Adsorption of Ni²⁺ and Cd²⁺ from Aqueous Solution by Using Natural Zeolites

Mekdes Gerawork[*], Amare Ayalew and Daniel Moges

Department of Chemistry, College of Natural and Computational Sciences, Debre Berhan University, P.O. Box 126, Debre Berhan, Ethiopia

[*]**Corresponding author:** Gerawork M, Department of Chemistry, College of Natural and Computational Sciences, Debre Berhan University, P.O. Box 126, Debre Berhan, Ethiopia, Tel: +251-913155005; E-mail: mgerawork2009@gmail.com

Abstract

Heavy metals from wastewater are major pollutants of the environment. To remove these pollutants adsorption by natural zeolite has been used. The physico-chemical properties of the adsorbent were characterized by AAS and FTIR spectrophotometers. Then the adsorption efficiency of the adsorbent was optimized as a function of pH, dose of the adsorbent, initial concentration of adsorbate and contact time. The findings of this study showed the optimal metal adsorption was 98.94% for Cd and 91.2% for Ni at pH 6, 0.002 g/mL dose of the adsorbent, 120min contact time and 0.001 g/mL initial concentration of the adsorbate. Indeed, the adsorption and isotherm studies were discovered that kinetics and adsorptions were well described by the pseudo-second order and the Freundlich isotherm model fitted to the equilibrium data better than the Langmuir model did. So, this study confirmed that adsorption of heavy metals from aqueous solution by natural zeolites was very promising and efficient.

Keywords: Adsorbent; Adsorption; Heavy metals; Natural zeolites; Pollutants

Introduction

Contamination of Cadmium, Copper, Lead, Arsenic, Chromium and Nickel metal ions is the major concern because of their poisonous and non-biodegradable property. Many industries are discharging these heavy metals in the environment through their wastewaters. High levels of heavy metals in the environment are serious causes for human health disorders if they are above the permissible concentration. Cadmium exposure causes renal dysfunction, bone degeneration, liver and blood damage [1]. The other toxic heavy metal is nickel which causes reduction in cell growth, cancer and nervous system [2]. As a result, earlier researchers have been used numerous conventional methods such as chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electro dialysis, etc. But these methods were not effective, are expensive, require high energy, generation of secondary sludge [3]. So, it is necessary to shift in to other advanced and environmentally friendly treatment methods like adsorption. Therefore, these problems were leads to widespread research by

developing effective methods for the removal of heavy metals from industrial wastewater particularly by using natural zeolites which are naturally available, economically effectives, selective, can be regenerate and effectiveness to remove these metal wastes. Moreover, these adsorbents are very successful to remove the pollutants completely than conventional methods. This is due their unique structure and ion exchange capacity characters for selection of these inorganic materials. Means that their aluminosilicate structure, there is partial substitution of Si^{4+} by Al^{3+}, results in the formation of excess negative charges. Then it is balanced by mono and divalent exchangeable cation such as Na^+, Ca^{2+}, K^+, and Mg^{2+}. These cations are coordinated with the defined number of water molecules, and located on specific sites [4]. Therefore, the purpose of this research was to investigate the effectiveness of natural zeolites as adsorbents for the removal of Cd^{2+} and Ni^{2+} from the targeted aqueous solution. Batch process technique was used as a function of initial concentration of the adsorbate, effect of dosage of adsorbent, pH of the solution and contact time. And also the property of the adsorbent was characterized by using FTIR and the adsorption of the metals by AAS spectrophotometers.

Materials and Methods

Materials

Beaker, stirrer, test tube, Spatula, measuring cylinder, conical flask, Hot plate, digital balance, siever shaker, rotatory shaker, pH meter, funnel, Oven, AAS (model-NOVAA 400), FTIR (Shimadzu model 8400S, German) are among the apparatus and instruments that the researchers were used during this study. All chemicals were analytically graded in this experiment. The compound $CdCl_2$, $Ni(NO_3)_2.6H_2O$, distilled water, natural zeolite, HNO_3, NaOH and HCl were taken from laboratory of chemistry, Debre Berhan University.

Methods

Preparation of adsorbent and metal solutions

The particle size distribution of the samples was determined in a sieve shaker. Natural zeolite was treated with hydrochloric acid (5% volume) over a period of 24 hrs and distilled water to remove fine powders and contaminants and was dried at 110°C for 1h before use Then by taking Stock solutions of 1000 mg/L of metals were prepared by weighing 4.9 g of Ni $(NO_3)_2.6H_2O$ and 1.63 g $CdCl_2$ which were dissolved in distilled water. The stock solution then diluted into 100 mg/l working solution [5].

Techniques for sample characterization

Atomic Absorption Spectroscopy (AAS) was used for characterization of metals composition. The percent of metal ions removal (%) from the investigated solution were calculated by the formula [6,7]:

$$\% \ Adsorption = \frac{(C_o - C_e)}{C_o} \times 100$$

.... (1)

Where C_o and C_e are the initial and final concentration (mg/L)

FTIR was used to identify organic (and in some cases inorganic) materials with their corresponding vibrations. The infrared absorption bands identify molecular components and structures.

Batch sorption experiment

Sorption experiment was carried out by varying pH value, contact time, concentration of adsorbate and adsorbent by using the necessary adsorbent in conical flask containing metal ions solution.

Effect of pH

The effect of pH on the adsorption of Cd^{2+} and Ni^{2+} ions on natural zeolite were studied by mixing 0.025 g of natural zeolite with 25 ml of aqueous solution containing 100 ppm of Cd^{2+} and Ni^{2+} at room temperature. 25 ml solutions were taken and finally, the metals in the supernatant were analyzed using the atomic adsorption spectrometer (AAS - model - NOVAA 400) [8].

Effect of contact time

The effects of contact time on the removal efficiency of natural zeolite for nickel and cadmium metal cations were studied. The rate uptakes of these metal ions were studied by using natural zeolite as absorbent by varying the contact time from 30 min to 180 min [8].

Effect of initial concentration of adsorbate

The effects of the adsorbate concentration were studied at room temperature by varying the adsorbate concentration at 25 mg/L to 150 mg/L. The waste water was prepared at different Ni^{2+} and Cd^{2+} ion concentration, 25 mg/lL 50 mg/L, 100 mg/L, and 150 mg/L, and their pH value were adjusted at pH 6 then 0.025 g of natural was added to each conical flask containing a sample of Ni^{2+} and Cd^{2+}. The final concentration of Cd^{2+} and Ni^{2+} in the aqueous solution was determined by AAS [7]. The concentrations of adsorbed species on adsorbent were calculated using the following equation [8]:

$$Qe=\left|\frac{(Ci-Cf)V}{m}\right| \qquad (2)$$

Where Qe is the final concentration of metal ions on adsorbent (mg. g^{-1}), C_i and C_f are the concentration of metal ions in the initial and final Solutions (mg/L), respectively, V is the volume of aqueous solution (L) and m is the mass of adsorbent used (g)

Effect of dosage of adsorbents

Adsorbent dosage is one of the most important parameter in adsorption which is used to determine the capacity of adsorbent at a given concentration of the adsorbate. Different concentration of natural zeolite 0.25 g/L, 0.5 g/L, 1 g/L and 2 g/L were added to the aqueous solutions which contained Cd^{2+} and Ni^{2+} ions separately. Then the suspensions were filtered and the concentration of Cd^{2+} and Ni^{2+} ions were determined by AAS [8-12].

Adsorption isotherm models

The adsorption isotherms are very important in describing the adsorption behavior of solutes on the specific adsorbents. In these studies, two important isotherm models such as Langmuir and Freundlich model were studied.

Langmuir isotherm models

The isotherm describes quantitatively the buildup of a layer of molecules on an adsorbent surface as a function of concentration of adsorbed materials in the liquid phase in which it is in contact.

The mathematical expression of Langmuir isotherm models are

$$\frac{Ce}{qe} = \frac{1}{qmKL} + \frac{Ce}{qm} \qquad (3)$$

Where qe is the amount of solute adsorbed per unit of adsorbent (mg/g), Ce the equilibrium concentration of solute in the bulk solution (mg/L), qm the monolayer adsorption capacity (mg/g) and KL is the Langmuir constant which reflects the binding strength between metals ions and adsorbent surface (L/mg). KL is the reciprocal of the concentration at which half saturation of the adsorbent is reached [13].

Freundlich isotherms models

This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [14].

$$Log\ q_e = KF + \frac{1}{n}\log C_e \qquad (4)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), Ce the equilibrium concentration of solute in the bulk solution (mg/l), KF a constant indicative of the relative adsorption (mg/g) and the constant 1/n indicates the intensity of the adsorption. n is considered as the heterogeneity of the adsorbate and its affinity for the adsorbent. A higher value of n (or a smaller value of 1/n) indicates a stronger bond between the adsorbate and the adsorbent.

Adsorption kinetics

The kinetics of heavy metal adsorption onto the natural zeolite can be predicted using pseudo-first order and pseudo-second order models. Pseudo-first order model assumes that the metal cation binds only one sorption site on the sorbent surface while the pseudo- second order equation assumes that the metal cations can bind to two binding site on the adsorbent surface. The equation can be expressed as shown in equation 5 and 6 respectively.

Results and Discussion

Characterization of the adsorbent

FTIR analysis: Fourier transformation infrared spectroscopy (FTIR) analysis was carried out in order to detect the functional groups in the adsorbent that be involved in the adsorption process. As shown in FIG. 1A, the frequency value between 3630-3487 stretching vibrations confirms the presence of –O-H group. The weak bands between 1652-1646 are attributed to the bending mode of water molecule. The Bands between 825-407 cm^{-1} region are mostly attributed to internal tetrahedral vibration of Si-O and Al-O of the materials. As shown in FIG. 1A other bands appear at 1023 cm^{-1} arise from asymmetric stretching vibration mode of internal T-O bond in TO$_4$ tetrahedral (T=Si and Al) [9]. FTIR spectrums of natural zeolite after the adsorption of nickel and cadmium have shown in FIG. 1B and 1C respectively.

Batch adsorption experiment: In this study the solution pH, dose of adsorbent, contact time and initial concentration of adsorbate were investigated towards cadmium and nickel adsorption on natural zeolite.

Effect of pH

The effect of pH on the metal ions adsorption by the natural zeolite was studied in the pH range between 3 to 7. The effect of pH was shown in FIG. 2. The pH was limited to values less or equal to 7 because of precipitation at higher pH and prevent further adsorption [10]. The removals of cadmium and Nickel by adsorption on natural zeolite were found to increase from 84.65 to 87.61% and 52.13 to 67.80% respectively when the pH was increased from 3 to 7. The optimum pH was 6 and the maximum cadmium and Nickel removal at this pH was 87.61% and 67.80% respectively. The low removal efficiency at low pH is apparently due to the presence of higher concentration of H^+ ions in the solution which complete with the Cd^{2+} and Ni^{2+} ions for the adsorption sites of the natural zeolite. With the pH increasing, the H^+ ions concentration decrease leading to increase Cd^{2+} and Ni^{2+} uptake. In higher acidic environment, several functional groups become protonated and act as positively charged species, resulting in reduced attraction between the metals and the minerals. Deprotonation of functional groups occurs at increasing pH and these behave as negatively charged species, attracting heavy metals. However, precipitation occurring at alkaline environment masks the true extent of metals sorption on natural zeolite.
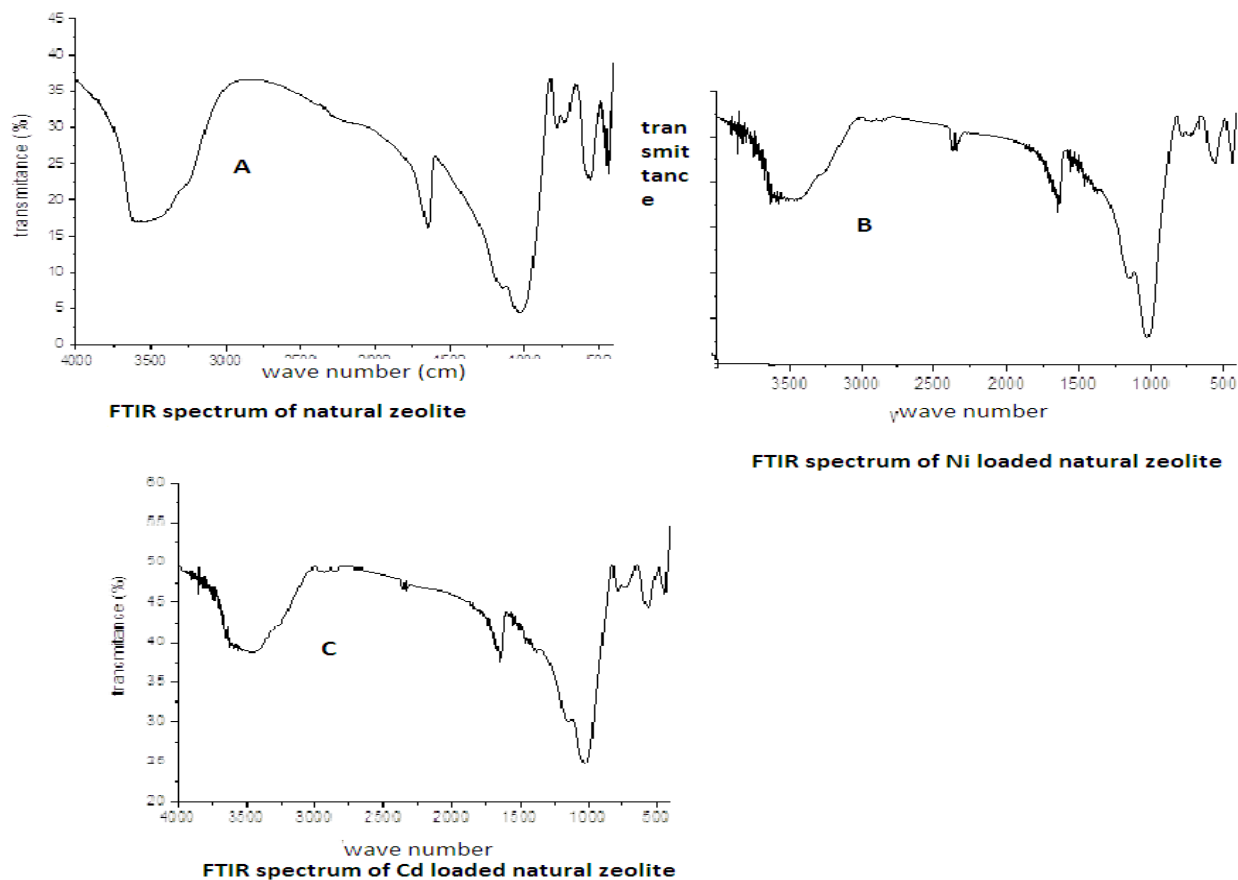

FIG. 1. **FTIR spectrum of natural zeolite: A) for natural zeolite B) Ni loaded zeolite C) Cd loaded zeolite.**
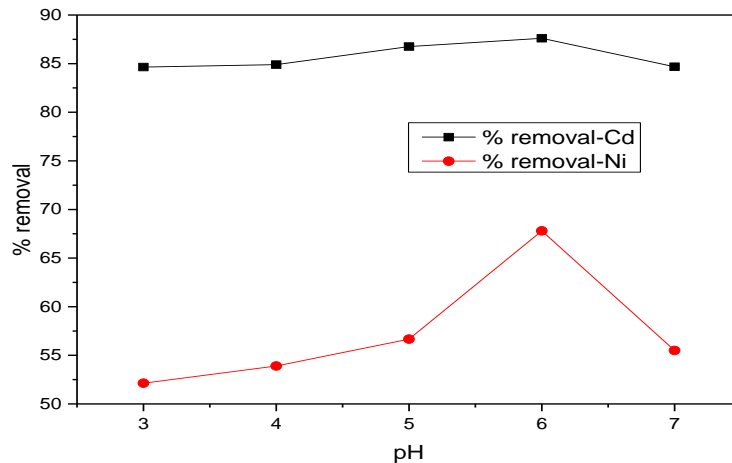
FIG. 2. **The effect of pH on the removal efficiency of natural zeolite for cadmium and nickel from solution.**

Effect of dose of adsorbent

The effect of adsorbent dosage on natural zeolite to adsorb Ni^{2+} and Cd^{2+} ions from aqueous solution was investigated. In this study the effect of the dose of natural zeolite were investigated by varying the adsorbent dose from 0.00025 g/mL to 0.002 g/mL on a 0.001 g/mL initial concentration of nickel and cadmium ions at pH 6. It can be seen from FIG. 2 that removal efficiency increased (FIG. 3 and 4). The removal efficiency gradually increased from 59.19% to 91.2% for nickel and from 84.93% to 98.94% for cadmium metal as the dose increased. However, more increment of the adsorbent dose was decreased the efficiency of natural zeolite from 91.2% to 47.32% for nickel and from 98.94% to 86.94% for cadmium. Generally, an increase in the adsorbent concentration increases the available area and the number of binding sites for the same solution volume. However, an increase in the adsorbent aggregation decreases the available active site. Several studies have reported the same impact of concentration on adsorption capacity and heavy metals removal efficiency of various heavy metals [11].
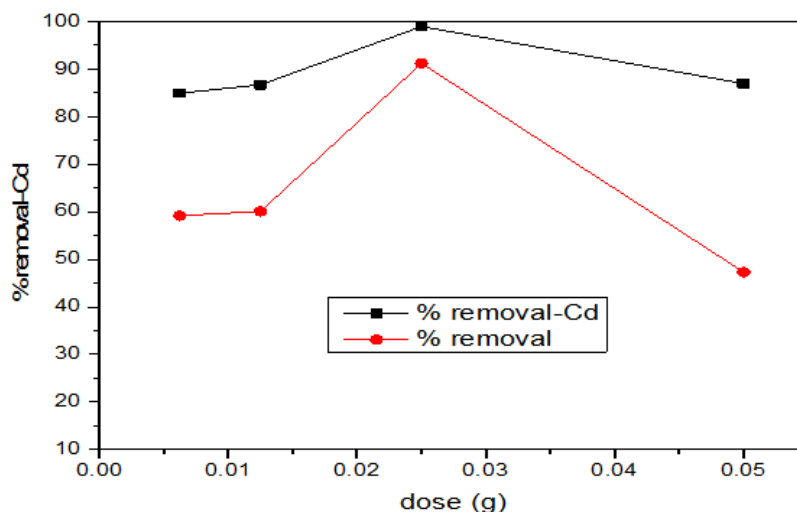

FIG. 3. **Effect of adsorbent dose on the removal of cadmium and nickel metals.**

Effect of contact time

As shown in FIG. 4, the effect of contact time on the removal of Cd^{2+} and Ni^{2+} ions using 0.025 g of natural zeolite was done. This was achieved by varying the contact time from 30 min to 180 min in separate experimental runs. The equilibrium adsorption was attained through 120 min for both cadmium and nickel metal and the equilibrium were determined at 65.76 mg/g and 60.19 mg/g respectively. The adsorption rate was observed as rapid in the first 90 min, followed by a gradual stage was with time until equilibrium adsorption was noticed at 120 min. This can be explained by the fact that initially, the rate of ion uptake was higher because all sites on the adsorbent were vacant and the ion concentration was high. The attainment of equilibrium adsorption might have been due to reduction in the available active adsorption sites on the adsorbent with time resulting to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of adsorbent. Different studies have reported the same impact of contact time on the removal efficiency of natural zeolite [5].
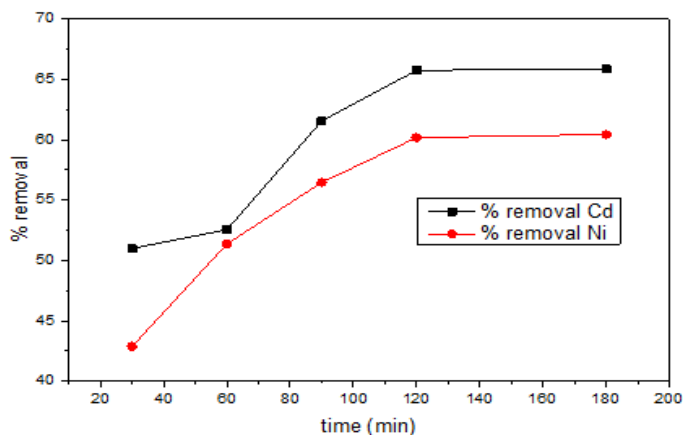

FIG. 4. **The effect of contact time on the removal of efficiency of cadmium and nickel.**

Effect of initial concentration

To find the optimum concentration, experimental studies were carried out for a wide range of metals concentration between 25 g/L to 150 mg/L. The capability of sorption process was found to be stable and reached a maximum value at concentration 100 mg/L. FIG. 5 represents the results of this investigation.
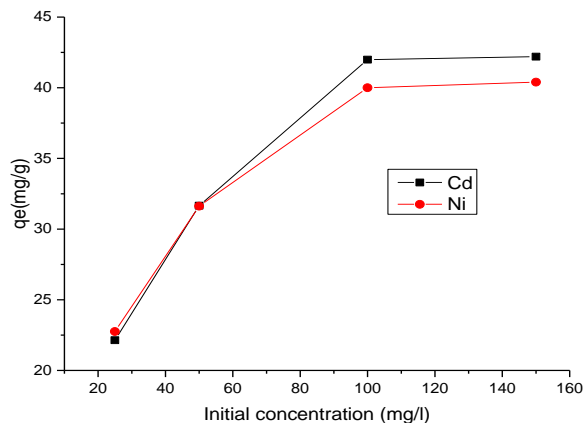

FIG. 5. **The effect of initial concentration to remove Cd and Ni from solution.**

The above results (FIG. 5) indicate that the amount of Ni and Cd adsorbed on natural zeolite were increased as the initial concentrations were increased until the system reached at equilibrium. The increase in the amount of Cd and Ni adsorbed as the initial concentration increase is a consequence of an increase in the concentration driving force. The concentration deriving force is responsible for overcoming the mass transfer resistance associated with the adsorption of metals from solution by the natural zeolites [12]. Therefore, as initial concentration increase, the driving force also increase resulting in an increase in metals uptake by the natural zeolite.

Adsorption Isotherms

Langmuir isotherm

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. According to Langmuir isotherm formula:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Plot of Ce/qe *vs.* Ce gives a straight line with slope $1/q_m$ and intercept $1/q_m K_L$. From this study, R_L value for Cd^{2+} and Ni^{2+} ions adsorption ranged from 0.13 to 0.48 and 0.057 to 0.27. Therefore, the adsorption process is favorable (FIG. 6 and 7).
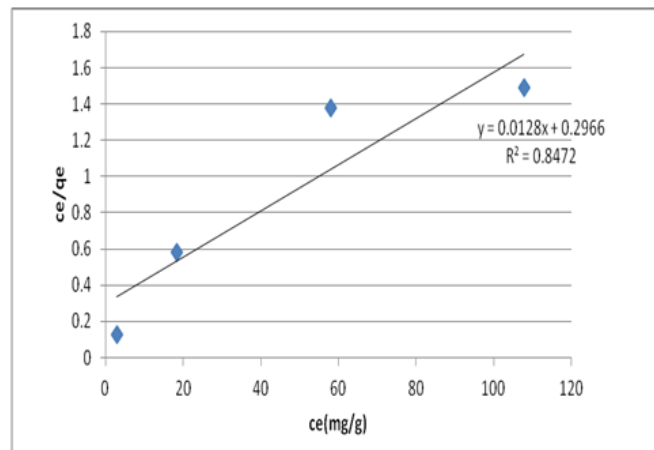

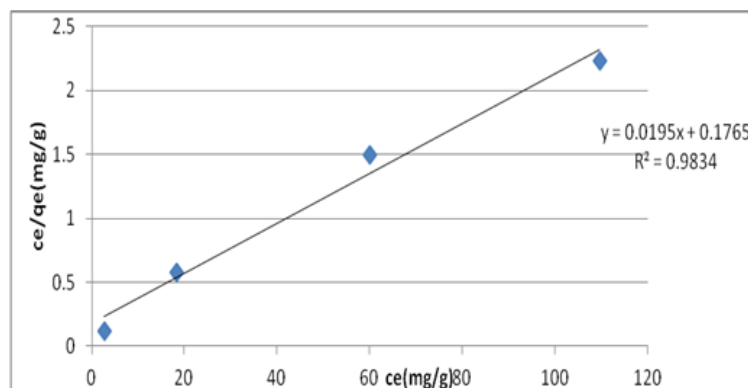FIG. 6. **Langmuir isotherm for Cd^{2+} adsorption onto natural zeolite.**

FIG 7. **Langmuir isotherm for Ni^{2+} adsorption onto natural zeolite**

The Freundlich Isotherm

The Freundlich equation is one the earliest empirical equations used to describe equilibrium data. This model can be applied to non-ideal adsorption (FIG. 8 and 9). It often represents an initial surface adsorption followed by a condensation effects resulting from extremely strong solute- solute interactions. The Freundlich equation:

$$\log q_e = \log K_F + 1/n \log C_e \text{ (linear form)},$$

The plot of lnqe *vs.* lnCe gives straight line with slope 1/n and intercepts $\ln k_F$. The values of the Freundlich constants together with the correlation coefficient are presented below in FIG. 8.
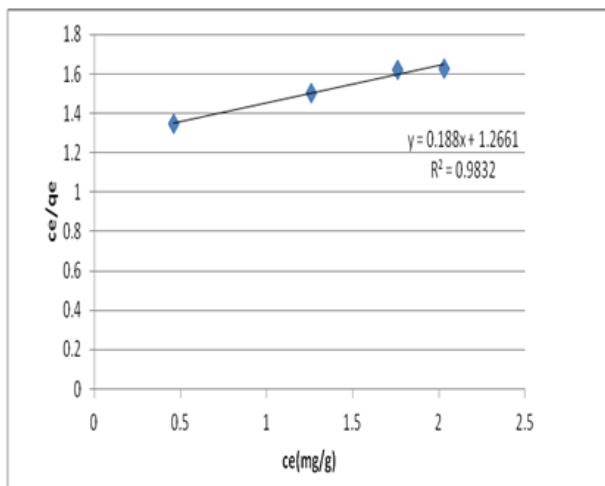

FIG. 8. Freundlich isotherm for Cd^{2+} adsorption onto natural zeolte.
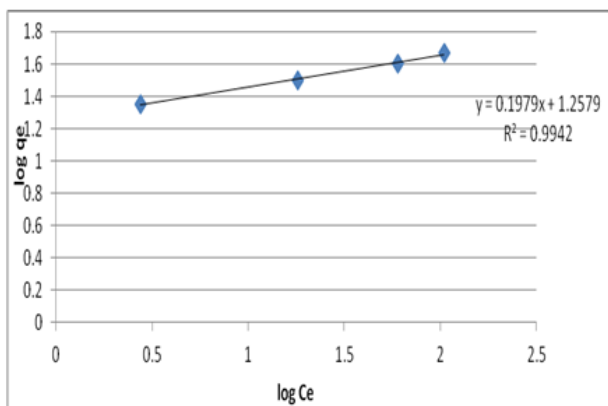

FIG. 9. Freundlich isotherm for Ni^{2+} adsorption onto natural zeolite

It appears that the Freundlich isotherm gave a better fit than the Langmuir isotherm. The regression coefficient value of the Freundlich isotherm 0.9832 and 0.9942 for Cd^{2+} and Ni^{2+} respectively are better than that of the Langmuir isotherms 0.8472 and 0.9834 for Cd^{2+} and Ni^{2+}.

Kinetics studies

The kinetic dada of the adsorption of cadmium and nickel onto natural zeolite were evaluated using pseudo-first order and pseudo-second order kinetics models.

Pseudo-first order model

The model assumes that the metal cations bind only one sorption site on the adsorbent surface. The pseudo-first order is expressed by the equation:

$$\ln (q_e - q_t) = \ln q_e - k_1 t, \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(5)$$

Where: qe and qt are the amount of heavy metal adsorbed (mg/g) at equilibrium and at the time t (t min) and k1 is the rate constant for the pseudo-first order adsorption process (min^{-1}) Linear plots of log (qe-qt) versus t are used to predict the rate constant (K1) and adsorption at equilibrium (mg/g), which are obtained from the slop and intercept respectively (FIG. 10 and 11).
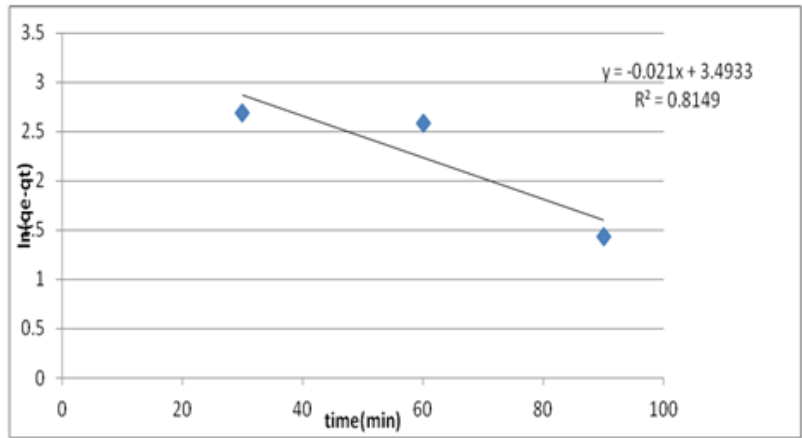

FIG. 10. **Pseudo-first order kinetics model of Cd^{2+} adsorption onto natural zeolite.**
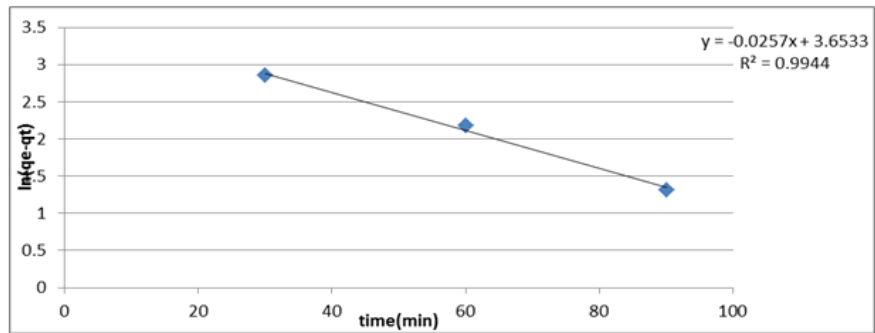

FIG. 11: **Pseudo-first order kinetics model of Ni^{2+} adsorption onto natural zeolite**

Pseudo- second order model

$$\frac{t}{q_t} = \frac{1}{kqe2} + \frac{t}{q_e} \qquad (6)$$

Where *qt* and *qe* are the amount of metal adsorbed per unit weight of adsorbent (mg/g) at time *t*, and at equilibrium respectively (FIG. 12 and 13). K$_2$ is adsorption rate constant of the pseudo-second order equation (g/mg min). A plot of *t/qt* versus time (*t*) would yield a line with a slope of 1/*qe* and an intercept of 1/k$_2$q$_e$^{2}.
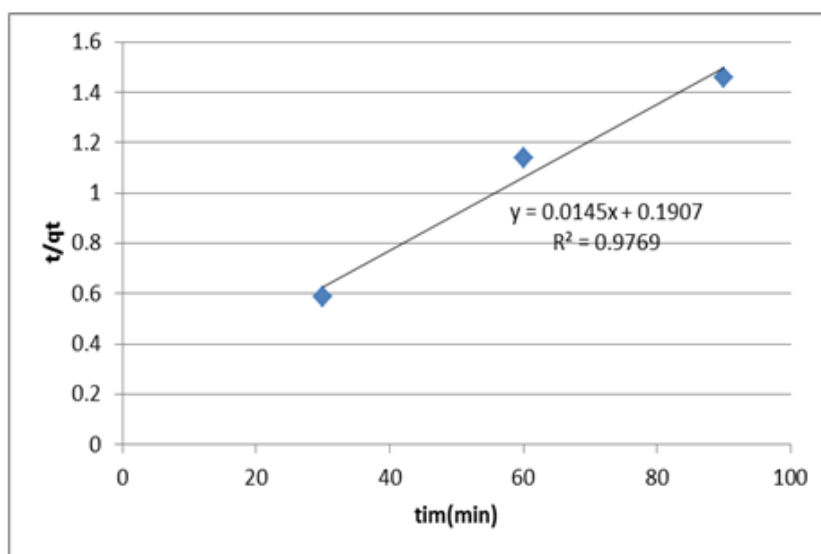
FIG. 12. **Pseudo-second order kinetic model of Cd^{2+} adsorption onto natural zeolite.**
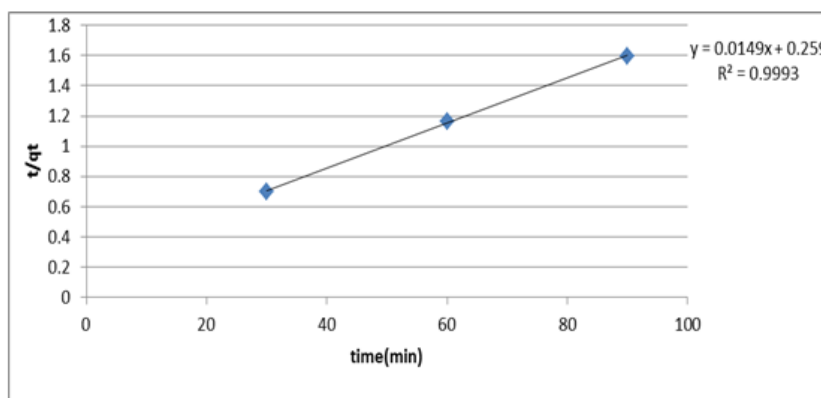

FIG. 13: **Pseudo-second order kinetic model of Ni^{2+} adsorption onto natural zeolite.**

Pseudo-first order rate constant k_1 and equilibrium uptake q_e were determined from the pseudo-first order plot of ln (qe-qt) vs. t (FIG. 10 and 11). The slope and intercept for cadmium were 0.021and 3.493, and 0.0225 and 4.01 for nickel respectively. While the slope and intercept for cadmium were 0.0145 and 0.190, and 0.0135 and 0.5067 for nickel respectively in pseudo second order kinetic model. From this finding, the pseudo-second order kinetic model favoured the adsorption process with a regression correlation (R^2) of 0.9769 for cadmium and 0.9692 for nickel while the pseudo-first order kinetic regression correlation gave 0.816 for cadmium and 0.9439 for nickel. The correlation coefficient using pseudo second order model is more than that of the first order model, therefore the adsorption of Cd^{2+} and Ni^{2+} ions are not suitable using the pseudo first order model.

Conclusion

This study revealed that natural zeolite can be effectively employed as a good adsorbent for the removal of Ni^{2+} and Cd^{2+} ions from aqueous solution. The removal of Ni^{2+} and Cd^{2+} ions from aqueous solution were dependent on pH, adsorbent dose, contact time and initial concentration of adsorbate. The data obtained in this study was described by Langmuir and Freundlich isotherm. Freundlich adsorption isotherm fitted best implying that there was multilayer coverage of the metal ions

on the surface of the adsorbent. The adsorption data also fitted well for Pseudo-second order model. Therefore, natural zeolites as adsorbents of heavy metal were very sensitive to remediate the environment by naturally available and environmental friendly inorganic materials.

REFERENCES

1. Sharma SK. Heavy metals in water: Presence, removal and safety JECRC University, Jaipur, India. 2004; pp: 4-5.

2. Tizro S, Baseri H. Heavy metals removal from wastewater by using different kinds of Magnetite Nano adsorbents. Journal of Advanced Materials and Processing. 2016;4(4):15-29.

3. Siddiquee S, Rovina K, Azad SA, et al. Heavy metals contaminants removal from wastewater using the potential filamentous fungi biomass. Journal of Microbial and Biochemical Technology. 2015;7:384-93.

4. Peric J, Trgo M, Medvidovic NV. Removal of zinc, copper, and Lead by natural zeolite - A comparison of adsorption isotherms. Water research. 2004;38:1893-99.

5. Pang M, Kano N, Imaizumi H. Adsorption of chromium (IV) from aqueous solution using zeolite. J Chem Eng. 2015;9:433-41.

6. Khachatryan SV. Heavy metal absorption by Armenian natural zeolite from natural aqueous solution, proceeding of the Yervan state Univ. Chemistry and Biology. 2014;2:31-5.

7. Shaheen SM, Derbalah AS, Mogham FS. Removal of heavy metals from aqueous solution by zeolite in competitive sorption system. International Journal of Environmental Science and Development. 2012;3(4):363.

8. Ansanay A S, Lemenech C, Hurel C, et al. Adsorption of nickel and arsenic from aqueous solution of natural sepiolite. International Journal of Nanotechnology. 2012;9:208.

9. Taslimah S, Suyati L. Synthesis of zeolite from sugarcane bagasse ash using cetyltrimethyl ammonium bromide as structure directing agent. Indonesia J Chem. 2018;18(1):159-65.

10. Ghomri F, Lahsini A, Laajeb A. The removal of heavy metal ions (copper, zinc, nickel, cobalt) by natural Beatonite. Larhyss J. 2013;37-54.

11. Hommaid O, Hamdo JY. Adsorption of Cr (VI) from an aqueous solution on a Syrian surfactant modified zeolite. Int Journal of Chem. Tech Res. 2014;6(7):3753-61.

12. Barrer RM. Zeolite and clay minerals as sorbents and molecular sieves, Academic press Int. London, UK. 1978.

13. Ho YS, McKay G. Competitive sorption of copper and Nickel ions from aqueous solution using peat. Journal of the International Adsorption Society. 1999;5:409-17.

14. Van Loon GM, Duffy SJ. Environmental chemistry. (2nd edn), Oxford University Press Inc. New York, USA. 2005; pp: 308-18.