

KINETICS OF GANKI LAUMONTITE-ZEOLITE AS EFFECTIVE ADSORBENTS IN WASTEWATER TREATMENT

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ABSTRACT

Zeolite is an important mineral that has been used as an adsorbent. The present study explores the application of modified laumonite from Ganki deposit for treatment of heavy metal polluted water. Batch adsorption technique was adopted to evaluate the effect of time and adsorbent dosage on the removal of lead, nickel, cadmium and chromium from water. AAS was used in determining the metal ion concentration in the various solutions. Langmuir and Freundlich adsorption model were used to carry out the kinetic studies. Percentage removal of the metals was 94.40%, 63.63%, 65.70% and 82.55% for lead, nickel, cadmium and chromium, respectively. The removal data were fitted into the Langmuir and Freundlich isotherm equation and the value of their corresponding constant was determined. The modified laumonite from Ganki deposit is found to be very effective for removal of the heavy metals. The modified laumonite could be used affectively for the treatment of heavy metals polluted water and industrial effluents.

Keywords: Absorption, Kinetics, Laumontite, Wastewater, Zeolite

1 INTRODUCTION

Numerous studies have confirmed that chemically modified natural zeolite have excellent performance on the removal of metal cation from wastewater [1]. It is known that heavy metals are toxic and are non-degradable. Thus, they have ability to reach living organisms through the food chain [2]. Having this in mind, they must be eliminated or reduced from wastewater [3]. Recently, researchers around the globe have shown more interest in natural zeolites as adsorbents in water and wastewater treatment, their properties and possible modification of natural zeolites. Different natural zeolites around the world have also shown good exchange capabilities for cation such as heavy metal [4]. The effectiveness of the natural zeolites in wastewater treatment depends on their physio-chemical properties that are tightly connected to their geological deposit. Natural zeolites have the advantage of low cost because of its availability naturally. They also have abundance of cation exchange capability, acts as a molecular sieve and have a high surface area. The advantages of natural zeolite attract the interest of many researchers in exploiting natural zeolite as an adsorbent for the adsorption of heavy metals in waste waters. Modification of natural zeolites can be performed by several methods such as acid treatment, ion exchange and surfactant functionalization. Modified zeolites show high adsorption capacity also for organic matter anions. Motsi *et al.* [5] used natural zeolite modified as an adsorbent for adsorption of Fe^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} and reported that the sequence of adsorption of the heavy metals are $\text{Fe}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+}$. Erdem *et al.* [6] used natural zeolite to adsorb Co^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} ions in industrial waste. They found that the natural zeolite, clinoptilolite has a good ability to adsorb these ions; an optimum ions adsorption sequence was $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. Vujakovic [7] modified natural clay by treating with hydrochloric acid and subsequently neutralizing the resultant solution by the addition of sodium hydroxide. They used the modified clay for the removal of nickel, copper and zinc. It was found that the uptake capacity of the modified clay did significantly increase. In recent years, natural zeolite and its modified forms have also been reported for removal of anions and

organics from water systems and in cation adsorption using natural zeolites as well as their modified forms for removal of anions and organic compounds in water and wastewater treatment [8]. In this work, kinetics study for the removal of heavy metal ions such as Lead, Nickel, Cadmium and Chromium ions in waste water samples using the modified laumontite deposit in Ganki of Fufure Local Government Area of Adamawa state, Nigeria as an adsorbent was exhausted.

2 METHODOLOGY

2.1 Sorption isotherm models

In this work, batch adsorption technique was selected to study the adsorption and kinetics models for lead, nickel, cadmium and chromium uptake. The adsorption experimental results of lead, nickel, cadmium and chromium on laumontite were analyzed according to well-known isotherm model (Langmuir and Freundlich). The Langmuir model makes assumptions such as monolayer and constant adsorption energy while the Freundlich models deals with heterogeneous adsorption. The uptake of heavy metal through a sequence of batch test was calculated using equation 1.

$$q_e = (c_i - c_f) \frac{V}{m} \quad (1)$$

where q_e is the weight of the heavy metal uptake per unit of laumontite (mg/g); C_i is the initial concentration of the metal in solution before the sorption analysis (mg/L); C_f is the final concentration of the metal in solution after the sorption analysis (mg/L); m is the dry weight of laumontite (g); V is the solution volume (L). Langmuir equation of adsorption is given by equation 2 [9].

$$q = \frac{Q_{\max} K C_f}{1 + K C_f} \quad (2)$$

It is linearized to the form equation 3.

$$\frac{1}{q} = \frac{1}{Q_{\max}} + \frac{1}{K Q_{\max} C_f} \quad (3)$$

where Q_{\max} and K are Langmuir constants. The Freundlich equation of adsorption isotherm is given by equation 4 [9].

$$q_e = k_f C_f^{1/n} \quad (4)$$

Its linearized form is represented by equation 5.

$$\log q_e = \log K_r + \left(\frac{1}{n}\right) \log C_f \quad (5)$$

2.2 Adsorption studies

Batch adsorption experiment was conducted for removal of the studied heavy metal at $30 \pm 0.1^\circ\text{C}$ temperature. A 0.1g of pure and modified Ganki laumontite was left in contact with 10 ml of heavy metal ion solutions (100 mg/L). Samples were collected at different time until the equilibrium adsorption was attained through 140 min. After equilibration, the samples were centrifuged, clarified supernatants decanted, and the content of metal ions in them determined by AAS to obtain the equilibrium concentrations in solution (C_f). The ions uptake (q), expressed as ions removal per unit mass of adsorbent material (mg. g), was calculated from the experimental data (C_i , v , m and C_f) in each sample according to Equation 1. Where, V is the volume of the solute aqueous solution, C_i corresponds to the initial solute concentration, C_f , the final solute concentration and m is the mass of adsorbent material. Therefore, the experimental data fitted very well to Langmuir model.

3 RESULTS AND DISCUSSION

3.1 Adsorption studies

The prepared Ganki laumontite was used as adsorbent in the removal of toxic metal ions in aqueous solution. The removal efficiency of the metal ions on this adsorbent show good affinity of this material for a number of ions such as Lead, Nickel, Cadmium and Chromium ions in water. The amount of metal ion removed by zeolite at equilibrium (q_e) was calculated from Equation (1) which is based on AAS analysis data [10]. To optimize the adsorption system, the effects of various parameters such as

adsorbent dose, and contact time on the adsorption of Lead, Nickel, Cadmium and Chromium ions were studied.

3.1.1 Effect of contact time

The effect of contact time on adsorption of different heavy metals is shown in Figure 1. It is clear from the figure that the contact time needed to reach the maximum removal of metal by laumontite was dependent on the heavy metals. The equilibrium adsorption was attained through 140 min for Lead, Nickel and Cadmium, while 120 min for Chromium metals and the equilibrium adsorption were determined at 91.60, 58.748, 59.30 and 64.506 for lead, nickel, cadmium and chromium, respectively. This implies that the Rate of adsorption of lead is greater than chromium which is greater than cadmium which is greater than nickel ($Pb > Cr > Cd > Ni$) with respect to contact time, respectively. The figure shows decrease in the concentration of the Heavy metal ions with increase in contact time [11].

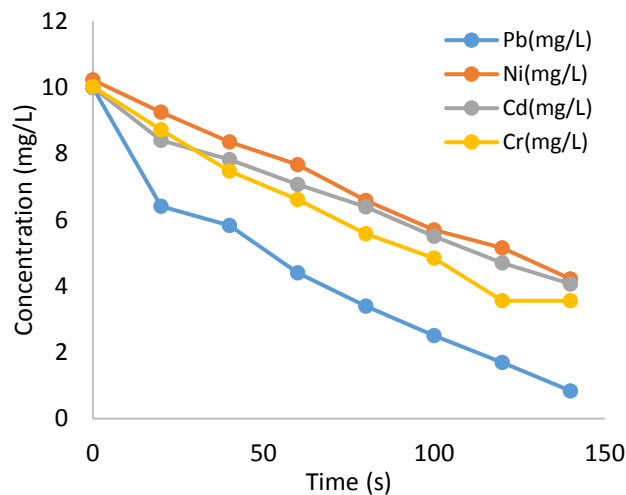


Figure 1. Concentration of Heavy Metals ions as a function of contact time

3.1.2 Effect of dosage

The effect of Laumontite load on the uptake efficiency of Lead, Nickel, Cadmium and Chromium is presented in the Figure 2. The adsorption percentage increased with laumontite mass in case of both Lead, Nickel, Cadmium and Chromium and when the adsorption reaches beyond 70g it became steady [11]. The adsorption percentage was found to be 94.40, 63.63, 65.70 and 82.55% in the case of lead, nickel, cadmium and chromium, respectively. This means that the percentage of Lead is greater than Chromium which is greater than cadmium, which is greater than Nickle ($Pb > Cr > Cd > Ni$) [12].

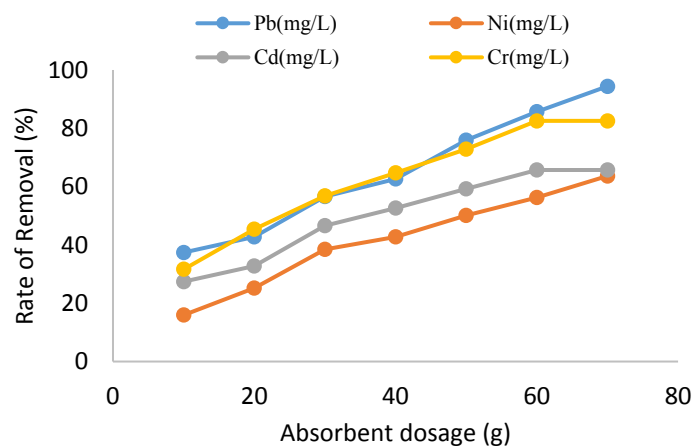


Figure 2. Percentage removal of Heavy metal ions as a function of adsorbent Dosage

3.1.3 Percentage removal of heavy metal ions by the modified laumontite material as a function of contact time

The percentage removal of Lead, nickel, cadmium and chromium ions was presented in Figure 3. The percentage removal of lead was observed to increase with time from an initial 35.9% at 20 minutes to a maximum of 91.60% at 140 minutes, while the percentage removal of nickel was observed to increase with time from an initial 9.48% at 20 minutes to a maximum of 58.74878% at 140 minutes. The percentage removal of cadmium was observed to increase with time from an initial 15.9% at 20 minutes to a maximum of 59.30% at 140 minutes and that of chromium the percentage removal was observed to increase with time from an initial value of 12.96% at 20 minutes to a maximum of 64.51% at 140 minutes [2, 13].

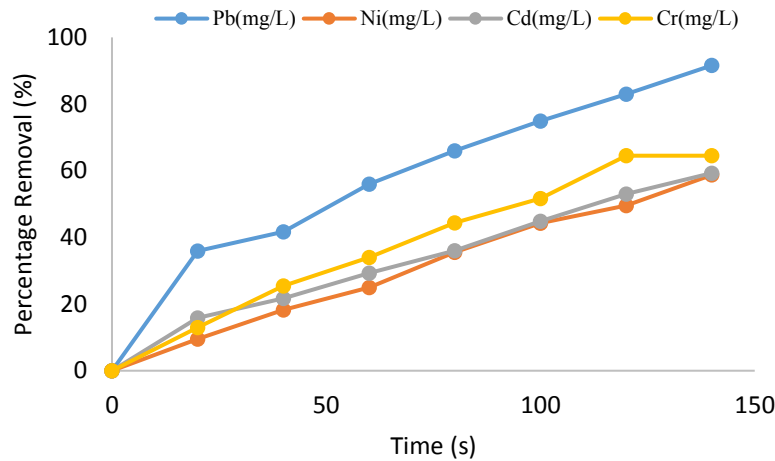


Figure 3. Percentage removal of heavy metal ions by modified laumontite

3.1.4 Percentage removal of Heavy metal ions by the modified Laumontite material as a function of Adsorbent dosage

The percentage removal of heavy metal ions is presented in Figure 4. The percentage removal of lead was observed to increase with dosage from 37.4% at 10g to a maximum of 94.40% at 70g. On the other hand, the percentage removal of nickel ions was observed to increase with dosage from an initial 15.93% at 10g to a maximum of 63.64% at 70 g. Likewise, the percentage removal of cadmium ions was observed to increase with dosage from 27.40% at 10g to a maximum of 65.70% at 60 g and the percentage removal of chromium ion was observed to increase with dosage from 31.07% at 10g to a maximum of 82.55% at 60g [5].

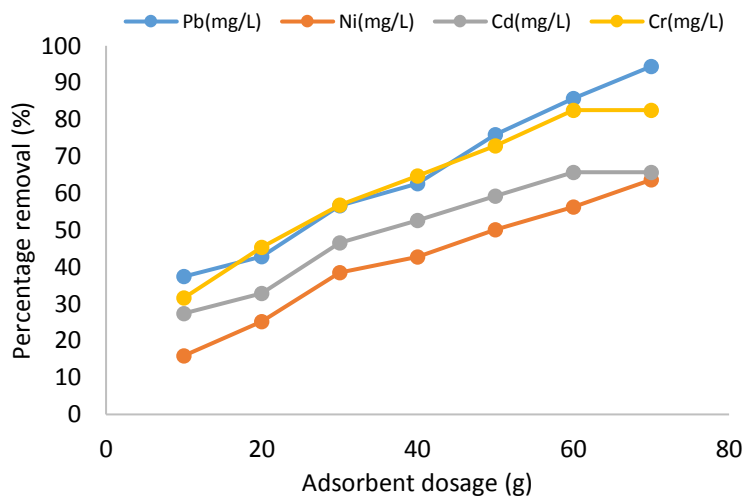


Figure 4. Percentage removal of heavy metal ions by modified laumontite as a function of adsorbent dosage

3.2 Sorption Isotherm Model

3.2.1 Absorption isotherms of the laumontite as a function of contact time

The figures below are the absorption isotherms of the Lead ions absorbed on the zeolite. Figure 5 shows the Freundlich isotherm for the absorption while Figure 6 shows the Langmuir isotherm. From both figures, the isotherm model is observed to be Type III isotherm model, which is best represented by Freundlich isotherm, hence the lead ions can be describe to be absorbed unto the surface of the zeolite in multilayers [8, 10].

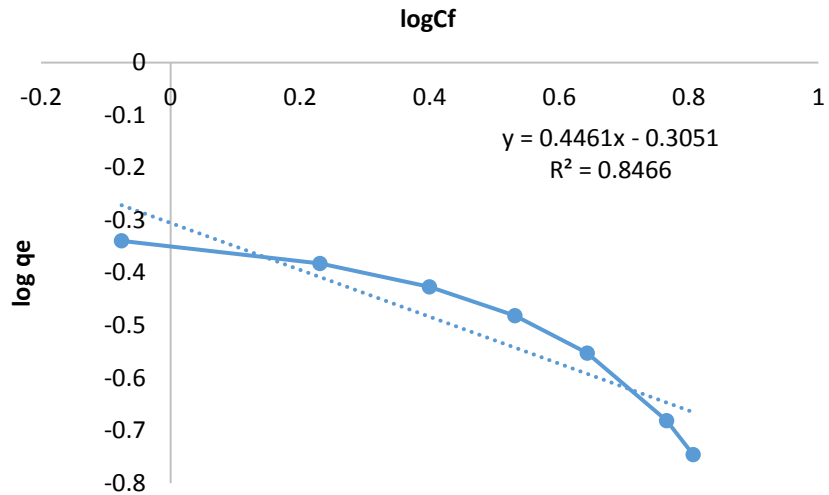


Figure 5. Freundlich isotherm at room temperature of lead ions absorbed from synthesized waste water

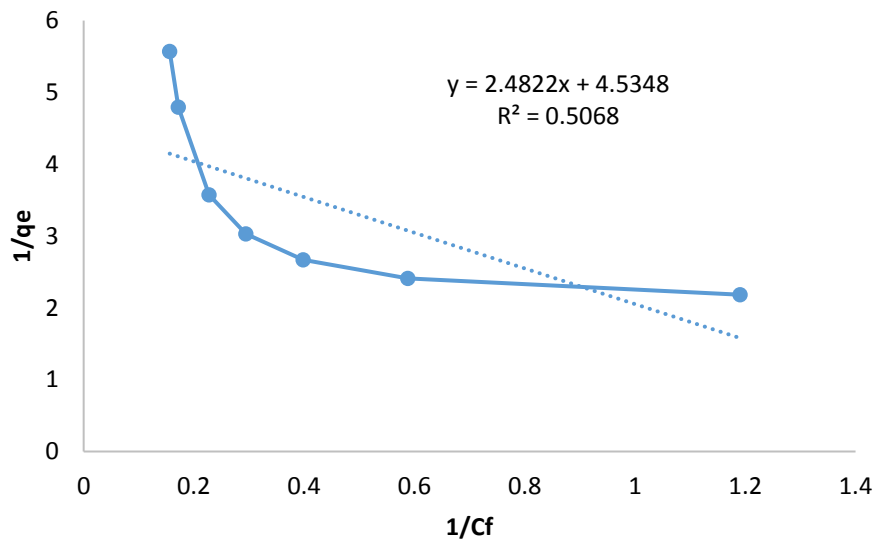


Figure 6. Langmuir isotherm at room temperature of lead ions absorbed from synthesized waste water

Figure 7 shows the Freundlich isotherm for the absorption of nickel while Figure 8 shows the Langmuir isotherm. From the figure, the isotherm model is observed to be Type II isotherm model. Type II absorption isotherm best describe the monolayer absorption hence same can be said of nickel ions unto the zeolite materials [11].

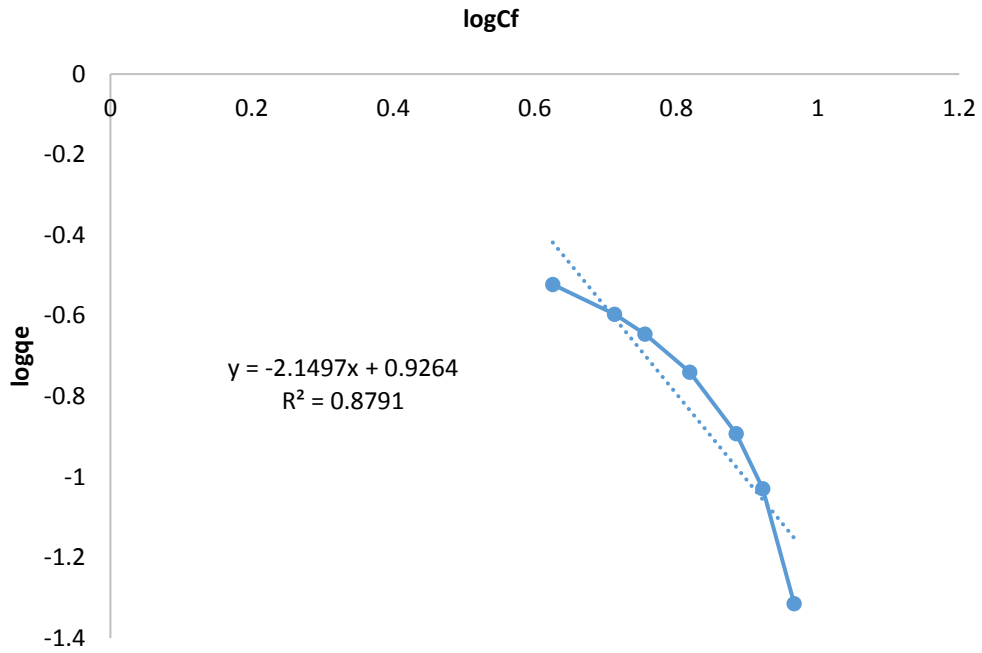


Figure 7. Freundlich isotherm at room temperature of Nickel ions absorbed from synthesized waste water

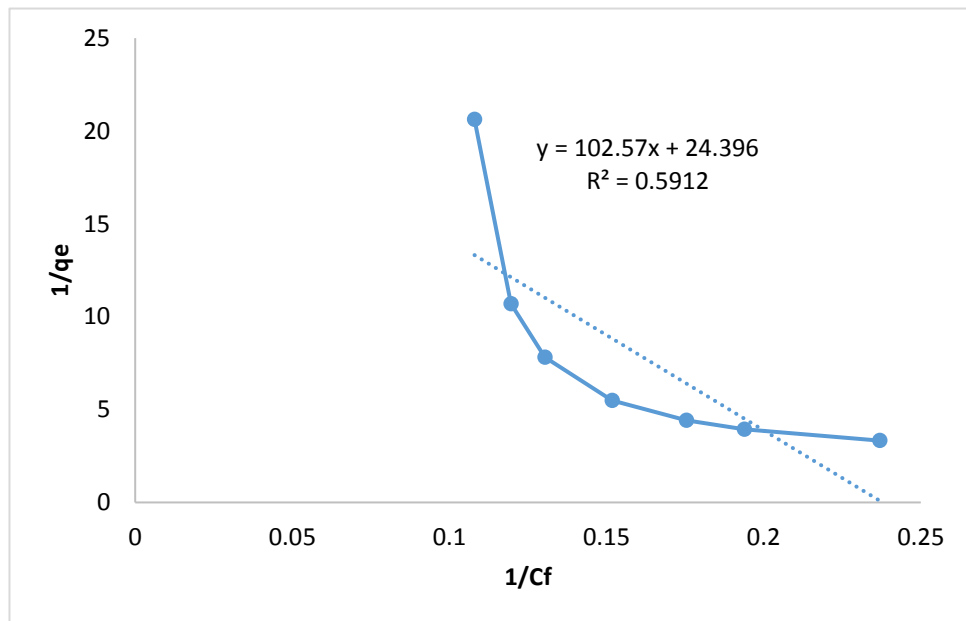


Figure 8. Langmuir isotherm at room temperature of nickel ions absorbed from synthesized waste water

Figure 9 shows the Freundlich isotherm for the absorption of cadmium while Figure 10 shows the Langmuir isotherm. From both representations, the isotherm models are observed to be Type II and Type IV isotherm model, respectively [13].

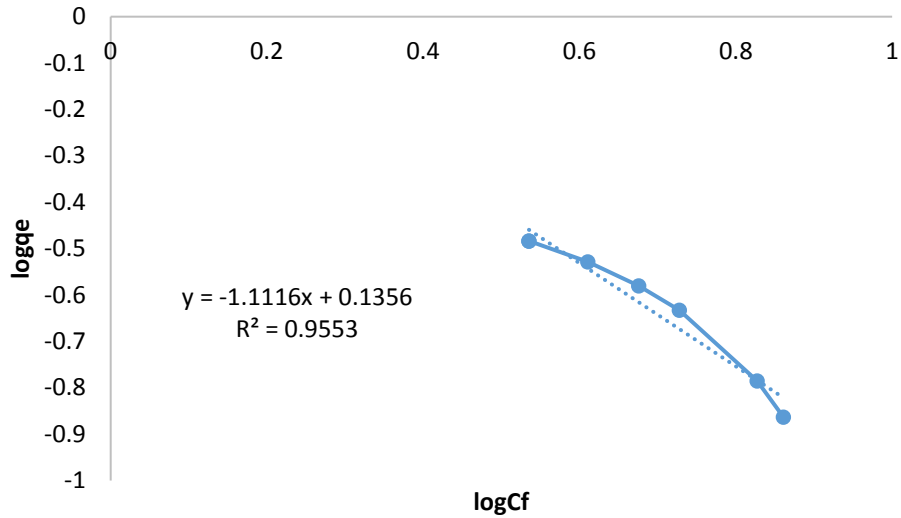


Figure 9. Freundlich isotherm at room temperature of Cadmium ions absorbed from synthesized waste water

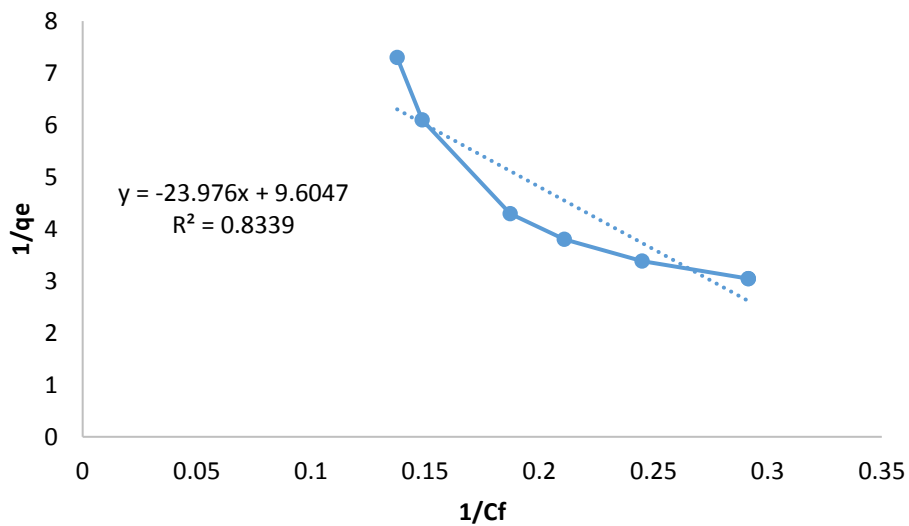


Figure 10. Langmuir isotherm at room temperature of Cadmium ions absorbed from synthesized waste water

Figure 11 shows the Freundlich isotherm for the absorption of chromium, while Figure 12 shows the Langmuir isotherm. From both representations, the isotherm models are observed to be Type I and III, respectively [13].

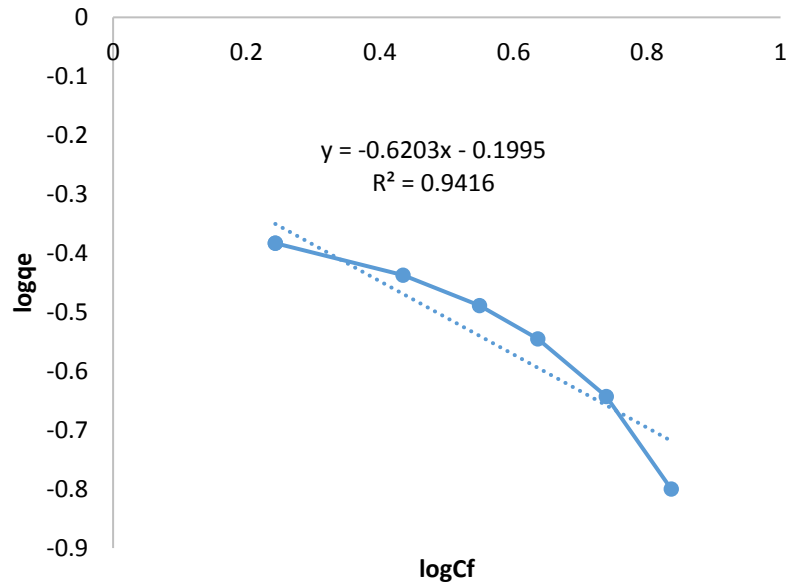


Figure 11. Freundlich isotherm at room temperature of Chromium ions absorbed from synthesized waste water

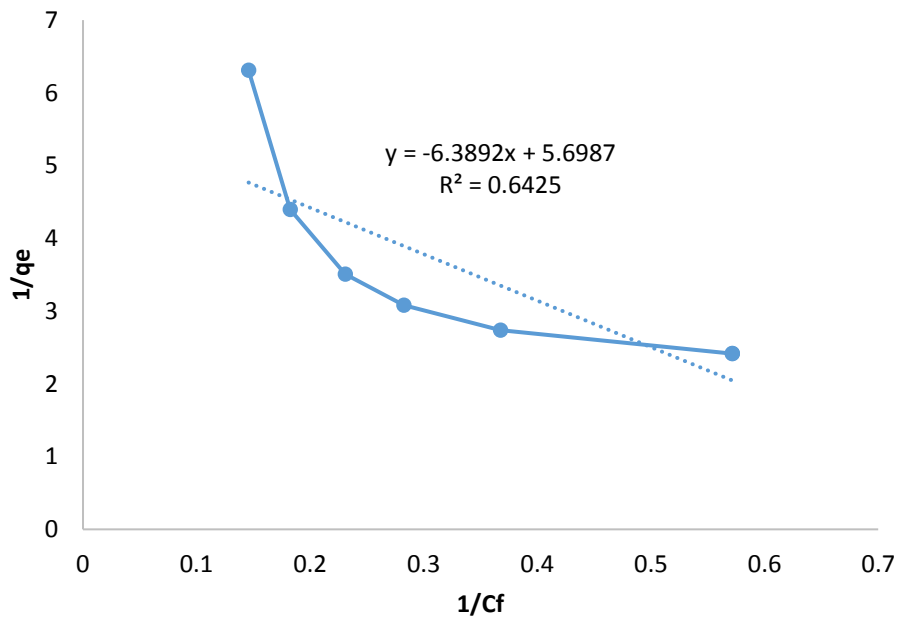


Figure 12. Langmuir isotherm at room temperature of Chromium ions absorbed from synthesized waste water

The values of k_f , C_f and N that best fitted the data as well as the corresponding correlation coefficients are presented in Table 1.

Table 1. The values of k_f , C_f and N that best fitted the data as well as the corresponding correlation coefficients

Kinetics parameter	Lead (Pb)	Nickel (Ni)	Cadmium (Cd)	Chromium (Cr)
K_f	0.49	8.44	1.3665	0.6317
C_f	0.84	4.27	4.07	3.56
N	2.24	-0.465	-0.8996	-1.6121

4 CONCLUSIONS

Natural Ganki laumontite can be used to remove heavy metals from wastewater. The result from this work found that treatment of wastewater with Ganki laumontite is as effective as the water alkalization leading to heavy metal removal. Modification of natural zeolite increased its uptake ability. The work shown that the amount of lead ion sorbed onto Ganki laumontite is 0.458 is higher than other ions present. The metals uptake process by natural zeolite obeys the kinetic equation describing adsorption. This fact together with the correlation found between the uptake of heavy metals and amounts of exchangeable ions of the Ganki laumontite released into solution shows that ion exchange adsorption is the basic mechanism of heavy metals uptake by zeolite.

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