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Adsorption of the herbicide 2,4-dichlorophenoxyacetic acid by Fe-crosslinked chitosan complex in batch mode

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ABSTRACT

It is essential to remove herbicide from solution. In this research, composite of Fe-crosslinked chitosan complex (Ch-Fe) was synthesized and characterized by scanning electron microscopy, X-ray fluorescence analysis and was used as adsorbent for removal of 2,4-dichlorophenoxyacetic acid (2,4-D) from solution. Batch experiments were performed to evaluate the effects of several experimental parameters, such as solid–liquid ratio, pH value, coexisting ions, contact time and concentration of 2,4-D. There was slight change of adsorption quantity at various solution pH from 4.0 to 11.0. The kinetic process was better described by the pseudo-second-order kinetic model. The adsorption equilibrium data were better fitted by Langmuir model and Koble–Corrigan model with higher determined coefficients (R^2) and low value of error and this suggested that adsorption be monolayer adsorption and the active sites be all energetically equivalent. The adsorption quantity was 473 mg g^{-1} from experiments at 293 K. Solution of 0.1 mol L^{-1} hydrochloric acid was the best to regenerate spent Ch-Fe and only 9% of adsorption capacity lost after three cycles. The mechanism between 2,4-D and Ch-Fe was discussed. High adsorption capacity and good cycling performance showed the potential application in removal of herbicide from aqueous solutions.

Keywords: Fe-crosslinked chitosan complex; 2,4-Dichlorophenoxyacetic acid; Adsorption; Regeneration

1. Introduction

One herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D, a synthetic plant somatotropic hormone), is widely used in worldwide, due to its low price and high selectivity for broadleaf weed [1,2]. It is estimated that approximately 21 million kg of 2,4-D are consumed each year in the later 1990s, especially in forestry and agriculture [3,4]. So there is residual in the environment. As 2,4-D can conjugate with protein or amino acids, it can not only disturb cell normal function but also lead to its death as it affects the enzymes activity [5]. As one of endocrine disrupting compounds, 2,4-D has negative effects on many organs such as eye, thyroid, kidney and adrenals. Besides, the maximum allowable concentration in drinking water is 0.1 mg L^{-1} (World Health Organization) [6]. 2,4-D is a moderately persistent chemical with a half-life between 10 and 50 d and it is also poorly biodegradable pollutant [4,7]. Therefore, the development of an effective method for removal of this pollutant is essential and important. Several methods include electrooxidation [8,9], membrane process [10], photodegradation [11–14], etc. But there are some drawbacks about these methods, such as high equipment investments, operation costs and no easy operation. However, adsorption may be a good choice for wastewater disposal due to its high efficiency, relatively low cost, easy operation and design [15].

As a derivative of abundant natural biopolymer, chitosan has caught our attention because of its eco-friendly, easy modification and degradation properties [16]. Effective functional groups or charge can be enhanced by modification [17].

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There are a large number of free hydroxyl and amino groups, which can coordinate with many common metal ions. These metal-binding biopolymers can be used in wastewater treatment and there is good adsorption performance. Since these metal ions containing positive charge, their binding can increase the positive charge of chitosan structure, therefore, increasing the efficiency of its adsorption for anionic pollutants. Fe^{3+} is common cation, low toxic and widely used as modifying agent. Chitosan–Fe(III) complex (Ch-Fe) has exhibited excellent adsorption performance in some anion solution, such as perchlorate [18], Cr(VI) [19–21], As(III) [22] and phosphate [23]. But few papers were about removal of organic anions from solution.

The aim of this work was to study the possibility of the utilization of Ch-Fe for removal of 2,4-D from aqueous solution. The system variables studied included contact time, solution pH, adsorbent dose, salt concentration, and 2,4-D concentration at different temperature to study their effects of adsorption quantity. The constants of adsorption models were obtained using non-linear regressive analysis. The property of regeneration and reuse was assessed. Finally, mechanism of adsorption was discussed.

2. Materials and methods

2.1. Preparation of chitosan–Fe(III) complex

Chitosan and some chemicals used in this study were purchased from Zhengzhou Chemical Corporation in China. The process of preparation was modified according to the method mentioned in reference [18]. Briefly, 2.0 g chitosan powder was dissolved into 100 mL of 1% (V:V) acetate acid solution. After stirring for 4 h at room temperature (293 K), 4.0 g $FeCl_3{\cdot}6H_2O$ was added and mixed with a stirrer for 2 h. Then chitosan–Fe(III) complex were obtained after adding ethanol, meanwhile washed the complex with ethanol to remove excess Fe(III). After drying at 353 K, it was screened through a set of sieves to get geometrical sizes of 40–60 mesh. The complex was immersed in 5% glutaraldehyde ethanol solution for 12 h, then washed the complex and dried at 353 K. The product was named as Ch-Fe. Normal-crosslinked chitosan (NCS) without iron was also prepared.

The exterior surface of NCS and Ch-Fe was obtained by scanning electron microscopy (SEM; JEOL6335FSEM, Japan). Elemental compositions were obtained by X-ray fluorescence spectrometer (Philips PW 2404 X-ray fluorescence, Netherlands).

2.2. Preparation of 2,4-D solution

The stock solutions of 2,4-D (1,000 mg L^{-1}) were prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration.

2.3. Adsorption performance

Adsorption was operated in batch mode. All adsorption experiments were performed by mixing adsorbent in 50-mL conical flasks containing 10 mL 2,4-D solution. The mixtures were shaken in a temperature-controlled shaker at 150 rpm at the designed conditions. Effects of several factors, including adsorbent dose (0.4–1.4 g L^{-1}), solution pH (2–11), coexisting ions, contact time, initial 2,4-D concentration (100–500 mg L^{-1}), temperature (293–313 K) were investigated. Kinetics and equilibrium studies were conducted at optimum adsorbent dose and solution pH. Kinetics process was carried out at different initial concentrations (100, 150 and 200 mg L^{-1}). Adsorption isotherms at 293–313 K were obtained by changing initial 2,4-D concentration (100–500 mg L^{-1}). The needed pH of the solution in each flask was adjusted using 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl solutions. The samples were withdrawn from the shaker at regular intervals until equilibrium was reached, and the concentration of supernatant was determined. Absorbance was measured at 280 nm (Shimadzu Brand UV-3000) and 2,4-D concentration was calculated according to adsorption law. The amount of 2,4-D adsorbed onto the unit weight of Ch-Fe (q, mg g^{-1}) and the removal efficiency (p %) was calculated by the following expressions:

$$q = \frac{V(C_0 - C)}{m} \tag{1}$$

$$p = \frac{C_0 - C}{C_0} \times 100\% \tag{2}$$

where V is the solution volume in L, C_0 is the initial 2,4-D concentration (mg L^{-1}), C is 2,4-D concentration (mg L^{-1}) at any time t and m is the mass of Ch-Fe (g).

2.4. Desorption and regeneration studies

Desorption studies were also performed in batch mode. Mass of 8 mg Ch-Fe was added to 10 mL 300 mg L^{-1} 2,4-D solution at optimum pH and shaking for 2 h at 303 K. Then the 2,4-D-loaded Ch-Fe was collected and washed with distilled water to remove feeble-adsorbed 2,4-D and dried at 353 K. Microwave desorption was carried by putting 8 mg dry 2,4-D-loaded Ch-Fe into a crucible, then microwave irradiated 10 min at different microwave power (450, 600 and 900 W). Similar to adsorption studies, solution desorption experiments were performed by mixing 2,4-D-loaded Ch-Fe in 50 mL conical flasks containing 2,4-D solution. In this experiment five solution were tested for desorption, they were H_2O, ethanol, 0.1 mol L^{-1} HCl, 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} NaCl. The mixtures were shaken in a temperature-controlled shaker at 150 rpm for 10 h in order to ensure desorption completely, the 2,4-D-loaded Ch-Fe after desorption was washed and reused in adsorption experiments and the adsorption–desorption cycle was repeated for three times. The regeneration efficiency was calculated as the ratio of values of q_e before and after regeneration.

3. Results and discussion

3.1. Characterization

The SEM analysis can show the surface microstructures of the NCS and Ch-Fe. The SEM images were shown in Figs. 1(a) and (b). There was relative smooth and compact surface of NCS while there was layered surface structure of

Ch-Fe. The irregular and porous structure of Ch-Fe efficiently increased superficial area, which was advantage of the diffusion and adsorption of 2,4-D molecules on Ch-Fe surface.

The X-ray fluorescence analysis was performed and the results were listed in Table 1. According to Table 1, the content of Fe after modification was increased significantly from the 0.142 to 1.247. So the chitosan was successfully modified by iron ions.

3.2. Effect of adsorbent dose

The amount of adsorption and 2,4-D removal efficiency at different adsorbent dose (solid–liquid ratio) were shown in Fig. 2. It was observed that the value of q_e decreased with the increase in adsorbent dosage and removal efficiency increased with the increase of dosage. The primary factor explaining the decrease in q_e value was that the adsorption sites remained unsaturated during the adsorption reaction and the 2,4-D molecule had not fully covered the active sites of Ch-Fe. On the other hand, it provided more adsorption sites for 2,4-D absorption with the increase of adsorbent mass. The trend showed that the Ch-Fe did not aggregate at experimental conditions. In the following test, the adsorbent dose was 0.8 g L^{-1}.

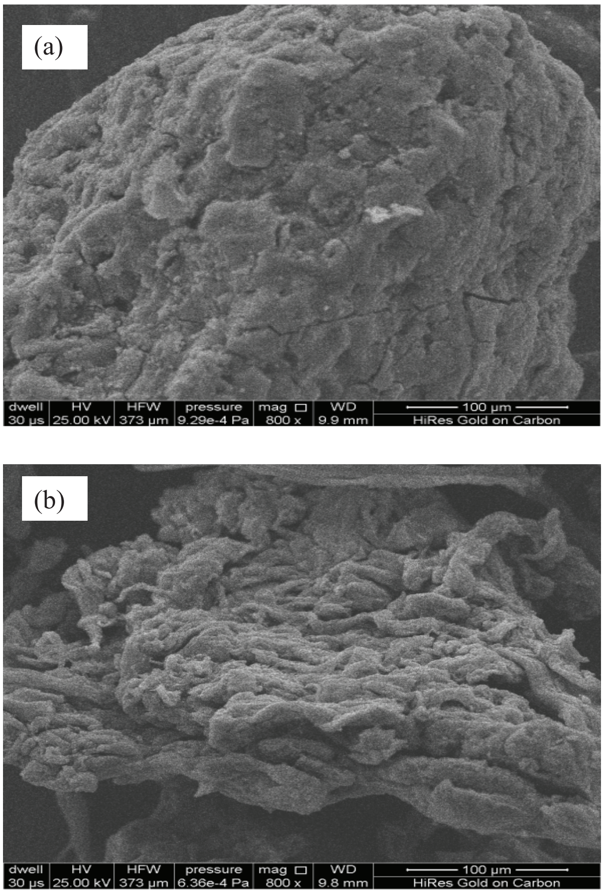

Fig. 1. SEM micrograph of: (a) NCS and (b) Ch-Fe.

Table 1
Result of X-ray fluorescence analysis

Element	Z	Content	
		NCS	Ch-Fe
S	16	0.0567	0.0593
P	15	0.394	0.409
Fe	26	0.142	1.274
Cl	17	0.241	17.86
Ca	20	0.411	0.159

3.3. Effect of initial pH on the adsorption

Solution pH is an important parameter in the adsorption process because it can affect the surface charge of Ch-Fe and the form of 2,4-D [17,24]. Experiments were performed in the pH range of 2.0–11 and the results were illustrated in Fig. 3. It was found that adsorption quantity of 2,4-D onto Ch-Fe dramatically increased when solution pH increased from 2.0 to 4, then kept relatively stable at pH 4.0–11.0. For NCS, curve was first sharply up and then rapidly down. This implied that Ch-Fe has practical significance in water treatment and sometime expand the range of application. Both NCS and Ch-Fe showed better uptake at pH 3. It was also observe that Ch-Fe

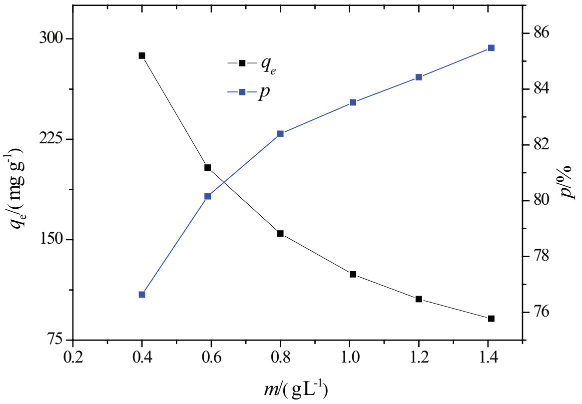

Fig. 2. Effect of adsorbent dose on adsorption quantity and efficiency (C_0 = 150 mg L^{-1}, T = 303 K).

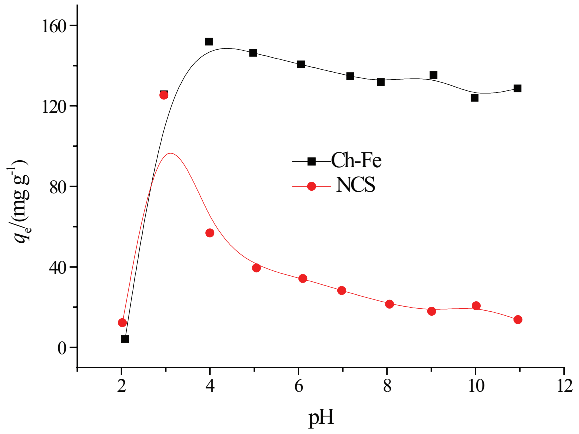

Fig. 3. Effect of solution pH on adsorption quantity (C_0 = 150 mg L^{-1}, T = 303 K, adsorbent dose = 0.8 g L^{-1}).

still had relatively good uptake in weak acidic medium and even in alkaline condition, this suggested that electrostatic attraction be not the only mechanism. The adsorption quantity of 2,4-D onto Ch-Fe was higher at pH over 3. This showed that Fe-modified chitosan was in favor of 2,4-D adsorption. Furthermore, Ch-Fe can be applied in the solution pH 3–11 while range of pH about NCS was narrower. In the following test, pH of 2,4-D solution was adjusted to 5.

3.4. Effect of coexisting ion on the adsorption

2,4-D cannot exist alone in actual water, coexisting negative ion such as Cl^-, SO_4^{2-} may exist in practical water. The research of coexisting ions is not only with the actual situation but also help interpreting adsorption mechanism. Three common salts, Na_2SO_4, $CaCl_2$ and NaCl, were chosen for the experiments and the results were shown in Fig. 4. It was seen from Fig. 4 that there was negative effect on adsorption quantity when coexisting ions were existed in solution and the increase in the salt concentration resulted in a decrease of adsorption quantity. The order of negative effect was Na_2SO_4 > $CaCl_2$ > NaCl. So ion exchange or electrostatic attraction may have participated in the adsorption process. Another reason was that ionic strength (salt concentration) increased, the activity of 2,4-D and the active sites decreased, so the adsorptive capacity of Ch-Fe toward 2,4-D declined. Although the total charge of Na_2SO_4 and $CaCl_2$ were the same with same concentration, but they showed different effect on 2,4-D adsorption. The difference is the ratio of charge toward radius (z/r) of the anions and SO_4^{2-} > Cl^-. With the higher z/r value of the anions, there was stronger interaction between the anion and the adsorbent [25].

3.5. Effect of contact time on the adsorption and the kinetic studies

The kinetic of adsorption is important as it can offer some useful information. A rapid adsorption process is desirable in practical water treatment. The effect of contact time on adsorption quantity was shown in Fig. 5. It was observed that adsorption rates increased dramatically in the first 60 min and subsequently kept constant. In order to describe the kinetic behavior and investigate Ch-Fe adsorption mechanism, the non-linear forms of pseudo-first-order kinetic model and pseudo-second-order kinetic model were applied to predict the adsorption process.

The pseudo-first-order kinetic model is expressed as [26]:

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

The pseudo-second-order kinetic model is expressed as [26]:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), k_2 is the rate constant of pseudo-second-order adsorption ($mg\ g^{-1}\ min^{-1}$), q_e is the amount of 2,4-D adsorbed ($mg\ g^{-1}$) at equilibrium and q_t is the amount of the adsorption ($mg\ g^{-1}$) at any time t. Usually, both linear regressive analysis and non-linear regressive analysis can be applied to obtain the parameters of models, but later is better as the form of equation is not transformed [27,28]. So non-linear regressive analysis was used to get the values of q_e, k_1 and k_2 with sum of least squares according to Eqs. (3) and (4) using the kinetic data. The calculated rate constants (k_1 and k_2) and regression coefficient values (R^2) were presented by Table 2. Meanwhile, in order to identify whether the model is suitable or not, average relative standard error (ARS) analysis was carried out. The expression for ARS analysis is [27]:

$$\text{ARS} = \sqrt{\left(\sum((q_c - q_e)/q_e)^2\right)/(n-1)} \tag{5}$$

where n is the number of count in the graph, q_e and q_c are adsorption quantity from experiments and models. According to Fig. 5 and Table 2, it clearly showed that both kinetic modes can described the kinetic data with high coefficient values (R^2 > 0.98). There was lower value of average relative standard (ARS) error about pseudo-second-order kinetic model. This showed that chemical adsorption was the rate-limiting process

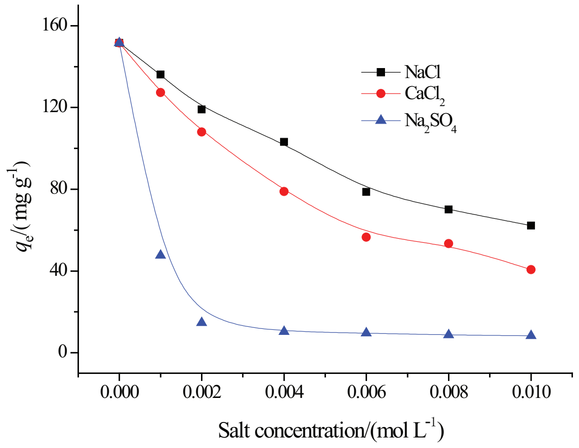

Fig. 4. Effect of coexisting ions on adsorption quantity (C_0 = 150 mg L^{-1}, T = 303 K, adsorbent dose = 0.8 g L^{-1}, pH = 5.00).

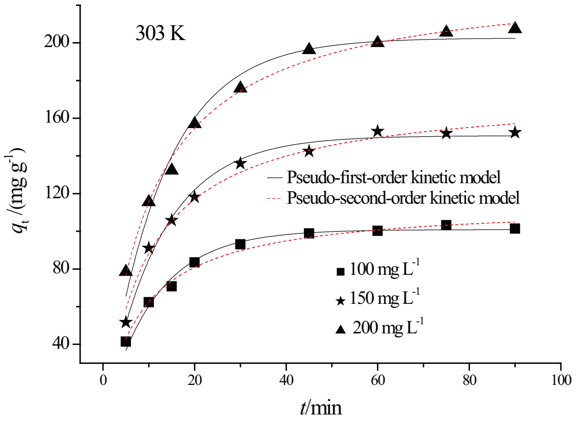

Fig. 5. Adsorption kinetics of 2,4-D (adsorbent dose = 0.8 g L^{-1}, pH = 5.00).

Table 2
Kinetic constants for the adsorption of 2,4-D by Ch-Fe

C_0 (mg L^{-1})	$q_{e,\exp}$ (mg g^{-1})	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
		$q_{e,\mathrm{cal}}$ (mg g^{-1})	k_1	R^2	ARS	$q_{e,\mathrm{cal}}$ (mg g^{-1})	$k_2 \times 10^{-3}$	R^2	ARS
100	103.2	100.9	0.091	0.984	0.0420	114.7	1.04	0.986	0.0216
150	153.1	150.7	0.083	0.990	0.0299	174.1	0.59	0.986	0.0281
200	207.3	202.6	0.078	0.976	0.0669	234.5	0.41	0.994	0.0223

[26]. The calculated values according to pseudo-first-order equation ($q_{e,\mathrm{cal}}$) were 100.9, 150.7 and 202.6 mg g^{-1} for the solution concentration 100, 150 and 200 mg L^{-1}, respectively. They all showed good agreements with the experimental results. Moreover, the fitted curves of pseudo-first-order kinetic model were closer to experimental points. This implied that pseudo-first-order kinetic model be better to predict the equilibrium adsorption quantity from kinetic process.

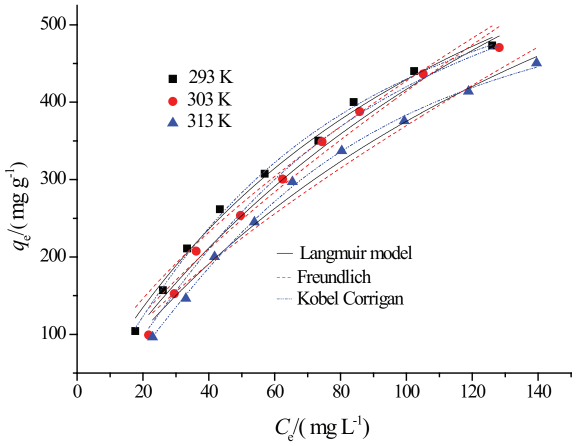

Fig. 6. Adsorption isotherms for adsorption of 2,4-D (adsorbent dose = 0.8 g L^{-1}, pH = 5.00).

3.6. Isotherm study of the adsorption

The analysis of adsorption process needs equilibrium to better understand the adsorption process. The effects of 2,4-D equilibrium concentration on adsorption quantity (adsorption isotherms) were shown in Fig. 6.

As seen from Fig. 6, equilibrium uptake increased with the increasing of 2,4-D concentrations at the range of experimental concentration. This was due to the increase in the driving force from the concentration gradient. The bigger adsorptive capacity of 2,4-D was also observed in lower temperature and the adsorption quantity was 473 mg g^{-1} at experimental conditions. The decrease of the equilibrium adsorption with the increase of temperature indicated that the adsorption of 2,4-D ions onto Ch-Fe was exothermic in nature.

The equilibrium adsorption isotherm is essential to design an adsorption system and it can offer some information of affinity and capacity of the adsorbent. The Langmuir model is perhaps the most famous model. It assumes monolayer sorption onto a homogeneous surface, and all active sites are energetically equivalent and independent [29]. A non-linear form of the Langmuir equation is represented as [30]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

where q_e is the amount of 2,4-D adsorbed at the equilibrium (mg g^{-1}); C_e is the equilibrium solution concentration (mg L^{-1}); K_L is the Langmuir adsorption constant (L mg^{-1}) and q_m is the monolayer capacity of the Ch-Fe (mg g^{-1}).

In order to discuss the suitability of adsorbent toward 2,4-D, a dimensionless constant separation factor was utilized. The separation factor R_L is defined as follows [31]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

where C_0 is the initial 2,4-D concentration (mg L^{-1}) and K_L is the Langmuir adsorption equilibrium constant (L mg^{-1}). R_L is an essential constant for Langmuir isotherm as it can predict whether an adsorption system is favorable or not through following criteria, irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$).

The Freundlich as an empirical model was widely used to describe non-ideal multilayer adsorption on heterogeneous surfaces and assumed the distribution of heat in adsorption is non-uniform. A non-linear form of the Freundlich model is represented as [32]:

$$q_e = K_F C^{1/n} \tag{8}$$

where K_F is a measure of adsorption capacity (L mg^{-1}) and n is the heterogeneity factor.

Koble–Corrigan model is a three-parameter empirical model and a combination of the Langmuir and Freundlich models. Its form is expressed as [32]:

$$q_e = \frac{A C_e^n}{1 + B C_e^n} \tag{9}$$

where parameters of A, B and n are Koble–Corrigan parameters, respectively. When $n = 1$, it is identical to Langmuir model.

All relative parameters of the three models, the correlation coefficients (R^2), and the values of ARS were listed in Table 3 with non-linear regressive analysis. Compared with the correlation coefficients and values of ARS in Table 3, Koble–Corrigan model and Langmuir model were more suitable than Freundlich model to describe the absorption process. The fitted curves were also shown in Fig. 6. It can be seen that the fitted curves from Koble–Corrigan model and Langmuir model were more close than that from Freundlich model. That was to say the adsorption was more inclined to a monolayer adsorption. This was in accordance with Koble–Corrigan parameter of n (near 1). The values Freundlich parameter ($1/n$) was $0.1 < 1/n < 1$ at three temperatures and this indicated favorable adsorption of 2,4-D at experimental conditions. The values of R_L for sorption of 2,4-D at three temperatures were >0 and <1, indicating that the uptake of 2,4-D onto Ch-Fe was favorable.

Table 3
Isotherm constants for the adsorption of 2,4-D by Ch-Fe

Isotherm parameters	Temperature (K)		
	293	303	313
Langmuir			
$K_L \times 10^{-3}$ (L mg^{-1})	8.31	5.50	5.55
q_m (mg g^{-1})	946	1,175	1,052
R^2	0.992	0.987	0.987
ARS	0.067	0.102	0.095
Freundlich			
K_F	19.87	13.75	13.35
$1/n$	0.67	0.74	0.72
R^2	0.975	0.973	0.971
ARS	0.12	0.14	0.13
Koble–Corrigan			
A	3.26	1.64	0.98
$B \times 10^{-2}$	0.48	0.24	0.17
n	1.28	1.42	1.53
R^2	0.995	0.995	0.998
ARS	0.029	0.046	0.019

Table 4 listed the adsorption capacity of different adsorbents used for the removal of 2,4-D. Compared to other adsorbents listed in Table 4, there was some competitive for Ch-Fe with higher adsorption quantity. This also provided strong evidence for the potential applications in removal of herbicide from aqueous solutions.

3.7. Desorption and reuse ability

To make the adsorption process more economical, it is necessary to regenerate the spent adsorbent. The reuse of the spent adsorbent is of importance in industrial practice [40–43]. Results of various methods were shown in Fig. 7. It was seen that both 0.1 mol·L^{-1} HCl and 0.1 mol L^{-1} NaCl as eluents were effective while there was smallest regenerated efficiency for NaOH and H_2O. But there were middle efficiency for microwave irradiation and ethanol elution. The reusability of 2,4-D-loaded Ch-Fe for 2,4-D adsorption was shown in Fig. 8. Compared with the fresh adsorbent, the adsorption capability of the 0.1 mol L^{-1} NaCl regenerated

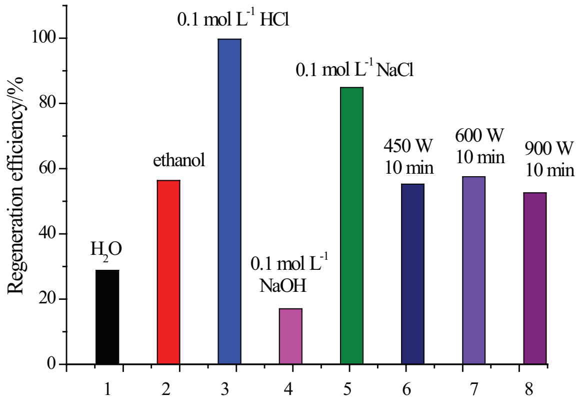

Fig. 7. 2,4-D regeneration efficiency of Ch-Fe after first regeneration.

Table 4
Comparison of 2,4-D uptake by selected adsorbents

Adsorbent	Solid–liquid ratio (g L^{-1})	Adsorption capacity (mg g^{-1})	T (K)	References
Pristine biomass	2	88.42	298	[17]
Aminated biomass	2	269.67	298	[17]
ZnAlZr LDH	0.5	1,304.14	–	[33]
Corncob-activated carbon	1	300.17	303	[34]
Granular-activated carbon	–	0.688	–	[35]
Chitosan	–	11.157	–	[36]
Chitin	–	6.079	–	[36]
Cu–Fe–NO_3 LDH	0.2	1,428	308	[37]
Zn_2–Al–Cl	1	587.97	–	[38]
Modified jute	–	38.5	298	[39]
Ch-Fe	0.8	473	293	This work

Note: LDH – layered double hydroxides.

adsorbent was markedly decreased with the increase of cycling times. But for 0.1 mol L^{-1} HCl solution, regenerated adsorbent showed more stable with the increase of cycling times and only 9% regeneration lost in three cycles. In HCl solution, chloride ions can exchange the 2,4-D anions loaded in Ch-Fe while 2,4-D in solution was existed in neutral molecular. Moreover, amino group existed in chitosan was protonated. So the interaction between adsorbent and 2,4-D was weak and more 2,4-D loaded in Ch-Fe can be desorbed into solution. It was also seen from Fig. 8 that the regeneration efficiency was still higher after cycle use. This result implied that the 2,4-D-loaded Ch-Fe can be reused as adsorbent to effectively remove 2,4-D from solution.

3.8. Adsorption mechanism

It is necessary to elucidate the adsorption mechanism and the structure of the adsorbate and the adsorbent surface properties can be considered. According to the literature, $-NH_2$ and –OH groups can bind the metal ions and Fe(III) coordinated with chitosan in the form of pentacoordinate, that is 2 mol of monomeric sugar units of the ligand are present in the coordination sphere of Fe(III) [20]. From FTIR of Ch-Fe (figure not shown), there was broad and strength peak at 3,423.36 cm^{-1}, which was due to stretching vibration of –COOH and $-NH_2$. Besides good adsorption properties in strong acidic conditions, Ch-Fe still had relatively good uptake in faintly acidic medium and in alkaline condition, it also suggest that electrostatic attraction be not the only mechanism. Competitive adsorption or ion exchange may have taken place between anion and 2,4-D, as the coexisting ions significantly affect adsorption. The possible main mechanism of adsorption was ion exchange and electrostatic attraction while non-polar and non-polar interactions were also existed. A schematic possible reaction between Ch-Fe and 2,4-D was shown in Fig. 9.

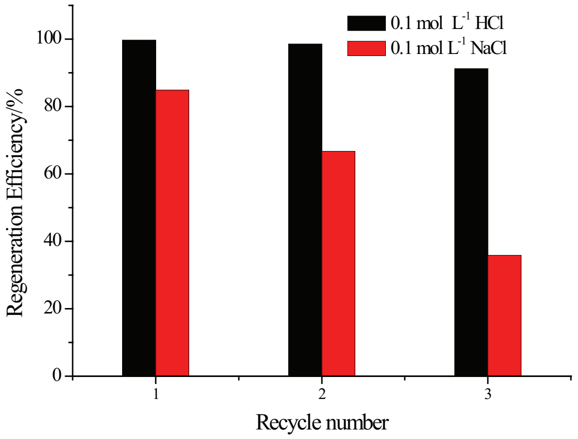

Fig. 8. 2,4-D regeneration efficiency of Ch-Fe after different cycle.

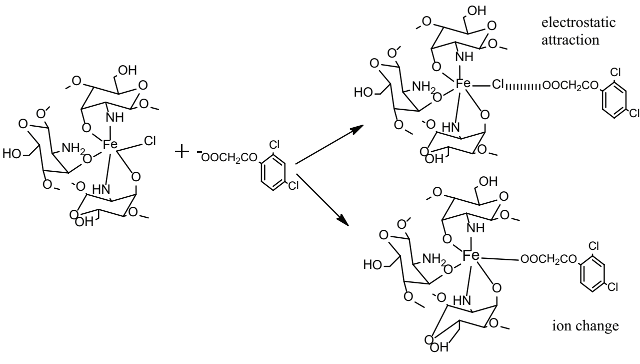

Fig. 9. A schematic representation of actions between Ch-Fe and 2,4-D.

4. Conclusion

An effective absorbent was prepared from chitosan and its adsorption behavior of 2,4-D was presented. The Koble–Corrigan and Langmuir model are more suitable than Freundlich model to describe the adsorption process. Beside, adsorption process was successfully described by pseudo-first-order model. Spent adsorbent can be effectively regenerated by 0.1 mol L^{-1} HCl solution. It can be concluded that Ch-Fe be very attractive and potential of practical application for removal of 2,4-D in water.

Acknowledgments

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