Removal of heavy metals Cd (II), Fe (III) and Ni (II), from aqueous solutions by natural (clinoptilolite) zeolites and application to industrial wastewater

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ABSTRACT

The adsorption mechanism of Cd, Fe, and Ni, ions on natural (clinoptilolite) zeolites, a regional low-cost natural available adsorbent was studied in a batch adsorption system. The effect of several parameters such as contact time, zeolite dose, particle size, the effect of pH, and initial concentration of metal ions in the adsorption process was estimated. The optimum adsorption was found to occur at pH 6.0, adsorbent dose 1.0 g/L, and initial concentration 2, 20 and 10 mg/L for Cd, Fe, and Ni, respectively. The adsorption efficiency also increases with decreasing particle size of zeolites and the effect of retention time on adsorption ratio shows that 80% of the Cd, Fe, and Ni, are adsorbed by zeolite during first 120 minutes. Under these optimum conditions, the removal efficiency was 78.8, 89.1, and 65.5% of Cd^{+2}, Fe^{+3} and Ni^{+2}, ions, respectively. Sorption data have been interpreted in terms of Langmuir and Freundlich isotherms. The adsorption efficiency of heavy metals in industrial wastewater as application mode was also investigated using zeolites and these results showed that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater and confirms the potential use of zeolite for the removal of heavy metals from industrial wastewater via adsorption. It was concluded that zeolite is very promising for the removal of metal ions from aqueous solution and hence we encourage the utilization of zeolites in environmental applications.

Keywords: Natural (clinoptilolite) zeolites, Adsorption, Heavy metals, Industrial Wastewater.

1. INTRODUCTION

Heavy metals pollution is one of the most serious problems facing human and other organisms due to its non-biodegradability and accumulation in the living organisms [1]. There are many sources of the heavy metals in the ecosystem that come with the wastewater streams such as electroplating, smelting, paint pigments, batteries, mining operations and agriculture activities [2]. The main concern of environmentalists toward heavy metal is that these elements are highly toxic and their serious impact on human health and surroundings can't ignore [3]. Nowadays, many studies are working on how to remove the toxic heavy metal contaminants from aqueous waste streams especially from industrial wastewater. Conventional methods, including, electro dialysis [4], chemical precipitation [5], reverse osmosis [6], ion-exchange [7], ultrafiltration [8], and adsorption used for removal of heavy metal ions from aqueous solutions. While most of these techniques are expensive and inapplicable on a large scale, ion exchange and adsorption method, among all above-mentioned processes, is the most preferable one because it is economically advantageous, high efficient and applicable [9,10], especially when using low-cost natural sorbents such as clay materials, biomass, perlites, diatomite, and zeolite. In this regard, naturally occurring

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zeolites hold great potential to use as packing material in subsurface reactive barriers intercepting groundwater plumes and for fixed bed reactors designed to remove heavy metals from industrial wastewater [11]. Zeolites have a framework silicate with a three-dimensional cage structure. Their structure bears negative charges which can balance by adsorption of exchangeable cations [12]. Due to the high deposit of zeolite in nature, its low cost, stable structure, even at an acidic environment, strong adsorption capacity, it has recently drawn attention to use in the treatment of industrial wastewater. According to these attracting properties of zeolite, interest has been increased towards the method of heavy metal adsorption from aqueous solution. There are several studies carried on the effectiveness and the importance of using natural zeolite for the adsorption of heavy metals under different empirical conditions such as pH, temperature, granular phase volume, concentration, and induction speed [16 - 20].

In the present study natural zeolite was tested as an efficient adsorbent for removing of ions of Cd^{+2}, Fe^{+3}, and Ni^{+2}, from aqueous solutions and wastewater. This article aims to investigate the parameters that affect removal rates, such as contact time, particle size, pH of the initial solution and zeolite dose. Also, the maximum adsorption capacity of natural zeolite, which is used to remove the studied metal ions through equilibrium reactions, was determined. As well as comparing the empirical data of adsorption balance with Langmuir and Freundlich sorption models to evaluate the adsorption performance of natural zeolite.

2. MATERIAL AND METHODS

2. 1 Preparation of Materials

Analytical grade chemicals were employed in all experiments. Compounds, $Cd(NO_3)_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$ and $Ni(NO_3) \cdot 4H_2O$, were purchased from Sigma Aldrich (USA) and used in the experiments. Adequate amounts of the metal salts were dissolved in de-ionized water (DIW) to yield the stock solutions of concentration 1000 mg/L. Various concentrations used in the adsorption studies were obtained by dilution of stock solution with DIW. All glassware was washed with soap, followed by 10 % HNO_3 and then rinsed many times with DIW before use. Adjustment of pH was done using either 0.1 M HNO_3 or 0.1M NaOH, and pH was measured with a pocket pH meter model Orion 210. Natural zeolite from Alex Trading & Commercial Agencies Company was used. Grain size fractions were used as received from the company in two Size: <0.5 mm (fraction I), 2.0 – < 6mm (fraction II).

2. 1. 1 Characterization

The main chemical composition of zeolite analyzed by X-ray diffraction(XRD) and X-ray fluorescence(XRF) methods, as well as other Physical properties such as particle size, density, humidity, fire loss, water, porosity, surface area, and hydrogen ion concentration carried at the Central Metallurgical Research Institute (CMRDI).

2.1. 2 Industrial wastewater

Industrial wastewater samples were collected from collecting industrial wastewater treatment plant from Adabiya area at Suez Bay, Egypt. Two main samples from the inlet and outlet of this plant were collected, and then stored in acid-washed polyethylene bottles for analysis. All the precautions recommended by [21], to minimize risks of sample contamination were followed during the collection and treatment of samples.

2.2 Batch Adsorption Studies

To evaluate the process of single adsorption of Cd^{+2}, Fe^{+3}, and Ni^{+2} from aqueous solution, different parameters and factors were studied. The aqueous solutions were agitated at

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different time intervals in a room temperature and on a mechanical shaker at 200 rpm. After the reactions, the supernatant was collected in a syringe and filtered through a 0.2µm membrane filter to measure the metal ion concentrations using a flame atomic absorption spectroscopy (Perkin Elmer A Analyst 100). Samples were diluted before the required analysis to set the calibration linear range.

2.2.1 Effect of pH

To investigate the optimum pH of adsorption, 50 ml of aqueous solution containing 2 mg/l of single metal ions (Cd^{+2}, Fe^{+3}, and Ni^{+2}) and having a pH range from 2 to 8 was mixed with 0.5 g of adsorbent in a 250 ml conical flask. After 180 min of contact time, the suspension was filtered and analyzed for heavy metal ions by atomic- absorption spectrophotometer.

2. 2. 2 Effect of Adsorbent Dose

Furthermore, to evaluate the optimum dosage of the, adsorbent dose studies were carried out in 0.25, 0.5, 0.75, 1, 1.5, 2 and 4.0 g adsorbent and 50 ml of solution containing 2 mg/l of heavy metal ion concentrations at optimum pH obtained from the section above during the contact time of 180 min at room temperature.

2. 2. 3 Effect of particle size

In order to investigate the grain size effect of zeolite, the batch experiment was performed in two sizes: < 0.5 mm (fraction I), 2.0 – < 6mm (fraction II). A 50 ml of a solution containing 2 mg/l of heavy metal ion concentrations at optimum pH and adsorbent dose, the contact time of 180 min at room temperature.

2.2.4 Effect of initial heavy metal ions concentration

The kinetic study of metals was performed using different concentrations (1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 100.0 mg /l) of each single metal ion. Optimum conditions such as pH and adsorbent dose determined previously in the batch studies were applied.

2.2.5 Effect of contact time

The time-dependent behavior of Cd^{+2}, Fe^{+3}, and Ni^{+2} adsorption was studied by varying the contact time between the adsorbate and the adsorbent at 5, 15, 30, 60, 90, 120, and 180 min at room temperature. The optimum conditions of the solution such as pH, adsorbent dose, and metals concentrations determined previously in the batch studies were used to determine the effect of contact time on the adsorption behavior of zeolite.

2.3 Equilibrium

The main objective of the equilibrium studies was to determine the maximum capacity of natural zeolite towards Cd^{+2}, Fe^{+3} and Ni^{+2} 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. The adsorption capacity formula is given by the following equation: qe (mg⁄g) $= \frac{x}{m} = (Ci - Ce)x\ V/m$, where qe is the quantity of dissolved adsorbed material in mg per g of the adsorbent at equilibrium, Ci: initial concentration of contaminant in solution at equilibrium (mg/l), V: volume of water phase (l), M: mass of solid phase (g). Percentage of metal removal can also be displayed by the percentage of metal removal as follows: Metal removal (%) =100 (Ci − Ce) / Ci.

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2. 3. 1 Langmuir Adsorption Isotherms

The Langmuir model suggests that adsorption occurs on the monolayer of the surface which contains an unlimited number of adsorption sites of equal energy. The linearity of Langmuir equation is expressed as follows: $\frac{Ce}{qe} = \frac{1}{q0\ b} + \frac{Ce}{q0}$ .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 q0 can be extrapolated from the slope of the linear plot of $\frac{Ce}{qe}$ with the index of Ce [22, 23, 24].

2. 3. 2 Freundlich Adsorption Isotherms

Freundlich model suggests energetically heterogeneous surface of porous matter so that adsorption capacity is due to adsorption temperature. Linear equation of Freundlich model is as follows: $\ln qe = \ln K + \frac{1}{n} \ln Ce$, 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 < refer to heterogeneous adsorbents while those values close or equal to 1 refer to relatively homogenous adsorbents at binding sites [23, 25], ln K, 1/n can be extrapolated from the slope of linear plot ln qe with index of In Ce.

2. 4 Application test on industrial wastewater:

Wastewater samples were preconcentrated with APDC-MIBK extraction procedure according to the standard methods [26]. Total metal concentrations were measured by flame atomic absorption spectrophotometer (FAAS; Perkin Elmer A Analyst 100). Concentrations of heavy metals are expressed as (mgL^{-1}). Zeolite (chloropitolite), were applied to the same samples at the optimum conditions (C_i= 2 ppm; pH = 6; m=0.5g; V=50ml; t=180 min; particle size < 0.5 mm), then simulated the removal rate of metals in wastewater. The same extracted method was applied to the wastewater after adsorption with zeolite.

3. RESULTS AND DISCUSSION

3. 1 Properties of studied zeolites

Zeolite sample is a non-dusting, hard and resistance to attrition, non-clouding in liquids (due to absence of clays), good permeability, and relatively high density and high water retention. The qualitative composition of natural (clinoptilolite) zeolites, has obtained by X-ray spectroscopy analysis, where the physical properties and chemical compositions present in the peaks of compounds as shown in Figure 1, and presented in Tables 1& 2.

3.1.1 Mineral component, %

The natural (clinoptilolite) zeolites were composed mainly of SiO_2 and Al_2O_3 components whose Si/Al ratio becomes 1.88 that means there are two Si atoms for each single Al atom. While the MnO and K_2O contents were very low. The zeolite contained large amounts of CaO as compared with the other component, thus appears that a high CaO content might enable the formation of hydroxy Sodalite. It has higher contents of calcium compound so it's called calcium zeolite.

The XRD patterns of zeolite and iron dust are shown in Figure1. The XRD pattern of zeolite proved that Clinoptilolite is the major part of it [13]. The zeolite structure causes zeolite to have negatively charged surface which can be used for adsorption of alkali earth metals. The oxygen atom in the tetrahedral structure of zeolite (Si-O-Al) leads to a negative charge

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on the adsorbent surfaces that are available sites for metal adsorption. Therefore, Si/Al ratio decline and the presence of oxygen atoms in zeolite structure are considered as two potential factors in the metals adsorption process [27].

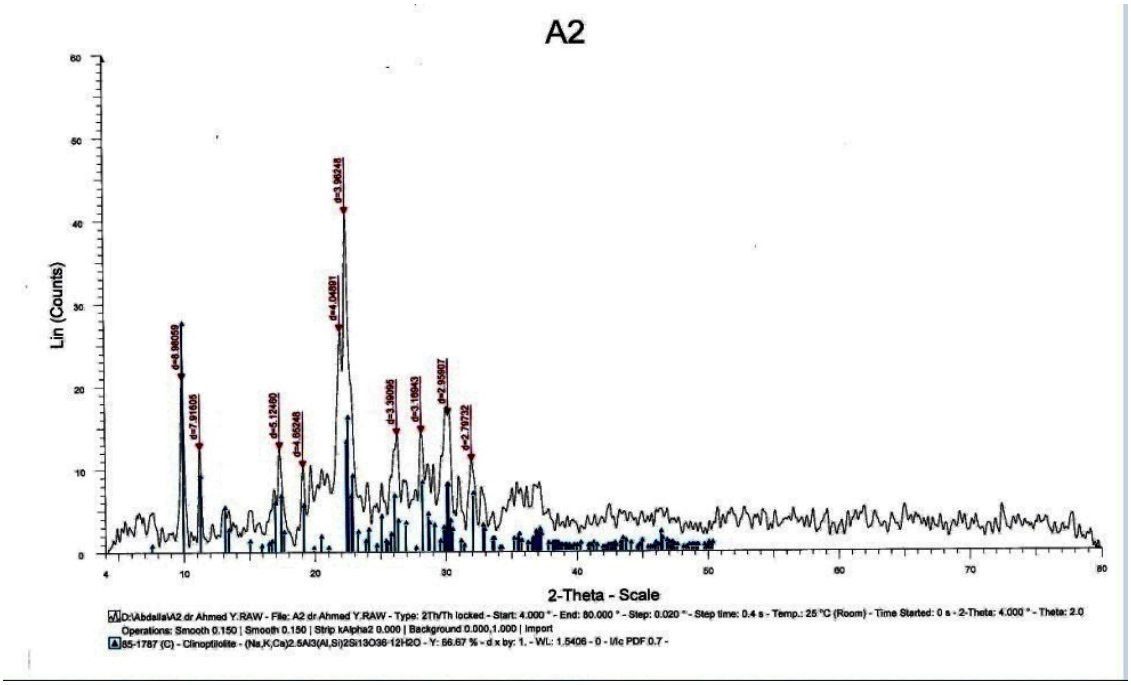

Figure 1. The XRD pattern of the sample confirming its Clinoptilolite mineralogy.

Table 1: Physical properties of natural (clinoptilolite) zeolites:

Physical properties	Values
Bulk (particle) Density, $gmcm^{-3}$	1.83
Overall Surface area, m^2gm^{-1}	89.82
Porosity, %	27.80
Total pore area, m^2gm^{-1}	35.836
Average pore diameter, µm	0.0181
Solubility, %	7.38
Swelling Index	2.52
pH	6.8
Apparent (Skeletal) Density, $gmcm^{-3}$	2.377
Appearance (Color)	Greyish-white
Humidity, %	6.75
Loss on ignition %	13.6
Hardness, Moh' no.	4
Grain Size	< 6 mm

Also, zeolite has cages and tunnels that can loosely hold water molecules in contrast to other tecto-silicates such as feldspar and quartz, These channels and cages are adequate for adsorbing molecules smaller than these channels and/or tunnels, so in this regard, zeolites are known as “molecular sieves” [28].

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3.1.2 Chemical composition

Table 2: Chemical composition of natural (clinoptilolite) zeolites:

Cations, %		Major elements (oxides), %		Other elements, (trace)	
K_2O, %	3.266	SiO_2	62.22	Cl	0.025
CaO, %	3.583	Al_2O_3	11.096	BaO	0.085
Na_2O, %	0.780	Na_2O	0.78	P_2O_5	0.033
		MgO	0.599	ZnO	0.025
		CaO	3.583	SrO	0.047
		Fe_2O_3	4.033	PbO	0.002
		K_2O	3.266	MnO	0.120
		TiO_2	0.339	SO_3	0.035
		ZrO_2	0.112		

The replacement of tetravalent silicon by trivalent aluminum in the mineral's structure creates a net negative charge that is counterbalanced by the presence of cations (usually Ca^{2+}, Na^{+} and K^{+}) which are situated in cavities [29, 30]. The removal of the heavy metal ions with zeolite is a result of ion exchange and/or adsorption property of zeolite. Both processes are parallel, but one of them is prevailing depending on the solid to the liquid ratio, [31]. Ion exchange properties of zeolites are due to the weakly bonded extra-framework cations which are mobile and easily exchanged with solution cations [32]. As it has been stated, removal of heavy metals from aqueous solution by means of zeolite is mainly is based on adsorption and ion exchange process. However, other mechanisms such as physicosorption and chemisorption are employed by zeolites for the sorption [33].

3. 2. Batch Adsorption Studies

3. 2. 1. Effect of adsorbent particle size

It's noticed from Figure 2 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 [34, 23]. The 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 [34]. It's also noticed that Cd^{+2} and Fe^{+3} revealed the greatest affinity 80.9 and 79%, while Ni^{+2} revealed the lowest affinity (65.2 %). And the more metals were sorbed, however, by fine-grained zeolite than by coarse-grained zeolite [35].

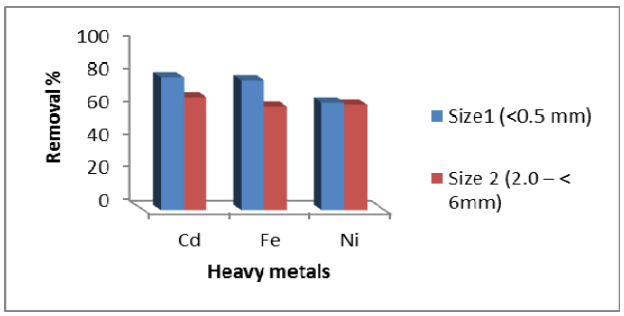

Figure 2. Adsorbent particle size affecting on the removal of Cd^{+2}, Fe^{+3} and Ni^{+2}, from the solution (C_i= 2 ppm; pH = 6; m=0.5g; V=50ml; t=180 min)

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3. 2. 2. Effect of pH on adsorption

The solution pH is one of the crucial parameters in the sorption of heavy metals by zeolites, because of its effect on the charge state of metals and also adsorbent surface [36]. The effect of pH on studied metals uptake by zeolite was evaluated and shown in Figure 3.

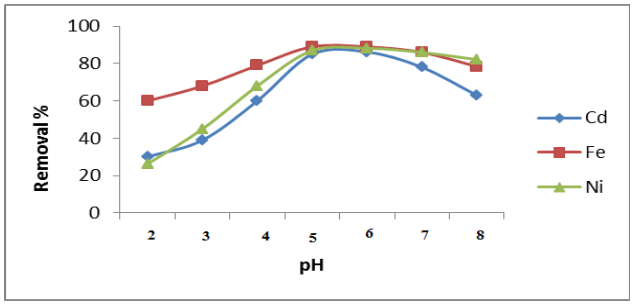

Figure 3. pH affecting on the removal of Cd^{+2}, Fe^{+3} and Ni^{+2} from the solution (C_i= 2 ppm; size < 0.5 mm; m=0.5g; V=50ml; t=180 min)

As is known, the cationic metals' adsorption efficiency is lower at acidic pH. It was observed that Cd^{+2}, Fe^{+3}, and Ni^{+2} uptakes increased with the increase of pH up to 6 and then it decreased with further increase in pH. Also, at pH below 6, hydrogen ions compete with positive charge ions for adsorption sites. Therefore, this condition limits the access of metal ions to the adsorption sites and decreases metal removal [37]. Furthermore, at alkaline pH values, the adsorption of metals decrease because soluble hydroxylated complexes of the metal ions are formed and compete with metal for adsorption sites. Apart from affecting the characteristics of heavy metal ions and their sorption, pH can also affect the structure of zeolites. Aluminosilicate structure is vulnerable to strong basic and acidic environments. Strong bases can lead to desilication, whereas strong acids can break Al atoms. Zeolite structure can be destroyed at extreme pH values, which in turn can reduce sorption [38, 33].

3. 2. 3. Effect of the initial heavy metal ion concentration

In the adsorption process, the initial concentration of ions in solution has a key role as a driving force to overcome the mass transfer resistance between the liquid phase and solid phase. Thus, it is expected that with an increase in metal ions the metal uptake will increase. [33]. The adsorption of Cd, Fe, and Ni as a function of their concentrations was studied at room temperature by varying the heavy metal ion concentration from 1 to 100 mg/L. The results are shown in Figure 4.

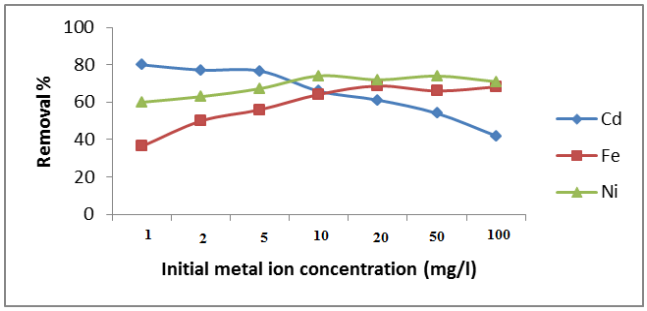

Figure 4. Initial heavy metal ion concentration (mg/l) affecting on the removal of Cd^{+2}, Fe^{+3} and Ni^{+2} from the solution (size < 0.5 mm; m=0.5g; V=50ml pH = 6; t=180 min)

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The maximum amount of Fe^{+3} and Ni^{+2} removal percentage of natural (clinoptilolite) zeolites at concentrations of 20 and 10 mg/l were obtained 68.7 and 74.1 %, respectively. Instead, the removal percentage decreased from 80 to 42% for Cd^{+2}, for concentration 2 to 100 mg/l. The results also, showed that Fe^{+3} and Ni^{+2} uptake rate was relatively high at the beginning of the process due to abundance available adsorption sites. However, the number of active sites for the adsorption gradually decreases with an increase in processing time and the adsorption rate slightly decreased, leading to the formation of the adsorption equilibrium. At low metal concentrations, adsorption sites are available and could easily be occupied since the ratio between the number of metal moles in solution and the available surface area is low. Therefore, adsorption is independent of the initial concentration. Nevertheless, at high concentrations of metal, the removal efficiency is dependent on the initial concentration because the number of available sites is less than the number of metal moles. [39], stated when the initial concentration increases, the removal rate decreases. At higher concentration, the number of ions competing for the available binding sites on the biomass surface increases and thus reduces the number of binding sites. Meanwhile, at higher concentration, the average distance between the adsorbed species will be reduced, which affects the distribution of surface charge. Thus, the ability of adsorbate to migrate to the adsorbent surface changes and, as a result, the fixation reduces [40].

3. 2. 4. Effect of adsorbent dose

The adsorbent dose is one of the important parameters in adsorption processes because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate under a given set of operating conditions [41]. To achieve this aim, a series of batch experiments were conducted with the adsorbent dose of 0.25, 0.5, 0.75, 1.0, 1.5, 2 and 4 g per 50 ml of test solution.

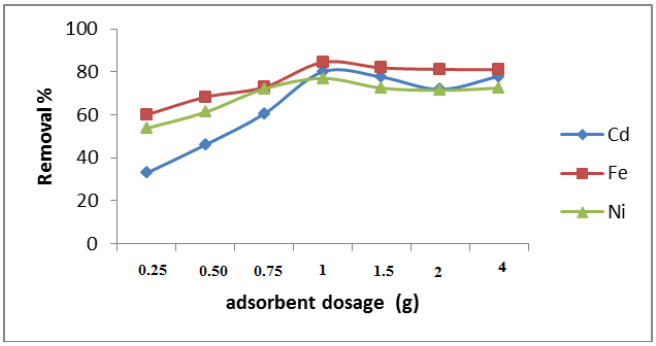

Figure 5. Adsorbent dose affecting on the removal of Cd^{+2}, Fe^{+3} and Ni^{+2}, from the solution (C_i= 2 ppm; size < 0.5 mm; pH= 6; V=50ml; t=180 min)

Figure 5 shows the effect of adsorbent dose on the adsorption of Cd^{+2}, Fe^{+3}, and Ni^{+2} ions. When the addition of the adsorbent dose increased, the percentage removal of metal ions also increased. A maximum removal of 80.1, 84.5 and 77% of Cd^{+2}, Fe^{+3}, and Ni^{+2} ions, respectively was obtained at 1.0 g of the adsorbent. It can be seen from Figure 3 that an adsorbent dose of 1.0 g is sufficient for optimal removal of metal ions in aqueous solutions. A further increase in the quantity of adsorbent dose will not have any significant effect on the removal of metal ions from the solution. The initial increment in adsorption capacity with the increase in adsorbent dose was expected because as the adsorbent dose increases the number of adsorbent particles increases, thus more surface areas were available for metal attachment [42].

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3. 2. 5. Effect of contact time

The effect of contact time on adsorption efficiency is depicted in Figure 6. It is clear from the Figure, that the contact time needed to reach the maximum removal of metal by zeolite was dependent on the type of heavy metal [43].

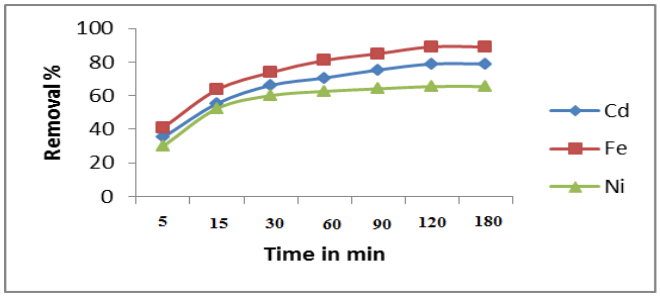

Figure 6. Contact time affecting on the removal of Cd^{+2}, Fe^{+3} and Ni^{+2}, from the solution (C_i= 2 ppm; size < 0.5 mm; pH= 6; V=50ml; m=0.5g)

The result of the effect of contact time on removal efficiency for Cd, Fe, and Ni, using 0.5 g zeolite at room temperature (25±0.1°C) is represented in Figure 6. The adsorption rate was observed as rapid in the first 30 min, followed by a gradual increase in time until equilibrium adsorption was noticed at 90 min. The fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the adsorbent surface. The attainment of equilibrium adsorption might have been due to the reduction in the available active adsorption sites on the adsorbent with time [41].

3.3 Adsorption isotherms

Adsorption isotherms are an important factor in system design and describe the interaction between the adsorbent and adsorbate. Freundlich and Langmuir isotherm curves for the adsorption of Cd^{+2}, Fe^{+3} and Ni^{+2} ions from solution as shown in Table 3 and Figure 7, reveal the reliability of experimental findings where the values of correlation coefficient R^2 range from 0.994 - 0.999, the maximal capacities of the given heavy metals adsorption q_0 according to Langmuir model are 10.08, 9.971, and 9.901 mg/g for Cd^{+2}, Fe^{+3}, and Ni^{+2} respectively.

Table 3. Calculated equilibrium adsorption isotherm constants for the uptake of Cd^{+2}, Fe^{+3} and Ni^{+2} from solution by natural zeolite.

Heavy metals ions	Langmuir			Freundlich		
	q_o (mg/g)	b	R^2	k	1/n	R^2
Cd	10.08	1.607	0.994	1.454	0.39	0.688
Fe	9.971	3.105	0.999	6.622	0.87	0.990
Ni	9.901	2.387	0.998	9.365	0.99	0.998

The maximal value is for Cd indicating to the higher selectivity of zeolite to Cd in comparison with other metals. Heterogeneity coefficient 1/n from Freundlich isotherm curve is less than 1

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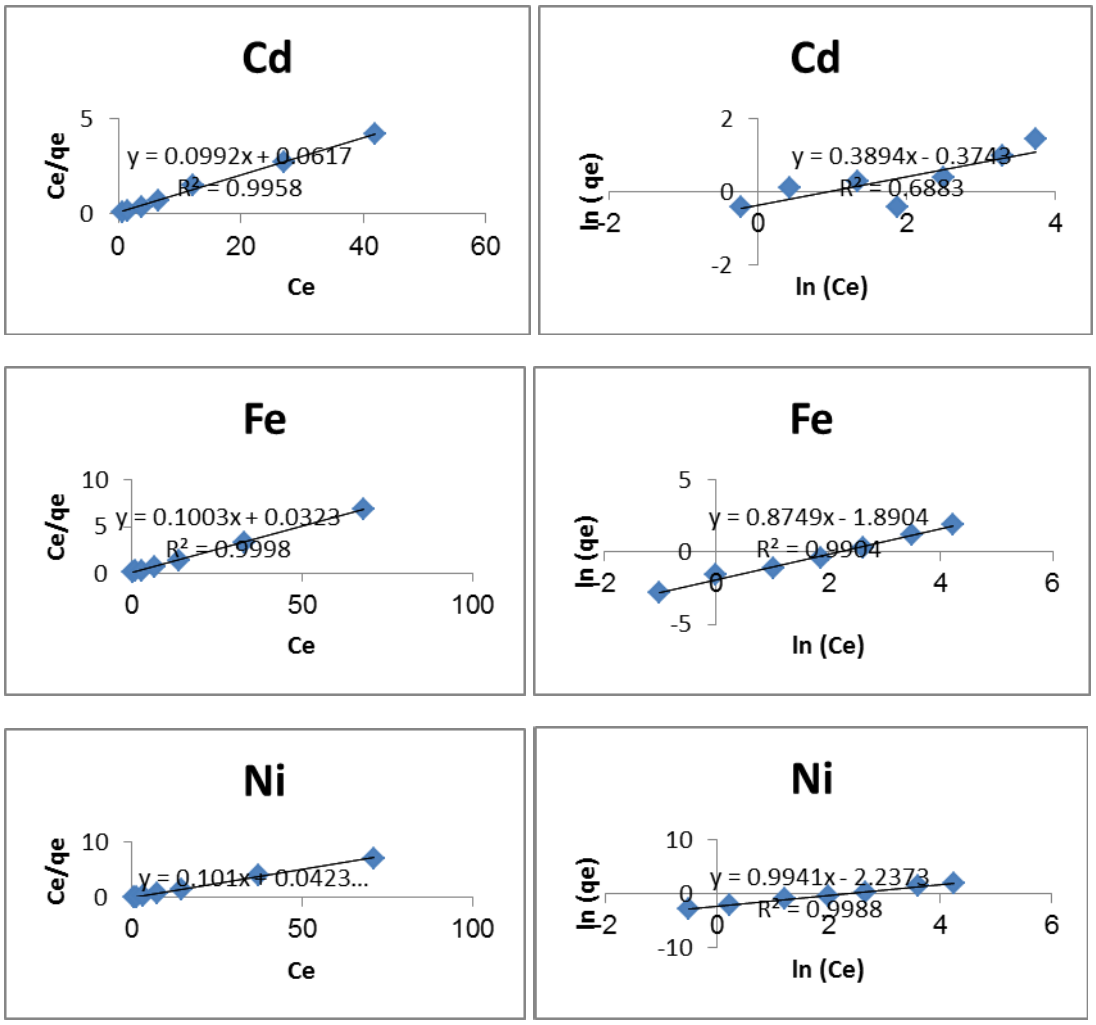
and thus the evaluations are 0.39, 0.87, and 0.99 for Cd, Fe, and Ni respectively. The values indicate a material with relatively homogenous binding sites of natural porous Zeolite. It's been noticed from Figure 7, the higher concentration of heavy metal ions the higher content of adsorbed metal per gram of natural Zeolite q_e 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 [43, 44]. The increase continues until the saturation point is achieved.



(a) Langmuir isotherms **(b) Freundlich isotherms**

Figure 7. Adsorption isotherms of Cd^{+2}, Fe^{+3}, and Ni^{+2} based on the Langmuir and Freundlich models

The removal efficiency (R%) of the metal ions on this adsorbent shows good affinity of zeolite for a number of ions such as Cd^{+2}, Fe^{+3} and Ni^{+2} ions in water. The Langmuir and Freundlich models were investigated for adsorption isotherms that the Langmuir isotherm fitted with equilibrium data better than the Freundlich isotherm.

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Application test on industrial wastewater:

The results presented in table 4, indicated relatively high concentrations of measured heavy metals from both inlet and outlet of wastewater treatment plant since this sample is taken from mixed industrial wastewater and is characterized by high concentrations of these elements [48].

Table 4. The concentration of different heavy metals at industrial wastewater before and after application of zeolite.

Heavy metals mgL^{-1}	Inlet to wastewater treatment plant			An outlet from wastewater treatment plant			Standard Limit Egypt
	Before	After	% removal	Before	After	% removal	
Cd	0.588	0.189	68.00	0.462	0.111	76.00	0.05
Fe	91.32	17.35	81.01	83.88	14.25	83.00	1.50
Mn	3.102	0.713	77.00	1.890	0.378	80.00	1.00
Ni	3.641	1.456	60.01	1.860	0.651	65.00	0.10
Pb	3.840	1.512	60.60	2.286	0.873	61.77	0.50
Zn	19.08	8.853	53.60	12.52	5.245	58.10	5.00

Industrial wastewater contains various metal ions with influence on the potentiality of adsorbent to treat wastewater in competition for exchange sites and within adsorbent [23].

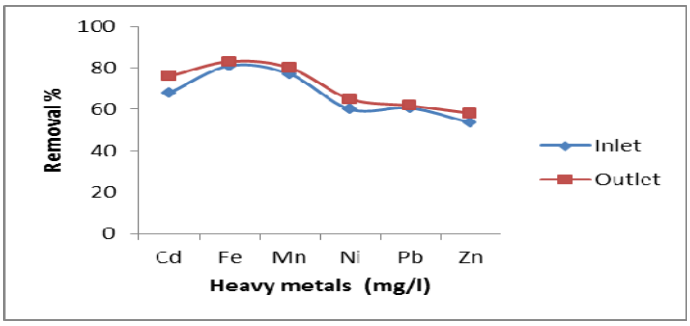

Figure 8. Removal % of different heavy metals in both inlet and outlet samples from industrial wastewater after applying of zeolite.

From table 4, it was observed that the metals in industrial wastewater follow the order: Fe > Zn > Pb > Ni > Mn > Cd, without application of zeolite. These variations depend on the amount and the type of the effluent drained in the study area [46, 47]. These concentration values for metals in both inlet and outlet samples exceed the maximum levels of the standard limitations for the discharge of industrial effluents in Egypt (Law 4/1994 for the disposal of the marine environment in Egypt). By applying zeolite the order became Fe> Mn > Cd > Ni > Pb > Zn. Each metal has unique electronegativities, ionic size and bond strength which influence the adsorption capacity of the zeolite [48]. During treatment with zeolite, the removal of heavy metals from industrial wastewater sample is high whereby the percentage of removal is more than 50 per cent of the initial concentration. The removal of heavy metals from industrial wastewater in an individual industry is effective using zeolite, but when using with mixed industrial wastewater, it can diminish the pollution problem to a certain and a considerable extent.

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4. CONCLUSION

The removal of heavy metals from aqueous solution was carried out in batch adsorption mode using natural (clinoptilolite) zeolites adsorbent. Natural zeolites exhibited effectiveness in the removal of Cd (II), Fe (III) and Ni (II) ions from aqueous solutions. Many factors affected the general reaction rate of adsorption process using natural zeolite from which contact time, zeolite dose, particle size, pH, and initial concentration of metal ions. It was found that the adsorption process is pH-dependent for studying metals, and the maximum uptake was obtained at the pH of 6. Optimal removal rate occurs after 2 hours of contact time when using adsorbent particles of small size. The best isotherm fit for Cd, Fe, and Ni was obtained with Langmuir model. By applying to industrial wastewater, the result of the experiments proved that the natural (clinoptilolite) zeolites could be used as an effective and low-cost method in removing metals from industrial wastewater. In the recommendation, the results obtained from this study show the need for further studies on the removal of the other toxic pollutant

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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