Removal of Ni (Ii) and Cd (Ii) Ions from Aqueous Solutions by Adsorption on to Synthetic Zeolite

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ABSTRACT

In this study, the removal of Ni (II) and Cd (II) ions from aqueous solutions using the adsorption process onto synthetic Zeolite has been investigated as a function of initial metal concentration, contact time, pH and temperature. In order to find out the effect of temperature on adsorption, the experiments were conducted at 20, 30, 40, 50 °C and 15, 30, 50 °C for Ni (II) and Cd (II) respectively. Kinetics data show that at higher temperatures, the rate of adsorption on the synthetic Zeolite is much higher compared to that on the lower temperatures. The optimum pH for Ni (II) and Cd (II) removal is found out to be 5.5 and 6 respectively. The batch method has been employed using initial metal concentrations in solution ranging from 25 to 100 mg/l for Ni (II) and from 10 to 25 for Cd (II) at optimum pH. An Atomic Absorption Spectrophotometer was used for measuring the heavy metal concentrations before and after adsorption. Langmuir, Freundlich, models were applied to adsorption equilibrium data to find the best amongst these models. This study has demonstrated that Zeolite was capable to remove 90% of nickel and cadmium from solution of different concentrations. This implies that Zeolite is an important in the removal process. These capabilities of Zeolite could lead to development of a viable and cost effective technology for removal of these pollutants from wastewater for countries like Iraq.

Keywords: Adsorption, Heavy metals, aqueous solutions, synthetic Zeolite, Kinetics.

أزالة آيونات النيكل والكادميوم من المحاليل المائية بواسطة الأمتزاز بأستخدام الزيولايت الصناعي

الخلاصة
في هذا الدراسة، تم التحقق في أزالة آيونات النيكل والكادميوم من المحاليل المائية بعملية الأمتزاز بأستخدام الزيولايت الصناعي كدالة لتركيز المعادن الابتدائي، الوقت، pH ودرجة الحرارة. ومن أجل معرفة تأثير درجة الحرارة على الأمتزاز، فقد تم ضبط درجات الحرارة على 20، 30، 40 و50 درجة مئوية للنيكل و 15، 30 و50 درجة مئوية للكادميوم على التوالي. أظهرت النتائج عند درجات الحرارة العالية تكون نسبة الأمتزاز على الزيولايت الصناعي أعلى اذا ماقورنت بدرجات الحرارة الواطئة. وكانت قيمة الـ pH المثلى للنيكل والكادميوم 5.5 و6 على التوالى. كما وظفت الدراسة أستخدام طريقة Batch بأستخدام تراكيز المعادن الأولية والتي تراوحت من 25 الى 100 ملغم/لتر بالنسبة للنيكل ومن 10 الى 25 بالنسبة للكادميوم على القيمة المثلى للpH. تم أستخدام جهاز الأمتصاص الذري لقياس تراكيز المعادن الثقيلة قبل وبعد الأمتزاز. كما تم تطبيق نموذج لانكماير وفراندلج للبيانات وذلك للعثور على الأفضل بين هذين النموذجين. أظهرت نتائج الدراسة ان الزيولايت قادر على أزالة 90% من النيكل والكادميوم وهذا يدل على أهمية الزيولايت في عملية الأزالة. نتيجة الكفاءة العالية للزيولايت في الأزالة، فيمكن ان تؤدي الى تطوير تكنولوجيا فعالة ومجدية من حيث الكلفة لأزالة الملوثات من المياه لدول مثل العراق.

INTRODUCTION

Cadmium and nickel and their compounds are toxic, non-biodegradable and relatively widespread in the environment and the systematic study on their removal from wastewater has considerable significance from an environmental point of view [1]. Cadmium is one of the heavy metals with the greatest potential hazard to humans and the environment. Chronic exposure to elevated level of cadmium is known to cause renal dysfunction, bone degeneration, liver damage, and blood damage. The chronic toxicity of nickel to humans and the environment is also well-known and high nickel concentrations cause gastrointestinal irritation and lung and bone cancers.

A number of methods are available for the metal ions removal from aqueous solutions: ion exchange, solvent extraction, reverse osmosis, biological methods, chemical precipitation and adsorption. Out of these methods, adsorption, which is considered as a third stage of wastewater treatment (first stage is primary/physical treatment: second stage is secondary/biological treatment: third stage is tertiary/chemical treatment), has been preferred over other processes because of its cheapness and the high quality treated effluents is produced [2]. Adsorption is a process by which a solid adsorbent can attract a component from the aqueous phase to its surface and thereby from an attachment through a physical or chemical bond, thus removing the component from the aqueous phase [3].

In the past two decades, research has been carried out focused on using low-cost effective sorbents for heavy metal adsorption and the sorption behavior of several natural materials and waste products has been investigated [4-6]. These cost-effective materials range from industrial byproducts or waste, such as waste rubber tires [7], to agricultural products such as wool, rice straw, coconut husks and peat moss [8]. Other known natural materials like clay [9–11] and other synthetic material like synthetic zeolite [12, 13] have been investigated for their potential use as adsorbents for heavy metal. In addition, zeolite has high sorption capacity and selectivity result from high porosity and sieving properties. Zeolites are natural silicate minerals; their capability to exchange cations is one of their most useful properties to remove heavy metals from industrial wastewater [14-16].

The objective of the present study is to investigate the adsorption potential of synthetic Zeolite in the removal of Cd (II) and Ni (II) ions from aqueous solution. The effects of pH, contact time and temperature on adsorption capacity of Zeolite have been investigated. The Langmuir and Freundlich isotherms models are used to investigate equilibrium data. The adsorption mechanisms of Cd (II) and Ni (II) ions onto Zeolite are also evaluated in terms of kinetics.

MATERIAL AND METHOD

Preparation of zeolites for the removal process

Zeolite has been used in this work for the removal of nickel and cadmium ions from aqueous solutions. Particles of zeolite represented by chemical formula $Na_{81}(AlO_2)_{81}(SiO_2)_{111}$ [17] having cylindrical shape with size of 1.5 mm and bulkdensity of 600 g/L, purchased from Central Drug House (C.D.H.), India were used as the adsorbent in this study. The adsorbent is contacted with 1M NaCl solution to convert it into a near homoionic state in Na form [18] followed by washing with deionised water and drying in oven at 373K. The dried adsorbent was stored over bed of silica gel putted in desiccators.

Chemicals

Double distilled water was used for all experiments. Stock solution of 100 mg/l of Ni (II) and Cd (II) was prepared by dissolving 447.9 mg of $NiSO_4.6H_2O$ and 203.1 mg $CdCl_2.2H_2O$ respectively in 1000 ml distilled water and this was diluted as per the requirements. Different buffers are prepared over a range of 3-7 pH so as to study the effect of pH on the removal efficiency of Zeolite. For maximum range of pH, Solution of Acetic acid and Sodium Acetate are used for maintaining the pH of the solution.

$NiSO_4$ and $CdCl_2$ are used for preparation of Nickel and Cadmium solution of particular solution.

Instrumentation

Nickel and Cadmium contents in solution are determined by Atomic Absorption Spectrophotometer (AAS-EC4141).

Batch mode adsorption studies

Removal of Ni and Cd using Zeolite was carried out by batch method and the influence of various parameters such as effect of pH, effect of temperature, contact time and initial sorbate concentration was studied. A series of 250 ml conical flask are employed. The procedure involves filling each flask with 250 ml of Ni and Cd of known concentration. One gram of zeolite was taken, then added into different flasks and stirred intermittently for four hours and then flasks are sealed and kept as such for 24 hours so that equilibrium can be achieved.

Effect of pH was studied in the range of 3-7 by adjusting pH with the addition of dilute aqueous solution of HCl or NaOH and buffer solutions. Effect of temperature was studied in the range of 20, 30, 40, 50 C° for Ni and 15, 30, 50 C° for Cd. Kinetics and effect of contact time on adsorption was determined at different time intervals of 10-220 min and 5-180 min for Ni and Cd respectively. Adsorption isotherms and effect of initial concentration were studied by varying the initial metal ion concentration from 25- 100 mg/L for Ni and 10-25 for Cd. Percentage removal was calculated using Eq. 1.

$$Ni, Cd\ removal(\%) = \frac{100(C_{Ao} - C_A)}{C_{Ao}} \quad ...(1)$$

Where, C_{Ao} and C_A are the Ni (II) or Cd (II) concentration (mg/L) in solution initially and at any time *(t)*.

Adsorption isotherm models

The experimental adsorption equilibrium data were analyzed in terms of Langmuir and Freundlich isotherm models for the purpose of interpolation and limited extrapolation.

The Langmuir model was used to quantify mainly the adsorption capacity of the adsorbent. The Langmuir model is:

$$q_e = q_m(bC_e / 1 + bC_e) \quad ...(2)$$

Where *qm* is the maximum or saturation uptake capacity of the adsorbent (mg/g) and b (L/mg) is the binding constant or energy of adsorption that reflects the slope of the isotherm in the low solution phase concentration range. This equation predicts that the equilibrium uptake of an adsorbent increases with increasing solution phase equilibrium concentration, finally leaving off at qm as the C_e term in the denominator becomes dominant. The values of qm and b can also be found out from a linear equation obtained by the rearrangement of the above mentioned equation, the resulting equation will be:

$$C_e / q_e = (1 / bq_m) + (1 / q_m)C_e \quad ...(3)$$

Where constants *b* and *qm* relate to the energy of adsorption and adsorption capacity respectively and their values are obtained from the slope and intercept of the plot of Ce/qe versus Ce.

The Freundlich isotherm equation has the following form:

$$\log\ q_e = \log\ K + 1 / n \log\ C_e \quad ...(4)$$

Where q_e is the amount of solute present in the adsorbent phase at equilibrium (mg/g), C_e is the equilibrium solute concentration in the solution phase (mg/L), K and n are constants representing adsorption capacity (mg/g) (L/mg) $^{1/n}$, and intensity of adsorbent respectively.

Kinetics of removal

The uptake of metal ions on zeolite is studied with respect to time till the equilibrium is reached. About 250 ml of Nickel metal solution of different concentrations from 25 to 100 mg/l and for Cadmium from 10 to 25 mg/L are taken in a 500 ml conical flask. The metal ion solutions are adjusted to the optimum pH and 1 g zeolite is taken for Ni and Cd. After a fixed interval of time a fixed amount of solution is taken out from the flasks and taken for the analysis. Batch kinetic experiments were conducted to determine the time required for Ni (II) and Cd (II) binding process to reach equilibrium.

RESULTS AND DISCUSSION

Effect of pH

One of the most important parameters that affect this mechanism is the pH of the solution. It is, therefore, planned to conduct experiments at different pH values of the solution. The uptake capacity of zeolite is found to be maximum at pH of 5.5 and 6 for Ni and Cd respectively, as shown in Figure (1).

It can be seen from the figure that the removal of metal ions is dependent on the pH of the solution. At low pH the metal ion uptake is relatively small.

The structure of zeolites, particularly with low Si/Al ratio may collapse in the presence of acids with pH lower than 4, but the severity will be more at pH below 3. In fact, pH less than 4.5 is not recommended for Zeolite. The loss in removal capacity at lower pH can therefore be described to the collapse of the structure of zeolites [19]

Effect of temperature

Temperature has an important effect on the process of adsorption. Different sets of experiments are conducted at different concentrations starting from 25 mg/L to 100 mg/L at different temperatures at 20, 30, 40 and 50 °C and it is evident in the Figure (2) that at low concentration, there is no noticeable change in adsorption capacity. The adsorption of Nickel increases with increase in the temperature at high concentration particularly concentration above 60 mg/L.

In case of Cd (II), as can be seen from the Figure (3) that as we increase the temperature, the rate of adsorption first increase with the same rate but after some time, the rate increases as we increase the temperature but in the end, near equilibrium, the rate of adsorption becomes nearly equal.

Kinetics of removal

The experimental study was found that nickel uptake by zeolite increases with lapse of time. It can be seen that Ni and Cd binding by the zeolite reached equilibrium after a contact time of 180, 160 minutes respectively, yielding a maximum percentage removal 90% for Ni. The adsorption of Ni and Cd was rapid up to period of 140 minutes after which the rate slowed down as the equilibrium approached as shown in the Figs. 4 and 5. The Figures (4 and 5) revealed that the remaining concentration of metal ions becomes asymptotic to the time axis such that there is no appreciable change in the remaining metal ion concentration after a definite time. Figure (6) shows the percentage removal for Ni (II) and Cd (II) at equilibrium contact time.

Adsorption isotherm

The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of Ni and Cd by Zeolite over the entire parameters range studied. Calculated Langmuir and Freundlich parameters are tabulated in Table (1). The adsorption capacity for Langmuir (*qm*) was 7.82 mg/g for Ni and 5.76 for Cd obtained from the slope and intercept of the plot of Ce/qe versus Ce as shown in Figs. 7 and 8. The adsorption capacity for Freundlich (K) was 1.62 mg/g for Ni and 0.97 for Cd, determined from the slope as seen in equilibrium curve (Figure 9 and 10).

Langmuir isotherm model for Ni shows better fitting (R^2 = 0.93) with the experimental data compared to Freundlich isotherm (R^2 = 0.79). This indicates the applicability of monolayer coverage of Ni (II) on the homogeneous surface of the adsorbent. It is also due to the fact that, Zeolite has greater surface area for metal adsorption [20]. The good correlation coefficient of Langmuir isotherm also indicates that Ni is strongly adsorbed to the surface of Zeolite. Therefore, it is verified that Zeolite has great potential to be a good adsorbent for the removal of Ni (II) in water treatment. Freundlich isotherm for Cd (II) shows very good fitting (R^2 = 0.99).

CONCLUSIONS

The adsorption behavior of Ni (II) and Cd (II) on zeolite was investigated in batch experiments. The adsorption was found to be drastically dependent on pH, temperature, initial sorbate concentration and contact time. The results show that synthetic zeolite can efficiently remove nickel and cadmium from solutions especially at pH close to 5.5 and 6 respectively. Kinetics data show that at higher temperatures, the rate of adsorption is higher for Zeolite. The kinetics experiments show that at definite time for Ni and Cd are 180 and 160 minutes respectively gives high removal percentage (90% for Ni) and indicates that the equilibrium can be achieved. The Langmuir and Freundlich isotherm model were used to describe the metal adsorption process. The Langmuir isotherm gives the best agreement over the Freundlich isotherm for Ni (II). While, for Cd (II), Langmuir isotherm has (R^2 = 0.96) and Freundlich isotherm (R^2 = 0.99), therefore, the Freundlich isotherm gives the best agreement over the Langmuir isotherm in case of Cd (II). Extensive studies are required to evaluate zeolite in terms of its cost, competitive adsorption properties and reaction chemistry for situations when other cations and anions are also present in the solution.

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Table (1) Values of Langmuir and Freundlich isotherm constants for Ni and Cd.

Adsorbent	Langmuir constants			Freundlich constants		
	qm (mg/g)	b (l/mg)	R^2	n	K (mg/g)	R^2
Ni (II)	7.82	0.21	0.93	1.944	1.621	0.79
Cd (II)	5.76	0.1808	0.96	1.665	0.977	0.99

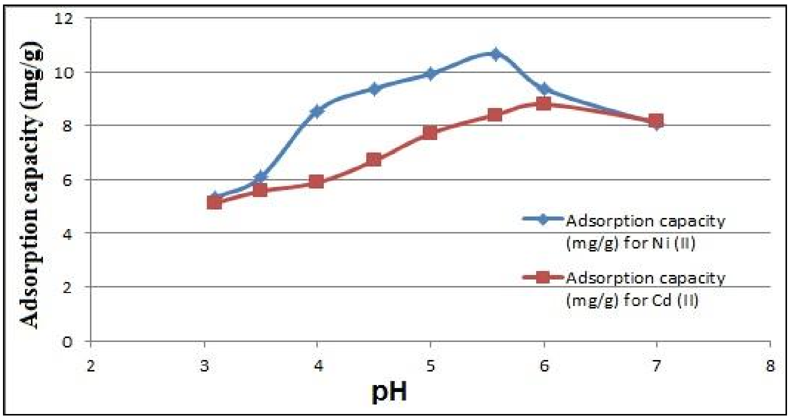


Figure (1) Effect of pH on adsorption of Ni (II) and Cd (II) onto Zeolite.

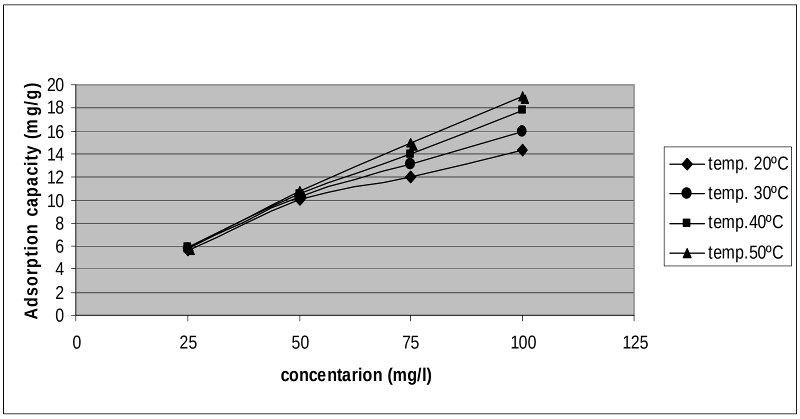


Figure (2) Effect of temperature on adsorption of Ni.

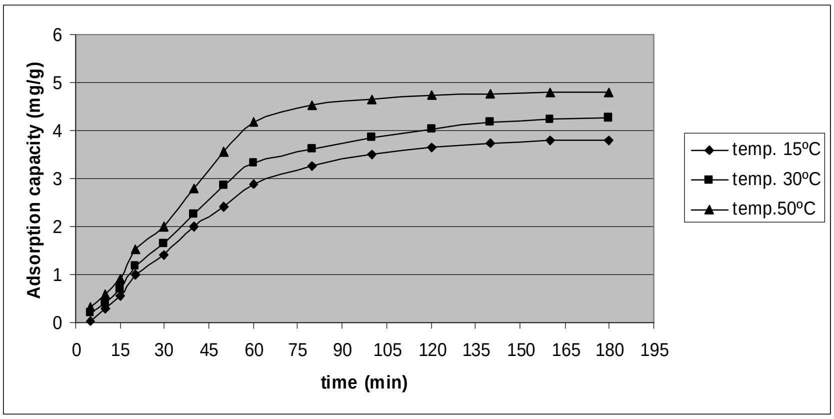


Figure (3) Effect of temperature on adsorption with time for Cd.

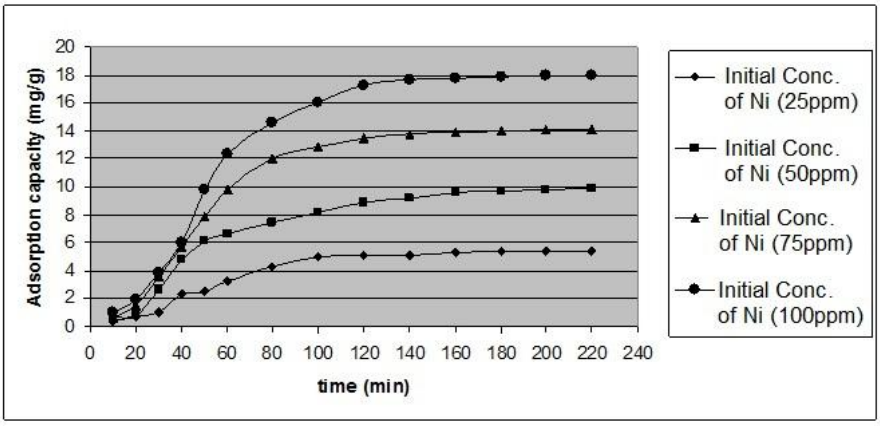


Figure (4) Variation of Adsorption capacity for Ni with time.

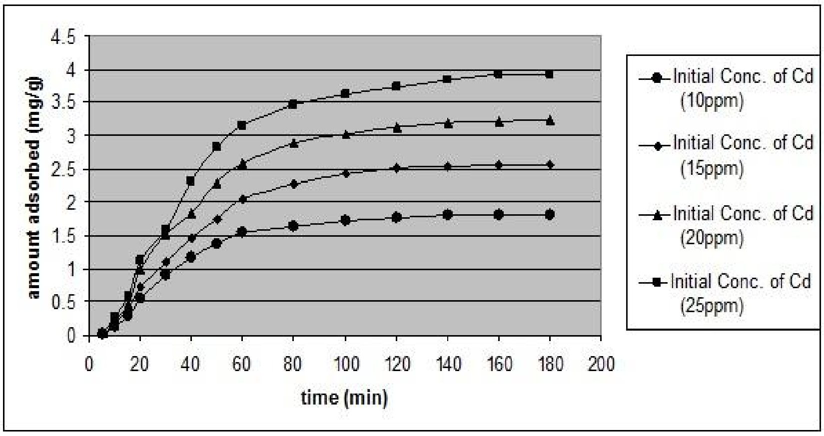


Figure (5) Variation of amount adsorbed for Cd with time.

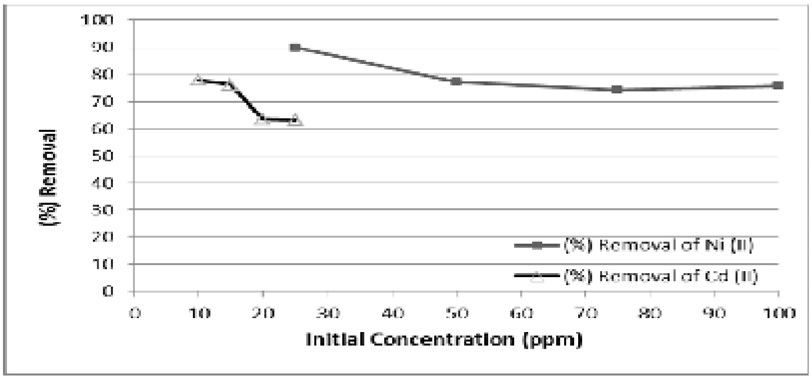


Figure (6) percentage removal for Ni (II) and Cd (II).

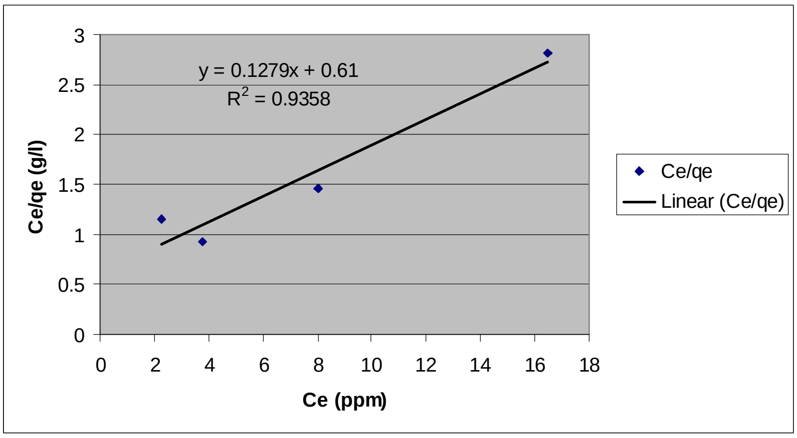


Figure (7) Langmuir isotherm plot for adsorption of Ni at optimum pH (5.5).

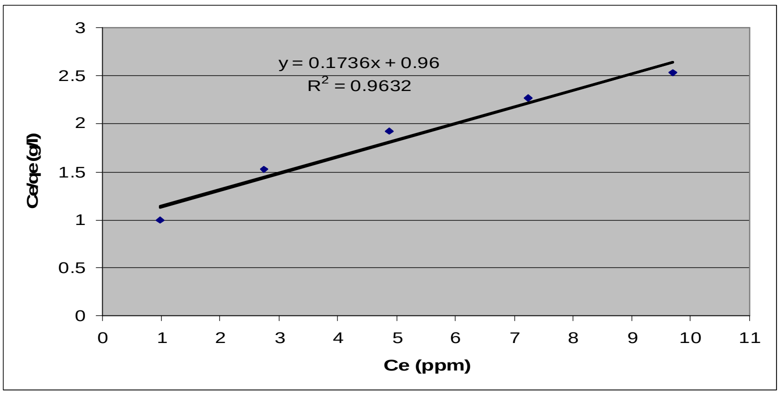


Figure (8) Langmuir isotherm plot for adsorption of Cd at optimum pH (6).

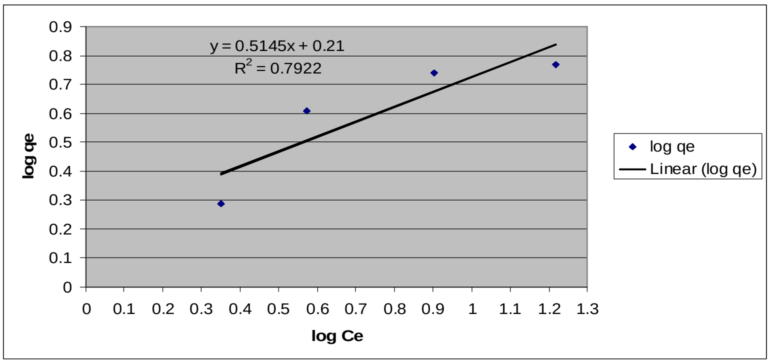
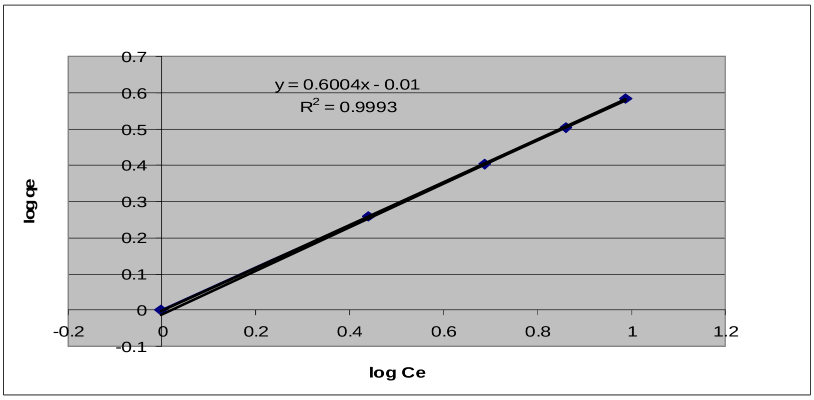


Figure (9) Freundlich isotherm plot for adsorptionof Ni at optimum pH (5.5).



Figure(10) Freundlich isotherm plot for adsorption of Cd at optimum pH (6).