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Adsorption Studies of Nickel(II) Metal Ions Uptake Using Fe_3O_4 Magnetic Nanoadsorbent

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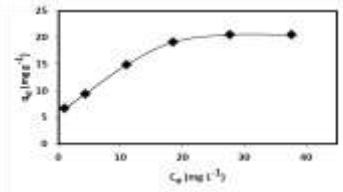
Graphical abstract



Abstract

In the present study, Fe_3O_4 magnetic nanoparticles (MNPs) synthesized in-housed using co-precipitation method was applied for the treatment of aqueous solutions contaminated by Ni(II) ions. Experimental results indicated that at 25ºC, the optimum pH value for Ni(II) removal was pH 6.0 and an adsorbent dose of 60.0 mg. The adsorption capacity of Fe_3O_4 nanoparticles for Ni(II) is 20.54 mg g^{-1}. Adsorption kinetic rates were found to be fast; total equilibrium was achieved after 180 min. Kinetic experimental data fitted very well the pseudo-second order equation and the value of adsorption rate constants was calculated to be 0.004 and 0.0008 g mg^{-1} min at 5 and 40 mg L^{-1} initial Ni(II) concentrations, respectively. The equilibrium isotherms were evaluated in terms of maximum adsorption capacity and adsorption affinity by the application of Langmuir and Freundlich equations. The maximum monolayer capacity obtained from the Langmuir isotherm was 24.57 mg g^{-1} for Ni(II). Results indicate that the Langmuir model fits adsorption isotherm data better than the Freundlich model.

Keywords: Fe_3O_4 magnetic nanoparticles, adsorption, nickel (ii) ions, langmuir and freundlich models

Abstrak

Dalam kajian ini, zarah nano magnet (MNPs) Fe_3O_4 yang disintesis menggunakan kaedah ko-pemendakan telah digunakan untuk rawatan larutan akueus yang dicemari ion Ni (II). Keputusan eksperimen menunjukkan bahawa pada 25ºC, nilai optimum pH untuk penyingkiran Ni(II) ialah pH 6.0 dan dos penjerap ialah 60.0 mg. Keupayaan penjerapan zarah nano Fe_3O_4 untuk Ni(II) ialah 20.54 mg g^{-1}. Kadar kinetik penjerapan didapati cepat; keseimbangan jumlah dicapai selepas 180 min. Data kinetik eksperimen menepati dengan baik persamaan tertib pseudo kedua dan nilai pemalar kadar penjerapan yang dihitung ialah 0.004 dan 0.0008 g mg^{-1} min masing-masing pada kepekatan awal Ni(II) 5 dan 40 mg L^{-1}. Isoterma keseimbangan telah dinilai berdasarkan keupayaan penjerapan maksimum dan afiniti penjerapan dengan menggunakan persamaan Langmuir dan Freundlich. Keupayaan maksimum lapisan mono diperoleh daripada isoterma Langmuir ialah 24.57 mg g^{-1} untuk Ni(II). Keputusan menunjukkan bahawa model Langmuir menepati data isoterma penjerapan lebih baik daripada model Freundlich..

Kata kunci: Zarah nano magnet Fe_3O_4 , penjerapan, ion nikel (ii) , model langmuir dan freundlich

1.0 INTRODUCTION

Nickel Ni(II) is mostly used in contemporary industry. Too much exposure of Ni(II) in humans can cause important influences such as cardiovascular, kidney and lung diseases.[1] Currently the Environmental Protection Agency (EPA) standard for Ni(II) in drinking water is 0.04 mg L^{-1}.[2] Several pollutants sources of Ni(II) ions have been identified in water samples such as electroplating, mining, machinery, and steel making industries. [3] Several adsorbents have been reported for the removal of Ni(II) from aqueous solutions, including chitosan,[1] zeolite,[2] functionalized polymers,[3] activated carbon[4] and multi-walled carbon nanotubes.[5] Among these purification adsorbents, the adsorption of metal ions using magnetic nanoparticles[6] is preferred due to their lower costs, high adsorption capacities, durability and high efficiency, especially for metal ions with trace and ultra-trace concentration level. In this study, an in-house synthesized Fe_3O_4 magnetic nanoparticles (MNPs) adsorbent was evaluated for its feasibility in the adsorption of Ni(II) metal ions from aqueous solutions. Adsorption experiments were investigated by kinetic and isotherm adsorption models.

2.0 EXPERIMENTAL

2.1 Chemicals and Reagents

All vessels were cleaned and soaked in diluted nitric acid for more than 12 h before use. Deionized water (18.2 MΩ) was obtained from a Simplicity 185, Millipore water filtration system from Merck (Darmstadt, Germany) and used for preparation of the standards and sample solutions. Stock solution (1.0 g L^{-1}) of Ni(II) was purchased from Merck (Darmstadt, Germany), ferric chloride hexahydrate (iron(III) chloride) $FeCl_3.6H_2O$, ammonium ferrous sulfate hexahydrate $(NH_4)_2Fe(SO_4)_2.6H_2O$, concentrated ammonia solution (NH_4OH 28.0%), nitric acid (HNO_3 65.0%) were all purchased from Sigma–Aldrich (St. Louis, MO, USA). Hydrochloric acid (HCl 37.0%) was purchased from Fluka Chemika (Buchs, Switzerland).

2.2 Instrument

Perkin-Elmer AAnalyst 400 flame atomic absorption spectrometer (Waltham, MA USA), equipped with a hollow cathode lamp for copper and with a deuterium lamp for background correction was used to determine the absorption of Ni(II) solution. The hollow cathode lamp was operated at 8.0 mA and the wavelength was set at 232.0 nm. The flame composition was operated with an acetylene flow rate of 1.8 L min^{-1} and air flow rate of 10.0 L min^{-1}.

2.3 Adsorption Experiments

2.3.1 Adsorption Isotherms

Adsorption isotherm experiments were performed in batch-mode. In a typical experiment, 60.0 mg of Fe_3O_4 nano-adsorbent was weighed into a 500 mL glass beaker containing 100mL of Ni(II) metal ion solution. Ni(II) metal ion concentration ranged from 5.0 to 50.0 mg L^{-1}, and the solution pH was adjusted to pH 6.0 with 0.1 M HCl or 0.1 M NaOH, when necessary. The mixture was mechanically shakened at 25ºC for 180 min. The adsorbent was gathered by placing an external magnet and the supernatant was collected for the determination of Ni(II) by FAAS, when adsorption equilibrium has been reached. The equilibrium adsorption capacity of the Fe_3O_4 MNPs towards Ni(II) was calculated as:

$$q_e = \frac{C_o - C_e}{m} V \qquad (1)$$

where q_e is equilibrium adsorption capacity (mg g^{-1}), C_o and C_e (mg L^{-1}) are the initial and the equilibrium concentrations of the metal ions, respectively. V (L) is the volume of the solution and m (g) represents the weight of the adsorbent.

2.3.2 Kinetic Adsorption

In a typical run, 60.0 mg of Fe_3O_4 MNPs and 100 mL of 40.0 mg L^{-1} Ni(II) solutions were mechanically shakened at pH = 6.0, and 25ºC for 30 to 360 min. The same procedures were followed for the 5.0 mg L^{-1} Ni(II) solutions. The kinetic studies were examined at lower and higher concentration of Ni(II).

3.0 RESULTS AND DISCUSSION

3.1 Adsorption Isotherms

The adsorption capacities of as-obtained Fe_3O_4 MNPs were examined at pH 6.0, 25ºC with 60.0 mg of Fe_3O_4 MNPs and varied Ni(II) concentrations from 5.0–50.0 mg L^{-1} (Figure 1). The adsorption data were analyzed using Langmuir[7] and Freundlich[8] isotherms (Table 1). These isotherms model were expressed as the following equations, respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

where q_e is the amount of Ni(II) adsorbed on the absorbent at equilibrium (mg g^{-1}), q_m denotes the maximum adsorption capacity corresponding to complete monolayer coverage, C_e describes the equilibrium Ni(II) concentration (mg L^{-1}), and K_L is the Langmuir adsorption constant (L mg^{-1}). K_F and n are the Freundlich constant related to the maximum sorption capacity (mg g^{-1}) and heterogeneity factor (mg^{-1}), respectively.

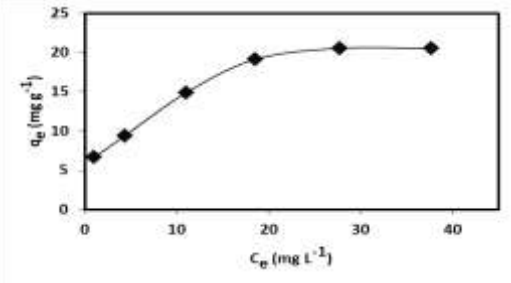


Figure 1 Adsorption capacity of Ni(II) on Fe_3O_4 MNPs. Conditions: weight of adsorbent 60.0 mg, Ni(II) concentration ranged from 5.0 - 50.0 mg L^{-1}, volume of solution 100 mL, pH 6.0, Temperature = 25ºC, contact time = 180 min

Table 1 Isotherm constants for the adsorption of Ni(II) onto as-synthesized Fe_3O_4 MNPs at 25ºC

q_m (exp.) (mg/g)	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (L/g)	R^2
20.54	24.57	0.14	0.9973	2.22	4.54	0.9696

The adsorption kinetics is essential for describing the solute uptake rate. Kinetics tests were carried out by adding 60.0 mg of Fe_3O_4 MNPs to 100 mL solutions each containing 5.0 and 40.0 mg L^{-1} of Ni(II) at pH 6.0, 25ºC with contact time ranging from 30 to 360 min. Figure 2 shows that the uptake of Ni(II) is quite effective initially, then slows down with lapse of time and reaches

equilibrium within 180 min. In order to evaluate adsorption kinetics of Ni(II) onto Fe_3O_4 MNPs, Lagergren pseudo-first order,[9] and Ho McKay pseudo-second order[10,11] kinetics models were applied to fit the experimental data (Table 2). Both the kinetic equations are shown as the following equations, respectively:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e and q_t are the sorption capacity (mg g^{-1}) at equilibrium and at time, t (min), K_1 and K_2 are the rate constants, in Lagergren pseudo-first order and Ho McKay pseudo-second-order model, respectively and R^2 is the coefficient of determination to express the uniformity between the experimental data and model-predicted values.

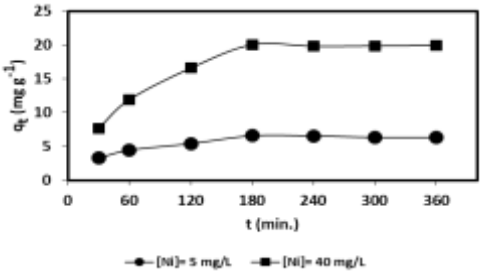


Figure 2 Kinetic data for Ni(II) uptake by Fe_3O_4 MNPs. Conditions: weight of adsorbent 60.0 mg , Ni(II) concentration = 5.0 and 40.0 mg L^{-1} , volume of solution = 100 mL, pH 6.0,Temperature = 25ºC, contact time from 30 - 360 min.

Table 2 Kinetic parameters of first and second order models fitted to experimental data

Initial Ni(II) conc. (mg/L)	q_e (exp.) (mg/g)	Pseudo-first order			Pseudo-second order		
		q_e (cal.) (mg/g)	K_1 (min−1)	R^2	q_e (cal.) (mg/g)	K_2 (g/mg min)	R^2
5.0	6.58	8.92	0.020	0.9034	7.04	0.004	0.9929
40.0	20.04	17.20	0.014	0.9575	23.47	0.0008	0.9912

4.0 CONCLUSIONS

In this study, the adsorption of Ni(II) from aqueous solution onto Fe_3O_4 MNPs adsorbent prepared with co-precipitation method was successfully studied. The Ho McKay pseudo-second-order model was the most suitable kinetic model, chemical sorption was the rate-limiting step, and Ni(II) adsorption equilibrium was achieved within 180 min. The isotherm analysis indicated that the adsorption data could be well represented by the Langmuir isotherm model and the maximum monolayer adsorption capacity was 20.54 mg g^{-1} at pH 6.0 and 25ºC. The adsorption process was exothermic in nature. Results showed that Fe_3O_4 MNPs had a high stability, which proposed that the Fe_3O_4 MNPs would be a potential candidate as a highly efficient, low-cost and renewable adsorbent for Ni(II) removal from aqueous medium.

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