

Removal Of Cd(II) From Aqueous Solution Using Modified Fe₃O₄ Nanoparticles

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Abstract: In this study, surface modification of Fe₃O₄ nanoparticles was carried out with sodium dodecyl sulfate (SDS). The obtained modified nanoparticles (SDS-Fe₃O₄ nanoparticles) were evaluated for Cd(II) removal from aqueous solution by batch adsorption method. Characterization of the SDS-Fe₃O₄ nanoparticles were performed by Scanning Electron Microscopy (SEM), Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analysis. The batch experiments showed that SDS-Fe₃O₄ nanoparticles can be effectively used to remove Cd(II) from aqueous solution. Maximum removal of Cd(II) was obtained at pH=6 and adsorption equilibrium was achieved in 30 min. The adsorption kinetics well fitted using pseudo second-order kinetic model. The adsorption isotherm data could be well described by the Freundlich equation. The maximum adsorption capacity of SDS-Fe₃O₄ nanoparticles for Cd²⁺ was found to be 7.466 mgg⁻¹. The results indicated that SDS-Fe₃O₄ nanoparticles can be used as an effective adsorbent for removing cadmium from contaminated water sources.

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1. Introduction

Heavy metal pollution of wastewater is a common environmental threat, since the toxic metal ions dissolved can eventually reach the top of the food chain and thus become a risk factor for human health (Rout et al., 2012). Cadmium is a toxic heavy metal of significant environmental and occupational concern (Waalkes, 2000). It has been released to the environment through the combustion of fossil fuels, metal production, application of phosphate fertilizers, electroplating, and the manufacturing of batteries, pigments, and screens (Sharma, 2008; Alloway and Steinnes, 1999; Perez-Marin et al., 2007).

The conventional technologies for the removal of heavy metal ions from aqueous solution include chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment and adsorption (Elouear et al., 2008). Among the different treatments described above, adsorption technology is attractive due to its merits of efficiency, economy and simple operation (Crini, 2005). A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash and activated carbon have been used for cadmium removal (Sharma, 2008; Tan and Xiao, 2009; Benguella and Benaissa, 2002; Meng et al., 2009; Soltani et al., 2009; Semerjian, 2010; Katsumi et al., 2010; Wang et al., 2010; Tashauoei et al., 2010; Visa et al., 2010). Compared to the traditional adsorbents,

magnetic nanoparticles not only can be manipulated or recovered rapidly by an external magnetic field but also possess quite good performance owing to high efficient specific surface area and the absence of internal diffusion resistance (Kohler et al., 2006).

Inorganic nanoparticles tend to aggregate into micron or larger particles because of direct interparticle interactions such as van der Waals forces and magnetic interactions. Aggregation reduces the specific surface area and the interfacial free energy, thereby decreasing particle reactivity and losing the unique property of nanoparticles (Elliott and Zhang, 2001; Xu and Zhao, 2007). To prevent agglomeration of nanoparticles, various stabilizers have been found effective for stabilizing nanoparticles, including carboxylic acids (Kataby et al., 1999), surfactant (Sun and Zeng, 2002), and polymers (Kim et al., 2003; Ditsch et al., 2005).

The objectives of this research were to synthesize and characterize sodium dodecyl sulfate (SDS) modified magnetite (Fe₃O₄) nanoparticles (SDS-Fe₃O₄). Furthermore, batch experiments were performed to investigate reaction kinetics, adsorption capacity and the effects of pH, contact time, initial concentration of cadmium and amount of adsorbent dosage on cadmium removal. Results from this study can be used to assess the utility of SDS-Fe₃O₄ nanoparticles for heavy metal removal, in particular cadmium adsorption, at the field scale.

2. Materials and methods:

2.1. Preparation and characterization of SDS-Fe₃O₄ nanoparticles:

The method of Si et al. (2004) was modified for synthesizing SDS-Fe₃O₄ nanoparticles. First, 50 mL of an aqueous solution of FeCl₂.4H₂O (5.0 gL⁻¹ as Fe) was added dropwise to a 50 mL aqueous solution of 0.625% (w/v) sodium dodecyl sulfate (NaC₁₂H₂₅SO₄) with continuous stirring. The mixture was stirred for 30 min to complete the formation of the iron – SDS complex. Then, the pH of the solution was increased slowly to 11 by adding 0.5 M NaOH solution. The reaction mixture was subsequently aged for 1 h with constant shaking. After the reaction, excess SDS was removed by washing with double distilled water. The resultant solid magnetite materials were then dried in a vacuum oven at 40 °C for 12 h.

Scanning Electron Microscopy (SEM) characterization was performed to identify surface morphology and size distribution of SDS-Fe₃O₄ nanoparticles. The functional groups presenting in SDS-Fe₃O₄ nanoparticles was investigated using the Fourier transform infrared (FTIR) technique. X-ray diffraction (XRD) analysis was performed to identify the structure and the composition of freshly synthesized SDS-Fe₃O₄ nanoparticles.

2.2. Adsorption experiments

Laboratory batch experiments were carried out to study the adsorption of cadmium on SDS-Fe₃O₄ nanoparticles. The experiments were performed at room temperature (20±2 °C) using 250 mL Erlen Meyer containing 50 mL cadmium solution. The Cd solution was prepared by dissolving Cd(NO₃)₂.4H₂O in 0.1 M KNO₃ solution. A known amount of SDS-Fe₃O₄ nanoparticles was added to 50 mL of the corresponding Cd solution over a period of time on a shaker at 120 rpm. After the aqueous phase was separated magnetically, the concentration of Cd in the solution was determined by using an atomic absorption spectrometer (Vario6).

The adsorption of cadmium by SDS-Fe₃O₄ nanoparticles was investigated at pH range of 3-8. The initial pH of the solution was adjusted by using 0.1 M HCl or 0.1 M NaOH. The effects of contact time (2, 5, 10, 15, 30, 60, 90 and 120 min), initial concentration of cadmium (10, 25, 50, 75 and 100 mgL⁻¹) and amount of adsorbent dosage (0.1, 0.2, 0.3, 0.4 and 0.5 g) were also examined throughout the experiments at 20±2 °C and 120 rpm shaking speed. The amount of Cd removal was calculated from the difference between Cd taken and that remained in the solution. The removal efficiency (R) of cadmium was calculated as:

$$R = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

The amount of cadmium adsorbed on the sorbent phase (mg g⁻¹) was calculated as:

$$q = \frac{C_i - C_f}{m} \times V \quad (2)$$

Where q is the amount of cadmium adsorbed per unit weight of adsorbent, V is the volume of the liquid phase (L), m is the weight of adsorbent (g) and C_i and C_f are the initial and final concentrations of cadmium (mg L⁻¹) in water.

3. Theory

3.1. Adsorption kinetics

Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion into the interior of the pores. In order to study the controlling mechanisms of the adsorption process, Lagergren's pseudo-first-order (Lagergren, 1898) and Ho's pseudo-second-order (Ho et al., 1996) kinetic models were used to test the experimental data.

A simple kinetic analysis of adsorption is the Lagergren's pseudo-first-order differential equation:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

Where q_e and q_t are the amounts of cadmium adsorbed (mg g⁻¹) at equilibrium and at time t (min), respectively, and k_1 (min⁻¹) is the rate constant of first-order adsorption.

The pseudo-second-order model can be expressed in the form:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

Where k_2 is the pseudo-second-order rate constant (g mg⁻¹ min⁻¹).

3.2. Adsorption isotherm models

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Cd²⁺ ions by SDS-Fe₃O₄ nanoparticles was modelled using two adsorption isotherms.

The Langmuir isotherm (1918) assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved

(Boparai *et al.*, 2011). The Langmuir model is given as (Langmuir, 1918):

$$q_e = \frac{K_L q_m C_e}{(1 + K_L C_e)} \quad (5)$$

Where C_e is the equilibrium cadmium concentration (mg L^{-1}) in the solution, q_e is the equilibrium cadmium concentration (mg g^{-1}) on the adsorbent, q_m is the maximum adsorption capacity (mg g^{-1}) and K_L (L g^{-1}) is the Langmuir constant related to the adsorption energy (Tan and Xiao, 2009; Barkat *et al.*, 2009; Chingombe *et al.*, 2006).

The Freundlich isotherm (1906) is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent (Yang, 1998).

$$q = K_F C_e^{\frac{1}{n}} \quad (6)$$

where K_F and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively (Tan and Xiao, 2009).

3.3. Goodness of model fit

In this research, the goodness of fit between experimental and model estimated data was assessed by the linear coefficient of determination (R^2) and Root mean square error ($RMSE$) as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (q_e - q_c)^2}{n}} \quad (7)$$

Where q_e and q_c are the measured and model estimated amounts of Cd^{2+} adsorbed, respectively, and n is the number of measurements. A lower $RMSE$ value and higher R^2 value are regard to show goodness of agreement between measured and estimated Cd^{2+} adsorbed data.

4. Results and discussion

4.1. Characterization of adsorbent

The surface and textural morphology of SDS- Fe_3O_4 nanoparticles by SEM image is illustrated in Fig. 1. As shown in Fig. 1, SDS- Fe_3O_4 nanoparticles prepared are in the range of 40–60 nm in diameter.

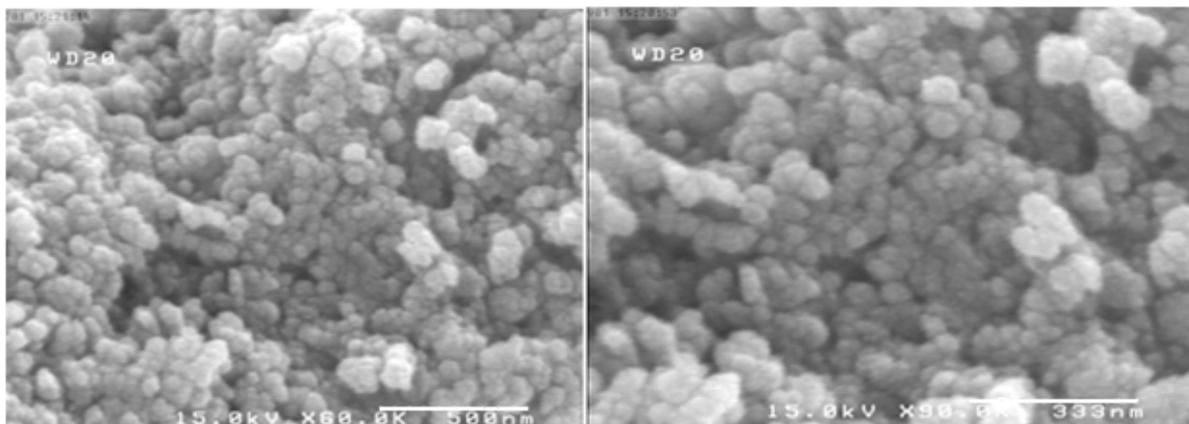


Figure 1. SEM images of the SDS- Fe_3O_4 nanoparticles

The XRD analysis of the SDS- Fe_3O_4 nanoparticles is shown in Fig. 2. The peaks at 2θ values of 30.300, 35.675, 37.160, 43.300, 57.175, 62.900, 71.290 and

74.380 that are maximum peaks corroborate the presence of Fe_3O_4 .

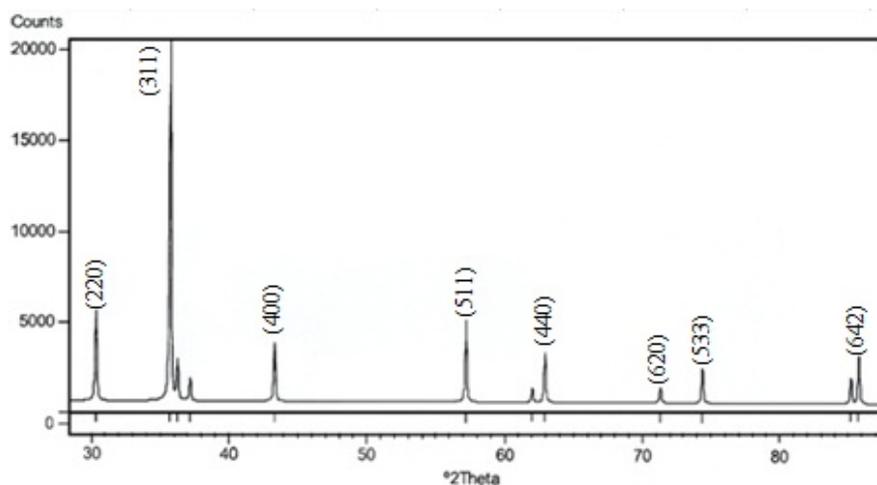


Figure 2. XRD image of the SDS-Fe₃O₄ nanoparticles

The FTIR spectra using KBr of Fe₃O₄ and SDS-Fe₃O₄ nanoparticles are shown in Fig. 3. Infrared spectrums at the low wave numbers (≤ 700 cm⁻¹) were obtained from vibrations of Fe-O bonds. The presence of magnetite nanoparticles can be seen by absorption bands at 578.371, 690.989 and 726.075 cm⁻¹. The bands

at 3402.03, 3853.15, 3443.35, 2341.11 and 2917.89 cm⁻¹ indicated the presence of stretching O-H vibrations. Other peaks at 1627.73, 1480.63 and 1020.42 cm⁻¹ were due to C=O, (CH₂)_n and C-O, respectively. Therefore, the composition of the both samples were magnetite.

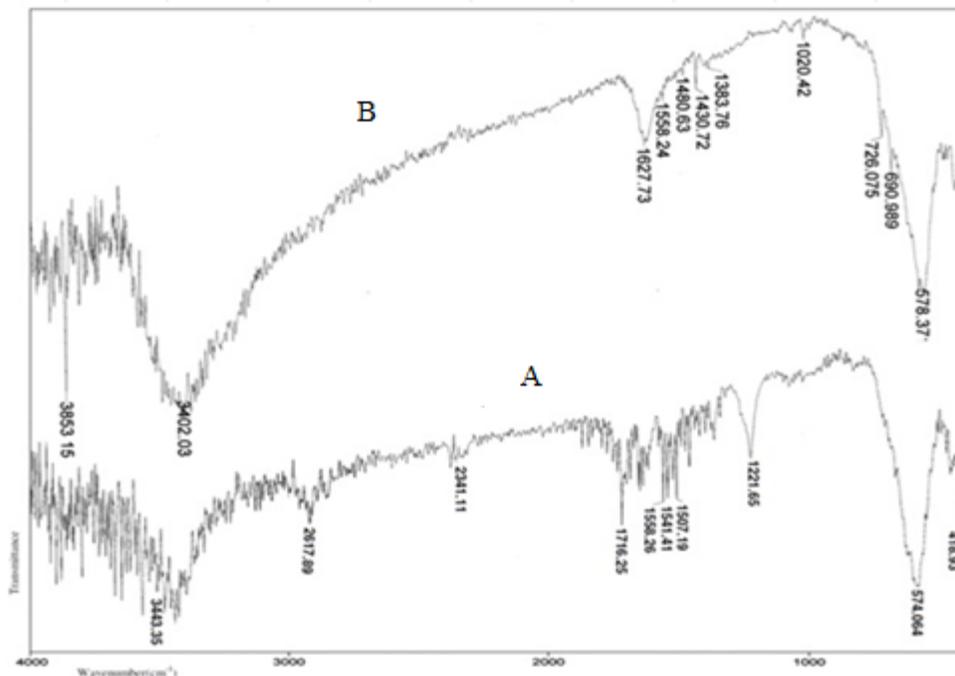


Figure 3. FTIR spectra of (A) bare Fe₃O₄ nanoparticles and (B) SDS-Fe₃O₄ nanoparticles

4.2. Adsorption studies

4.2.1. Effect of initial pH

The percentage of cadmium (II) ion removed by SDS-Fe₃O₄ nanoparticles as a function of equilibrium solution pH is shown in Fig. 4. Because pH affects the surface charge of adsorbents, it can influence the adsorption of charged ions (Martinson and Reddy, 2009). Under different pH conditions, the removal efficiency of Cadmium ions by the SDS-Fe₃O₄ nanoparticles was measured. As presented in Fig. 4, the removal efficiency (R %) increased from 47% to 89% when the initial pH varied from 3 to 6, then at pH>6

removal efficiency decreased with increasing solution pH.

Thus, the optimal pH for Cd²⁺ ions removal was found to be 6.0. At pH 3 and 4, competition between H⁺ and Cd²⁺ ions could thus explain the weak adsorption in acid medium. In pH 5 and 6, cadmium adsorption was increased because of OH⁻ enhancement. Decrease of cadmium adsorption at pH>6 was due to formation of dissolved hydroxyl groups (Rahmani *et al.*, 2010; Shih and Dong, 2009; Krishnan and Anirudhan, 2003).

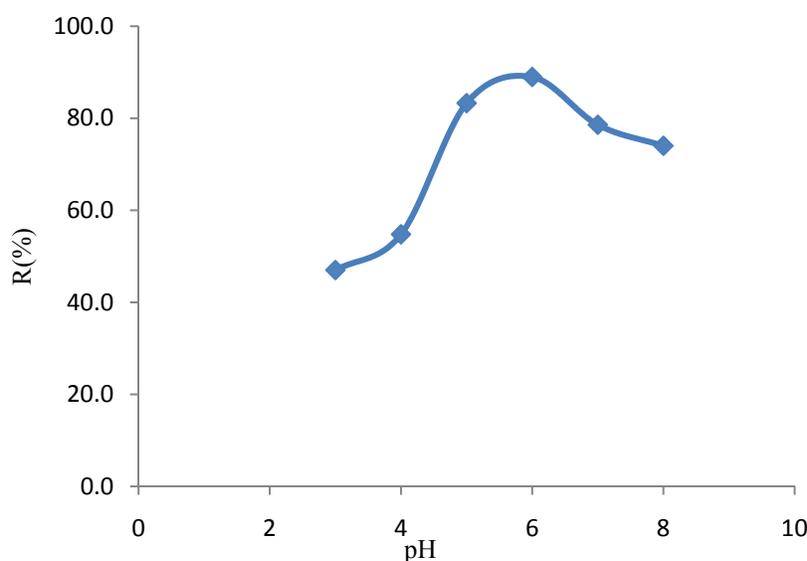


Figure 4. Effect of pH on the adsorption of Cd²⁺ ion by SDS-Fe₃O₄ nanoparticles adsorbent (cadmium initial concentration 10 mg L⁻¹, adsorbent loading 0.1 g, adsorption time 12 h)

4.2.2. Effect of contact time

Fig. 5 illustrates the variation in the amount adsorbed as a function of time for Cd. The removal

efficiency increases with time in the first 30 min. Then the adsorption curve reached equilibrium after this time (Ozmen *et al.*, 2010).

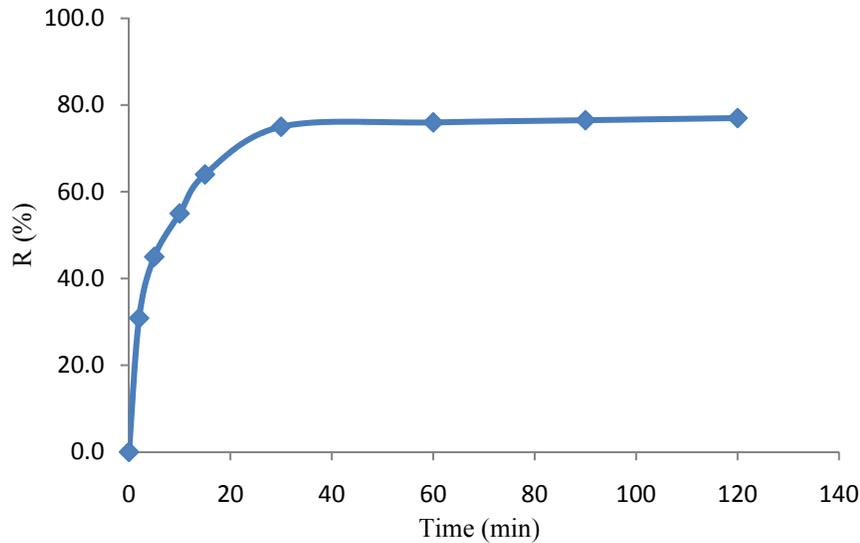


Figure 5. Effect of contact time on the adsorption of Cd²⁺ ion by SDS-Fe₃O₄ nanoparticles adsorbent (cadmium initial concentration 10 mg L⁻¹, adsorbent loading 0.1 g, pH=6)

4.2.3. Effect of initial Cd (II) concentration

Solutions of different initial Cd(II) concentrations (10, 25, 50, 75 and 100 mgL⁻¹) were used to investigate the effect of concentration on the removal of Cd(II) by 0.25 g sorbent at pH 6. As presented in Fig. 6, adsorption yields (%) were decreased with increasing concentration of solution. Although percent of adsorption (%) decreased, equilibrium adsorption capacity of SDS-Fe₃O₄ nanoparticles increased with increasing initial Cd(II) ion

concentration. At low initial solution concentration, the surface area and the availability of adsorption sites were relatively high, and the Cd(II) ions were easily adsorbed. At higher initial solution concentration, the total available adsorption sites are limited, thus resulting in a decrease in percentage removal of Cd(II) ions. The increased q_e at higher initial concentration can be attributed to enhanced driving force.

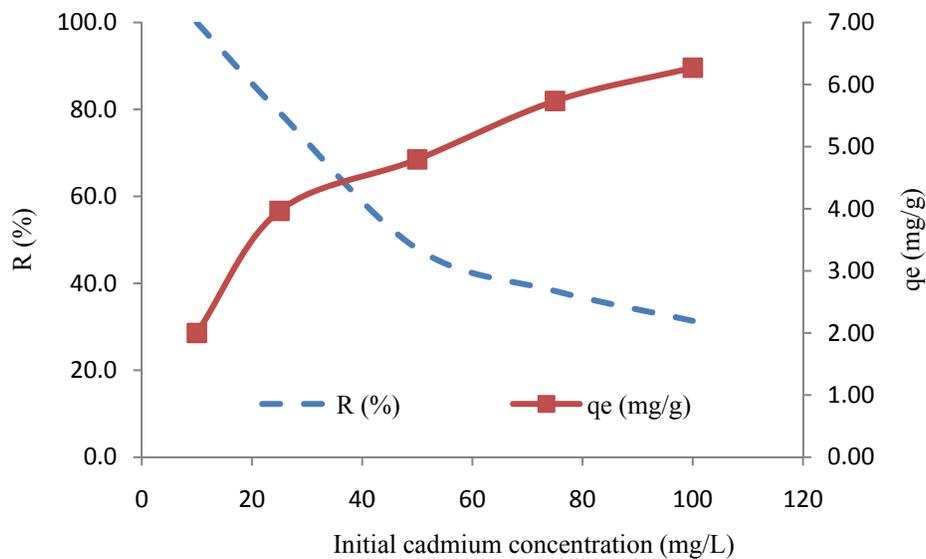


Figure 6. Effect of initial concentration on the adsorption of Cd²⁺ ion by SDS-Fe₃O₄ nanoparticles adsorbent

4.2.4. Effect of adsorbent dosage

The other variable chosen for studying Cd(II) adsorption was the amount of adsorbent, which was varied from 0.1 to 0.5 g while keeping the Cd (II) concentration as 50 mgL⁻¹ (Fig. 7). The increase in

adsorbent dosage from 0.1 to 0.5 g resulted in an increase from 28 to 90.8% in adsorption of Cd(II), while the adsorption capacity decreased from 7.00 to 4.54 mgg⁻¹. This was because of the availability of more binding sites for complexation of Cd(II) ions.

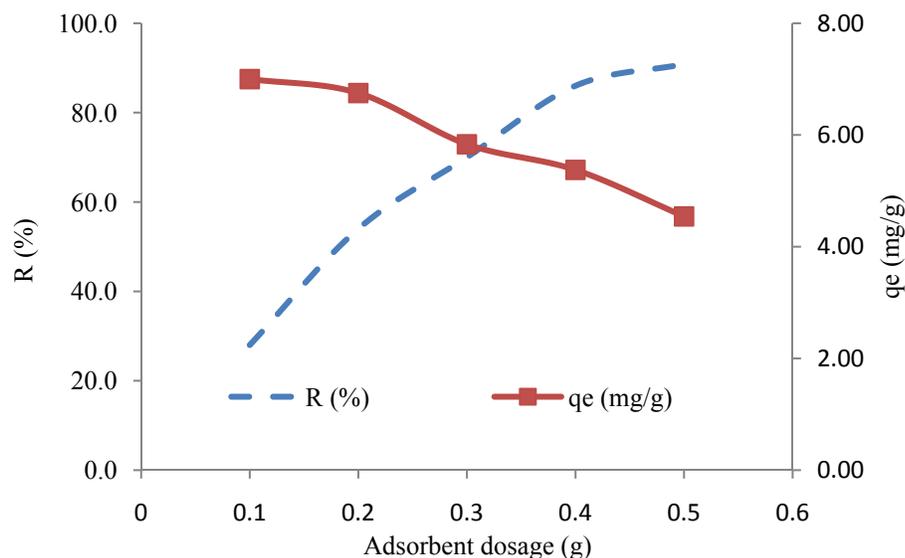


Figure 7. Effect of adsorbent dosage on removal of cadmium by SDS-Fe₃O₄ nanoparticles adsorbent

4.2.5. Kinetic study

The fittings of the experimental kinetic results to the two models are shown in Fig. 8 and the estimated parameters values are presented in Table 1. It can be seen that the pseudo second-order model gives the best fit with more R^2 and less $RMSE$ but its predicted q_e value (3.345 mgg⁻¹) is overestimated as compared to the

experimentally observed value (3.210 mgg⁻¹). In pseudo first-order, predicted q_e value (3.115 mgg⁻¹) is lower than experimentally observed value (3.210 mgg⁻¹). Therefore, pseudo second-order model could be used for prediction of the kinetics of adsorption of Cd²⁺ on the SDS-Fe₃O₄ nanoparticles.

Table 1: The kinetic models parameters for adsorption of Cd²⁺ ions by SDS-Fe₃O₄ nanoparticles in aqueous solution.

First-order kinetic model					Second-order kinetic model				
$q_e(\text{exp})(\text{mg/g})$	$K_1(\text{l/min})$	$q_e(\text{cal})(\text{mg/g})$	R^2	$RMSE$	$K_2(\text{g}/(\text{mgmin}))$	$q_e(\text{cal})(\text{mg/g})$	R^2	$RMSE$	
3.210	0.172	3.115	0.921	0.219	0.081	3.345	0.983	0.103	

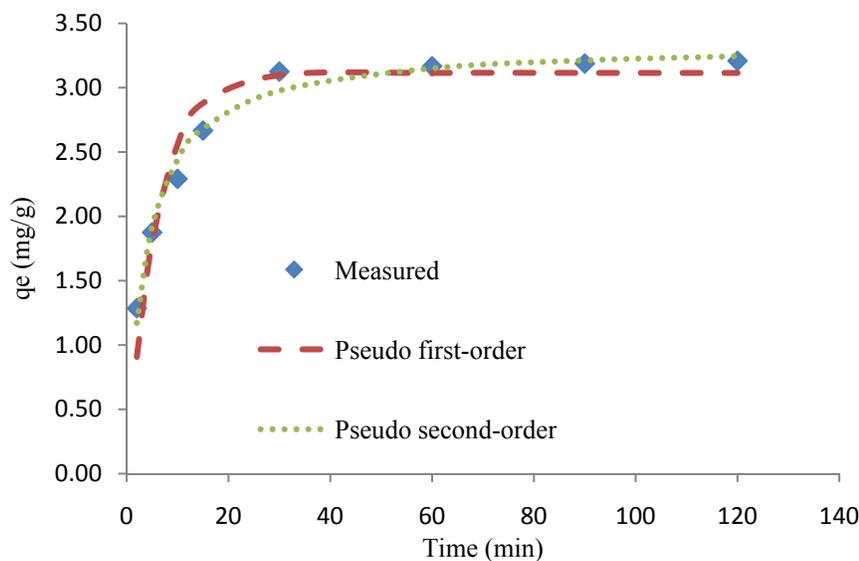


Figure 8. The fitting of kinetic models for Cd^{2+} on SDS- Fe_3O_4 nanoparticles

4.2.6. Adsorption isotherm

Fig. 9 displays a comparison of the fitting of the experimental data with Langmuir Freundlich adsorption isotherms. It suggests that the Freundlich model is more suitable in simulating the adsorption isotherm of Cd^{2+} onto SDS- Fe_3O_4 nanoparticles. The related parameters have also been summarized in table 2. It is observed that the Freundlich model possesses

higher R^2 and less $RMSE$ than the Langmuir model, which means the heterogeneity of SDS- Fe_3O_4 nanoparticles surface. Moreover, the maximum adsorption capacity (q_m) was 7.466 mgg^{-1} which is more than values of cadmium adsorption on activated carbon (3.37 mgg^{-1}) (An *et al.*, 2001) and hematite (4.96 mgg^{-1}) (Singh *et al.*, 1998).

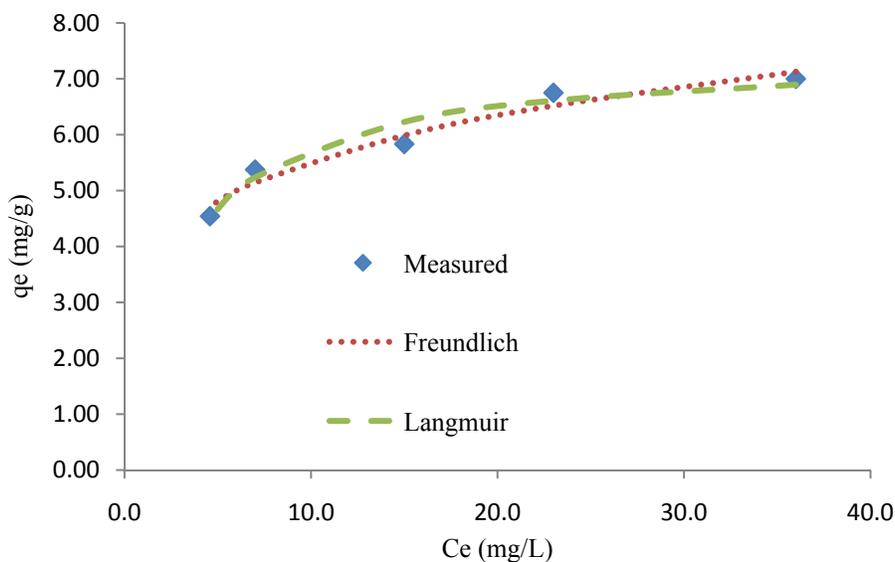


Figure 9. Cd^{2+} adsorption isotherms by SDS- Fe_3O_4 nanoparticles

Table 2: Equilibrium model parameters for adsorption of Cd²⁺ ions by SDS-Fe₃O₄ nanoparticles

Langmuir isotherm				Freundlich isotherm			
q_{max} (mgg ⁻¹)	K_L	R^2	RMSE	K_F	n	R^2	RMSE
7.466	0.335	0.948	0.265	3.491	5.022	0.954	0.249

5. Conclusion

SDS-Fe₃O₄ nanoparticles can be used as an effective adsorbent for removing cadmium from contaminated water sources. Examined experimental parameters, such as pH, contact time, initial Cd²⁺ concentration and adsorbent dosage influenced the removal of Cd²⁺ ion by SDS-Fe₃O₄ nanoparticles. The cadmium removal was optimal at pH=6 and 30 minutes equilibrium time in batch experiments. Higher initial cadmium concentration led to lower removal percentages but higher adsorption capacity. As the adsorbent dose increased, the removal of cadmium increased, while the adsorption capacity decreased. The cadmium adsorption data was fitted to the Freundlich model, thus, indicating the heterogeneity of SDS-Fe₃O₄ nanoparticles surface. The pseudo second-order kinetic model accurately described the adsorption kinetics. Based on the results, it can be concluded that SDS-Fe₃O₄ nanoparticles is a suitable adsorbent for cadmium removal and it can be recommended for use in water sources treatment.

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