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Highly Concentrated Ferrus Removal from Groundwater Using Powdered Activated Carbon as Adsorbent

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KEYWORDS

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ABSTRACT: In this study, powdered activated carbon was used as an absorbent to reduce Fe (II) ions concentration of groundwater. The adsorption behavior of Fe (II) ions was studied by varying parameters including the dosage of powdered activated carbon, pH of solution, initial concentration of Fe (II) and contact time. Equilibrium adsorption isotherms and kinetics were also investigated based on Fe (II) adsorption tests. The optimized adsorption conditions were used for reducing iron concentration of groundwater derived from deep wells in Marand Plain with agricultural purposes in April 2017. An increase in contact time and adsorbent dosage resulted in increase of adsorption rate. The optimum condition of Fe (II) removal process was found at pH=4, 0.45 g adsorbent dosage, 10 mg/l initial concentration of Fe (II) and contact time of 30 min. The removal percent was equal to 97.21 at optimal conditions. Langmuir and Freundlich's models were employed to analyze the experimental data. Langmuir model fitted well with the correlation coefficient (R^2=0.995) with adsorption capacity of q_{max}=205.2 mg/g. According to results of analysis of the kinetic data by the pseudo-first-order and pseudo-second-order equations, we found that the adsorption of Fe (II) using PAC follows the pseudo-second-order kinetic model with correlation coefficients (R^2) equals to 0.9995, 0.9996 and 0.9993 for 10, 20 and 30 mg/l Fe (II) concentrations, respectively. In addition, the reaction is spontaneous and endothermic. In optimal conditions, this adsorbent can be suitable for improving the quality of ground water containing high iron concentrations.

INTRODUCTION

Protecting water sources is vital to ensure human health. Annually, about five million people die from diseases related to water including cancer in the gastrointestinal tract and lungs, severe diarrhea, and

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qualm bleeding also kidney and gastric damage and so on. One of its reasons is existence of heavy metals concentrations exceed acceptable limits [1].

Heavy metals such as Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Fe^{2+}, and Zn^{2+} are elements having atomic weights greater than 50 gr and a specific gravity greater than 5.0 [1]. They appear in wastewater discharged from hospitals and different industries such as smelting, metal plating, Cd-Ni battery production, phosphate fertilizer manufacture, pigment mining, stabilizer production, leather tanning, refining, electroplating, and alloy manufacturing [2-7].

There are several available processes for removing heavy metal ions from wastewater such as precipitation, bioremediation, ion exchange, adsorption, membrane filtration and electrochemical [8, 9]. However, to reduce metal ion concentration of wastewater to permissible concentrations, most of the technologies are ineffective and very expensive [9, 10], the adsorption process is considered as the most widely used method for removing metal ions from types of industrial effluents with respect to its lower process costs and higher treatment efficiency compared to the above-mentioned processes [11].

Activated carbon (AC) is a useful porous carbon material as an adsorbent [12, 13] with extensive industrial usage [14] and high adsorption capacity [15]. Moreover, it has several functional groups containing oxygen on its surface. The other features include great specific surface area, desired pore structure; reactivate ability, appropriate chemical resistance [13]. Today, AC can be produced from a large number of achievable and low-cost materials containing a low inorganic content and high carbon content including coconut shell [16], rice husk [9], cherry stones [17], peanut shell [18], walnut shell [19], hazelnut husks [20], pomegranate peel [21], etc. Physical and chemical activation are intermittent processes for preparing AC [22]. Physical activation is performed at higher temperature in the presence of gases including steam, carbon dioxide and so on. [22]. Chemical activation is performed by dehydrating agents and oxidants including $ZnCl_2$, NaOH, KOH, and HNO_3. Shorter activation time in lower temperatures and higher efficiency are some benefits of chemical activation in comparison with physical activation which were reported in the literatures [23].

Many types of research have been conducted in the field that indicated the high potential of ACs for adsorbing heavy metals such as Fe (II). AC was prepared from pomegranate peel in order to remove Fe (II) from aqueous solution to a batch operation [21].

The aim of this study was to find optimal conditions such as contact time, pH, and the effects of temperature and metals ions initial concentration. Pseudo-second-order equation has a better control on the adsorption process. In addition, Langmuir adsorption model fitted well the experimental equilibrium data, with maximum Fe (II) adsorption capacity of 18.52 mg/g at temperature 29 °C and pH6.

Hejazi [3] could remove different metals ions (Ni^{2+}, Fe^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+}) with the concentration range of 20-60 mg/L by the AC produced from rice husk and fly ash. In addition, the optimum pH required for maximum adsorption was found to be 6-7. According to the best performance for adsorption of Pb^{2+}, Ni^{2+}, Fe^{2+}, and rice husk had the highest efficiency among the mentioned adsorbents.

Since iron is the most useful metal in many countries and one of the main components of steel devices that have essential utilization in many industries, the considerable amount of effluent contacting iron is produced as a by-product. Meanwhile, using iron pipes for water transportation, and distribution by considering the iron corrosion phenomena in water and also the unpleasant taste and odor of water, there are considerable amount of iron in urban water [24].

Iron has two oxidized forms: ferrous and ferric. The solutions normally contain only ferrous forms, it is completely soluble in the solution and the solution is clear but ferric shows a different behavior. It is soluble in pH<3.5 but by increasing pH, it is insoluble and yellowish orange participation is observed [25].

Recently, our research group applied some selective polymer based materials as an adsorbent for uptake and removal of some significant medicinal molecules in pharmaceuticals, effluents and biological fluids [26-32].

The main purpose of the present study was ferrous removal from ground water containing high iron concentration by using powdered activated carbon (PAC) as adsorbent. The results obtained on its ability to remove Fe (II) from dilute aqueous solutions are discussed. The effects of solution pH, temperature, and initial metal concentration on adsorption of Fe (II), were evaluated in detail. Accordingly, the equilibrium isotherms, kinetics, and thermodynamics studies of adsorption process have been conducted.

MATERIALS AND METHODS

Materials

All chemicals used in this study such as hydrochloric acid, sodium hydroxide, 5-Sulfosalicylic acid, Powdered Activated Carbon and $FeSO_4.7H_2O$ were of analytical grade and were purchased from Merck Company.

Case study

To examine the Fe (II) ions concentration of groundwater, samples were taken from wells with depth of 90 to 160 m located in the Southern and South-Eastern of Marand Plain used for agricultural purposes in April 2017. The Fe (II) concentration was in range of 1.8-3.1 mg/l, which according to WHO standards, should be lowered up to 0.3 mg/l.The analysis of wells samples conducted after obtaining the optimal conditions for Fe (II) removal in laboratory.

Preparation of solutions

A proper amount of $FeSO_4.7H_2O$ was dissolved in distilled water in order to prepare the stock solution of Fe (II) ions with a 1000 mg/l concentration. Fresh dilutions are prepared based on the working Fe (II) concentrations for adsorption experiment. Sodium hydroxide and Hydrochloric acid (0.1 M) were used to set the pH of test solutions.

Adsorption experiments

Batch experiments were performed to assess the effect of some parameters including PAC dosage, initial concentration of Fe (II), pH, temperature and contact time, and examine isotherm models, kinetic models, and thermodynamic studies.

Each parameter effect was exclusively studied in each step. Each experiment was performed by changing one parameter while other parameters are kept constant. At the beginning of each step, some 100-ml flasks containing 50 ml of Fe solution with considered concentration were prepared. The pH of solutions was set by pH meter to a considered value. Then, considered amount of PAC was added to flasks, and then they were placed in incubator shaker and shaken for 180-rpm speed and equilibrium time. At the end of each step, the supernatant liquids were filtered using 15-mm circular paper filter and the Fe (II) concentrations were determined using an atomic adsorption spectrophotometer (PerkinElmer AAS 100, Wellesley, MA, /USA). The amount of Fe adsorbed on PAC (q) was calculated using the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where C_0 and C_e are the initial concentration of Fe and remaining Fe concentration after equilibrium time, respectively. V and M are the volumes of the solution (L) and the mass of the adsorbent, respectively. The Fe (II) removal efficiency (% R) was calculated using the following formula:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

Adsorption isotherm

The adsorption isotherm was studied by adsorption of different concentration ranging from 10 to 50 mg/l (Fe ion), 0.45 gr adsorbent dosage, pH=4 and T=20, 30 and 40 ^{o}C for 120 min. the Langmuir and Freundlich models are two isotherm models that describe the equilibrium sorption. The Langmuir model is shown by the following non-linear equation:

$$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e} \qquad (3)$$

where q_e is the sorption capacity of adsorbent at equilibrium (mg/g), and q_{max} and k_L are the maximum Fe ions adsorbed per unit mass of adsorbent (mg/g) and Langmuir constant (L/mg), related to energy of sorption with quantitatively indicates the affinity between the adsorbent and Fe ions, respectively [33,34]. They can be determined from the plot of q_e versus C_e [35].

The adsorption intensity of the Fe ions towards the adsorbent can be determined using Freundlich model. The non-linear form of the equation is represented by the following equation [33]:

$$q_e = k_f C_e^{1/n} \qquad (4)$$

Where K_f is Freundlich constant and shows the adsorption capacity (mg/g (1/mg) 1/n) and the constant n indicates the adsorption intensity. They can be determined from the plot of q_e versus C_e [35].

Kinetic study

To determine the adsorption kinetics of Fe ions on PAC, the adsorption process parameters for contact time ranging from 5 to 120 min for 10, 20 and 30 mg/l initial Fe concentrations were studied. The Pseudo-first-order and pseudo-second-order models were applied to study the kinetics of the process.

Pseudo-first-order

The assumption of the pseudo-first order model is that the solute uptake rate changes directly with time and is proportional to the variation in the saturation concentration and the amount of adsorbate uptake through time [33]. The pseudo-first-order kinetic model is described by the following equation [35]:

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (5)$$

where q_e and q_t (mg/g) are the sorption capacity at equilibrium and elapsed time t, respectively. T (min) is contact time, and k_l (1/min) is the pseudo-first order rate constant. xk_l and equilibrium sorptive capacity (q_e) can be determined from the plot of q_t versus time, t.

Pseudo-second order

The proposed pseudo-second-order velocity by Kaymakci shows the dependence of velocity to the capacity of adsorption in the solid phase, and it is independent of the concentration of the adsorbed substance [35]. The pseudo-second-order kinetic model can be expressed in the following linear form:

$$q_t = \frac{k_2 q_e{}^2}{(1 + k_2 q_e t)} t \qquad (6)$$

where k_2 (g/mg.min) is the pseudo-second-order rate constant. The values of k_2 and q_e can be calculated from the plot of q_t versus t [35].

Thermodynamic study

The investigation of adsorption thermodynamics gives an insight about heat management of the adsorption process to achieve efficient removal. Temperature-dependent experimental data obtained for the uptake of Fe (II) onto the PAC were used to evaluate the thermodynamic parameters such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) in temperatures 20, 30 and 40 °C and initial concentration 10 mg/l.

The standard Gibbs free energy change (ΔG^0) is defined by the following equation:

$$\Delta G^0 = -RTLnK_{eq} \qquad (7)$$

Where T is the absolute temperature (K), R is the gas constant (8.314 j/mol.K) and K_{eq} is the equilibrium constant that relates concentration in adsorbed and bulk phase defined as follows:

$$K_{eq} = \frac{C_{ads}}{C_e} = \frac{C_0 - C_e}{C_e} \qquad (8)$$

where C_{ads} and C_e indicate the amount of Fe (II) concentration on the adsorbent and in the aqueous phase (mg/l), respectively.

ΔH^0 and ΔS^0 that represent the change in enthalpy (kj/mol) and entropy (kj/mol.K), respectively, are related to Gibbs free energy (ΔG^0) as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

Substituting Eq. (7) into Eq. (9) gives:

$$LnK_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{10}$$

Enthalpy (ΔH^0) and entropy (ΔS^0) changes were evaluated from the slope and intercept of LnK_{eq} plot versus $1/T$ [36].

RESULTS AND DISCUSSION

Effect of PAC dosage

To determine the effect of PAC dosage on the removal efficiency of Fe ions, a number of experiments were conducted at several PAC dosages over the range of 0.05 to 1.0 g/50 mL as shown in Figure 1. The removal efficiency of Fe ions rapidly increased (from 89.37% to 95.9%) with an increase in PAC dosage from 0.05 to 1.0 gr. This increase was expected because of the increase of absorbent resulted in greater availability of exchangeable sites for Fe ions [33]. Increase in removal efficiency continued with increase in PAC dosage. This increase is less than the initial increase ignored. The percentage of removal reached 93.82% at PAC dosage of 0.45 gr.

The adsorption efficiency has been increased with increase of adsorbent dosage, which may be due to the higher number of available active sites and the larger surface area, hence favoring more Fe (II) ion adsorption but the adsorption capacity decreased [37]. Hence, 0.45 gr adsorbent dosage was selected as optimum dosage.

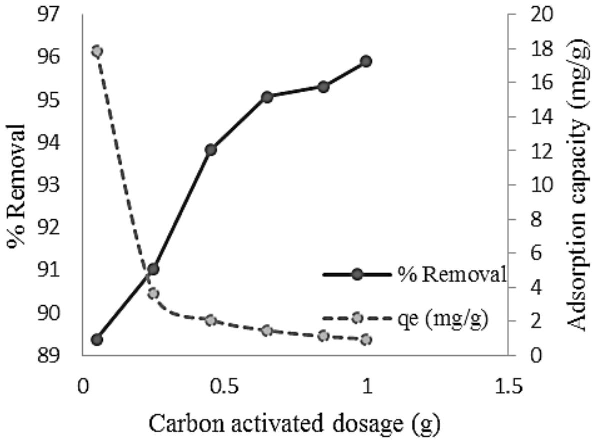


Figure 1. Effect of adsorbent dosage on removal efficiency and adsorption capacity.

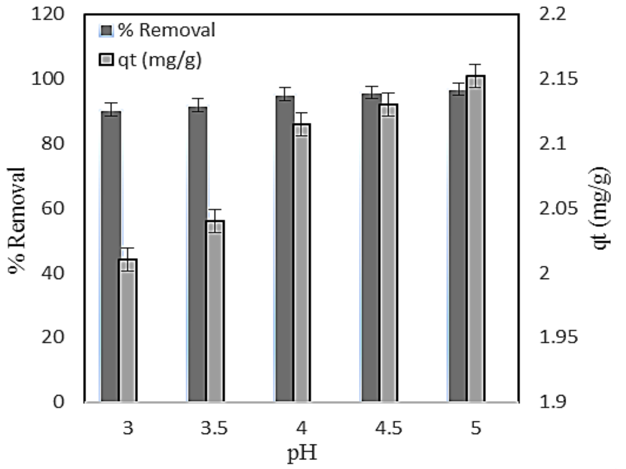
Effect of pH

The pH of the solution is a significant parameter in the heavy metals adsorption by an adsorbent that contributes to sites of metal ion adsorption on the adsorbent surface as well as chemical structure of the metal in water [35]. After increasing of pH, the control surface charge of adsorbent surface reached to more negative region. It can be a good index for positive Fe (II) ions adsorption [36]. Accordingly, at high grade of pH, due to visual aspect of the OH-front groups, iron ions precipitation is predictable.

Hence, to ensure that iron ions removal occurs exclusively due to adsorption, the solution pH was set lower than precipitation pH (pH 5) according to our previous work [37].

Therefore, the effect of pH on the removal efficiency of Fe (II) by PAC was studied in the pH range 3-5, while the other operational parameters including adsorbent dosage, initial ion concentration, and temperature were kept constant at 0.45 gr, 50 mg/l and 20^{o}C, respectively (Figure 2). Removal efficiencies of Fe (II) increase from 90.4% to 96.85% by raising the initial pH of the solution. Since after pH 4, the removal efficiency increased slowly, thereafter, the pH 4 was selected as the optimal pH for further adsorption studies.

Figure 2. Effect of pH on removal efficiency and adsorption capacity of Fe (II).



Effect of initial concentration

The effect of initial metal concentration on the adsorption capacity was studied at several initial concentrations of Fe (II) solutions to the range of 10-50 mg/l at optimal pH 4.0 with 0.45 g/l adsorbents at 20 ^{o}C and contact time of 60 min. Figure 3 shows the equilibrium adsorption capacity of Fe (II) increased from 2.16 mg/g to 10.25 mg/g when the Fe (II) initial concentration increased from 10 to 50 mg/l.

Indeed, higher initial metal concentration provided a greater driving force for movement towards Fe (II) ions from aqueous phase to the solid surface. With increase in Fe (II) ion concentration of the solution, interactions between Fe (II) ions and the active sites on the activated carbon surface increased, which enhanced the adsorption process [37, 38].

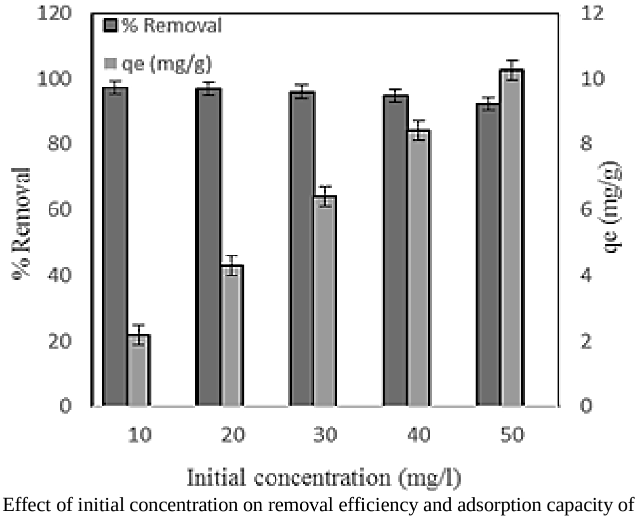


Figure 3. Effect of initial concentration on removal efficiency and adsorption capacity of Fe (II).

Effect of Temperature

To assess the temperature effect, equilibrium experiments were conducted at several temperatures, 20, 30, 40 ^{o}C, at the initial concentration of 10 mg/l, pH 4 and adsorbent dosage of 0.45 g/l (Figure 4). Fe (II) removal efficiency increased while the temperature reached to 40 ^{o}C, indicating the Fe (II) adsorption is endothermic [38].

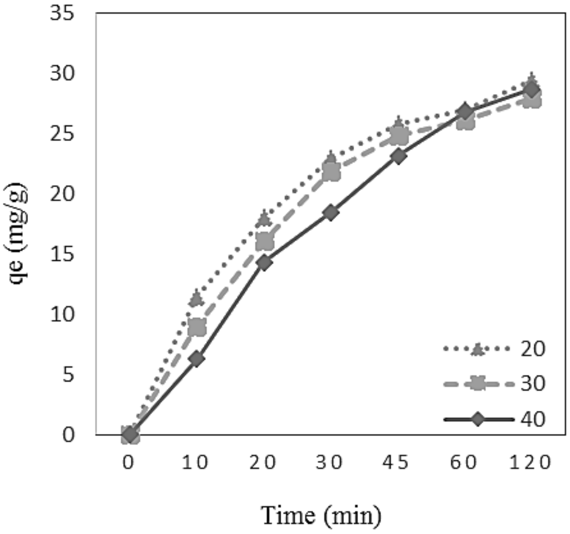


Figure 4. Effect of temperature on adsorption capacity of Fe (II).

Effect of contact time

The impact on contact time for the removal efficiency of Fe (II) at initial concentrations 10 mg/l, pH 4.0, adsorbent dosage of 0.45 g/l and temperature of 20 ^{o}C, was studied (Figure 5). About 98.5% of Fe (II) removal occurred at the first 60 min and equilibrium was achieved after 120 min. At the beginning, the rate of Fe (II) removal was high and then increased gradually until it reached equilibrium. The transfer rate of Fe (II) ions shows the availability of a plenty of active sites on the adsorption surface.

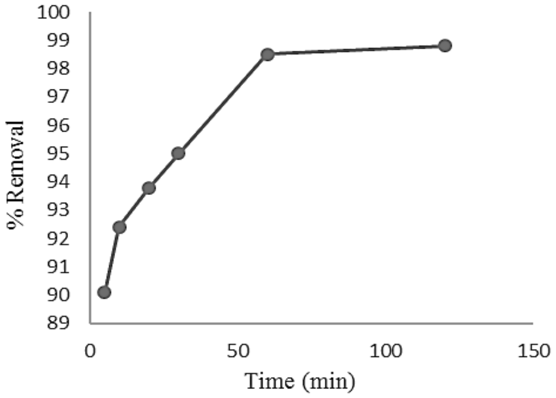


Figure 5. Effect of contact time on removal efficiency of Fe (II)

However, later, adsorption becomes slower as the results of dominance of intraparticle diffusion mechanism for the diffusion of Fe (II) into the adsorbent pores [36].

Adsorption isotherm

Evaluation of the equilibrium distribution of adsorbate between the adsorbent and the solution is essential in order to determine the maximum sorption capacity [33]. Table 1 shows the constants and correlation coefficients for the Langmuir and Freundlich isotherm models. The Langmuir isotherm showed better fit to the experimental data onto high correlation coefficient (R^2=0.995). Based on the assumptions of the Freundlich model, the surface of PAC is heterogeneous, and there is an interaction between the adsorbed species on adjacent active sites [36].

Kinetics of adsorption

The parameters of two kinetic models were calculated and listed in Table 2. The experimental data showed very low correlation coefficients for the pseudo-first-order model. In contrast, the fitting of experimental data onto the pseudo-second-order model was good, and this model provided high correlation coefficients. Therefore, the pseudo-second-order kinetic can ideally describe the adsorption process of Fe (II) onto PAC.

Adsorption Thermodynamics

The thermodynamic parameters recovered from the linear fitting of the temperature-dependent experimental data are summarized in Table 3.

The ΔG^0 negative values showed the feasibility of the adsorption process and verified the adsorption of Fe (II) on the PAC occurred spontaneously. The spontaneity of the Fe (II) adsorption onto the adsorbent increased by increasing temperature (Table 3). The decreasing trend of ΔG^0 with an increase in tem perature suggested that the adsorption is more favorable at higher temperature. The ΔH^0 positive value demonstrated the endothermic nature of the adsorption. This is supported by the increase in the Fe (II) adsorption capacity of the adsorbent with increasing temperature. The positive value of ΔS^0 can be attributed to the increase in irregularity and randomness at the solid solution interface during adsorption. Some researchers [36, 38] have reported similar results from/of the adsorption of Fe (II).

Finally, by applying the optimal conditions on some wells samples collected from deep wells in Tehran suburb, the final concentration of Fe (II) ions are decreased at the best condition from 1.8-3.1 to 0.02-0.009 mg/L which is less than allowable limit that recommended in WHO standard and this showed that the proposed adsorbent and method are appropriate for removal of excess Fe (II) ions from water.

CONCLUSIONS

The adsorption of Fe (II) ions to PAC is forcefully dependent on the initial pH of solution. Increasing PAC dosage leads to increase the removal efficiency of Fe (II) ions. In addition, increasing initial concentration of Fe (II) leads to increase and decrease concentration of Fe (II) ions adsorbed per PAC unit weight (q_e) and the removal efficiency of Fe (II) ions, respectively. The pseudo-first-order model has a better description of the adsorption kinetics of Fe (II) onto PAC. The experimental data were fitted to Langmuir and Freundlich models. Moreover, the Langmuir isotherm model showed better fit of the equilibrium data. Besides, this reaction is spontaneous and endothermic. In optimal conditions, PAC can be suitable for improving the quality of ground water containing high iron concentrations.

Table 1. Equilibrium isotherm parameters for the removal of Fe (II)

Freundlich			Langmuir				
R^2	N	k_F (mg/g(l/mg)$^{1/n}$)	R_L	R^2	q_{max} (mg/g)	k_L (l/mg)	T (^{0}C)
0.9907	1.102	2.354	0.9-0.64	0.9912	205.2	0.011	20
0.986	1.294	3.41	0.82-0.48	0.9896	104.1	0.02168	30
0.993	1.303	3.641	0.41-0.12	0.9952	28.38	0.143	40

Table 2. Parameters of kinetic equations in different concentration

	pseudo-second-order				pseudo-first-order			
C_i (mg/l)	R^2	$K_2 \times 10^3$ (g/mg.min)	q_e (mg/g)	$q_{e,exp}$ (mg/g)	R^2	$K_1 \times 10^2$ (g/mg.min)	q_e (mg/g)	$q_{e,exp}$ (mg/g)
10	0.9995	1513	2.206	2.25	0.9991	73.44	3.394	2.25
20	0.9996	901	2.409	4.422	0.9994	74.85	4.477	4.422
30	0.9993	761	6.596	6.67	0.999	73.82	6.616	6.67

Table 3. Thermodynamic parameters for Fe (II) adsorption

Initial concentration	ΔH (kJ.mol^{-1})	ΔS (J.Mol^{-1}.K^{-1})	-ΔG (kJ.mol^{-1})	K_{eq}	Ln K_{eq}	1/T (K^{-1})	T (K)
10	22.489	103.01	7.33	23.39	3.152	0.0034	294
			8.72	34.71	3.547	0.0033	303
			9.75	40.15	3.693	0.0032	313

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Conflict of interest

The authors declare that there is no conflict of interest.

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