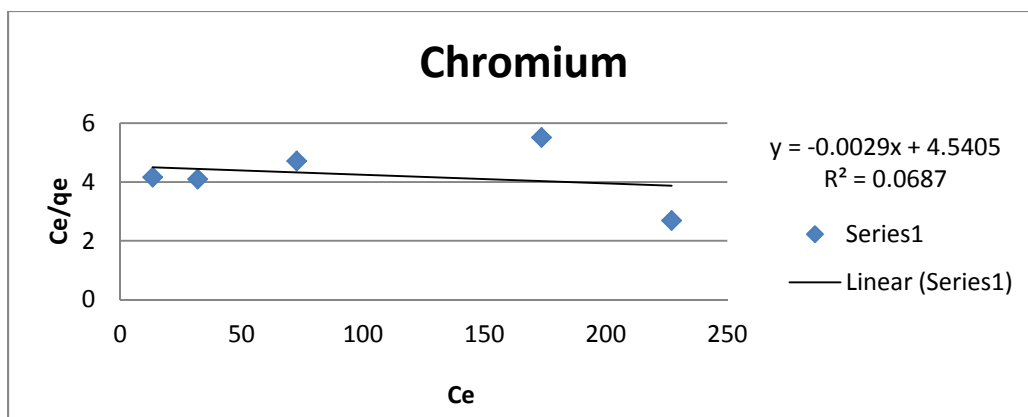


Figure 31. Chromium Langmuir Isotherm.

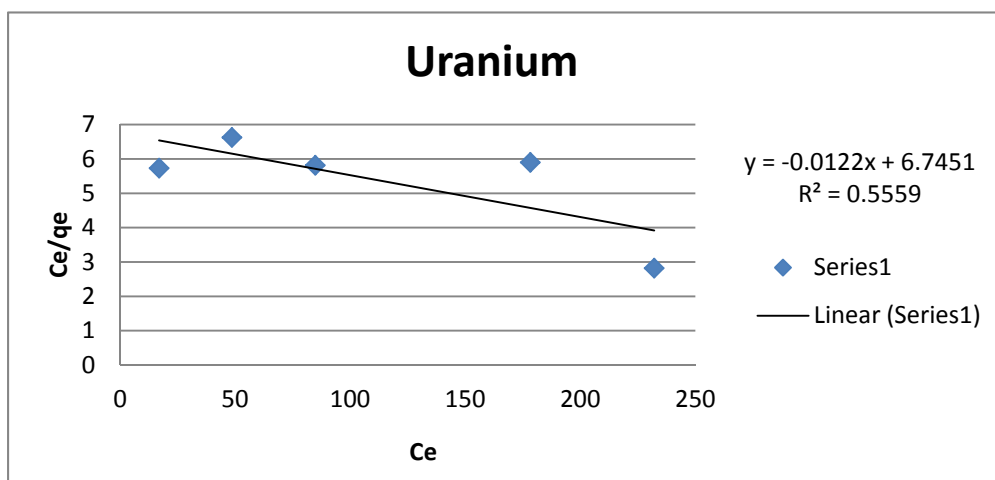


Figure 32. Uranium Langmuir Isotherm.

7.8.3 Lines of Best Fit

From the actual data obtained theoretical data were generated using the constant derived from the slope and intercept. These are used to determine the best line of best fit between the Freundlich and Langmuir models. The two fits are shown in Figures (33, 34, and 35). It can be observed that the Freundlich fit the experimental data, Thus it is the best line of fit. This case is more true for all the three metals (As, Cr and Uranium), and it was found that the Freundlich isotherm generally represent the equilibrium sorption of the three metal ions in solution.

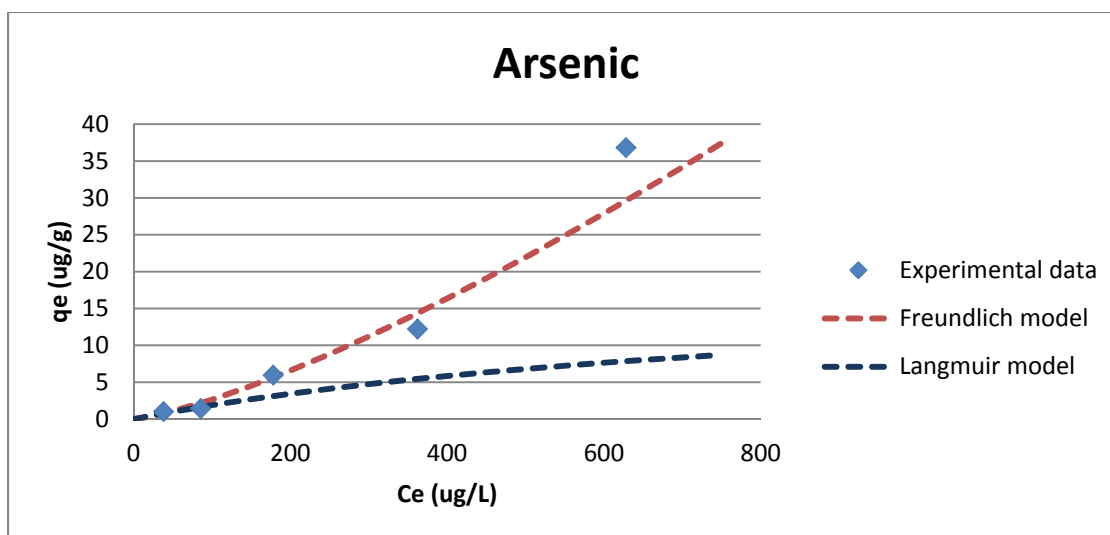


Figure 33. Freundlich Fit and Langmuir Fit for Arsenic.

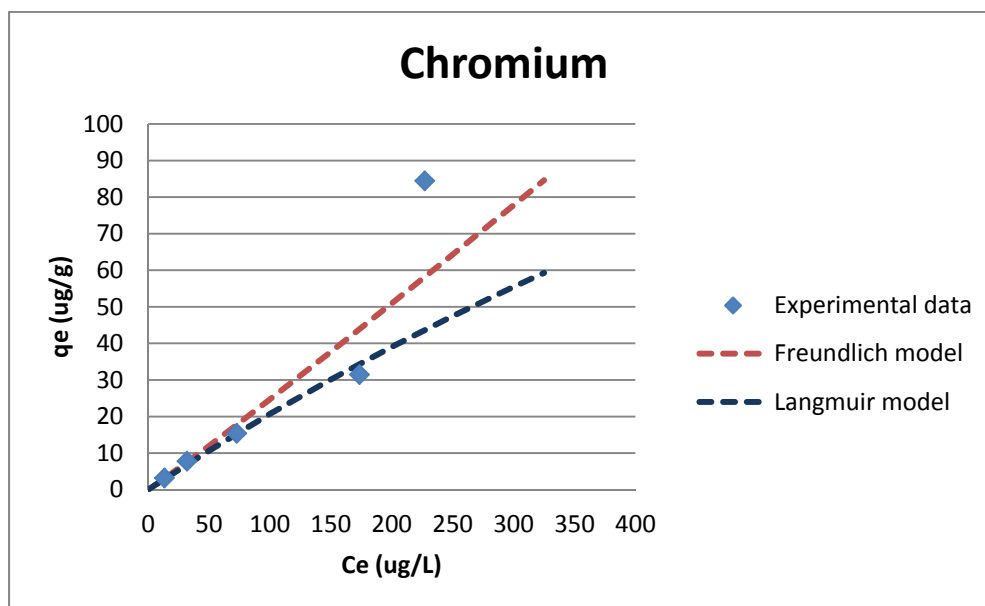


Figure 34. Freundlich Fit and Langmuir Fit for Chromium.

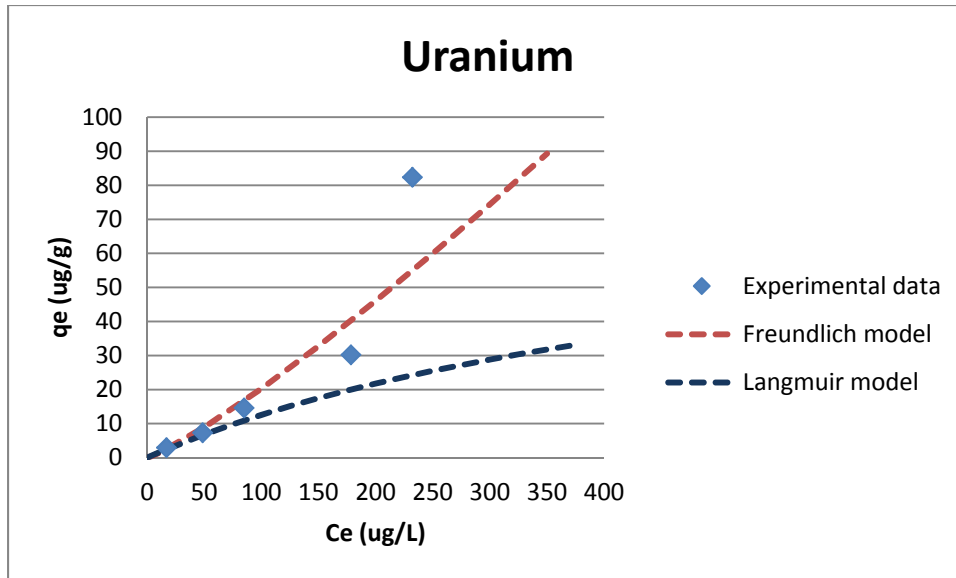


Figure 35. Freundlich Fit and Langmuir Fit for Uranium.

7.9 Breakthrough Column Result

The pH and conductivity of the solution in the column is shown the graphs in Figure 36 to 38. The pH decreased from pH 7 at the start of the column run until it reaches a time of 48 hours. It stabilized for the next 7 hours at pH 4. There was no significant change in the conductivity measured, except in the early hours.

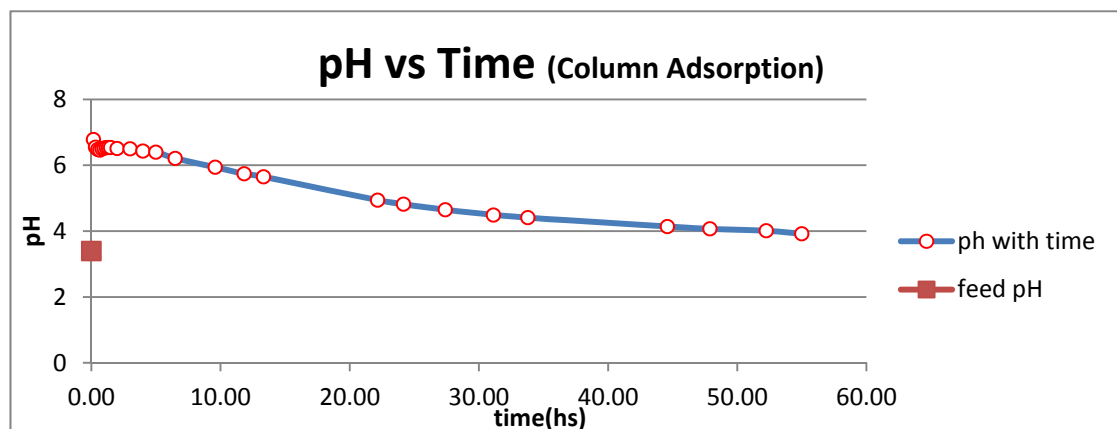


Figure 36. Change in Solution pH with Time.

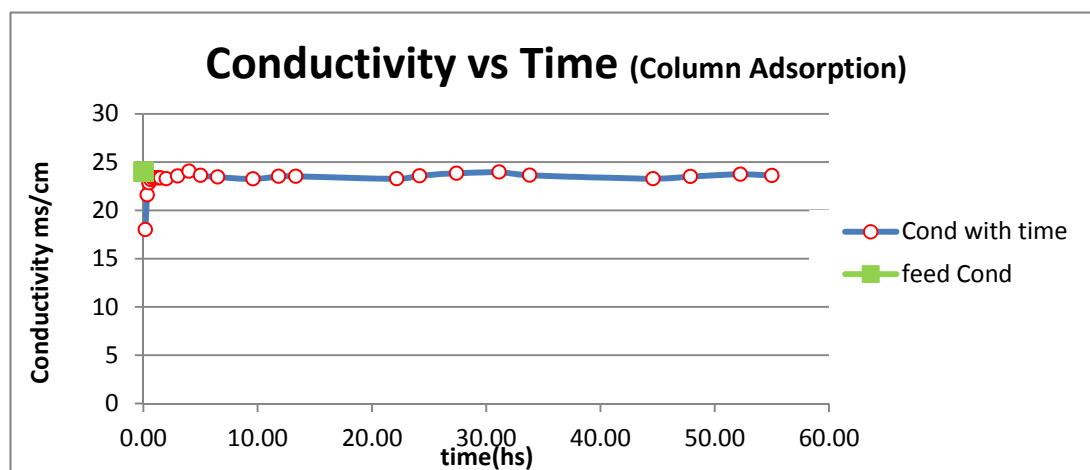


Figure 37. Change in Solution Conductivity with Time.

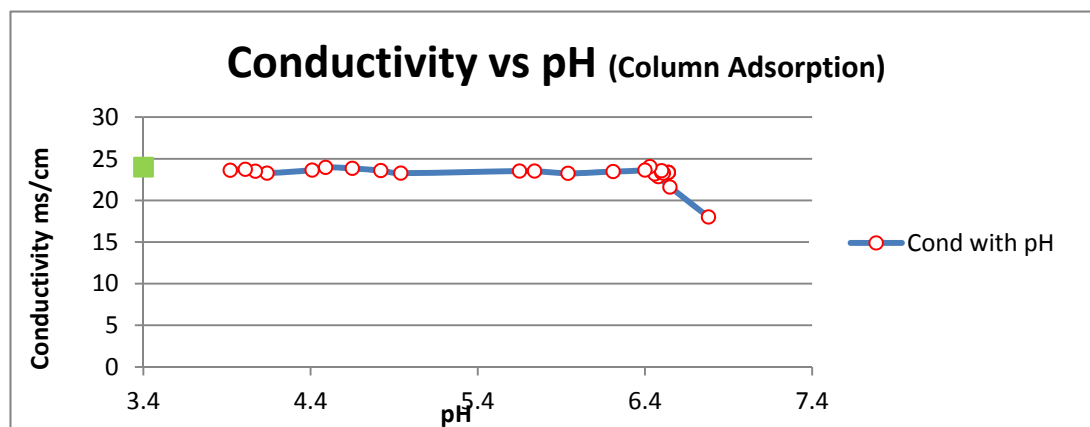


Figure 38. Change in Solution Conductivity with pH.

It could be observed from the graph in (Figure 39) that chromium has the highest adsorption and arsenic the least amongst the three metals. The breakthrough for the arsenic ion was early, this is an indication that clinoptilolite is not removing the arsenic. The chromium took 25 h to reach a breakthrough, and the uranium breakthrough time was about 21hr. At the reported breakthrough times, 90% of the chromium was removed and 82% of the uranium was removed. Afterward there was a sporadic increase in the effluent concentration of the metals. Grab samples at about 55 h of adsorption process showed concentration of the three metals close to the feed concentration of 500 µg/L. This was an indication of complete bed exhaustion.

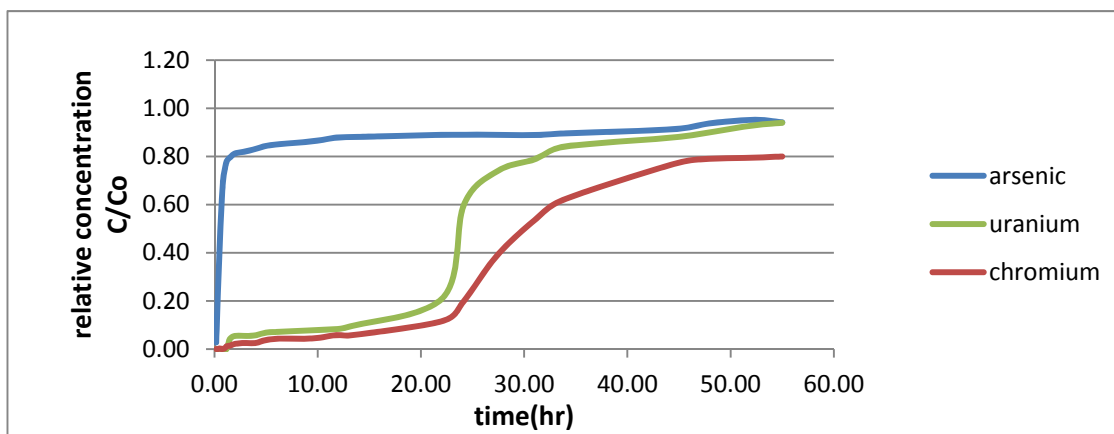


Figure 39. Breakthrough Curve (Full Column Adsorption).

7.9.1 A Comparison of Batch and Column Process for the Amount of Metal ions Adsorbed

The data collected in both batch and column experiments were analyzed for the amount of chromium and uranium adsorbed. The data from the column was compared with the batch process for q_e .

The breakthrough point for chromium was 24 h, the column had processed about 1.9 L of solution and the total amount of Cr in the effluent was 73.7 µg, which was determined by integrating the area under the chromium curve in Figure 39 and multiplying that value by the flow rate. The total amount of Cr fed to the column was 906.4 µg, so the net loading was $(906.4 - 73.7)/35 = 24.74$ µg of chromium per gram of clinoptilolite, and the removal was 92%. The average concentration of Cr in the effluent was 38.8 µg/L. In Figure 34, the value of q_e

associated with Ce of 38.8 $\mu\text{g/L}$ was about 8 $\mu\text{g/g}$. So a batch treatment to produce an effluent with 38.8 $\mu\text{g/L}$ of chromium would require about 3 times as much clinoptilolite as a column treatment.

The Uranium breakthrough occurred at 22 h. The column had processed about 1.73 L (831.4 μg) of solution and the total amount of uranium in the effluent was 105 μg , so the loading was 20.6 $\mu\text{g/g}$. The average effluent concentration of the uranium was 60.8 $\mu\text{g/L}$. The value of q_e corresponding to Ce of 60.8 $\mu\text{g/L}$ was about 9 $\mu\text{g/g}$ (Figure 35). Thus a batch treatment to produce an effluent with 60 $\mu\text{g/L}$ of chromium would require twice as much clinoptilolite as a column treatment. The column experiment proved to be much faster and more effective than the batch process, and the use of a column would be appropriate for the treatment of large volume of wastewater. The result of the half column operation showed very early breakthrough for the three metals. Overlapping curves were noticed, which could be an indication of short circuiting or the waste water not having much residence time.

Table 2. The q (mg/g) of Batch and Column Experiments.

Sample	Batch Experiment q ($\mu\text{g/g}$)	Column Experiment q ($\mu\text{g/g}$)
Chromium	8	24.74
Uranium	9	21.41

7.9.2 Regeneration of Clinoptilolite

The analysis of the spent acid used to regenerate the column of clinoptilolite is shown in Table 3 below. It can be observed that the spent acid solution contains more chromium ions and less arsenic. This is expected because the clinoptilolite effectively removed more chromium than the

other metals during the column experiment. The values represent the characteristic of the wastewater that was used as the feed solution to the diffusion dialysis.

Table 3. Metal Ion Concentration of Spent Acid Solution.

Feed Acid	As ($\mu\text{g/L}$)	Cr ($\mu\text{g/L}$)	U ($\mu\text{g/L}$)
HCl 0.1N	13.8	188.6	63.08

7.9.3 Diffusion Dialysis Result

During the demonstration, the diffusion dialysis recovered on average about 77% of the hydrochloric acid content of the feed acid and rejected 94% of the chromium, 71.7% of the uranium and 0% of the arsenic metal content as shown in Table 8. This shows that the arsenic ions in the acid were poorly rejected by the anion-exchange. After performing the overall material balance for each trial it is evident that osmosis was substantially diluting the feed acid and causing the concentration of acid in the diffusate to be significantly lower than that of the feed. The result shows the differences in acid concentration between the feed and diffusate. The values in Tables 4 and 5 represent the normality of the HCl and chromium concentration of the synthetic solution. The result from the diffusion dialysis indicated that 91.4% of the HCl was recovered and 80.69% of the chromium was rejected from the synthetic solution as presented in Tables 6 and 7. The result from Table 8 shows that the arsenic ions in the acid were poorly rejected by the unit. The pH and the conductivity of the two effluent streams (diffusate and the dialysate) are shown in Tables 9 and 10. The relationship between the pH and the conductivity was observed. The dialysate pH is lower (more acidic), thus it has high conductivity than the diffusate due to its high H^+ concentration and mobility. This was expected because the dialysate stream recovered the spent HCl and it was more concentrated.

Calculations

$$\% \text{ Acid Recovery} = \frac{100 \times C_f}{C_i}$$

C_i = Initial Concentration of Acid

C_f = Final Concentration of Acid in the diffusate stream

% Acid Recovery from the synthetic solution = $100 \times 0.17/0.186 = 91.4\%$

% Acid Recovery from the regenerant solution = $100 \times 0.08/0.1 = 77\%$

$$\% \text{ Metal Rejection} = \frac{100 \times (C_{mf})}{C_{mi}}$$

C_{mi} = Initial Concentration of Metal

C_{mf} = Final Concentration of Metal in Dialysate stream

% Chromium ion rejection from the synthetic solution = $100 \times 403/500 = 80.6\%$

% Arsenic ion rejection from the regenerant's solution = $100 \times 13.65/13.8 = 0\%$

% Chromium ion rejection from the regenerant's solution = $100 \times 177.3/188.66 = 94\%$

% Uranium ion rejection from the regenerant's solution = $100 \times 43/60.08 = 71.6 \%$

Table 4. Synthetic Solution.

Synthetic solution	ACID (N)	CHROMIUM ($\mu\text{g/L}$)
	0.186N	500

Table 5. Titration of the Synthetic and Column Spent Acid Solution.

Sample	Volume of acid (ml)	Volume of base (ml)	Base Normality (N)	Acid Normality (N)
Synthetic	25	21.3	0.2	0.17
Feed Solution	25	9.6	0.2	0.077

Table 6. Percentage Acid Recovery of Synthetic and BTC Spent Acid Solutions.

SAMPLE ID	Feed-Acid Normality (N)	Diffusate-acid Normality (N)	Dialysate-acid Normality (N)	ACID recovery, %
synthetic	0.186	0.17	0.01	92.4
Regenerant solution	0.1	0.08	0.03	77

Table 7. Percentage Metal Rejection of the Synthetic Solution.

Synthetic	Feed-metal Concentration($\mu\text{g/L}$)	Diffusate-metal Concentration($\mu\text{g/L}$)	Dialysate-metal Concentration($\mu\text{g/L}$)	METALS rejection, %
chromium	500	3.4	403	80.6

Table 8. Percentage Metals Rejection of BTC Spent Solution.

Metals	Feed-metal	Diffusate-metal	Dialysate-metal	METALS
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	Concentration($\mu\text{g/L}$)	Concentration($\mu\text{g/L}$)	Concentration($\mu\text{g/L}$)	rejection, %
Arsenic	13.8	13.65	0	0
Chromium	188.6	1.355	177.33	94
Uranium	60.08	5.02	43	71.6

Table 9. The pH and Conductivity of Diffusate and Dialysate of Synthetic Solution

Sample	pH	Conductivity (mS/cm)
Diffusate	0.95	76
Dialysate	2.0	21.2

Table 10. The pH and Conductivity of Diffusate and Dialysate of Synthetic and Spent Acid Solution

Sample	pH	Conductivity (mS/cm)
Diffusate	1.3	33
Dialysate	1.66	14

7.94 Performance Evaluation

These calculations are not the actual percentages. They are estimates based on the flow rate and concentrations of the dialysate and diffusate. The actual value of the % acid recovery using titration analysis is already in the table above and the actual % metal ion rejection based on the result of the ICP OES is also included. These calculations are based on the flow rate and the effluent concentration of the two streams.

Synthetic Solution

$$\% \text{ Acid Recovery} = 100 \times (F_{\text{diff}} \times C_{\text{Acid diff}}) / [(F_{\text{diff}} \times C_{\text{Acid diff}}) + (F_{\text{dial}} \times C_{\text{Acid dial}})]$$

Where,

F_{diff} = Diffusate flow rate = 0.663ml/min

C_{Aciddiff} = Diffusate acid concentration = 0.17N

F_{dial} = Dialysate flow rate = 0.675ml/min

C_{Aciddial} = Dialysate acid concentration = 0.01N

$$\% \text{ Acid Recovery} = 100 \times (F_{\text{diff}} \times C_{\text{Aciddiff}}) / [(F_{\text{diff}} \times C_{\text{Aciddiff}}) + (F_{\text{dial}} \times C_{\text{Aciddial}})]$$

$$\% \text{ Acid Recovery} = \frac{100(0.663 \times 0.17)}{[(0.663 \times 0.17) + (0.675 \times 0.01)]} = 94.3\%$$

$$\% \text{ Cr Ion Rejection} = 100 \times (F_{\text{dial}} \times C_{\text{Metdial}}) / [(F_{\text{diff}} \times C_{\text{Metdiff}}) + (F_{\text{dial}} \times C_{\text{Metdial}})]$$

Where,

F_{dial} = Dialysate flow rate = 0.675ml/min

C_{Metdial} = Dialysate metal concentration = 177.333 (μg/L)

F_{diff} = Diffusate flow rate = 0.663ml/min

C_{Metdiff} = Diffusate metal concentration = 1.355 (μg/L)

$$\% \text{ metal rejection} = \frac{100(0.675 \times 403)}{[(0.675 \times 403) + (0.663 \times 3.4)]} = 99\%$$

Spent Acid Recovery

$$\% \text{ Acid Recovery} = 100 \times (F_{\text{diff}} \times C_{\text{Aciddiff}}) / [(F_{\text{diff}} \times C_{\text{Aciddiff}}) + (F_{\text{dial}} \times C_{\text{Aciddial}})]$$

Where,

F_{diff} = Diffusate flow rate = 0.587ml/min

C_{Aciddiff} = Diffusate acid concentration = 0.08N

F_{dial} = Dialysate flow rate = 0.675ml/min

C_{Aciddial} = Dialysate acid concentration = 0.03N

$$\% \text{ Acid Recovery} = 100 \times (F_{\text{diff}} \times C_{\text{Aciddiff}}) / [(F_{\text{diff}} \times C_{\text{Aciddiff}}) + (F_{\text{dial}} \times C_{\text{Aciddial}})]$$

$$\% \text{ Acid recovery} = \frac{100(0.587*0.077)}{[(0.587*0.077) + (0.675*0.026)]} = 70\%$$

Cr %

% Cr Ion Rejection =

$$100 \times (F_{\text{dial}} \times C_{\text{Metdial}}) / [(F_{\text{diff}} \times C_{\text{Metdiff}}) + (F_{\text{dial}} \times C_{\text{Metdial}})]$$

Where,

F_{dial} = Dialysate flow rate= 0.675 ml/min

C_{Metdial} = Dialysate metal concentration= 177.33 (µg/L)

F_{diff} = Diffusate flow rate = 0.587 ml/min

C_{Metdiff} = Diffusate metal concentration= 1.355 (µg/L)

$$\text{Cr \% Ion Rejection} = \frac{100(0.675*177.33)}{[(0.675*177.33) + (0.587*1.355)]} = 99\%$$

Uranium % Ion Rejection =

$$100 \times (F_{\text{dial}} \times C_{\text{Metdial}}) / [(F_{\text{diff}} \times C_{\text{Metdiff}}) + (F_{\text{dial}} \times C_{\text{Metdial}})]$$

Where,

F_{dial} = Dialysate flow rate= 0.675 ml/min

C_{Metdial} = Dialysate metal concentration= 43 (µg/L)

F_{diff} = Diffusate flow rate = 0.587 ml/min

C_{Metdiff} = Diffusate metal concentration= 5.02 (µg/L)

$$\text{Cr \% Ion Rejection} = \frac{100(0.675*43)}{[(0.675*43) + (0.587*5.02)]} = 90\%$$

Conclusion

On the basis of the studies and the results and discussion presented, the following conclusions were drawn;

- Adsorption has continued to be a proven technology for removal of metals from water if optimum conditions for the treatment process are fully taken into consideration.
- According to the equilibrium studies, the adsorption selectivity sequence in both single and multiple systems can be given as $Cr > U > As$.
- The Freundlich equation was the most suitable adsorption model for the adsorption equilibrium data with R^2 values of 0.9726, 0.9972, and 0.9918 As, Cr, and U respectively.
- The column experiment proved to be much faster and more effective than the batch process, and the use of a column would be appropriate for the treatment of large volume of wastewater.
- The adsorption studies showed low affinity by clinoptilolite for the removal of arsenic (37.2%) compared to both chromium (88.6%) and uranium (87.5%) at initial maximum concentration of 1000 ($\mu\text{g/L}$) in the multiple adsorption system.
- The presence of sodium chloride in the solution increased the adsorption capacity of natural clinoptilolite for heavy metals.
- The percent removal of metals increase with adsorbent concentration or mass.
- The clinoptilolite needs to be modified to suit the adsorption of arsenic, because of the charge complexes it forms at certain pH and its common issue with peaking.
- This project demonstrated that diffusion dialysis is effective at recovering hydrochloric acid from metal contaminated acid streams.
- The only acid streams where diffusion dialysis may not be technically viable are those where the major metal contaminants form charged complexes with the acid anion such as arsenate.

- The processes of ion exchange and adsorption on natural zeolite occur concurrently with the process of hydrolysis.

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