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Adsorption kinetics of Cd (II) from aqueous solution by magnetite

Xue Song Wang*, Fei Liu, Hai Jie Lu, Peng Zhang, Hong Ying Zhou

Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang, Jiangsu, 222005, China
Tel.: +8651885895408; Fax: +8651885895409; email: snowpine1969@yahoo.com.cn

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ABSTRACT

Magnetite was applied to remove Cd (II) from aqueous solution. The influence of initial Cd (II) concentration, adsorbent concentration, particle size and reaction temperature on adsorption kinetics was investigated. The highly crystalline nature of the magnetite structure with diameter of around 10 (±3) nm (dry particles) was characterized with transmission electron microscopy (TEM) and X-ray diffractometry (XRD). The surface area was determined to be 115 (±10) m^2/g. The estimated value of the solid pH_{zpc} was found to be nearly 7.3. The Cd (II) uptake was governed by surface complexation adsorption. The Cd (II) adsorption was pH-dependent. Kinetics of adsorption of Cd (II) were found not to conform to the pseudo-first-order equation, pseudo-second-order equation and Elovich equation, but to follow the Fractional power equation well.

Keywords: Cd (II); Magnetite; Adsorption; Kinetics

1. Introduction

Environmental contamination by heavy metals is of growing concern because of health risks on humans and animals. Among the heavy metals of public concern, cadmium has received attention, probably because of its toxicity. The adverse effects of cadmium have been reported by various researchers [1,2]. Cadmium has many industrial applications which serve as potential sources of contamination. These industries include metallurgical alloying, ceramics, electroplating, photography, pigment works, chemical industries and lead mines and drainage [3]. The U.S. Environmental protection Agency has set new stringent standards for cadmium at 5.00 μg/L. Existing purification technologies including precipitation, ion exchange, fluidized bed separation and floatation do not attain the required efficiency in Cd (II) removal from water needed to meet these regulations [4].

A potential method for attaining better removal of heavy metals from wastewater is the adsorption of heavy metals on iron oxide [4]. Among the various iron oxides, magnetite has been the most popular. Numerous studies have been performed to apply magnetite to remove heavy metals including Cr (VI) [5–9], Hg (II) [10], As (V) [4,11], Sb (V) [12], Se (IV) [13], V (V) [5], Pb (II) [4,9]. However, very few experimental studies were reported in the literature on the other common heavy metal ions (e.g. Cd (II)) interactions with magnetite. In this study, magnetite particles were used to remove Cd (II) from aqueous solution. The batch studies were performed to investigate the influence of initial Cd (II) concentration, adsorbent concentration, particle size and reaction temperature on the adsorption kinetics. The adsorption mechanism was also discussed.

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*Corresponding author

2. Materials and methods

All chemical reagents used were analytical grade or better. All glassware was washed with 1 mol/L HNO_3 and rinsed thoroughly with deionized water prior to use. Solutions were made with deionized water purified by passage through a milli-Q water system.

The magnetite samples were purchased from Nanjing Emperor Nano Material Co., Ltd, China and used as received.

2.1. Particle characterization

Magnetite particles were characterized via powder X-ray diffraction (XRD) using a Bruker D8ADVANCE diffractometer with a Cu-Kα source (λ = 0.154 056 nm). Data collection ranges were 5–80° 2θ. The diffraction pattern was compared to PDF (powder diffraction file) No. 72-2303 for magnetite.

The specific surface area was determined from seven-point N_2-BET (Brunauer-Emmett-Teller) adsorption isotherms performed on a Quantachrome Nova 1200 surface area analyzer. Fourier transform Infrared spectroscopy (FTIR) on KBr pellets was performed on a WGH-30A spectrophotometer. The size and morphology of magnetite were determined using TEM (transmission electron microscopy, JEOL-2010). Potentiometric titrations were performed to find out the zero point charge, pH_{zpc}, following the methodology of Davranche et al. [14]. The hydrodynamic diameter distribution for particle suspensions at pH 7.5 was determined by Winner 2000Z Laser Particle Analyzer (Jinan Winner Co. Ltd, China).

2.2. Cd (II) uptake experiments

Stock solutions of Cd (II) (~1 mol/L) were prepared by dissolving cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$) in de-ionized water. All following experiments were performed in triplicate.

The adsorption experiments were carried out by mixing together a constant adsorbent with a constant volume of the aqueous solution of cadmium ions. The contents in the flasks were agitated by placing them in constant temperature water bath thermostat. The pH was adjusted with 1 mol/L HNO_3 or NaOH using a PHS-3C pH meter (Jiangsu Jiangfen Instrumental Factory, China) using a combined glass electrode. After shaking, the solution samples were withdrawn at predetermined time intervals and were then passed through a 0.2-μm filter and the residual Cd (II) concentration was measured using atomic absorption spectroscopy (TAS-990, Beijing Puxi Scientific Instrumental Factory, China). The following conditions were maintained for different sets of experiments:

Effect of pH: Magnetite concentration 10 g/L; Cd (II) concentration 1.7 mmol/L; temperature 298 K; contact time 120 min; stirring speed 150 rpm.

Kinetics:

1. *Effect of initial Cd (II) concentration*: Magnetite 10 g/L; Cd (II) concentration 1.33 or 1.7 mmol/L; temperature 298 K; pH 7.5; stirring speed 150 rpm;
2. *Effect of adsorbent concentration*: Magnetite 5, 10 or 15 g/L; Cd (II) concentration 1.7 mmol/L; temperature 298 K; pH 7.5; stirring speed 150 rpm;
3. *Effect of particle size*: Magnetite 10 g/L; Cd (II) concentration 1.7 mmol/L; temperature 298 K; pH 7.5; stirring speed 150 rpm;
4. *Effect of reaction temperature*: Magnetite 10 g/L; Cd (II) concentration 1.7 mmol/L; temperature 298, 308, 318 K; pH 7.5; stirring speed 150 rpm;

2.3. Data analysis

The amount of Cd (II) ions adsorbed at time t, q_t, was calculated according to the following equation

$$q_t = \frac{(C_0 - C_t)V}{m}, \tag{1}$$

where q_t (mmol/g) is the amount of solute adsorbed onto the unit mass of the adsorbent at time t (min); C_0 and C_t (mmol/L) the concentration of the solute in the initial solution and in the aqueous phase at time t, respectively; V the solution volume of the aqueous phase (L); and m the amount of adsorbent used (g).

The percent removal (%) was calculated using the following equation:

$$\text{removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100, \tag{2}$$

where C_e (mmol/L) is the concentration of the solute at equilibrium.

3. Results and discussion

3.1. Primary particle characterization

The particle FT-IR spectrum is shown in Fig. 1. The peak at 582 cm^{-1} may be assigned to the Fe–O stretching band of Fe_3O_4 which characteristically occurs at around 580 cm^{-1} [15]. At 1,633 cm^{-1}, this is the Fe–OH groups on the magnetite nanoparticles surface and 628 cm^{-1} is the presence of nonstochiometric magnetite or some maghemite [15]. The occurrence of broad peak

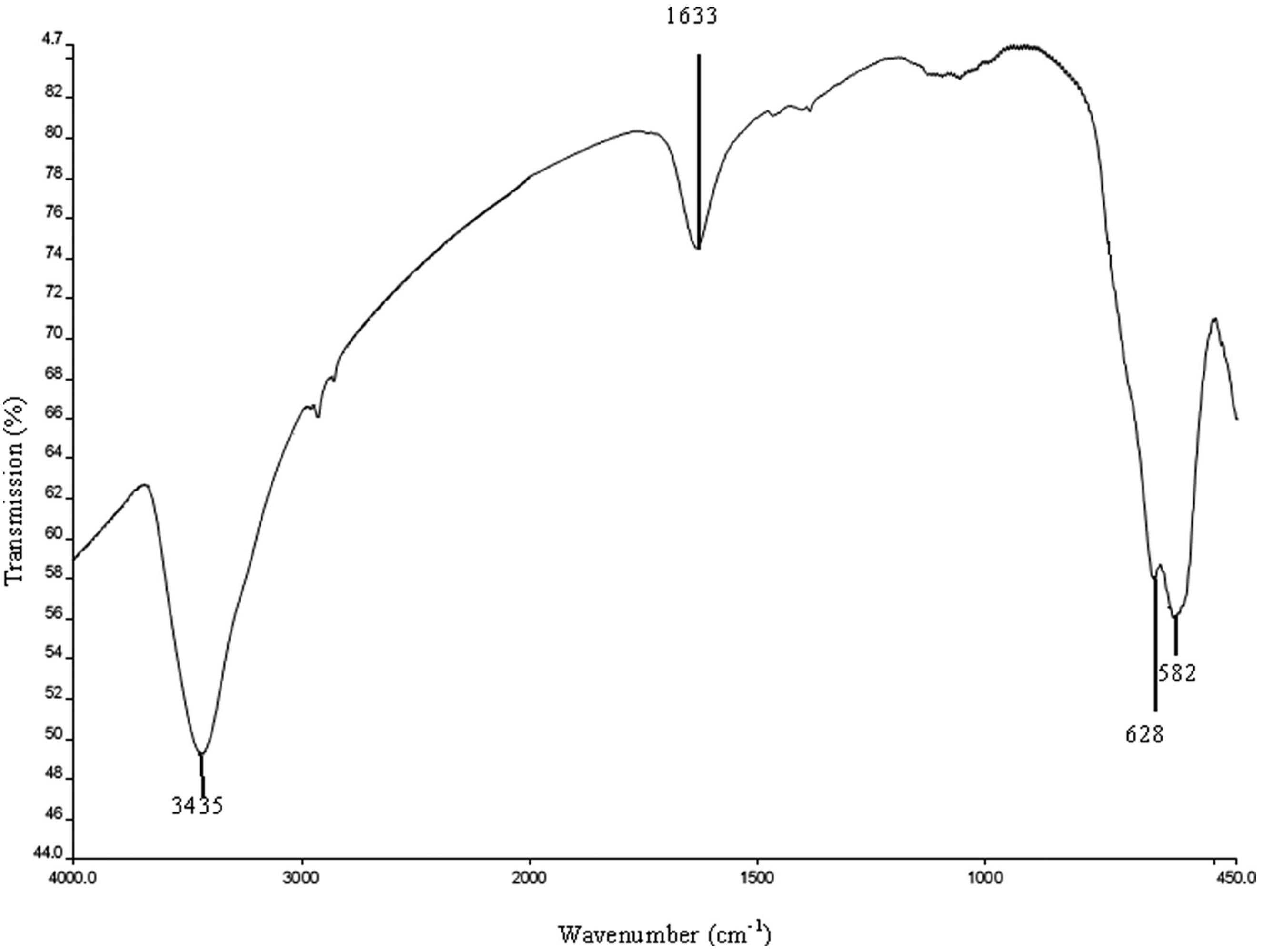

Fig. 1. FT- IR spectrum of magnetic Fe_3O_4 particles.

at 3,435 cm^{-1} was due to the moisture present in the KBr used to prepare the pellets for IR analysis.

The XRD spectrum (not shown) exhibits peaks at 2θ values of 35.5°, 43°, 57° and 62.6°, respectively, which correspond to the normal positions (JCPDS-Magnetite No. 72-2303). A typical TEM micrograph for the magnetic sample applied is shown in Fig. 2. The particles are spherical and mean diameter is 10 (±3) nm. The specific surface area measured by BET method was 115 (±10) m^2/g.

Magnetite, an ampoteric solid can develop charges in the protonation and deportation reactions of $\equiv F_eOH$sites on surface. Thus, we obtain

$$\equiv \mathrm{FeOH} \leftrightarrow \equiv \mathrm{FeO}^- + \mathrm{H}^+ \quad K^s_{a1} \tag{3}$$

$$\equiv \mathrm{FeOH}_2^+ \leftrightarrow \equiv \mathrm{FeOH} + \mathrm{H}^+ \quad K^s_{a2} \tag{4}$$

and the corresponding acidity constants,

$$K^s_{a1} = \frac{[\mathrm{H}^+]\{\equiv \mathrm{FeO}^-\}}{\{\equiv \mathrm{FeOH}\}} \tag{5}$$

$$K^s_{a2} = \frac{[\mathrm{H}^+]\{\equiv \mathrm{FeOH}\}}{\{\equiv \mathrm{FeOH}_2^+\}}, \tag{6}$$

where [] is the solution species concentration in mol/L and {} is the solid surface concentration in mol/L.

The surface charge of a solid, Q in unit mol/g, corresponds to

$$Q = \{\mathrm{FeOH}_2^+\} - \{\mathrm{FeO}^-\} \tag{7}$$

The solid surface charge as a function of pH is plotted in Fig. 3 and the estimated value of the solid pH_{zpc}, the pH where the curve cross the x-axis ($Q = 0$), was found to be nearly 7.3.

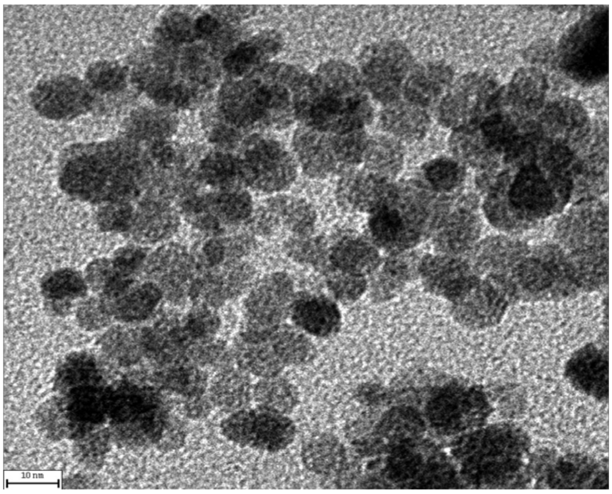

Fig. 2. Transmission electron micrograph of magnetic Fe_3O_4 particles

Fig. 4 suggests that particles extensively aggregated in pH 7.5 suspensions, as large aggregates settled if the suspensions were not mixed. The mean hydrodynamic diameter of particles is 0.69 μm.

3.2. Effect of initial solution pH on Cd (II) adsorption

The effect of initial solution pH on Cd (II) removal was studied and the result is shown in Fig. 5. With an increase in pH, the percent removal increased progressively by increasing pH up to 7.53. At higher pHs, the precipitate was observed. This pH dependency has previously been attributed to the protonation and deprotonation of surface Fe^{II} [16 and reference therein]:

$$\equiv \mathrm{Fe^{III}OFe^{II}OH} \leftrightarrow \equiv \mathrm{Fe^{III}OFe^{II}O^{-}} + \mathrm{H^{+}} \tag{8}$$

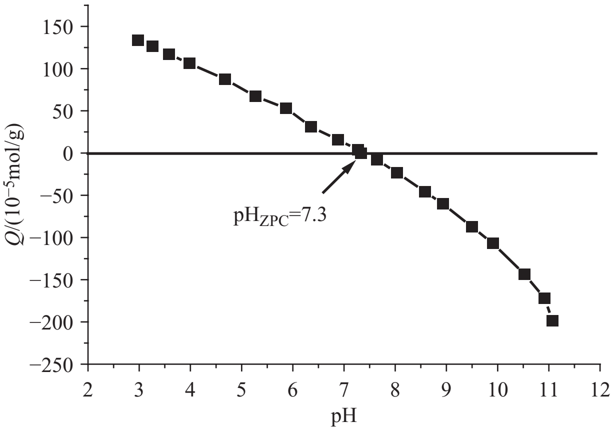

Fig. 3. The solid surface charge, Q, as a function of pH.

With an increase in pH, the equilibrium shifts such that a greater number of sites are present in the more reactive deprotonated form.

It is important to realize that negative, positive and neutral functional groups can coexist on the oxide surface. At pH's < pH_{zpc}, the $FeOH_2{}^+$ groups predominate over the FeO^- groups, i.e., although the surface has a net positive charge, some FeO^- groups are still present. At the pH_{zpc}, the number of $FeOH_2{}^+$ groups equals the number of FeO^- groups and at pH increases, the number of FeO^- groups increases [15]. The zero point of charge (pH_{zpc}) was determined to be pH 7.3. Accordingly, at pH > 7.3, magnetite particles would have much more negative charge and readily sorbed positively charged cation (Cd (II)) due to electrostatic attractions.

3.3. Adsorption kinetics

3.3.1. Influence of initial Cd (II) concentration on adsorption kinetics

The effect of initial Cd (II) concentration on Cd (II) adsorption kinetics is shown in Fig. 6. As expected, the overall trend was an increase of the adsorption capacity with increasing initial Cd (II) concentrations and this confirmed strong chemical interactions between cations and magnetite particles [17]. On changing the initial concentration of Cd (II) solution from 1.33 to 1.7 mmol/L, the amount adsorbed increased from 0.04 (29.7% removal) to 0.09 (56.8% removal) mmol/g at 25°C, pH 7.5.

In order to analyze the Cd (II) sorption kinetics, four kinetic models were tested including the fractional power equation, Elovich equation, pseudo-first-order equation and pseudo-second-order equation. The validity of each model was checked from the linear plot and the inapplicability of the Elovich equation, pseudo-first-order equation and pseudo-second-order equation to describe the kinetics of Cd (II) adsorption on to magnetite particles was observed (data not shown). Thus, kinetics of Cd (II) adsorption on to magnetite particles were analyzed only using the Fractional power model.

The Fractional power function model is a modified form of the Freundlich equation and may be expressed as [18]

$$q_t = at^b, \tag{9}$$

where q_t (mmol/g) is the amount of Cd (II) adsorbed by magnetite at a time t (min), while a and b are constants with $b < 1$. The function ab is also a constant, being the specific sorption rate at unit time, i.e., when $t = 1$.

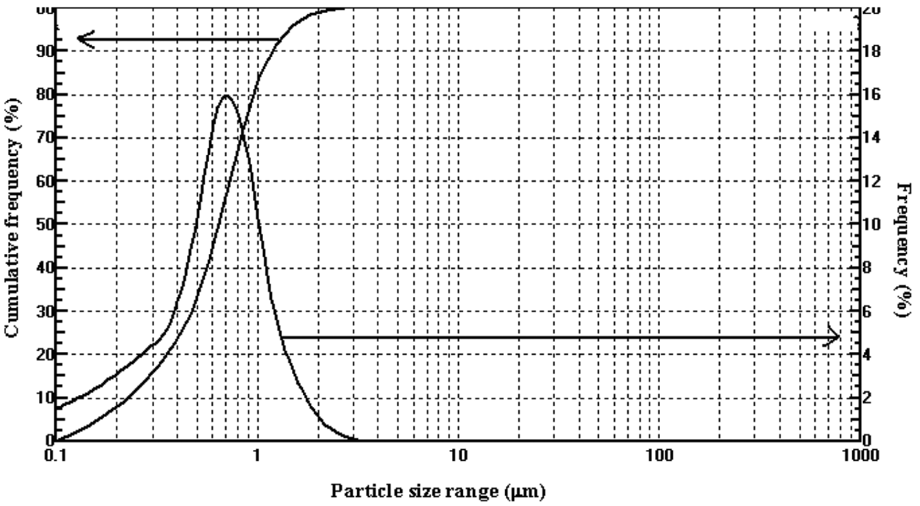

Fig. 4. Hydrodynamic diameter distribution for particle suspensions at pH 7.5.

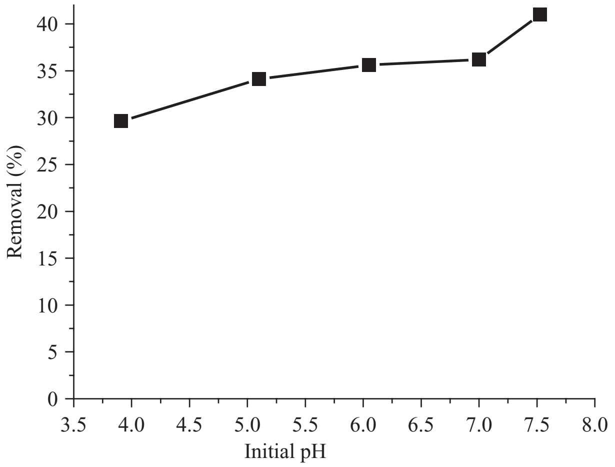

Fig. 5. Effect of initial solution pH on Cd (II) removal (Initial Cd (II) concentration:1.7 mmol/L, Magnetite concentration:10 g/L, reaction time: 2 h, reaction temperature: 298 K).

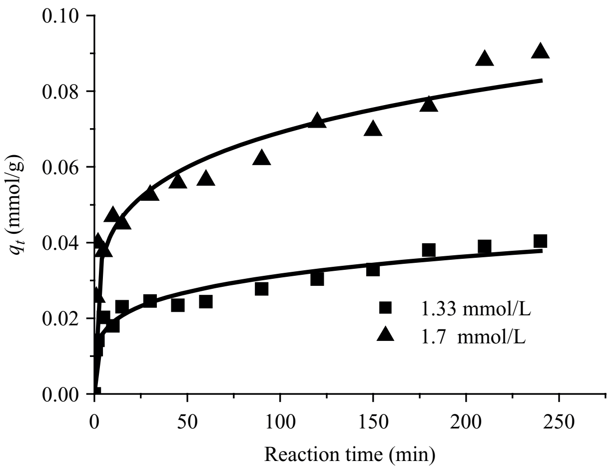

Fig. 6. Kinetics of adsorption of Cd (II) by magnetite particles for various initial Cd (II) concentrations. The experimental data were fitted to fractional power equation. (Magnetite concentration: 10 g /L; Temperature: 298 K; pH: 7.5).

Both parameters (*a* and *b*) were evaluated by nonlinear regression and the values are listed in Table 1. The data showed a good compliance with the Fractional powder equation.

3.3.2. *Influence of adsorbent concentration on adsorption kinetics*

An attempt to enhance Cd (II) adsorption was evaluated by examining the effect of adsorbent concentration. Fig. 7 shows the effect of adsorbent concentrations on the Cd (II) kinetics. By employing 1.7 mmol/L Cd (II) and by increasing adsorbent concentration from 5 to 15 g/L, at 240 min, the adsorption capacity increased from 0.06 to 0.11 m mol/g. This is likely due to the fact that at higher adsorbent concentration more surface area is available, which means higher number of adsorption. Overall, at low adsorbent concentration (5 g/L) equilibrium was readily reached but at higher adsorbent concentration (15 g/L), much longer time would be needed to ensure adsorption equilibrium.

The experimental kinetic data were also fitted by the Fractional power function model and the values of constants together with correlation coefficients are listed in Table 2. The high correlation coefficients (r^2 > 0.96) also indicate that the Fractional power function model provided a good fit to the experimental data.

Table 1
Parameters of the Fractional power equation for various initial Cd (II) concentrations

Initial Cd (II) concentration (mmol/L)	*a*	*b*	r^2
1.33	1.1×10^{-2}	0.21	0.96
1.7	2.6×10^{-2}	0.21	0.96

Table 2
Parameters of the Fractional power equation for various adsorbent concentrations

Adsorbent concentration (g/L)	*a*	*b*	r^2
5	3.7×10^{-2}	0.09	0.97
10	2.6×10^{-2}	0.21	0.96
15	2.6×10^{-2}	0.24	0.97

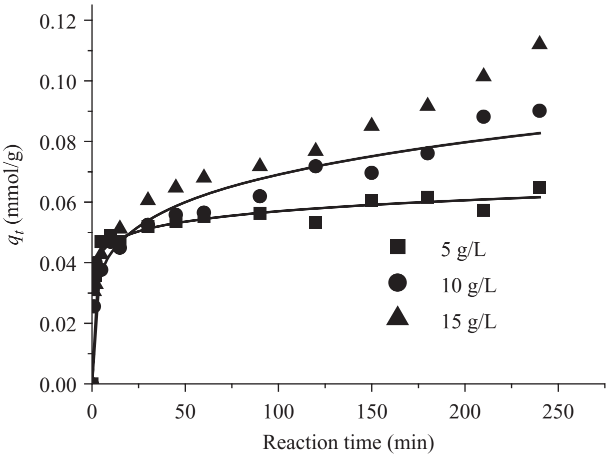

Fig. 7. Kinetics of adsorption of Cd (II) by magnetite particles for various adsorbent concentrations. The experimental data were fitted to fractional power equation. (Cd (II) initial concentration: 1.7 mmol/L; Temperature: 298 K; pH: 7.5).

3.3.3. Influence of adsorbent particle size on adsorption kinetics

Adsorbent particle size has a significant effect on the kinetics of adsorption due to the change of easily available adsorption sites [19]. Fig. 8 presents the influence of adsorbent particle size on Cd (II) adsorption kinetics. As expected, the relatively higher adsorption rate and adsorption capacity by smaller particles may be attributed to the fact that smaller particles yield a larger external surface area. The experimental data were also fitted to the Fractional power function model and the values of constants together with correlation coefficients are listed in Table 3.

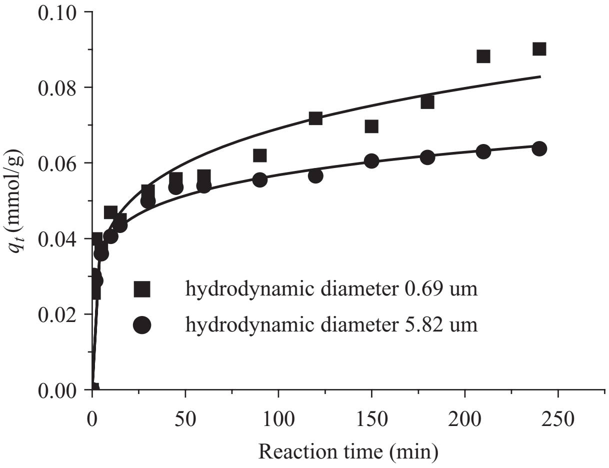

Fig. 8. Effect of particle size on adsorption kinetics. The experimental data were fitted to Fractional power equation. (Cd (II) initial concentration: 1.7 mmol/L; Magnetite concentration: 10 g /L; Temperature: 298 K; pH: 7.5).

Table 3
Parameters of the Fractional power equation for different particle sizes

Particle size (nm)	*a*	*b*	r^2
10	2.6×10^{-2}	0.21	0.96
20	2.9×10^{-2}	0.15	0.99

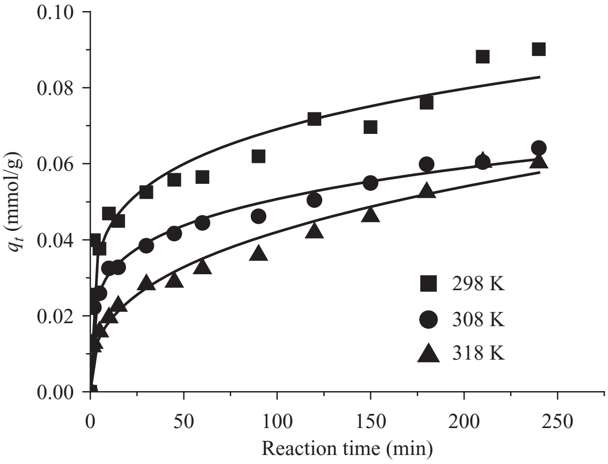

Fig. 9. Effect of reaction temperature on adsorption kinetics. The experimental data were fitted to fractional power equation. (Cd (II) initial concentration: 1.7 mmol/L; Magnetite concentration: 10 g /L; pH: 7.5).

3.3.4. Influence of reaction temperature on adsorption kinetics

Fig. 9 shows the influence of reaction temperature on the Cd (II) adsorption kinetics. It is obvious that

Table 4
Parameters of the Fractional power equation for various reaction temperatures

Temperatures (K)	a	b	r^2
298	2.6×10^{-2}	0.21	0.96
308	2×10^{-2}	0.21	0.99
318	1×10^{-2}	0.36	0.98

by increasing the reaction temperature, the adsorption rate and adsorption capacity was decreased; likely indicating the adsorption process was exothermic. The experimental data conformed to the Fractional power equation well (Table 4).

4. Conclusions

The magnetite particles applied consisted of spherical particles around 10 nm. The estimated value of the solid $\mathrm{pH_{zpc}}$ was found to be nearly 7.3. The Cd (II) adsorption was pH-dependent. An increase of Cd (II) uptake by magnetite was observed with (i) higher initial Cd (II) concentration (ii) higher adsorbent concentration (iii) small particle size and (iv) lower reaction temperature. Kinetics of adsorption of Cd (II) were found not to conform to the pseudo-first-order equation, pseudo-second-order equation and Elovich equation, but to follow the Fractional power equation well.

Acknowledgements

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