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Adsorption of Fe(II) ions from aqueous phase by chitosan adsorbent: equilibrium, kinetic, and thermodynamic studies

Hamideh Radnia[a], Ali Asghar Ghoreyshi[a,*], Habibollah Younesi[b], Ghasem D. Najafpour[a]

[a]*Chemical Engineering Department, Babol Noshirvani University of Technology, Babol, Iran*
Tel. +981113234204; Fax: +981113234201; email: aa_ghoreyshi@nit.ac.ir
[b]*Department of Environmental Science, Faculty of Natural Resources and Marine Science, Tarbiat Modares University, Noor, Iran*

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ABSTRACT

The aim of present study was to investigate the adsorption properties of chitosan for the removal of Fe(II) ions from aqueous phase in a batch equilibrium system. The effects of adsorbent dose, initial pH, concentration, and temperature of the solution on adsorption were investigated. Adsorption experiments were carried out at initial concentration range of 10–50 $\mathrm{mg\,l^{-1}}$ in a temperatures range of 20–40°C. The adsorption isotherm data were well fitted with Langmuir–Freundlich model. The kinetics of Fe(II) on chitosan followed the nonlinear form of pseudo-first-order model and the model parameters were confidently recovered. The examination of kinetic data also revealed that the adsorption rate was dominated by intraparticle diffusion mechanism. The calculated negative values of standard Gibbs free energy and enthalpy changes confirmed the spontaneous and exothermic nature of Fe(II) adsorption on chitosan adsorbent. Finally, chitosan showed to be a good potential adsorbent for removing Fe(II) ion from aqueous solution with maximum loading capacity of 28.7 $\mathrm{mg\,g^{-1}}$ with removal efficiency of 92.9%.

Keywords: Adsorption kinetics; Adsorption thermodynamics; Chitosan; Iron removal; Isotherm models

1. Introduction

Iron is a commonly used metal in many industries; therefore, large amount of wastewater containing iron should be treated before being discharged into environment. Although iron is one of the essential micronutrients for humans, animals, and plants; however, at high concentration can cause undesirable problems in ecosystems or in industrial processes. It also can cause an unpleasant taste or odor in drinking water and block pipes or transmission lines in industrial processes due to precipitation of iron hydroxide [1]. Different methods have been used to remove iron from aqueous phases such as membrane technologies [2], ion exchange [3], extraction [4], precipitation [5], electro coagulation [6], adsorption [7,8], etc. Recently, Fu et al. [9] reviewed the current methods that have been used to treat wastewater containing heavy metals. As a result, adsorption was recognized as an effective and economic method for heavy metal removal. Adsorption is a mass transfer operation in which a fluid, either liquid or gas, is contacted with a porous solid and it is allowed mass transfer to take place from the fluid phase to solid phase [10]. The adsorption process is an

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*Corresponding author.

effective and flexible operation and offers high removal efficiency conditioned to choose a suitable adsorbent for treating effluents. Therefore, synthesis and development of low-cost adsorbents are essential to have an effective and economical operation for treatment of wastewater containing heavy metal [9] that attracted many researchers in recent decade [11–13]. Ahmaruzzaman [14] performed an overview of some industrial wastes as low-cost adsorbents for treatment of wastewater laden with heavy metals and compared their removal performance [14]. Chitin and especially chitosan have been extensively investigated as low-cost adsorbents for the removal of metal ions from water and wastewater [15]. Chitin is a natural polymer which is produced from fishery wastes such as shrimp shells [16]. Deacetylation of chitin results in chitosan—a crystalline polysaccharide [17].

A summary of relevant published data in terms of adsorption capacities of chitin and chitosan derivatives has been presented for the removal of various pollutants [18]. Wan Ngah et al. [19] reviewed adsorption of heavy metals and dyes by various chitosan composites. In a study, the adsorption of heavy metals including Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from sulfate and nitrate solutions was investigated on pristine chitosan prepared from cuttlefish wastes [20]. The high adsorption potential of chitosan can be attributed to high hydrophilicity due to large number of hydroxyl groups, flexible structure of the polymer chain, and high chemical reactivity. The last item is due to presence of large number of functional groups in its structure [13].

To the best of our knowledge, few researches were carried out on adsorption of iron by chitosan. Ngah et al. [21] have reported that the adsorption capacity of cross-linked chitosan with different agent decreased compared to pristine one. The main objective of the present study was to assess the adsorption capacity of ferrous iron by pristine chitosan for practical application. The second task was to identify the optimal condition for maximum removal efficiency. For this purpose, batch adsorption experiments were carried out at different conditions. Equilibrium data were analyzed in terms of different isotherm models. Kinetics of iron adsorption was also discussed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Thermodynamic analysis was also carried out to obtain information about thermal nature of Fe(II) adsorption by chitosan adsorbent.

2. Experimental

2.1. Chemicals and materials

Chitosan with minimum 85% deacetylation was purchased from Sigma-Aldrich (USA). All other chemicals used in this study were supplied by Merck (Ddarmstadt, Germany). All reagents were analytical grade and used without further purification. Stock solution of $1,000\,\mathrm{mg\,l^{-1}}$ of Fe(II) ions was prepared using crystalline heptahydrate ferrous sulfate salt. The stock solution was diluted to give appropriate concentrations when necessary. Distilled water was used to prepare all solutions.

2.2. Batch adsorption experiments

Batch adsorption experiments were conducted in 250 ml beakers with 100 ml of iron solution at certain concentration. The initial pH of solutions was adjusted using the required amounts of 0.1 M HCl or NaOH solutions. The mixture was equilibrated with chitosan at rotation speed of 180 rpm in incubator shaker (model KS 4000i control, IKA) for 240 min. All experiments were conducted at 30°C, unless otherwise was stated. Samples were taken at fixed time intervals to determine solution concentration. The samples were filtered with 0.45 μm syringe filter to remove the adsorbent. Iron concentrations in the filtrates were analyzed by 5-sulfosalicylic acid reagent, using a UV–vis Spectrophotometer (model 2100 SERIES, UNICO) at wavelength of $\lambda_{\max} = 425\,\mathrm{nm}$ [22]. A series of experiments were conducted to determine the effect of parameters such as adsorbent dose, pH, initial concentration, and temperature on equilibrium uptake of Fe (II) ions by chitosan.

The amount of metal ion adsorbed by chitosan was calculated according to following equation [23].

$$q_e = \frac{C_0V_0 - C_eV_e}{m} \tag{1}$$

Also removal efficiency is defined as:

$$\%\ \text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where q_e is the equilibrium concentration of Fe(II) in solid phase which is known as metal uptake capacity ($\mathrm{mg\,g^{-1}}$), C_0 and C_e are metal concentrations at initial and equilibrium time ($\mathrm{mg\,l^{-1}}$), V_0 and V_e denotes initial and final volume (l), respectively. Finally, m represents the mass of used adsorbent (g). Due to change in the volume of solution during sampling, the initial and final volumes in Eq. (1) have different values. High removal efficiency as well as high adsorption capacity obtained in this study demonstrated an effective adsorption process.

3. Result and discussion

3.1. Effect of adsorbent dose

Adsorbent dose is particularly important factor in adsorption; because it determines the extent of removal as well as the economics of operation [21]. So effect of chitosan dose on adsorption of iron was studied. Various amounts of adsorbent (0.05−1 g) were added to 100 ml of solutions at constant Fe(II) concentration (10 mg l^{-1}). The equilibrium experiments were conducted at the same time to ensure all conditions remained the same.

Fig. 1 shows the removal efficiency increased with an increase in adsorbent dose. In fact at high adsorbent dose, more adsorbent surface and exchangeable sites for adsorption are available for the metal ions.

Also, it was observed that the adsorption capacity of iron ions per unit weight of chitosan decreased from 8.86 to 0.878 mg g^{-1} with an increase in adsorbent dose from 0.05 to 1 g. In fact, with increase in adsorbent dose, more adsorbent active sites remain uncovered during the adsorption process, thus the metal uptake capacity may decrease. This is in accordance with previous results reported in the literature [23].

At adsorbent dose of 0.15 g, removal efficiency reached to about 91%. However, further increase in adsorbent dose did not show any appreciable improvement in iron removal but a sharp decrease in adsorption capacity was observed. Therefore, the adsorbent dose was fixed at 0.15 g/100 ml of solution (or concentration of 1.5 g l^{-1}) for all further experiments.

3.2. Effect of pH

For sorption studies, pH must be less than the pH at which metal ions precipitate. Although hydrolysis of ferrous ion occurs negligibly under acidic conditions but at higher pHs, it is very probable to hydrolyze and precipitates in the form of hydroxide [24].

Effect of pH on precipitation of Fe(II) was studied at the highest metal concentration used in this study (i.e. 50 mg l^{-1}). The pH of solutions was adjusted at different values varying from 3.5 to 6. The amounts of dissolved iron in solutions were determined to find the minimum pH at which precipitation occurs. Fig. 2 indicates that at pH less than 5, no significant change was observed in a fixed concentration of metal ions. At pH value of greater than 5, the OH^- ions available in the solution form some complexes with Fe(II) and the removal takes place by precipitation. Therefore, the adsorption process should be carried out at pH of less than 5 to ensure metal ions are removed just by adsorption and the effect of precipitation is eliminated.

The effect of pH on adsorption properties of chitosan was also studied. Amount of 0.15 g of adsorbent was added to the aqueous solutions with the concentration of 10 mg l^{-1} at the pH range of 3–5. Fig. 3 depicts both removal efficiency and adsorption capacity increase with an increase in pH.

The reason for higher adsorption at higher pH may be explained by the nature of the chemical interactions of F(II) ions with chitosan functional groups. At lower pH, the amino groups in chitosan molecules are protonated. Therefore, less competition between the protons and metal ions for the reactive sites leads to an increase in adsorption of metal ions. Mohan et al. [24] and Zhou et al. [25] reported similar phenomena.

In the present study, the sorption of Fe(II) was found to be very low at pH less than 3.5; the maximum removal efficiency was obtained at pH around 4

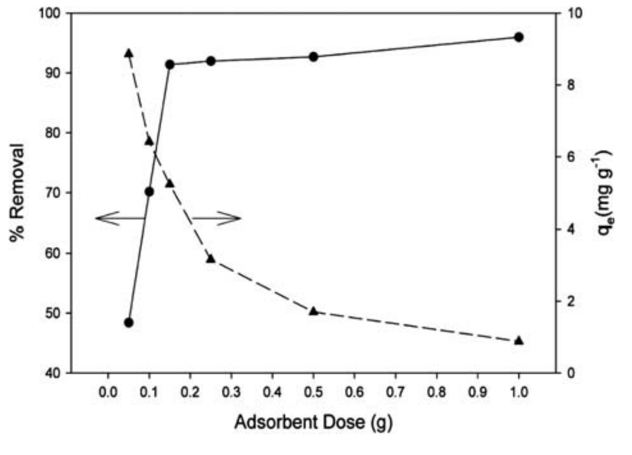

Fig. 1. Effect of chitosan dose on adsorption capacity and removal efficiency of Fe(II) ($C_0 = 10$ mg l^{-1} and $T = 30$°C).

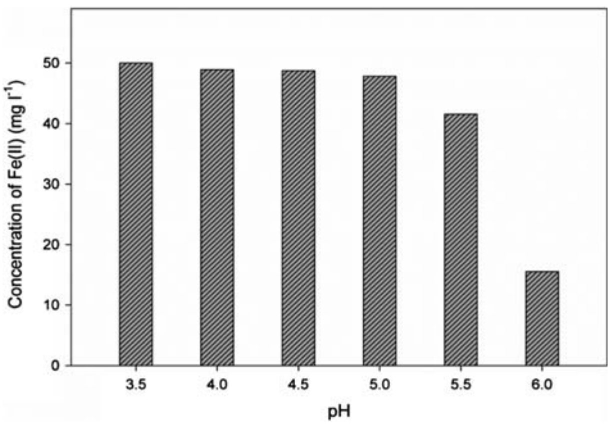

Fig. 2. Effect of initial pH on precipitation of Fe(II) in aqueous solution ($C_0 = 50$ mg l^{-1} and $T = 30$°C).

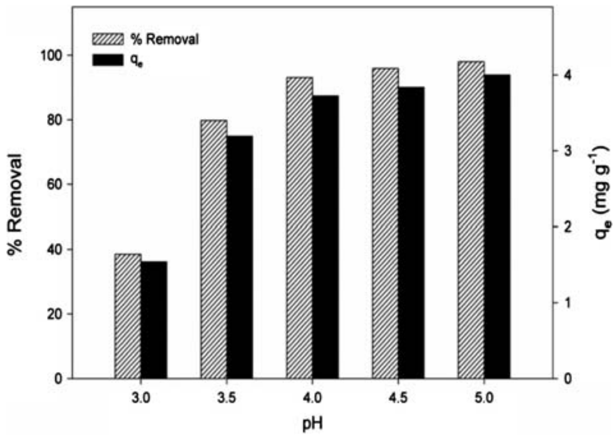

Fig. 3. Effect of initial pH on adsorption capacity and removal efficiency of Fe(II) ($C_0 = 10\,\mathrm{mg\,l^{-1}}$; $T = 30$°C; and adsorbent dose = 0.15 g).

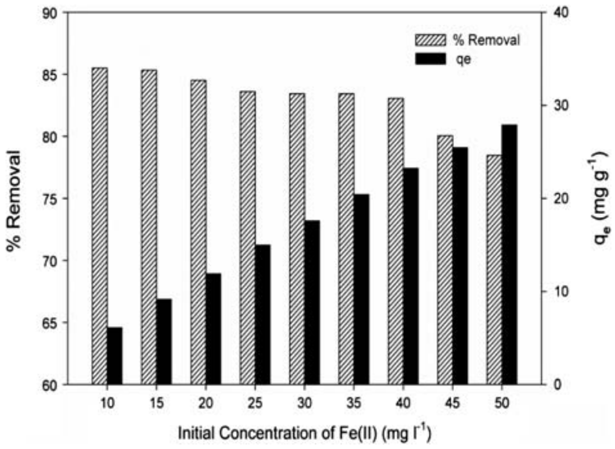

Fig. 4. Effect of initial concentration of Fe(II) on equilibrium adsorption capacity and removal efficiency (pH = 4; $T = 30$°C; and adsorbent dose = 0.15 g).

with the value of 93.1%. However, further increase in pH did not show any appreciable improvement in iron removal and adsorbent capacity. Therefore, further experiments were conducted at initial pH of 4 to achieve acceptable removal efficiency and metal uptake capacity and also to reduce the possibility of precipitation of iron ions during adsorption process.

Final pH of the solution was also measured. The final pH is affected by initial metal concentration, initial pH of the solution, and the amount of chitosan added to the solution [26]. The results obtained in this study indicated that the final pH varied in the range between 5.5 and 7.

In general, neutralization and sorption are parallel processes associated with adsorption of heavy metals by some adsorbents. As mentioned before, this is due to reaction of proton with amino groups of chitosan which leads to decrease in H^+ concentration and subsequently increase in pH.

3.3. Effect of Initial concentration

Ion removal is extremely concentration dependent process. This can be attributed to the mass transfer effects. The concentration of driving force is directly proportional to the initial concentrations. Subsequently, the removal of metals depends on the initial concentration [27–29].

In this study, metal solutions with different initial concentrations in the range of 10–50 mg l^{-1} at optimal pH of 4 were equilibrated with 0.15 g chitosan. Fig. 4 shows the ferrous ion equilibrium adsorption capacity increases with an increase in its concentration. In low initial concentrations, forming monolayer coverage of the molecules at the outer interface of the chitosan may govern the adsorption rate. Therefore, the adsorption process is very intense and fast, but most of adsorbent active sites remain unsaturated, consequently the uptake capacity decreases. At higher initial concentration, available adsorption sites would be surrounded by more metal ions; therefore, metal ions not only adsorbed in a monolayer at the outer interface of chitosan, but also diffuse within the chitosan particles. As a result, the sorption of ions would be carried out more effective. This is a common observed phenomenon referred frequently in adsorption literature [27,30]. In this study, maximum uptake capacity of Fe(II) by chitosan was 28.71 mg g^{-1} for initial concentration of 50 mg l^{-1}.

Fig. 4 also shows the removal efficiency decreased with an increase in initial Fe(II) ions concentration. In other words, for higher concentrations, more residual metal molecules remained in the solution. Hence, the percentage of adsorption decreased. But these variations are small in low concentrations because of the ratio of initial number of metal ions to the available adsorption active sites is low and therefore the removal efficiency will be less dependent on initial concentration. However, it will be more significant as the initial concentration increases.

3.4. Effect of temperature

To investigate the effect of temperature on adsorption rate, experiments were conducted at three different temperatures 20, 30, and 40°C. Samples were collected at fixed time intervals in the range of 10–240 min. Fig. 5 demonstrates the variation in amount of ferrous ion

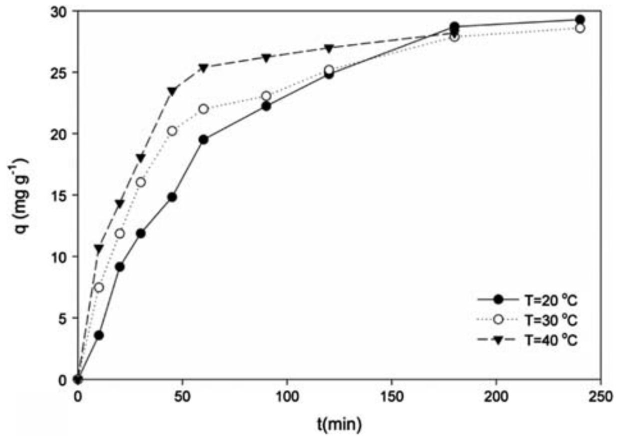

Fig. 5. Effect of temperature on adsorption of Fe (II) on chitosan (pH = 4; adsorbent dose = 0.15 g; and $C_0 = 50\,\mathrm{mg\,g^{-1}}$).

adsorbed by chitosan with respect to time from the solutions with initial concentration of $50\,\mathrm{mg\,l^{-1}}$.

As the plotted data show, a sharper slope was observed for the curves pertaining to higher temperatures. It means that the time required reaching equilibrium state, decreased at higher temperatures. This can be explained by knowing that an increase in temperature results in increasing the mobility of ions in solution; which expedites diffusion of the Fe(II) ions to the adsorbent surface. Fig. 5 also presents that adsorption capacity at equilibrium time decreased with an increase in temperature; as it was found that maximum capacity was at 20°C. It may be attributed to physical adsorption and nature of the process at which adsorbing sites are more deactivated at elevated temperature. Similar trends for the effect of temperature were reported in the literature dealing with adsorption of heavy metals by chitosan based materials. Kannamba et al. [31] studied the effect of temperature on adsorption of Cu(II) onto chemically modified chitosan. Temperature dependence of adsorption capacity of Cu(II), Co(II), and Ni(II) ions by modified magnetic chitosan chelating resin were also investigated by Monier et al. [32].

3.5. Isotherm Models

The experimental adsorption isotherm is a plot that shows the amount of equilibrium uptake vs. the concentration of ion in the solution at equilibrium state. This was obtained by the measurement of equilibrium uptake at initial concentration range of 10–$50\,\mathrm{mg\,l^{-1}}$ at various temperatures.

Equilibrium adsorption data were correlated with Langmuir, Freundlich, and Langmuir–Freundlich isotherms. Langmuir model is a widely used model in adsorption. The basic idea behind this model is the coverage of the surface by a monomolecular layer. This model is expressed as follows [33]:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{3}$$

The linearized form of Eq. (3) is determined as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_L} \tag{4}$$

k_L and q_m values are obtained by plotting C_e/q_e vs. C_e.

Freundlich isotherm is used for the adsorption on a heterogeneous surface with uniform energy. The Freundlich isotherm is given as follows [33]:

$$q_e = k_F C_e^{1/n} \tag{5}$$

Eq. (5) may also be rearranged to obtain a linear form:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{6}$$

n and k_F can be obtained from the slope and intercept of log q_e vs. log C_e.

Langmuir–Freundlich model is a three parameters model expressed by Eq. (7). This model can be used in the case of failure of the two-parameter isotherm models in describing the adsorption data [34]. In fact Langmuir–Freundlich isotherm behavior is similar to the Freundlich equation with exception of possessing a finite saturation limit when the concentration is sufficiently high [35].

$$q_e = \frac{q_m (k_{L\cdot F} C_e)^b}{1 + (k_{L\cdot F} C_e)^b} \tag{7}$$

Linearized form of Eq. (7) is presented as:

$$\log \frac{1}{q_e} = b \times \log \frac{1}{C_e} + \log \frac{1}{q_m^2 k_{L\cdot F}^b} \tag{8}$$

The plot of $\log(1/q_e)$ as a function of $\log(1/C_e)$ yields a straight line and b can be calculated from the slope of this line. The intercept also gives $q_m{}^2 k_{L.F}{}^b$. In fact, q_m and $k_{L.F}$ cannot be calculated individually.

In the above equations, q_e is the amount of metal adsorbed per unit weight of adsorbent at equilibrium ($\mathrm{mg\,g^{-1}}$), C_e is the equilibrium metal concentration in solution ($\mathrm{mg\,l^{-1}}$), q_m is the maximum uptake of adsorbate ($\mathrm{mg\,g^{-1}}$). k_L ($\mathrm{l\,mg^{-1}}$), k_F ($\mathrm{mg\,g^{-1}\,(l\,mg^{-1})^{1/n}}$), and $k_\mathrm{L.F}$ ($\mathrm{l\,mg^{-1}}$) are Langmuir, Freundlich, and Langmuir–Freundlich equilibrium constants, respectively; n and b are dimensionless heterogeneity coefficient in Freundlich and Langmuir–Freundlich models. Fig. 6 shows the experimental adsorption isotherms of Fe(II) at three temperatures (20, 30, and 40°C).

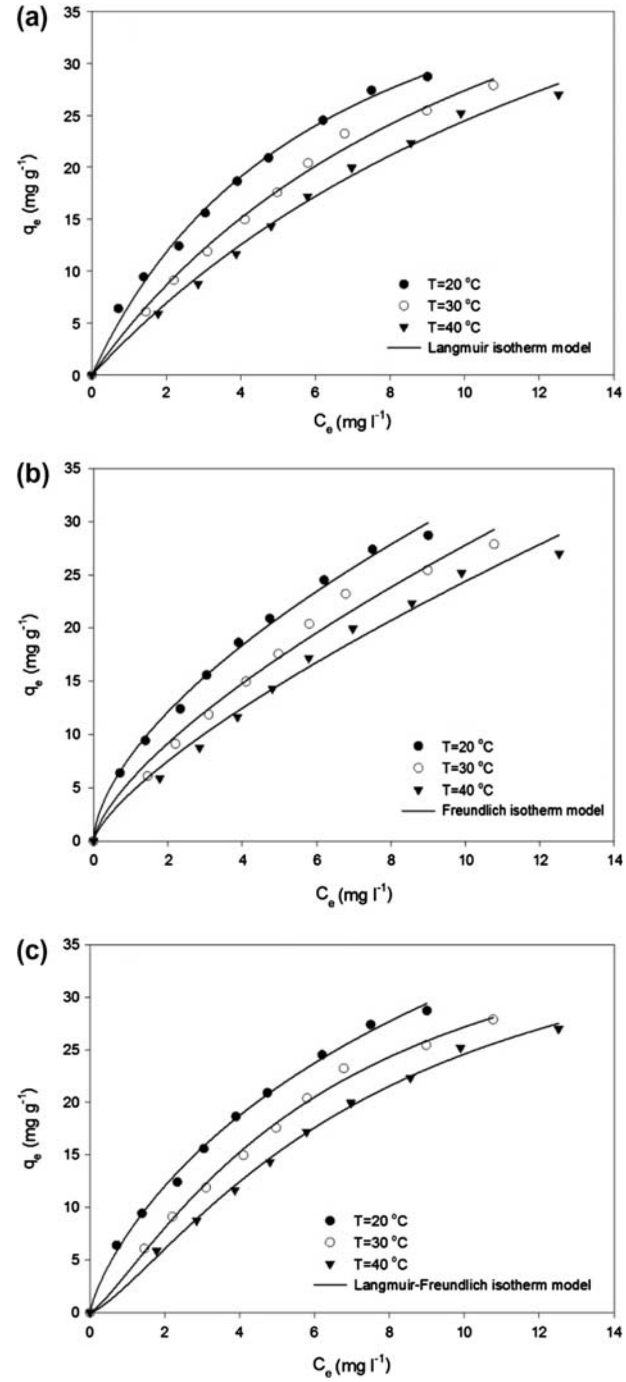

Fig. 6. Sorption isotherms of Fe(II) onto chitosan fitted to the (a) Langmuir, (b) Freundlich, and (c) Langmuir—Freundlich model at different temperatures (adsorbent dose = 0.15 g and pH: 4).

A comparison between linear and nonlinear of estimating the isotherm parameters was discussed by Kumar [36]. The results confirmed that the nonlinear method is a better way to obtain isotherm parameters. So adsorption isotherms of Fe(II) were fitted to nonlinearized form of Langmuir, Freundlich and Langmuir–Freundlich models. All three models are well fitted with experimental data (see Fig. 6). The models parameters are calculated and summarized in Table 1.

According to regression coefficient, data exhibit the best fit to Langmuir–Freundlich model. As well the maximum uptake capacity (q_m) predicted by Langmuir–Freundlich model decreases by an increase in temperature. The value of parameter n in Freudlich isotherm is an indicator of variation in bond energies with surface density [37]. From Table 1, all n values obtained are greater than 1 and lies in the range of 1.36–1.66. Therefore, it can be justified that in adsorption of ferrous ions by chitosan, bond energies decrease with the surface density.

The equilibrium constant of Langmuir isotherm model can be expressed in terms of a dimensionless separation factor (R_L). This factor is used to predict the favorability of adsorption process. The R_L is determined as follows [38]:

$$R_\mathrm{L} = \frac{1}{(1 + k_\mathrm{L} C_i)} \tag{9}$$

These values indicate the shape of the isotherm to be either unfavorable ($R_\mathrm{L} > 1$), linear ($R_\mathrm{L} = 1$), favorable ($0 < R_\mathrm{L} < 1$), or irreversible ($R_\mathrm{L} = 0$). All the values of separation factor (R_L) lie in the range 0–1, indicating favorable adsorption of Fe(II) ions onto chitosan.

3.6. Adsorption kinetics

Kinetics study is an important part of all researches focused on adsorption, because the mechanism of the process can be realized by kinetic constants. Knowledge about kinetic parameters leads to provide valuable insight into the reaction pathway. As well the rate limiting step can be determined by kinetics [39].

The pseudo-first-order rate expression of Lagergren is a widely used kinetic model for sorption analysis. This model is associated with physical adsorption indicating that the limiting stage of the adsorption process is a weak interaction between

Table 1
Constants of different isotherm models for adsorption of Fe(II) ions onto chitosan

T (°C)	Langmuir				Freundlich			Langmuir–Freundlich			
	k_L	q_m	R^2	R_L	k_F	N	R^2	$k_{L,F}$	q_m	b	R^2
20	0.1574	49.40	0.9953	0.11–0.38	8.0027	1.66	0.9955	0.0554	80.27	0.78	0.9972
30	0.0847	59.69	0.9947	0.19–0.54	5.6955	1.45	0.9862	0.1575	42.49	1.25	0.9967
40	0.058	66.65	0.9948	0.25–0.63	4.5222	1.36	0.9873	0.1311	41.74	1.32	0.9977

metal ions and adsorbent [40]. It is represented by the following equation [41]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{10}$$

where q_t is the metal uptake capacity (mg g^{-1}) at any time t, q_e denotes the metal uptake capacity (mg g^{-1}) at equilibrium, and k_1 is the observed rate constant of pseudo-first-order kinetic model (min^{-1}). Azizian [42] reported that k_1 is not the intrinsic adsorption rate constant which was mistakenly reported in the literature. He explained that it is a combination of adsorption (k_a) and desorption (k_d) rate constants.

Some sorption systems followed the pseudo-second-order kinetic model which is based on the assumption that the rate-limiting factor may be chemisorptions [40]. The rate equation for this system is expressed as follows [41]:

$$q_t = \frac{k_2 q_e^2}{1 + k_2 q_e^t} t \tag{11}$$

where k_2 (g mg^{-1}min^{-1}) is the observed rate constant of the pseudo-second-order model which is a complex function of the initial concentration of solute [42]. Intraparticle diffusion model was also tested for the kinetic data to identify the diffusion mechanisms. Existence of multilinearity in the plot of uptake amount with time square root would be an indicator of two or more steps in adsorption. This model is presented by the following equation:

$$q_t = k_{id} t^{0.5} \tag{12}$$

where k_{id} is the intraparticle diffusion rate constant (mg g^{-1}min$^{-1/2}$).

Fig. 7 shows the variation in amount of ferrous ion uptake by chitosan with respect to time. It indicates that with an increase in initial concentration, the time required to reach equilibrium increased. Also a sharp slope was observed for the curve pertaining to high temperatures. It means that the time required reaching equilibrium decreased at high temperature. In other words, with an increase in temperature, the adsorption rate increased. This can be explained by knowing that the adsorption in general takes place by two processes: fast diffusion and slow complexation. An increase in temperature results in increasing the mobility of the ions; consequently, both enhanced diffusion rate of Fe(II) ions to the adsorbent surface and complexation of the functional groups assisted the adsorption process [43].

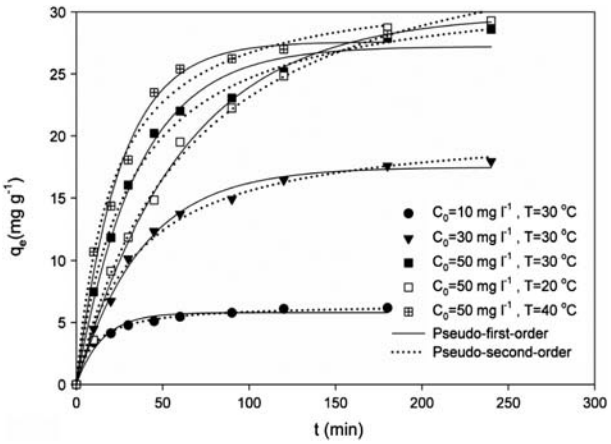

Fig. 7. Pseudo-first-order and pseudo-second-order kinetic models of Fe(II) adsorption on chitosan at different temperatures and concentrations (pH = 4 and adsorbent dose = 0.15 g).

Also Fig. 7 shows nonlinear form of both pseudo-first-order and pseudo-second-order models were able to fit kinetic data. From Table 2, there are no significant differences in the obtained nonlinear determination coefficients (R^2) for the pseudo-second-order model (ranging from 0.9887 to 0.9961) and those of the pseudo-first-order model (ranging from 0.9715 to 0.9955). The differences lie within the experimental error and therefore, both of them are statistically acceptable. However, the difference between the experimental adsorption capacity of Fe (II) and the value predicted from the pseudo-first-order model was considerably lower than those predicted by the pseudo-second-order. Hence, in this study the pseudo-first-order model can be considered as a suitable kinetic model to describe Fe(II) adsorption. Therefore it can be concluded that the adsorption of Fe(II) onto chitosan may take place through a physical adsorption process. Stronger evidence for dominant sorption mechanism is presented by the enthalpy of adsorption. The results are further approved by calculating the adsorption enthalpy in the next section.

Due to lack of a clear cut between pseudo-first-order and pseudo-second-order kinetic models to identify the diffusion mechanisms, the intraparticle diffusion model was also tested. The rate controlling step of adsorption may be external film diffusion (1), intra-particle diffusion (2), or interaction step (3) [44,45].

Fig. 8 shows the external surface sorption (stage 1) is absent; because of the fast adsorption. All plots have the same general features, initial linear portion (stage 2) followed by second linear portion (stage 3).

Table 2
Pseudo-first-order and pseudo-second-order kinetic model parameters for Fe(II) ions adsorption onto chitosan

			Pseudo-first-order			Pseudo-second-order		
T (°C)	C_0 (mg l^{-1})	$q_{e,exp}$ (mg g^{-1})	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
30	10	6.09	5.80	0.0666	0.9715	6.46	0.014914	0.9961
30	30	17.57	17.46	0.0262	0.9935	20.91	0.001386	0.9947
30	50	27.87	27.21	0.0283	0.9882	32.29	0.000994	0.9951
20	50	28.71	29.79	0.0162	0.9955	38.40	0.000393	0.9943
40	50	26.98	27.58	0.0395	0.9917	32.32	0.001463	0.9887

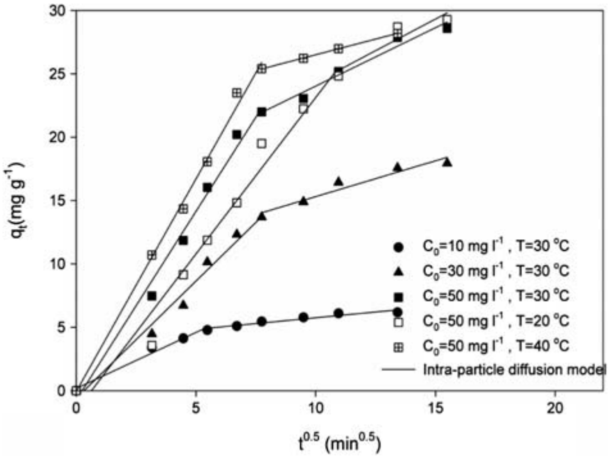

Fig. 8. Intraparticle diffusion kinetic model for the adsorption of Fe(II) on chitosan at different temperatures and concentrations (pH = 4 and adsorbent dose = 0.15 g).

The obtained fitting correlation coefficients and intraparticle rate constants are presented in Table 3. With respect to higher correlation coefficients, it can be concluded that the intraparticle diffusion model fitted well with the experimental data for an initial period (stage 2) of the adsorption process. The results also indicated that intraparticle rate constant increases with increasing in temperature and initial concentration.

3.7. Adsorption thermodynamics

Investigation on thermodynamics of adsorption provides valuable knowledge about the process that may be useful for conducting an efficient operation. Temperature dependence of equilibrium capacity can be explained by heat of adsorption. Also, evaluation of standard free energy change can give useful information about the nature of process, whether it is spontaneous or not [46,47]. These factors have been investigated in different adsorption systems by many researchers [48–51].

Standard Gibbs free energy change (ΔG°) is estimated from the variations of the equilibrium constant (K_{eq}) for the sorption reaction by the following equation:

$$\Delta G^o = -\mathrm{RT} \ln K_{eq} \tag{13}$$

where R is the gas constant (8.314 J mol^{-1}K^{-1}) and T is the absolute temperature (K). Different methods were applied to evaluate the equilibrium constant in literature [37,48,49,52,53]. Langmuir equilibrium constant has been widely used for this purpose. Liu [54] expressed that when the volumetric concentration of adsorbate is used in Langmuir model, K_{eq} can be reasonably approximated by the following equation:

$$K_{eq} = k_L M_{iron} \tag{14}$$

where k_L is the Langmuir equilibrium constant expressed in volumetric concentrations and M_{iron} is the molecular weight of iron. This fact has been neglected by many researchers and they have simply considered equilibrium constant as Langmuir constant. Enthalpy change (ΔH°) and entropy change (ΔS°) are calculated as follows:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{15}$$

Substituting Eq. (13) in (15) gives:

$$\ln K_{eq} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{16}$$

By plotting ln K_{eq} vs. $1/T$, the values of ΔH° and ΔS° can be estimated from the slope and intercept of the resultant line (see Fig. 9).

The pseudo-second-order observed rate constant (k_2 (g mg^{-1}min^{-1})) is expressed as a function of temperature by Arrhenius type relationship.

$$\ln k_2 = -\frac{E_a}{\mathrm{RT}} + \ln k_0 \tag{17}$$

where E_a is the Arrhenius activation energy of adsorption (J mol^{-1}), k_0 temperature independent factor

Table 3
Intraparticle diffusion kinetic model parameters for adsorption of Fe(II) ions onto chitosan

T (°C)	C_0 (mg l^{-1})	k_{id1} (mg g^{-1} min$^{-1/2}$)	R_1^2	k_{id2} (mg g^{-1} min$^{-1/2}$)	R_2^2
30	10	0.88	0.9807	0.18	0.9202
30	30	1.84	0.9814	0.56	0.9377
30	50	2.97	0.9889	0.92	0.968
20	50	2.47	0.9742	0.99	0.8789
40	50	3.35	0.9958	0.49	0.9998

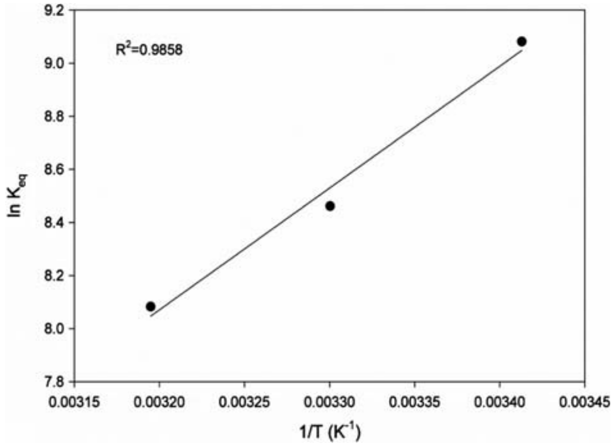

Fig. 9. Plot of ln K_{eq} vs.1/T for the adsorption of Fe(II) on chitosan.

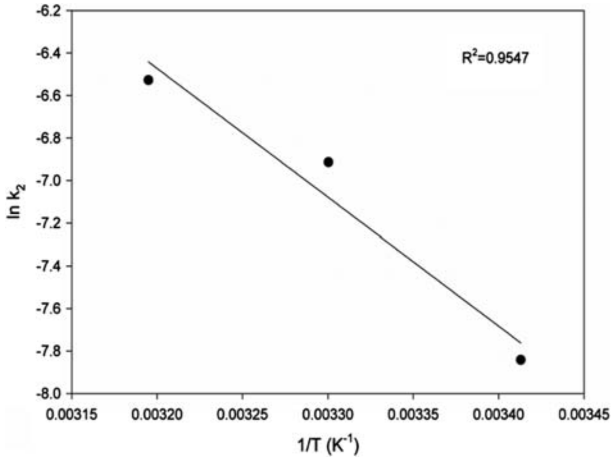

Fig. 10. Plot of ln k_2 vs.1/T for the adsorption of Fe(II) on chitosan.

(g mg^{-1} min^{-1}); R the gas constant (8.314 J mol^{-1}K^{-1}), and T is the solution temperature (K). When ln k_2 is plotted vs. $1/T$, a straight line with the slope of $-E_a/R$ is obtained (see Fig. 10).

Table 4 shows the calculated values of the thermodynamic parameters for the adsorption of Fe(II) onto chitosan.

The negative values of ΔG° show the feasibility of the process and it confirms that the adsorption of Fe (II) on chitosan occurs spontaneously. Decrease in the ΔG° value from 22.12 to 21.03 kJ mol^{-1} with an increase in temperature indicates that the adsorption process in more favorable at lower temperatures.

As mentioned before, there are some serious miscalculations made in determination of ΔG° of adsorption from the Langmuir constant (k_L). For example, Kannamba et al. [31] investigated removal of Cu(II) from aqueous solutions using chemically modified chitosan. In their study, volumetric concentration of Cu(II) was used in Langmuir equation. Although, they have reported negative value for ΔG°, however, with their calculations it becomes positive which means the adsorption process was unfavorable or nonspontaneous reactions. There are other examples for misuse of Langmuir isotherm equation in computing change in standard free energy in literature [51].

Table 4
Thermodynamic parameters for Fe(II) ions adsorption onto chitosan

T (°C)	$-\Delta G$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1}K^{-1})	$-\Delta H$ (kJ mol^{-1})	E (kJ mol^{-1})
20	22.12			
30	21.31	55	38.15	50.32
40	21.03			

The negative value of ΔH° shows the exothermic nature of the adsorption process. The calculated value of enthalpy change is 38 kJ mol^{-1}. The enthalpy value due to physisorption is generally lower than that of chemisorption which is in the range of 40 and 120 kJ mol^{-1} [55]. Physisorption is characterized as an adsorption mechanism with multilayer adsorption, low degree of specificity, possibility of desorption (adsorbed molecule keeps its identity), always exothermic (energy involved is less than ~40 kJ/mole), and reaching thermodynamic equilibrium rapidly [56]. Therefore, it was concluded that the adsorption of Fe(II) on chitosan is likely to be due to physisorption in which only van der Waals interactions play major role. Kinetic studies (Section 3.6) also revealed that the adsorption of Fe (II) onto chitosan may take place through a physical process. Moreover, the value of ΔS° obtained in this study is negative which indicates decrease in degree of freedom of adsorbed species during adsorption of ferrous ions. With respect to entropy concept, decreasing in ions uptake capacity at higher temperatures can be attributed to the increase in mobility of ions. Therefore, Fe(II) ions escape from the solid phase to the liquid phase at higher temperature.

4. Conclusion

High removal efficiency (92.9%) and uptake capacity (28.7 mg g^{-1}) demonstrate that chitosan can be used as an effective adsorbent for removal of Fe(II). In this study, the obtained results revealed that adsorption of Fe(II) by chitosan is strongly dependent on initial pH of the solution. The pH value of 4 was found to be an optimum pH for the adsorption process. Based on values of fitting correlation coefficients Langmuir–Freundlich isotherm model gives a better fit than Langmuir and Freundlich models. The adsorption kinetics followed nonlinear form of pseudo-first-order equation, which shows the adsorption is dominated by physisorption. The intraparticle diffusion model was also applied to identify the possible mechanism of transport. The results indicated that pore diffusion and surface diffusion occurred in parallel within chitosan particles during adsorption. The adsorption process was spontaneous ($\Delta G^\circ < 0$) and exothermic ($\Delta H^\circ < 0$), supporting that the physisorption is the dominating adsorption mechanism.

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