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## Use of Syrian natural zeolite for heavy metals removal from industrial waste water: Factors and mechanism

Hana Salman, Haitham Shaheen, Ghaiath Abbas and Nisreen Khalouf

#### Abstract

Using static adsorption techniques, the adsorption of heavy metals of  $V^{+5}$ ,  $Ni^{+2}$ ,  $Zn^{+2}$ ,  $Pb^{+2}$  was investigated on natural zeolite (NZ) mined from southern Syria. This study was performed in order to determine the adsorption capacity of low-cost zeolite used to remove heavy metals from desalter wastewater of crude oil, many heavy metals are contained in this wastewater and threaten human life and fauna when discharged without treatment. The effects of the following factors on adsorption process were studied: contact time, initial concentration, size of adsorbent particles, the competing ions and hardness. The results showed that the adsorption rate accelerates at the beginning adsorption. The optimal removal efficiency was reached during 6 hours. The Langmuir adsorption isotherm model was able to give good fits to experimental data. An increase in the concentration of exchangeable cations ( $Ca^{+2}$ ) was noticed in solution at equilibrium. This finding reveals that ion exchange between zeolite and solution is responsible for the removal of heavy metal ions from the solution. It was found that precipitation affects the removal rate of  $Pb^{+2}$  from solution while it has negligible effect on other three ions. The highest pH of equilibrium was higher than the minimum pH necessary for complete precipitation of  $Pb^{+2}$  as hydroxides. The regeneration ability of the studied zeolite was examined using NaCl salt at concentration (20 g/L). The results also showed that the highest selectivity of (NZ) was for  $V^{+5}$  and  $Pb^{+2}$ . Therefore their desorption efficiency is the lowest. The desorption series is a reversal of the adsorption series, desorption series  $Ni^{+2} > Zn^{+2} > Pb^{+2} > V^{+5}$ . So the locally - available NZ is considered a low - cost adsorption that can be applied to remove heavy metals.

**Keywords:** Industrial wastewater, desalting unit, heavy metals, Zeolite, adsorption, Langmuir, Freundlich

#### Introduction

The presence of accumulated heavy metals in the environment constitutes a serious threat to human life and the environment because of their toxicity. Many toxic heavy metals have been discharged into the environment as industrial wastes resulted from crude oil desalter annexed to oil refinery which is the major source for highly toxic industrial wastewater [1]. i.e. Baniyas refinery in Syria where discharge capacity is 125m<sup>3</sup>/h. Desalter's wastewater contains highly toxic heavy metals (such as V, Ni, Zn, Fe, Mn, Cu, Cd, Pb, Co, and Cr). The oil - contaminated wastewater is treated in a specialized unit for the recovery of oil after treatment, the discharged heavy metals to the Mediterranean sea reach 61% of their initial values [2]. In the recent years, the removal of heavy metals from industrial wastewater have been inclusively investigated. Most commonly used methods for this purpose include ionic exchange, adsorption, precipitation, ultrafiltration, reverse osmosis and electro dialysis. While most of these techniques are expensive and inapplicable on a large scales, Ionic exchange and adsorption are still preferable methods to be adopted using low cost natural materials i.e.  $ZnCl_2$ , activated carbon, metal sludge, crystalline hydroxyapatite, and metal hydroxides as adsorbents to remove heavy metals from aqueous solution [3, 4]. Due to high deposit of Zeolite in nature, and to its low cost, strong adsorption capacity, it has recently drew attention to be used in the treatment of industrial wastewater. Syria has high deposits of Zeolite thus its usage in the removal of heavy metals from industrial wastes offers a significant alternative to other traditional treatment techniques [5, 6]. Wastewater treatment in desalter essentially entails ion exchange reaction by natural Zeolite which has a special structure enable to displace exchange cations ( $Mg^{+2}$ ,  $K^{+}$ ,  $Ca^{+2}$ ,  $Na^{+}$ ) by heavy metal cations such as  $Pb^{+2}$ ,  $V^{+5}$ ,  $Zn^{+2}$ ,  $Fe^{+2}$ , and  $Ni^{+2}$ . The safety of using natural Zeolite is attributed to the non-toxicity of its metals that displace

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unfavorable toxic heavy metals from wastewater in the desalter.

Zeolite is structurally stable even at acidic environment that can be easily reproduced with some modification to improve its structure and adsorption capacity. Due to these attracting properties of Zeolite, interest has been increased towards the method of heavy metal adsorption from aqueous solution. Many studies reported the importance of using natural Zeolite for the adsorption of heavy metals under different empirical conditions such as temperature, pH, concentration, granular phase volume, and induction speed [7-10]. However, the treatment wastewater in the desalter hasn't had much interest. In the present study natural Zeolite was tested as an efficient adsorbent for the removal of ions of  $Pb^{+2}$ ,  $Zn^{+2}$ ,  $V^{+5}$ ,  $Ni^{+2}$  from desalter wastewater. This article aims to investigate the parameters that affect removal rate i.e. contact time, particle size, pH of initial solution and competitive ions, determination of maximum adsorption capacity of natural Zeolite which is used to remove the studied metal ions through equilibrium reactions, comparing the empirical data of adsorption balance with Langmuir and Freundlich sorption

models in order to evaluate the adsorption performance of natural Zeolite, then to establish an empirical equation with the objective of achieving results having high accuracy, and Studying of Zeolite regeneration using sodium chloride.

## 2. Materials and Methods

### 2.1. Study site

The present study focuses on the crude oil desalter at Baniyas refinery in Baniyas city northern Tartous and located near the shore of the Mediterranean Sea. Desalting method used in Baniyas refinery is based on thermal, electrical, physical and chemical techniques using a horizontal cylindrical vessel into where desalted fresh water pumped in order to dissolve the salts in oil at two points as shown in Fig1. The wastewater is driven from the desalter to the treatment unit of oil-contaminated wastewater, to recover residues of oil, free non emulsified oils, stable emulsified oil in water, undissolved solids and dissolved organics. It's well mentioned that direct disposal of industrial wastewater treatment unit negatively affects later biological treatment process [11].

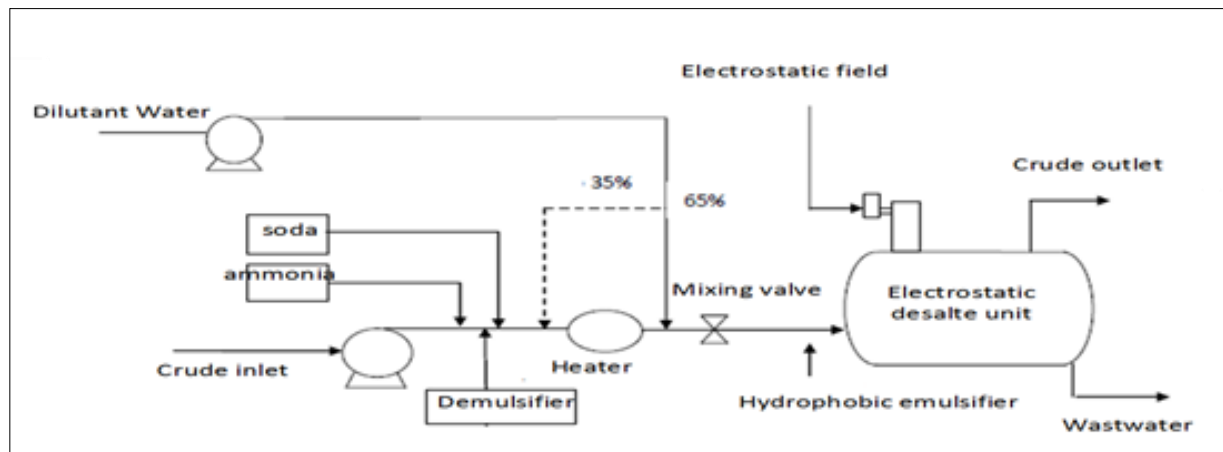


Fig 1: Desalting unit diagram [2]

### 2.2. Chemicals and Apparatus

Samples of Syrian rocks containing natural zeolite in southern Syria was studied and X-ray diffraction of zeolite sample was measured using X-ray crystallographer. The sample contains a mixture of phillipsite and chabazite as well as some additional rocky matrices such as Hematite, Diopside, Smectite. Standard solutions for minerals are used at concentration of 1000ppm to prepare stock solutions off different concentrations range from 50 to 600ppm. Heavy metals concentrations are measured using AAS (AA6800Shimadzu) with flame and graphite techniques. The pH of the solutions matches that of waters in refinery, that is pH/ was adjusted to  $6 \pm 0.1$  using HCl and NaOH. As for concentration measurements, assays were applied to low, average and high concentrations due to the fact that content of discharged heavy metals depends on the source of crude oil, nature and the various compositions of heavy metals in crude oil on one hand, and low levels can reach the detectable level quickly on the other hand. Thus, high level of concentrations are not taken into consideration. Size of adsorbent particle was determined using the grain size distribution analysis and the samples were shaken using mechanical shakers for 15 minutes needed to complete the separation process, the interval of particles diameters of (NZ) was (0.5-1mm). pH meter and electric mixer were also used.

### 2.2. Factors influencing on removal rate

Process of adsorption and its rate are very complicated in relation to many factors that effect on the general reaction rate. i.e. contact time, volume of adsorbent granule as well as pH and concentration of initial solution. The influence of these factors on the removal of the  $V^{+5}$ ,  $Ni^{+2}$ ,  $Zn^{+2}$  and  $Pb^{+2}$  from the studied solution using natural Zeolite as follows:

#### 2.2.1. Equilibrium time

Single component solutions for  $V^{+5}$ ,  $Ni^{+2}$ ,  $Zn^{+2}$ , and  $Pb^{+2}$  were prepared at a concentrations of 300mg/l in which 0.5 g of Zeolite with particle size range 0.5-1mm was placed in 50ml of solution and shaken for 24hours at 450 rpm using electrical shaker. 1ml of the solution was taken at different intervals 0.25, 0.50, 0.75, 1, 2,4, 6, 8, 24 hours. Each was transferred into calibrated flasks and diluted to the mark of 50ml. ions in the solution were determined using AAS analysis. The quantity of metal ions was calculated from the difference in solution concentration before and after adsorption as well as removal rate was deduced there after :

$$\text{Removal Efficiency \%} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where  $C_i$ : initial concentration of metal ions (mg/L),  $C_f$ : final concentration of the contaminant in the solution at equilibrium (mg/L).

### 2.2.2. Effect of adsorbent particle size

The effect of adsorbent particle size on the kinetics of sorption was investigated. three different sizes were used:  $0.5\text{mm} < dp < 1\text{mm}$ ,  $1\text{mm} < dp < 2\text{mm}$ ,  $2\text{mm} < dp < 4\text{mm}$ . 0.5 gr of adsorbent at the required particle size was mixed with 50 ml of solution of the appropriate single component solution at an initial concentration 100mg/L and shaken for 6 hours. All samples were then analyzed and the rate of adsorption was determined.

### 2.2.3. Effect of competing ions

Multi-component solutions containing equal concentrations of  $V^{+5}$ ,  $Ni^{+2}$ ,  $Zn^{+2}$  and  $Pb^{+2}$  were prepared at concentration of 100mg/l for each. The whole metal concentration would be 400mg/l when contact with natural Zeolite and shaken for 6 hours at pH of  $6 \pm 0$ . Tests were performed to investigate the influence of the presence of other cations on the adsorption capacity of natural zeolite for each of the cations under investigation in this study

### 2.2.4. Effect of Hardness

the presence of different elements such as dissolved salts of ammonia, calcium, magnesium, as well as other ions may interfere with adsorption of heavy metals that is the presence of some cations such as calcium, magnesium, and potassium significantly effect on the efficiency of the removal process so that calcium which is the major element in all types of water including the studied one is considered to be the most potent competitive element, thus, for that purpose, single component solutions of  $V^{+5}$ ,  $Ni^{+2}$ ,  $Zn^{+2}$ , and  $Pb^{+2}$  were prepared at concentration of 100mg/L and volume of 50ml to which 0.5gr of Zeolite was added. Moreover, calcium ions were added to the solutions at concentrations of 0, 20, 50, 100, and 150mg/L where pH =6 with continuous agitation for 6h at 450rpm until equilibrium is attained. The samples were then filtered and the content of heavy metals residues were determined. The variations of heavy metals removal rates with corresponding variations of concentrations of calcium ions were also graphed.

### 2.3. Equilibrium

The main objective of the equilibrium studies was to determine the maximum capacity of natural zeolite towards vanadium, nickel, zinc and lead removal under the studied conditions and according to make a selectivity comparison for these. Experimental data were fitted to conventional adsorption mathematical models. These were used to predict the adsorption performance of natural zeolite. adsorption capacity formula is given in the following equation:  $q_e$ (mg/g)

$$= \frac{X}{m} = \frac{(C_i - C_e) \times V}{m} \quad (2)$$

where  $q_e$  is the quantity of dissolved absorbed material in mg per g of the adsorbent at equilibrium [12]

$C_i$ : initial concentration of contaminant in solution at equilibrium (mg/l),  $V$ : volume of water phase (l),  $M$ :mass of

solid phase (g)

### I. Langmuir Adsorption Isotherms

Langmuir model suggests that adsorption occurs on monolayer of the surface which contains unlimited number of adsorption sites of equal energy. Linearity of Langmuir equation is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \quad (3)$$

where  $q_0$  is the maximal adsorption capacity at the surface availability of binding sites(mg/g)

$b$  is Langmuir constant which is related to the radical energy of adsorption.

$b$  and  $q_0$  can be extrapolated from the slope of linear plot of

$\frac{C_e}{q_e}$  with index of  $C_e$  [13-15]

### Freundlich Adsorption non Isotherms

Freundlich model suggests energetically heterogeneous surface of porous matter so that adsorption capacity is due to adsorption temperature [16-17] linear equation of Freundlich model is as follows:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (4)$$

where  $K$  is Freundlich constant related to maximal adsorption capacity.

$n$  is a constant related to adsorption density or binding strength

$1/n$  is heterogeneity coefficient i.e. values of  $1/n < 1$  refer to heterogeneous adsorbents while those values close or equal to 1 refer to relatively homogenous adsorbents at binding sites [15]

In  $K$ ,  $1/n$  can be extrapolated from the slope of linear plot  $\ln q_e$  with index of  $\ln C_e$ .

### 2.3. Regeneration

1 gr of natural Zeolite was mixed with 100 ml of single component solution of  $Pb^{+2}$ ,  $Zn^{+2}$ ,  $Ni^{+2}$ , and  $V^{+5}$  at a concentration of 100mg/L to be activated for 6h thereafter. The mixture was filtered and the result was analyzed using AAS. Solid matters with adsorbed heavy metal were rinsed thoroughly with deionized water and dried in oven. The dried material was then mixed with 100ml of the solution of NaCl at concentration 20g/l pH5.5 adsorption reagent and shaken for 3hours.

## 3. Results and Discussion

### 3.1. Equilibrium time

It's obvious from Fig 2 that adsorption occurred at two stages while the first stage is instant the second one is slower then it becomes at steady speed until the equilibrium is attained after 4-6 hours [9, 18]. Thus, the chosen time required for all trials is 6hours.

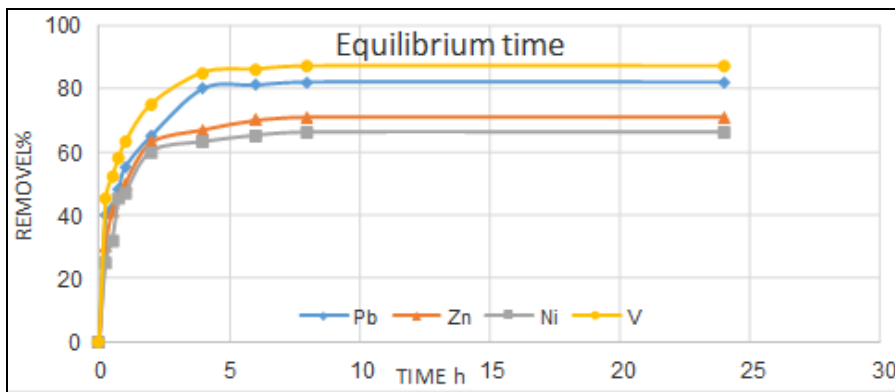


Fig 2: Equilibrium time for V<sup>5+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> & Ni<sup>2+</sup> at experimental conditions (C<sub>0</sub>= 300 ppm ϕpH = 6, m=0.5gr ϕV=50ml ϕ0.5-1mm)

**3.2. Effect of adsorbent particle size**

It's noticed from figure 3 that increasing the external surface area by reducing the adsorbent particle size, results in an increase in the number of available sites for metal uptake [19]. Moreover, smaller particle sizes result in the shortening of the

diffusion distance that heavy metals have to travel in order to get to an adsorption site, hence a faster rate of reaction. It's also noticed that Vanadium revealed the greatest affinity >90% for most of used sizes of particles while Nickel revealed the lowest affinity (70-85%).

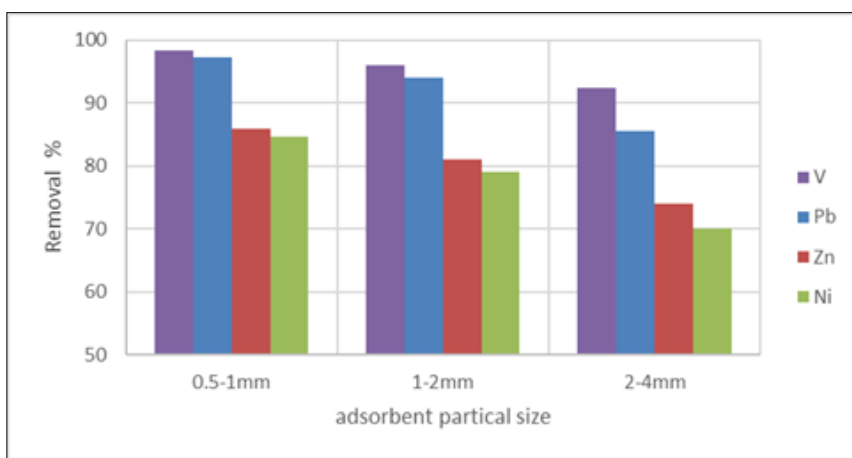
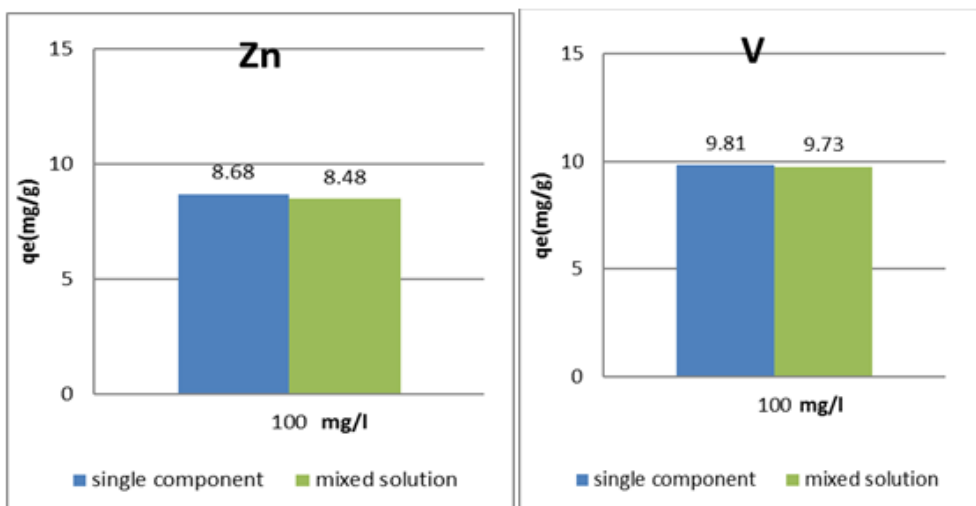


Fig 3: Adsorbent particle size affecting on the removal of V<sup>5+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, & Ni<sup>2+</sup> from the solution (C<sub>0</sub>= 100 ppm ϕpH = 6, m=0.5gr ϕV=50ml ϕT=6h)

**3.3. Effect of competing ions**

Wastewater from desalting unit contains various metal ions with influence on potentiality of adsorbent to treat wastewater in competition for exchange sites and within adsorbent. Confirmation trials were conducted for the influence of competitive ions on individual adsorption of each Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, and V<sup>5+</sup>. Fig 4 implies comparison between heavy metals ions adsorption from mono and multi component solutes

using natural Zeolites. So as a result it's been found that Nickel adsorption decreased due to competitiveness, while other metal ions adsorption were not influenced, that is adsorption capacity of these ions from single component solutions in comparison to multi component ones and at rate ranged 1-3% and 10% higher than nickel's. The difference can be attributed to the adsorption selectivity of Zeolite specific sites to which each metal ion is adsorbed in different ways.



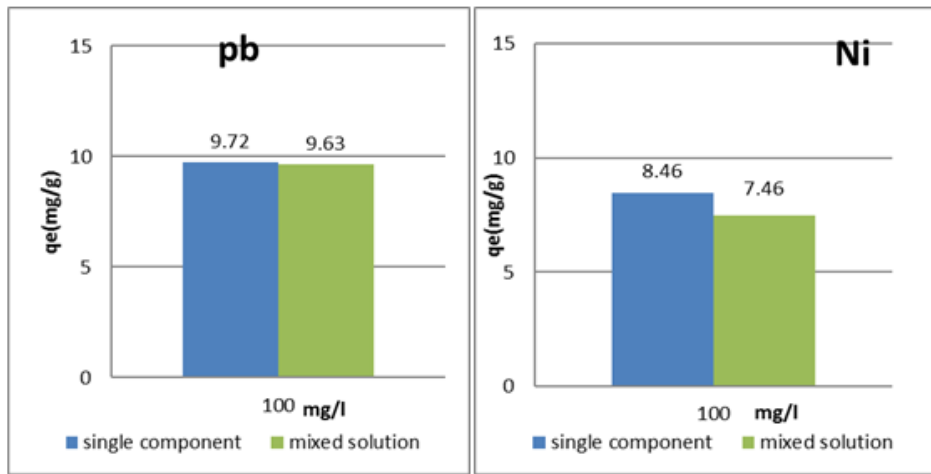


Fig 4: Comparison of the adsorption capacity of natural zeolite for  $V^{+5}$ ,  $Pb^{+2}$ ,  $Zn^{+2}$  &  $Ni^{+2}$  from single and multi – component solutions.

### 3.5. Effect of Hardness

Since desalting wastewater contains high concentrations of Calcium ions, it is considered hard water and majorly affect the removal of heavy metals from wastewater due to competing metal ions on exchange site of zeolite structure on one hand and to forming surface complexes of heavy metals ions bonded to surface on the other hand. Thus heavy metals removal from water is impeded as shown in Fig 5. It was noticed that the increase of Calcium ions concentration led to decrease in removal rate of Ni and Zn from 84.6%, 86.8% to 70.61%, 71.22% respectively, while both  $Pb^{+2}$  and  $V^{+5}$  were not influenced by Calcium ions so that removal rate decreased from 97.2% to 95.22% at high concentrations of Calcium with

potential exposure which led to increasing adsorption of Calcium in comparison with Pb ions. more over, hydration energy significantly effect on equivalent ions. i.e. the higher hydration energy the lower competitiveness of ion is. Thus, since hydration energy for  $Pb^{+2}$ ,  $Ca^{+2}$ ,  $Zn^{+2}$  and  $Ni^{+2}$  are 2105, 2025, 1677, 1495 KJ/mol respectively<sup>[20]</sup>, Zeolite selects Pb first in Pb-Ca displacement reaction then comes Calcium where removal rate of ions decreases. As vanadium, it's slightly influenced by calcium due to the fact that zeolites first select high valent ions in terms of electrostatic ion exchanges where electrostatic affinity is stronger<sup>[15]</sup> Thus, natural zeolite is very efficient in the removal of ions whether in presence or absence of water hardness agents.

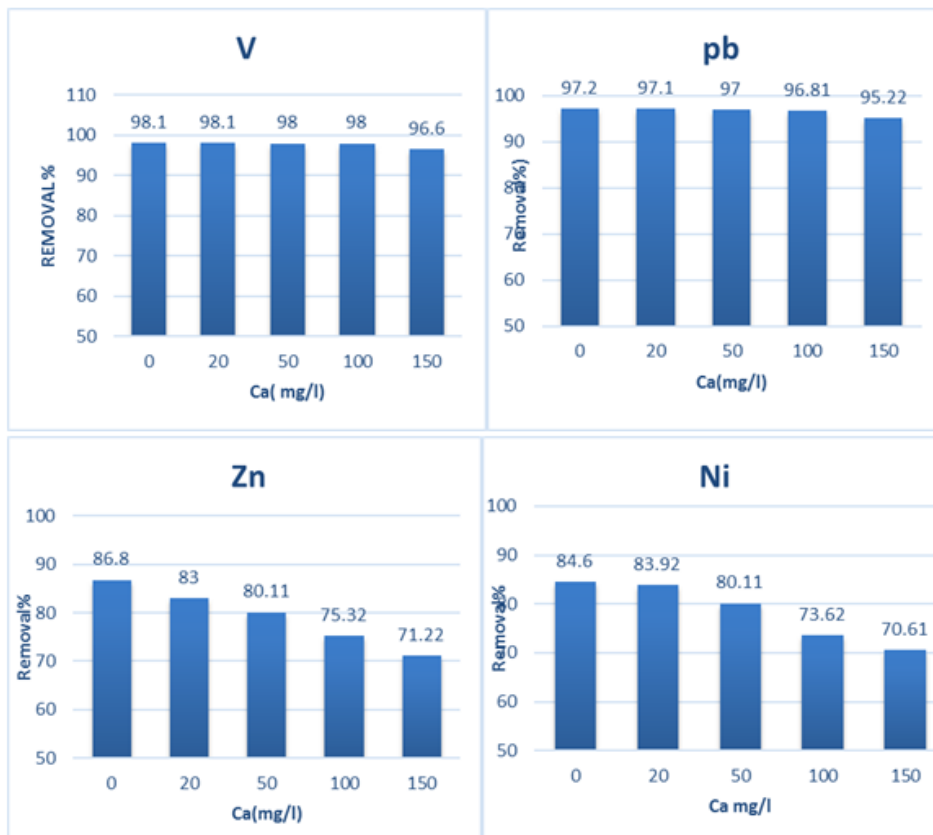


Fig 5 Calcium cations affecting the removal of  $V^{+5}$ ,  $Zn^{+2}$ ,  $Pb^{+2}$  &  $Ni^{+2}$  from single ionic solutes using Zeolite ( $C_0 = 100ppm$   $pH=6$   $V=50ml$   $m=0.5gr$ )

### 3.6 Equilibrium

Freundlich and Langmuir isotherm curves for the adsorption of four heavy metal ions from solution as shown in Tab 1

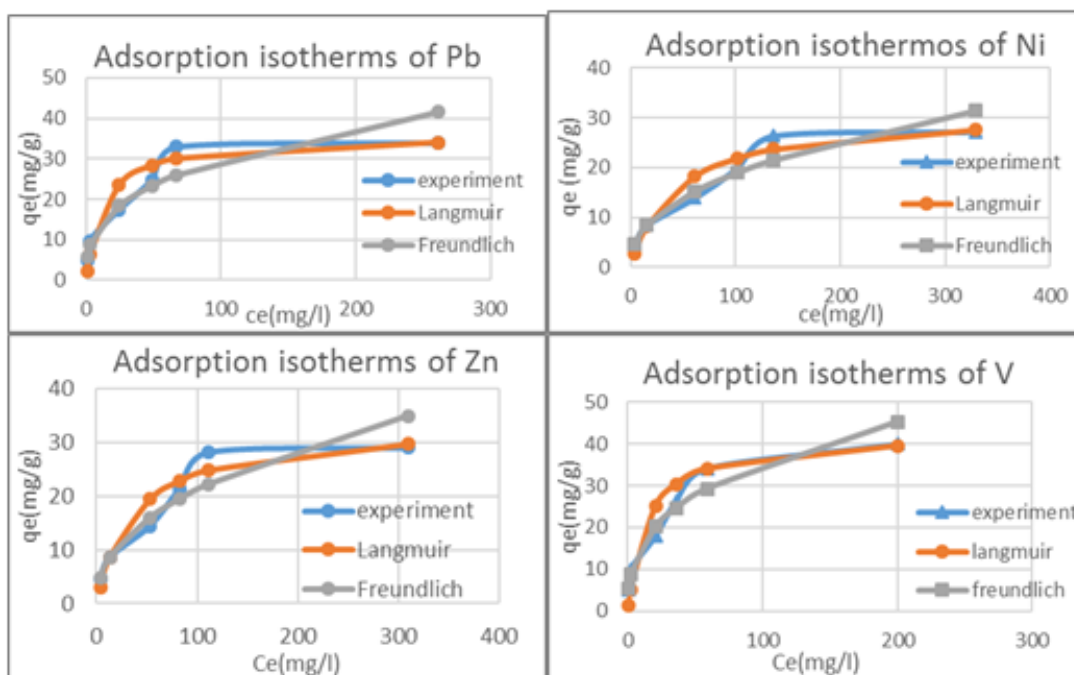
reveals the reliability of experimental findings where the values of correlation coefficient  $R^2$  range from 0.95-0.99, the maximal capacities of the given heavy metals adsorption  $q_0$

according to Langmuir model are 35.71, 31.25, 42.37, 33.33mg/g for Zn<sup>2+</sup>,V<sup>5+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> respectively. The maximal value is for vanadium indicating to the higher selectivity of zeolite to vanadium in comparison with other metals. Heterogeneity coefficient 1/n extrapolated from Freundlich isotherm curve is less than 1 and thus the evaluations are 0.43,0.34, 0.44 and 0.32 for Ni, Pb, Zn, and V respectively. The values indicate a material with relatively homogenous binding sites of natural porous Zeolite. It's been

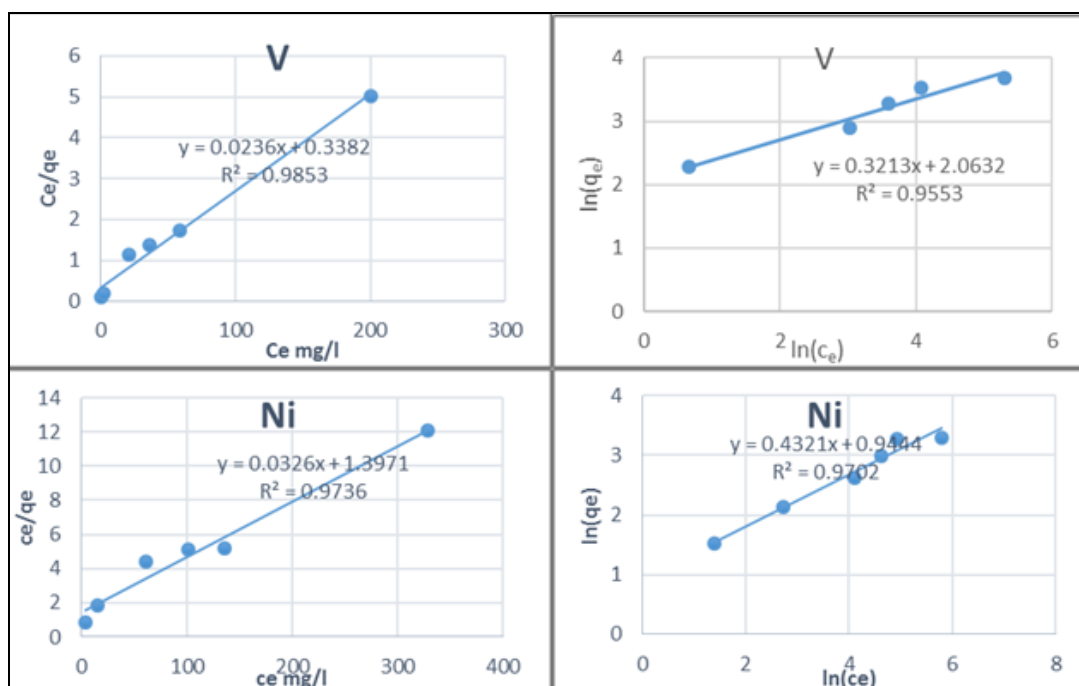
noticed from Fig6 the higher concentration of heavy metal ions the higher content of adsorbed metal per gram of natural Zeolite q<sub>e</sub> this is attributed to the fact that at high concentration of heavy metal there is a higher solute concentration gradient; and this provides the necessary driving force for metal ions to displace exchangeable cations on the surface and from the internal micro-pores of natural zeolite [21]. The increase continues until the saturation point is achieved.

**Table 1:** Calculated equilibrium adsorption isotherm constants for the uptake of V<sup>5+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup> from solution by natural zeolite.

Heavy metal ion	Experimental		Langmuir			Freundlich		
	q <sub>e</sub> max (mg/g)	C <sub>e</sub> (mg/l)	q <sub>o</sub> (mg/g)	b	R <sup>2</sup>	k	1/n	R <sup>2</sup>
V	40.00	200.10	42.37	0.069	0.99	7.87	0.32	0.96
Ni	27.19	328.51	31.25	0.023	0.97	2.57	0.43	0.97
Pb	33.89	261.07	35.71	0.079	0.99	6.09	0.34	0.95
Zn	29.02	309.82	33.33	0.026	0.98	2.72	0.44	0.95



**Fig 6:** Adsorption isotherms of V<sup>5+</sup>,Pb<sup>2+</sup>,Zn<sup>2+</sup>and Ni<sup>2+</sup> from solution using (NZ)



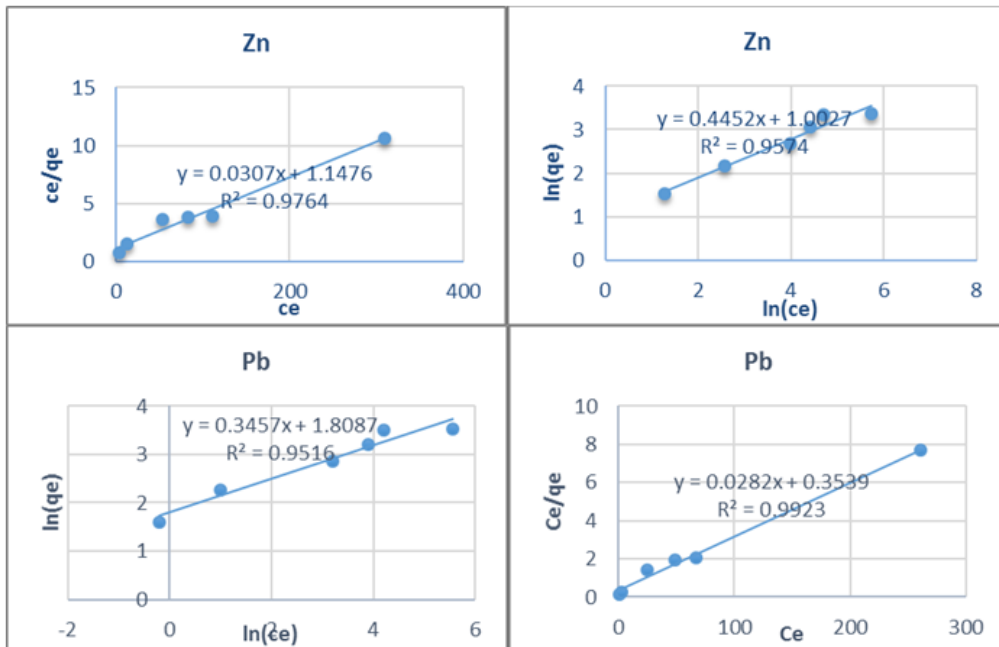


Fig 7: Freundlich isotherms

Fig 8: Langmuir isotherms

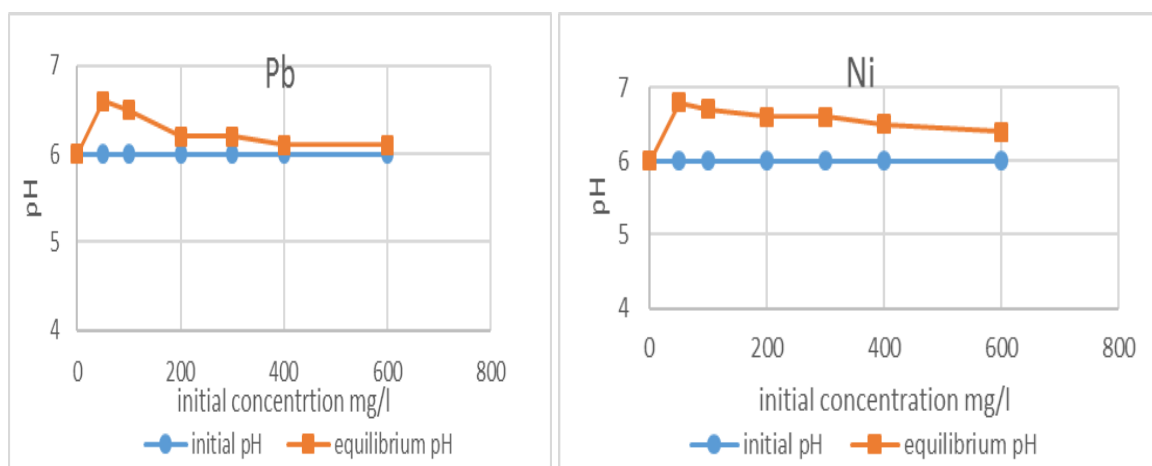
**3.7. Other potential removal Mechanisms**

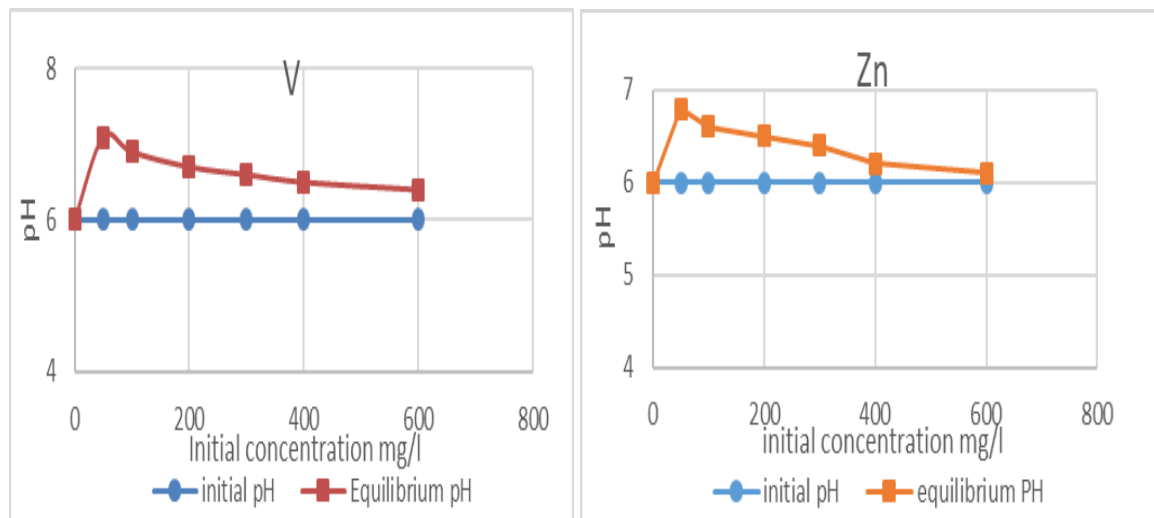
It's obvious from Fig 9 changes in pH at equilibrium point in proportion to the initial concentration of heavy metal ions, pH values become higher at equilibrium point than that at the initial point. The difference between pH values at the tow points decreases when the initial concentration increases. The increase in pH is a result of H<sup>+</sup> Adsorption from the solution. but as the initial concentration of heavy metal increases, the concentration driving force begins to favor the adsorption of heavy metal ions in preference to H<sup>+</sup> ions, this is why pH decreases when the heavy metals initial concentration increases. The equilibrium pH values for Zn<sup>+2</sup>, Ni<sup>+2</sup>, and V<sup>+5</sup> are 6.8, 6.7, and 7. 2 even though they are still lower than the minimum pH values of 8.4,9.3 and 8 which are required for the complete precipitation of Zn<sup>+2</sup>, Ni<sup>+2</sup>, and V<sup>+5</sup> as Hydroxides [22]. Thus no precipitation was occurred during the experiment. However, equilibrium pH value for Pb<sup>+2</sup> solution with concentration of <100mg/l has been higher or equal to the minimum pH value (6.3) which is needed to precipitation

[22]. So precipitation probably occurs. High removal capacity of Pb<sup>+2</sup> from solution can be attributed to adsorption and precipitation of Pb<sup>+2</sup> on Zeolite surface [6, 23], owing ion exchange property zeolite has been utilized in removal of V<sup>+5</sup> and Pb<sup>+2</sup> from solution at high sorption capacity, that is Zeolite has displaceable structural ions such as Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, and Na<sup>+</sup>. These ions should be available in solution at the point of equilibrium as ion exchange process occurring to remove heavy metal ions from the solution. Ca<sup>+2</sup> concentration was measured using ion exchange chromatography. High content of calcium zeolite was displaced from the zeolite thus, V<sup>+5</sup> and Pb<sup>+2</sup> concentrations noticeably increased. The increase in calcium ions at the point of equilibrium can be attributed to high content of adsorbed heavy ions which lead to great displacement of Ca<sup>+2</sup> cations from adsorption sites. Therefore ion exchange is one of efficient processes for heavy metal ions removal from solution using natural zeolite. Tab 2.

**Table 2:** The amount of Ca<sup>2+</sup> ions released from natural zeolite at equilibrium, for different initial vanadium, lead concentrations; initial solution pH = 6.

Initial concentration of V(mg/l)	50	100	200	300	400	600
q <sub>e</sub> (mg Ca/g zeolite)	0.065	0.305	0.325	0.36	0.41	0.44
Initial concentration of Pb(mg/l)	50	100	200	300	400	600
q <sub>e</sub> (mg Ca/g zeolite)	0.050	0.29	0.30	0.35	0.41	0.42





**Fig 9:** changes in pH at equilibrium point in proportion to concentrations of  $V^{+5}$ ,  $Pb^{+2}$ ,  $Zn^{+2}$  &  $Ni^{+2}$  with a lower error of  $\pm 0.1$

According to previous studies [24] increase in calcium ion concentration can be also attributed to natural zeolite at lower pH values (acidic conditions) which cause slight dissolution of natural zeolite and exchangeable ion would release to the solution. Thus the increase in  $Ca^{+2}$  can be as a result of potential processes of ion exchange and dissolution of natural zeolite. But the release of  $Ca^{+2}$  at  $pH=6$  indicates that ion exchange between zeolite and ions of  $V^{+5}$  and  $Pb^{+2}$  in solution is the reason for the increase of  $Ca^{+2}$  at the point of equilibrium.

### 3.8 Natural zeolite selectivity

Usually equilibrium deduction is very essential for the measurement of affinity of natural zeolite towards heavy metals at specific experimental conditions [25]. Langmuir isotherms was used to determine the maximal capacity of natural Zeolite by comparing maximal adsorption capacity  $q_0$  of natural zeolite for heavy metal ion. The result selectivity order was as follows  $V^{+5} > Pb^{+2} > Zn^{+2} > Ni^{+2}$  the differences in zeolite adsorption capacities for heavy metal ions can be attributed to different factors i.e. physicochemical factors hydration energy and diameter, thus high selectivity of zeolite for vanadium was due to electrostatic attraction between high valent vanadium cations and cations of solid adsorbent. In general zeolites and ion exchanges prefer high valent ions [15]. In case of equivalent cations, there are many factors that effect on the process of cation removal i.e. hydration energy of Pb, Zn and Ni: -1495, -2025, -2105Kj/mole [20]. Therefore,  $Pb^{+2}$  ions has highest adsorbent capacity is quiet expected due to its lowest value of hydration energy in comparison to the rest of studied ions [20].

### 3.9 Desorption/Regeneration studies

Desorption of heavy metal ions from an adsorbent or the regeneration of an adsorbent is of great importance that should be taken into consideration upon choosing adsorbent for any practical application [26]. A favorable adsorbent is one that can be regenerated and reused without a significant change in its adsorption efficiency after regeneration. Regeneration enables the reduction in volume of the waste material, which is of great practical and economic importance,

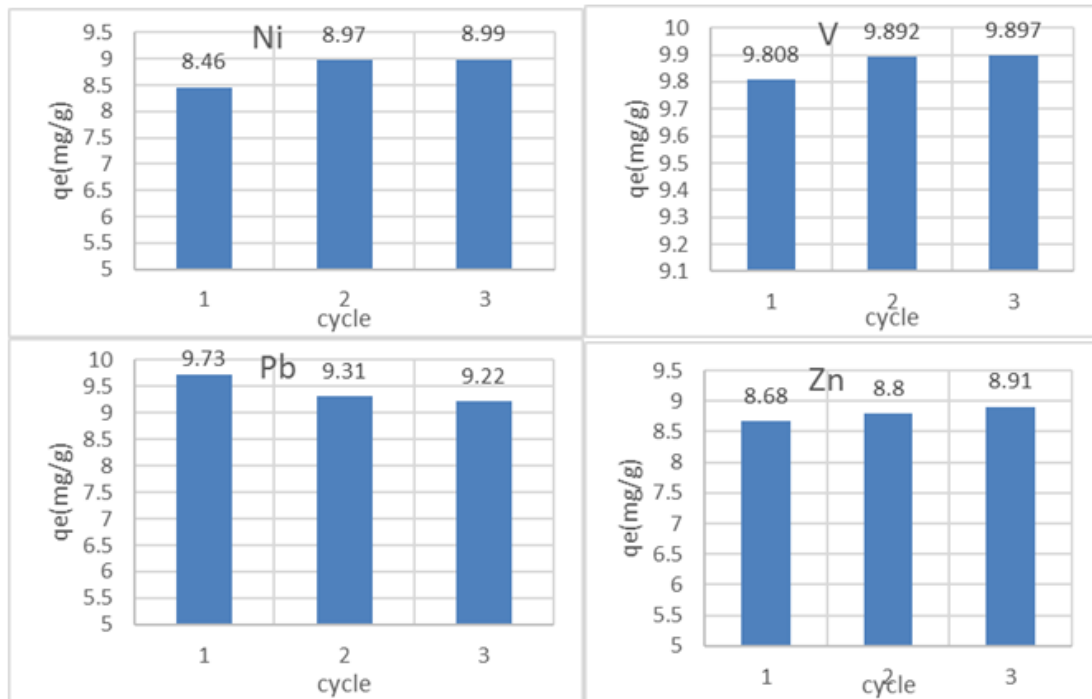
as this reduces the storage costs and land utilization. In this study the regeneration of natural zeolite was carried out using NaCl (20 g/l). The change in adsorption capacity of the natural zeolite was also investigated by contacting regenerated zeolite with single component solutions of the respective metal ions for 360 minutes. It's obvious from Table 3 that the recovery occurred due to the removal of heavy metal ions from adsorbent sites of zeolite and replaced with Na because of its high concentration in NaCl solution in one hand and high kinetics of sodium ions that are capable to replace higher contents of metal ions upon activation.  $Ni^{+2}$  was easily extracted from zeolite due to the lowest selectivity of zeolite towards  $Ni^{+2}$  as mentioned above, thus, it was easily removed from zeolite surface and from the internal micropores of natural zeolite which revealed a higher affinity to  $V^{+5}$  and  $Pb^{+2}$  ions of weak extractability i.e.  $V^{+5}$  and  $Ni^{+2}$  were hardly displaced from zeolite. So that the desorption series is a reversal of the adsorption series, desorption series  $Ni^{+2} > Zn^{+2} > Pb^{+2} > V^{+5}$  and adsorption series:  $V^{+5} > Pb^{+2} > Zn^{+2} > Ni^{+2}$

**Table 3:** The percentage recovery of heavy metals after zeolite regeneration

Heavy metals	% Recovered over 3 cycles		
	1 <sup>st</sup> cycle	2 <sup>nd</sup> cycle	3 <sup>rd</sup> cycle
Pb	73.83	68.97	73.21
Ni	83.48	82.69	84.02
Zn	78.56	76.46	79.25
V	70.02	71.23	69.71

as shown in Fig 10 The adsorption capacity of natural zeolite that has been regenerated using NaCl is either the same for the three adsorption stages or it changed slightly. Tab4 reveals the average percentage change in the adsorption capacity of natural zeolite for the 3 adsorption – desorption cycles. It was also noticed from Table 4 that the adsorption capacity of activated zeolite using NaCl was not negatively affected in general. In fact the adsorption of zinc, nickel and vanadium increased at rate of 2.06, 6.17 and 0.88% respectively as shown in Fig10. After pretreatment with NaCl, the adsorption capacity of zeolite increased [10, 27, 28].





**Fig 10:** changes in adsorption capacity of Zeolite due to regeneration.

**Table 4:** Average percentage of adsorption capacity over the three cycles

Heavy metals	Adsorption capacity mean%		
	1 <sup>st</sup> change ratio	2 <sup>nd</sup> change ratio	Mean
Pb	-4.3	-5.25	-4.78
Ni	+6.08	+6.29	+6.18
Zn	+1.42	+2.71	+2.07
V	+0.86	+0.91	+0.88

Natural zeolite has a low preference for Na<sup>+</sup> ions in comparison to most heavy metals; then Na<sup>+</sup> ions are easily displaced by heavy metals from the zeolite structure, therefore increasing the adsorption capacity of natural zeolite pre-treated with NaCl solution [20, 29, 30].

#### 4. Conclusions

There are many factors that affect the general reaction rate of adsorption process using natural zeolite. i.e. contact time, initial concentration of solution, size of adsorbent particles, and hardness. The optimal removal rate occurs after 6 hours of contact time, when using adsorbent particles of small size. Vanadium metal has the highest rate of adsorption >92%, while Nickel has the lowest one (70-85%). The effect of competing ions are also studied. We found that the studied zeolite has adsorption locations on its surface special for every metal. Each metal reacts with the corresponding adsorption location with different adsorption forms. Natural zeolite is highly efficient in the removal of the studied heavy metal ions from the solution regardless the presence of hardness. The maximal removal capacities of V<sup>+5</sup>, Pb<sup>+2</sup>, Zn<sup>+2</sup> and Ni<sup>+2</sup> have been experimentally found to be 40, 33.89, 29.01, 27.1 mg/g respectively. Freundlich and Langmuir isotherms were used to investigate adsorption of natural zeolite for V<sup>+5</sup>, Pb<sup>+2</sup>, Zn<sup>+2</sup> and Ni<sup>+2</sup>. Comparison between experimental data and model isotherms shows that they are highly correlated (correlation coefficient R<sup>2</sup> = 0.95-.099). Langmuir isotherms best fit the data (R<sup>2</sup> > 0.97). According to Langmuir isotherms the selectivity series of natural Zeolite for heavy metal ions is V<sup>+5</sup>>Pb<sup>+2</sup>>Zn<sup>+2</sup>>Ni<sup>+2</sup>. The increase in Ca<sup>+2</sup> concentration at the point of equilibrium,

indicates that ion exchange between zeolite and solution is responsible for the removal of heavy metals. Precipitation also affects the rate of removal and the quantities of heavy metals in solution. This is particularly true for Pb<sup>+2</sup> which has the lowest pH value necessary for precipitation between the studied ions. NaCl solution at 20g/L was used to activate NZ. The adsorption capacity of natural zeolite that has been regenerated using NaCl is either the same for the three adsorption stages or it changed slightly.

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