

## REMOVAL OF Pb (II) AND Cr (III) CATIONS FROM AQUEOUS SOLUTIONS USING NATURAL ZEOLITE

Dadi Dinku<sup>1</sup>, Gezahegn Faye<sup>1\*</sup>, Nestor Fernandez<sup>2</sup>

<sup>1</sup>Chemistry Department, College of Natural Sciences, Jimma University, Ethiopia.

<sup>2</sup>Inorganic Chemistry Department, Faculty of Chemistry, University of Havana, Cuba.

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\*Correspondence for

Author:

Gezahegn Faye

Chemistry Department, College  
of Natural Sciences, Jimma

University, Ethiopia,

[gez.wak1@yahoo.com](mailto:gez.wak1@yahoo.com)

### ABSTRACT

The removal of inorganic toxic heavy metals from water and its softening by using natural zeolites are widely used in the purifications treatment of water. Here within, the adsorption of Pb<sup>2+</sup> and Cr<sup>3+</sup> ions from an aqueous solution by Cuban (Tasajeras) natural zeolite (Clinoptilolite) with 150µm particle size were studied through batch experiment method. Optimization of contact time, zeolite dose, heavy metal ions (Pb<sup>2+</sup> and Cr<sup>3+</sup> ions) concentration and temperature were carried out to be 4hrs, 1g, 10ppm and 25<sup>0</sup>C respectively. Optimization of initial pH was also done and found to be 4 for Pb<sup>2+</sup> and 5 for Cr<sup>3+</sup>. Then, at these obtained optimum parameters and 260 rpm agitation speed, the removal efficiency of this natural zeolite was found to be

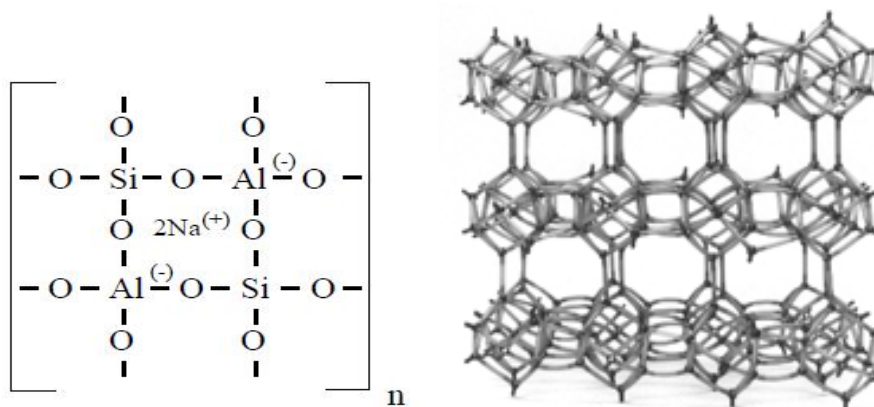
97.6% for Pb<sup>2+</sup> and 98.7% for Cr<sup>3+</sup>. Adsorption isotherm study using Langmuir and Freundlich model were considered and the data best fit with the Langmuir adsorption isotherm model.

**Keywords:** - Natural Zeolite ( Clinoptilolite), lead ion (Pb<sup>2+</sup>), chromium ion (Cr<sup>3+</sup>), Batch Adsorption Method, Adsorption Isotherm, Co-existing ions.

### INTRODUCTION

Waste material disposal from industries (paint, metal plating, mining operations, tanneries, radiator manufacturing, smelting and alloy industries [1]) into the environment are the major causes for soil and water pollution with toxic heavy metals [2 - 6]. Water is highly exposed to pollution; urbanization [1] and agricultural activities are also produce pollutants to waters. It is reported that about 80% of communicable diseases in the world are waterborne [4].

Among non-biodegradable inorganic material pollutants of water,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  are the major heavy metals, persistent, bio-accumulate in organism and causes variety of diseases and disorders on consumers organs such as kidney, nervous system and bone [5 - 11]. Since heavy metals are strongly toxic even at low concentrations [4, 12], the water should be purified from, i.e. elimination /minimization of this pollutants to the acceptable concentration level is very important to prevent public health [7, 8]. According to World Health Organization guidelines of drinking-water quality, the maximum tolerable concentration of lead is 0.01mg/L and 0.05mg/L for chromium [12, 13]. Many methods have been developed for the removal of such heavy metals from water. Some of these are precipitation, solvent extraction, vacuum evaporation, oxidation, ultrafiltration, reverse osmosis, electrodialysis, adsorption and ionic exchange [2, 3, 10, 11, 14, 15]. The use of adsorbents such as clay minerals, activated carbon, carbon nanotubes, biosorbents, metal oxides and zeolites [8] for the separation of heavy metal ions from water samples have been also reported. Currently, the use of low cost [3, 4] and locally available [4] adsorbents has been given attention and an alternative method for purifications of water from heavy metal ions. The most abundant naturally occurring zeolite (clinoptilolite) is an hydrated aluminosilicate mineral [16] adsorbent; locally available, low cost, non-toxic, relatively harmless exchangeable ions and high capacity sorption character makes its widely uses for the treatment of waste water [2, 6, 10, 14, 17]. Natural zeolite is an aluminosilicates, with a cage-like structure suitable for ion exchange due to isomorphous replacement of  $\text{Al}^{3+}$  with  $\text{Si}^{4+}$  in the structure. The chemical composition and structure of zeolite (clinoptilolite) in different area is different and thus, showed different adsorption capacity [2, 3]. Generally, zeolite removes heavy metals from water by a mechanism of ion-exchange [3, 16] and adsorption on the inner and outer surface [16]. The exchangeable cations are sodium, potassium, or calcium [3]. Zeolite has high cation exchange capacities and heavy metals selective properties [18]. Specially, zeolite with sodium charge balancing cations can easily exchange heavy metal cations in waste water [15, 18]. Clinoptilolite ('Beli Plast' mine, Bulgaria) with sodium ions as balancing cations has showed to have a selectivity order:  $\text{Pb} > \text{Cd} > \text{Cs} > \text{Cu} > \text{Co} > \text{Cr} > \text{Zn} > \text{Ni} > \text{Hg}$  [3]. Structural changes in various media play important roles in the potential utilization of zeolite as ion exchangers [10]. The most abundant natural zeolite [19], Clinoptilolite, has the chemical formula  $(\text{Na,K,Ca})_4\text{Al}_6\text{Si}_{30}\text{O}_{72}\cdot 24\text{H}_2\text{O}$  [10] and the structure given bellow (figure 1).



**Figure 1: The Clinoptilolite bonding and framework model**

Several natural zeolite deposits have been studied to evaluate their capacity for heavy metal removal. The adsorption characteristics of an abundant Cuban natural material containing clinoptilolite, for the removal of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  from metal-finishing and electroplating wastewaters were investigated [20]. This natural material from Cuban source could be useful for the removal of other dangerous cations from water sources used for household purposes. Here within, Lead ion ( $\text{Pb}^{2+}$ ) and Chromium Ion ( $\text{Cr}^{3+}$ ) removal from synthetic aqueous solution by natural zeolite (clinoptilolite) (From Cuba, Tasajeras ) has been presented.

## MATERIALS AND METHODS

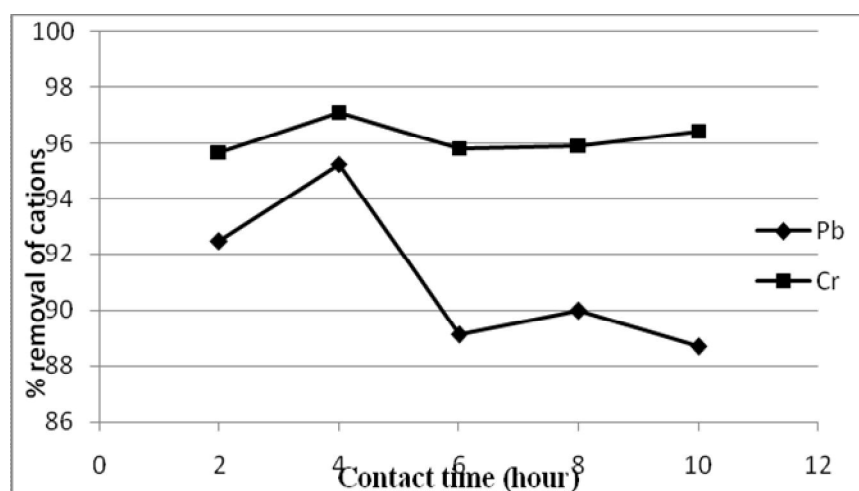
The natural mineral used was collected from the Tasajeras deposit in the middle-eastern part of Cuba. The major mineralogical components are clinoptilolite (up to 53%) and mordenite (up to 17%); with feldspar, quartz and calcite as the main impurities. The chemical composition of the zeolite sample are (wt%):  $\text{SiO}_2$  62.36;  $\text{Al}_2\text{O}_3$  13.14;  $\text{CaO}$  2.72;  $\text{K}_2\text{O}$  1.20;  $\text{Na}_2\text{O}$  3.99;  $\text{Fe}_2\text{O}_3$  1.63;  $\text{MgO}$  1.22; loss of ignition 13.15. The Physical properties of this material is very important for its adsorption capacity [20]. The mineral was used by crushing into small size and sieved with  $150\mu\text{m}$  size sieve.

For the adsorption experiments, analytical grade reagents were used to prepare stock solutions (1000mg/L) of the heavy metals cations lead(II) from  $(\text{Pb}(\text{NO}_3)_2)$  and chromium(III) from  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with deionized water. Batch adsorption method was considered for study. 0.1M NaOH and  $\text{HNO}_3$  were used for pH adjustment of the initial solution. The sample batches were placed in temperature controlled water bath and shaken by Grant GLS400 at 260 rpm for the desired time. Finally the solid was separated by filtration and the residual metal concentration in the filtrate was measured using Analytikjena novAA300 model Atomic Absorption Spectrophotometer.

## RESULT AND DISCUSSION

### Effect of Contact Time

The adsorption behavior of  $Pb^{2+}$  and  $Cr^{3+}$  ions by zeolite in relation to the effect of contact time was carried out by varying contact time from 2-10 hours. The concentration of  $Pb^{2+}$  and  $Cr^{3+}$  was fixed at 10ppm, zeolite dosage 1.0g, agitation speed 260 rpm, temperature  $25^{\circ}C$  and initial pH 6. Results showed that the adsorption equilibrium is four (4) hours at which the percent removal efficiency was found to be 95.3% for lead and 97.1% for chromium (Figure 2).



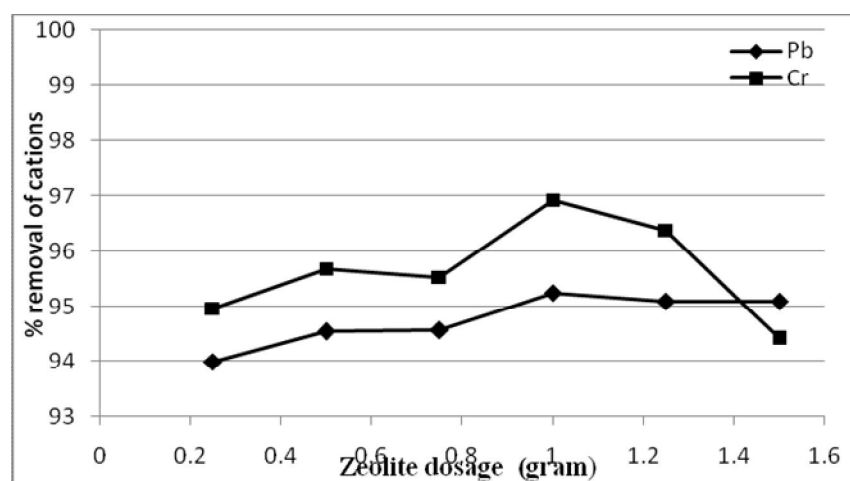
**Figure 2: Effect of contact time on Chromium (III) and Lead (II) ions removal by zeolite (Zeolite 1.0g, cation concentration 10ppm, agitation speed 260rpm, temperature  $25^{\circ}C$  and initial pH 6)**

According to figure 2, the adsorption efficiency is initially increased and then decreased with increasing contact time after equilibrium had been reached. This probably resulted from saturation of adsorbent surfaces with heavy metal ions followed by adsorption and desorption processes that occur after saturation [21]. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium [22].

### Effect of Zeolite Dosage

The study was taken place by using various amounts of zeolite dosage from 0.25g to 1.5g while the pH, agitation speed, temperature, concentration and contact time were fixed at: 6, 260 rpm,  $25^{\circ}C$ , 10ppm and 4hrs respectively. The results (Figure 3) indicated that the adsorption efficiency increased at the beginning as there are high exchangeable sites [12] and then decreased with increased in zeolite dosage. However, high zeolite dose increases the pH

of the system by increasing concentration of the hydroxide ion in the solution during adsorbing the water molecule which releases hydroxide ion, which successively affects the removal of heavy metals which enhances desorption [23]. The partial hydrolysis of aquacations  $[M(H_2O)]^{n+}$  as pH increases produces deprotonated species as  $[M(HO)_{n-1}OH]^{(n-1)+}$  and also others with higher degree of deprotonation which exhibit lower positive charge than the original and are less strongly retained by the adsorbent. The screening effect may be other factors for decrease in adsorption capacity with increase in the adsorbent dose, thus protection of the adsorption sites of the adsorbent [12]. As zeolite dosage increases the removal efficiency was increased until some optimum point and then decreases on addition of more zeolite.



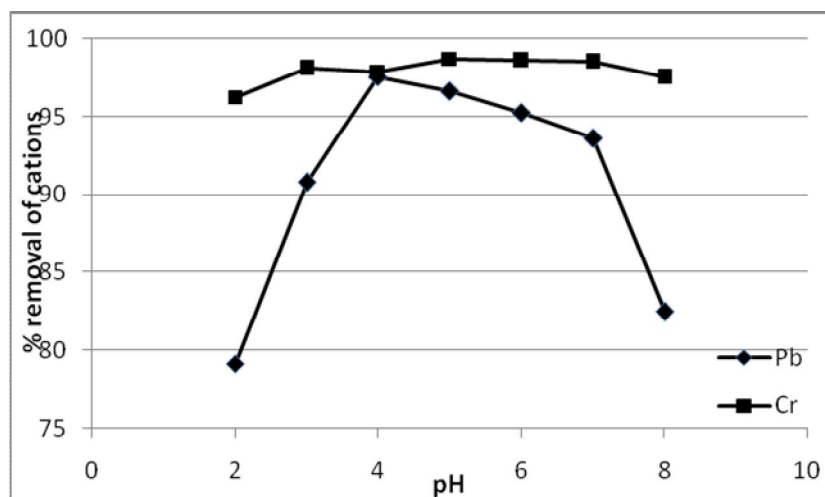
**Figure 3: Effect of zeolite dose on Chromium (III) and Lead (II) ions removal by zeolite (contact time 4 hrs, cation concentration 10ppm, agitation speed 260rpm, temperature 25°C and initial pH 6)**

### Effect of pH

Removal of heavy metal ions from aqueous solution is affected by pH, as it affects the charge of zeolite, solubility of the metal ions and exchangeable cations [24, 25]. The removal of  $Cr^{3+}$  and  $Pb^{2+}$  ions from aqueous solution by natural zeolite adsorbent at various initial pH of the solution was studied (Figure 4). Aqueous solutions with pH 2 to 8 were prepared by drop wise addition of 0.1 M nitric acid and/or 0.1 M sodium hydroxide. It is observed that with the increasing of the initial pH from 2 to 8 the removal of  $Pb^{2+}$  and  $Cr^{3+}$  ions in the solution was at first increased up to a certain point and then decreased. In highly acidic medium removal efficiency of the zeolite is observed to be lower which most probably due to strong competition of  $H^+$  with cations on the adsorption sites [26]. At higher pH (~8) the adsorption

of  $Pb^{2+}$  and  $Cr^{3+}$  onto the adsorbent is decreased as metals are precipitated in the form of hydroxides, hydrated oxides or basic salts in basic medium[26]. The optimum pH was found to be 5 for  $Cr^{2+}$  and 4 for  $Pb^{2+}$ .

In natural zeolite these metals seem to reach saturation, which means that the metal had filled possible available sites and further adsorption could take place only at new surfaces[5]. It is reported [27], that the optimal pH for lead is 5.0 and at pH higher than 5.0 the metal was precipitated as hydroxide.



**Figure 4: Effect of initial pH on Chromium (III) and Lead (II) ions removal by zeolite (time 4h, cation concentration 10ppm, agitation speed 260rpm, temperature 25°C and zeolite 1.0g)**

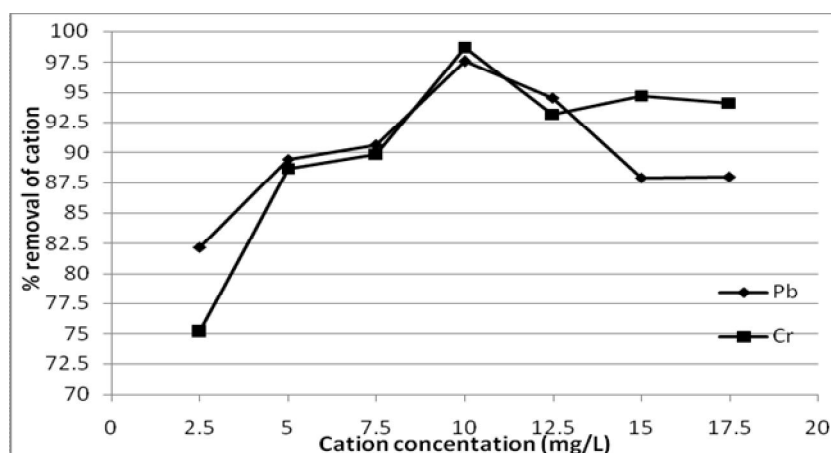
#### Effect of Cation Concentration

The effect of cation concentrations on removal efficiency of natural zeolite was studied with addition of 1.0 grams of adsorbent dosage, initial pH 5 for chromium and 4 for lead, contact time of 4hrs and temperature 25°C in different concentration of  $Cr^{3+}$  and  $Pb^{2+}$  ions from 2.5 to 17.5ppm. Results (Figure 5) showed that the optimum removal efficiency was obtained at 10ppm cation concentration of the solutions; a decrease after this value was observed. Later on, decreasing removal efficiency was detected with increasing initial heavy metal concentrations in the solutions. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and that as metal concentrations increase, these sites become saturated. That is, there is some metal concentration that produces the best adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available: all are occupied[28]. Research studies report contradictory observations regarding the effect of initial metal concentration in the removal of heavy

metals. The following three different sorption behaviors have been reported in the literature when the initial metal concentration is increased [23]:

- ❖ decrease in percentage uptake of heavy metal ions
- ❖ no effect on heavy metal sorption
- ❖ increase in sorption capacities of zeolites for uptake to certain initial metal concentration and then only a slight increase in sorption

In a typical experimental study to evaluate the influence of initial metal concentration, zeolite dose is usually kept constant; meaning the number of available sorption sites is constant. When the initial metal concentration is increased, the sorption sites available for the uptake of metal ions can be inadequate. This may be the possible reason for the first type of observation. As for the second observation, heavy metal ions were completely removed in the concentration range studied. This could have been due to the availability of an abundance of sorption sites in zeolite used in the study. In case of the third observation, zeolite could have been exhausted due to the occupation of active sites by the ions. Thus, a significant increase in heavy metal uptake was not observed. These observations demonstrate the close relationship between the metal concentration and zeolite dose.



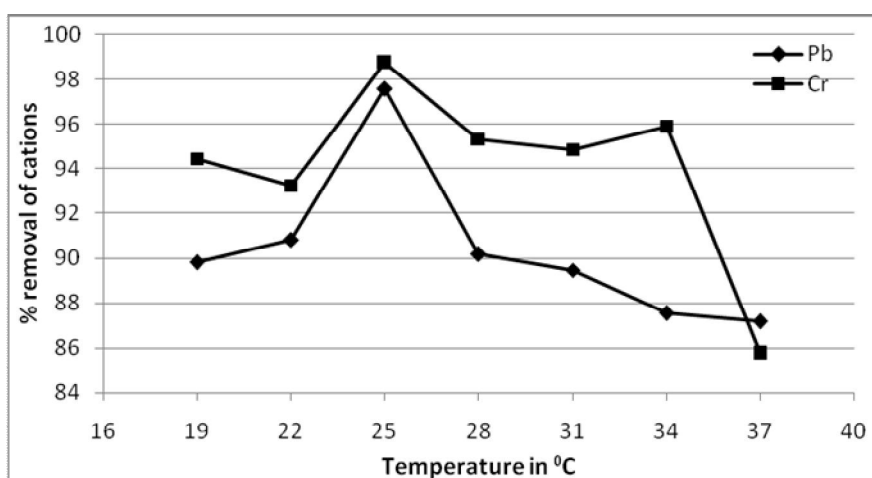
**Figure 5: Effect of concentration on Chromium (III) and Lead (II) ion removal by zeolite (time 4hrs, zeolite 1.0g, agitation speed 260rpm, temperature 25<sup>0</sup>C and initial pH 4 lead (II) and 5 chromium (III)).**

### Effect of temperature

The effect of temperature on removal efficiency of natural zeolite was studied with addition of 1.0 grams of zeolite dosage, initial pH 5 for chromium and 4 for lead, contact time 4hrs and cation concentration was 10ppm in different temperature range from 19 to 37<sup>0</sup>C. The

optimum removal was obtained at 25°C, a little increase before this value and decrease after this value was observed (Figure 6).

Temperature of solution influences the heavy metal sorption mainly by enhancing the diffusion of hydrated heavy metal ions. Heavy metal aqua-complex stability in solution decreases with increasing temperature. As a result, hydrated heavy metal ions strip off some of the water molecules from their hydrated complexes leading to a reduction of ionic size. This facilitates the diffusion of heavy metal cations into the pores and consequently increases sorption since metal ions can access the extra sorption sites available in the pores. It was reported [29] that increase in temperature from 25°C to 80°C has only reduced the distance between metal ion and water by approximately 0.005nm resulting only in a slight reduction in the size of heavy metal aqua complex. However, the size reduction can have an impact on some heavy metal ion complexes that have only a few water molecules in their complexes. . Additionally, studies have reported that increasing the temperature to 60°C results in only a slight increase in the sorption of zeolite possibly due to the insignificant impact on size reduction. Hence, enhancing sorption by increasing the temperature is not economically attractive as it involves the consumption of energy. Therefore, the effect of temperature appears to be dependent on other physical and chemical factors such as the strength of metal-water complexes and the characteristics of pores. Thus, the knowledge on the contribution of these factors can provide a basis in the selection of an optimum treatment temperature. Furthermore, in real world application, the energy consumption must also be considered in optimization [23].



**Figure 6:** Effect of temperature on Chromium (III) and Lead (II) ion removal by zeolite (time 4hrs, zeolite 1.0g, agitation speed 260rpm, concentration 10ppm and initial pH 4 lead(II) and 5chromium(III) )



A decrease in metal ion adsorption as temperature increases beyond the maximum may be due to increasing tendency to metal desorption from the interface to the solution by weakening of adsorptive forces between the active sites of the adsorbent species. Result indicates that the removal of  $\text{Cr}^{3+}$  and  $\text{Pb}^{2+}$  cations from the solution was lowered at lower and at higher temperatures which is consistent with some results reported in literature. Accordingly with some study [28], activated 2 grams of clinoptilolite in 100 ml water at pH 5.0 was tested for adsorption of  $\text{Pb}^{2+}$  at different sample temperature between 10 to  $50^{\circ}\text{C}$ . Results show that optimum working temperature was about  $30^{\circ}\text{C}$ . Removal of  $\text{Pb}^{2+}$  from the water was 88% at this temperature; it was lowered at lower and at higher temperatures. Similar result was obtained [22] when the effect of temperature on the adsorption was examined for solutions of 1000mg/L metal ion and 20g/L adsorbent at optimum pH, temperature was increased from  $25^{\circ}\text{C}$  to  $55^{\circ}\text{C}$ .

### Effect of co-ions

The desired concentration (10mg/L) of cations ( $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$ ) were prepared using deionized water in three different bottles. The initial solutions pH were controlled to be 4 for  $\text{Pb}^{2+}$ , 5 for  $\text{Cr}^{3+}$  and 5.8 for  $\text{Cu}^{2+}$ .  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  solutions prepared and 3g of zeolite were mixed in one reagent bottle. Then, the adsorption capacity of this Cuban Natural Zeolite were measured after the mixture was agitated with the speed of 260 rpm at a temperature of  $25^{\circ}\text{C}$  for 4hrs contact time. Results show that the removal efficiency of natural zeolite decreases for  $\text{Pb}^{2+}$  from 97.6% to 89.4% and for  $\text{Cr}^{3+}$  from 98.7% to 68.2%. As result indicates that a natural zeolite (Tasajeras) is more selective for  $\text{Pb}^{2+}$  than  $\text{Cr}^{3+}$  if they exist together in one solution. It can be seen with other zeolites [30] that in both two-component and four-component mixture solutions selectivity follows the same order:  $\text{Pb}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+} > \text{Cu}^{2+}$  which is consistent with the result of present work. Similar literature reports [16] show that normal drinking water contains several other ions, specially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which may compete with the active sites in the sorbent during chromium sorption. They showed the effect of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with a fixed all other parameters, such as contact time, pH, dosage and initial chromium concentration as constants. From this report the overall sorption capacity of AICs (Aluminum/Chitosan) composite was slightly altered by the presence of co-ions and hence there is reduction in sorption capacity due to co-ion competition for the surface binding sites and decrease in the amount of the chromium metal ion adsorbed as a result of the competition.

### Adsorption Isotherm models

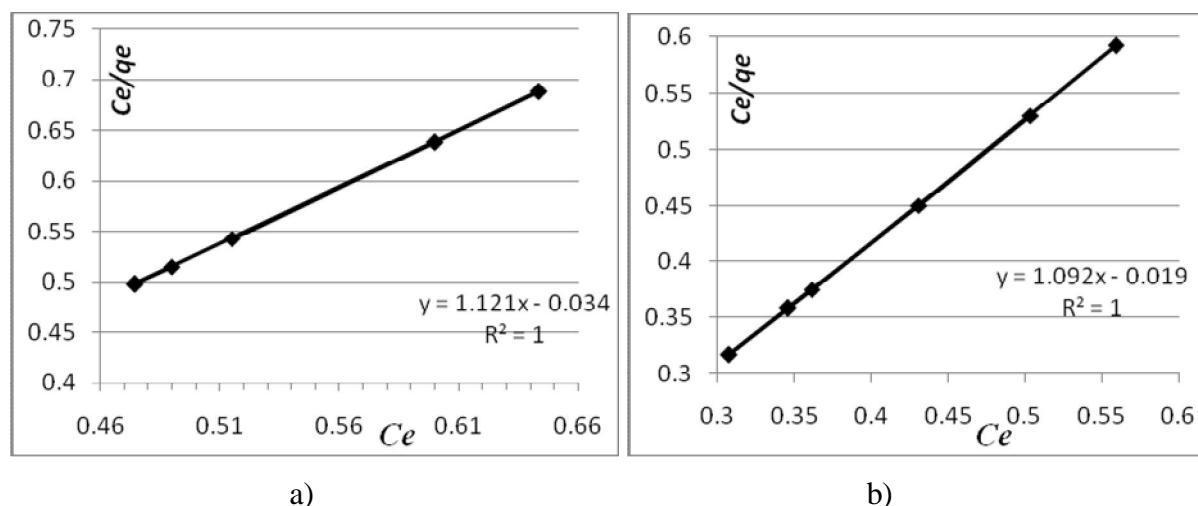
The equilibrium adsorption isotherm for lead(II) and chromium(III) on natural zeolite was done by varying adsorbent dose from 0.25 to 1.50g and fixing initial  $Pb^{2+}$  and  $Cr^{3+}$  concentration 10mg/L, contact time 4hrs, temperature 25<sup>0</sup>C and initial pH 4 and 5 for  $Pb^{2+}$  and  $Cr^{3+}$  respectively. Isotherms models were studied for characterization of the adsorption process such as Langmuir and Freundlich isotherm which provide information on the capacity of sorbent. These isotherms relate metal uptake per unit weight,  $q_e$  to the equilibrium metal ion concentration in the bulk fluid phase  $C_e$  [28].

The Langmuir adsorption isotherm is the best known of all isotherms describing sorption and it has been successfully applied to many sorption processes [31]. The Langmuir model been empirically most often used, contained the two parameters  $q_m$  and  $b$ , which reflect the two important characteristics of the sorption systems. Langmuir adsorption model was applied to the data:  $C_e/q_e = 1/q_m b + C_e/q_m$ . Where:  $C_e$  is the equilibrium aqueous metal ions concentration (mg/L),  $q_e$  the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg/g),  $q_m$  the maximum adsorption capacity (mg/g) and  $b$  is the Langmuir constant (mg/l). The values of  $q_m$  and  $b$  can be determined from the linear plot of  $C_e/q_e$  versus  $C_e$ .

Equilibrium concentration  $C_e$  and equilibrium capacity  $q_e$  were calculated for each metal concentration.  $C_e/q_e$  was plotted against  $C_e$  and a straight line was fitted in the data. Correlation factor  $R^2 = 1.0$  for both  $Pb^{2+}$  and  $Cr^{3+}$  indicate that sorption process fit to Langmuir adsorption isotherm model. The Langmuir plots for  $Pb^{2+}$  and  $Cr^{3+}$  isotherm adsorption data for natural zeolite adsorbent at 25<sup>0</sup>C have studied,  $R^2 = 1.0$  which clearly suggests the applicability of Langmuir adsorption model ( Figure 7 ). Values of Langmuir constants  $q_m$  and  $b$  were calculated from slope and intercept of line (Table 1).

**Table 1. Langmuir adsorption isotherm constants**

Metal ion	Langmuir isotherm			Freundlich isotherm		
	$q_m$	$b$	$R^2$	$K_F$	1/n	$R^2$
$Pb^{2+}$ ion	0.892	33.33	1.0	1.27	0.58	0.17
$Cr^{3+}$ ion	0.916	58.82	1.0	1.08	0.04	0.98



**Figure 7: Langmuir adsorption isotherm for a)  $Pb^{2+}$  ion adsorption by Natural Zeolite at  $25^{\circ}C$ . (Contact time 4hrs,  $Pb^{2+}$  ion concentration 10ppm, initial pH 4, agitation Speed 260 rpm). b)  $Cr^{3+}$  ion adsorption by Natural Zeolite at  $25^{\circ}C$ . (The same conditions except for initial pH = 5)**

Using the same obtained experimental data for  $q_e$  and  $C_e$  the Freundlich isotherm model  $\log q_e = \log k_F + 1/n \log C_e$  was checked. The correlation coefficient ( $R^2$ ) were 0.17 and 0.98 for  $Pb^{2+}$  and  $Cr^{3+}$  respectively, which indicate that Freundlich adsorption isotherm is not correctly fitted to the experimental data.

From the data obtained the adsorption is monolayer as it was fitted with Langmuir isotherm model and not fit with the Freundlich isotherm model.

## CONCLUSION

The present study shows that natural zeolite (Tasajeras) is an effective adsorbent for the removal of  $Pb^{2+}$  and  $Cr^{3+}$  ions from aqueous solutions. Removal efficiency of natural zeolite observed was 97.6% for  $Pb^{2+}$  removal and 98.7% for  $Cr^{3+}$  removal at optimum conditions; contact time 4 hrs, zeolite dosage 1g, cation concentration 10ppm, initial pH 4 for  $Pb^{2+}$  and 5 for  $Cr^{3+}$ , and temperature  $25^{\circ}C$ . The adsorption isotherm studies show that the Langmuir adsorption isotherm model fits well with the experimental data. By using Cuban natural zeolite effective removal efficiency is attained for  $Pb^{2+}$  and  $Cr^{3+}$  ions at optimum conditions. According to the experimental data of present work, the removal efficiency of Cuban natural zeolite is comparable to reported removal efficiency of other places natural zeolite. The main advantage of using natural zeolite for removal of heavy metal cation is the low-cost of this material and its economic feasibility, being a good alternative to water purification by removing lead and chromium from their solutions.

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