

Adsorptive Removal of Cr(VI) from Water by Anion Exchanger Based Nanosized Ferric Oxyhydroxide Hybrid Adsorbent

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A hybrid adsorbent (FOAE) prepared by loading ferric oxyhydroxide on anion exchanger was applied for adsorptive removal of Cr(VI) from water. Effects of initial Cr(VI) concentration, pH, temperature and competition of other anions on Cr(VI) adsorption were investigated in batch experiments. The equilibrium adsorption capacity (Q_e) of the FOAE increased with initial Cr(VI) concentrations (from 20 to 100 mg L⁻¹) and reached a plateau at the point of 100 mg L⁻¹ with the Q_e of 123 mg g⁻¹. The optimum conditions for adsorption were determined as pH 2 and 313 K with Q_e of 200 mg g⁻¹. Competition effect of other anions on Cr(VI) removal can be concluded in the following order: PO₄³⁻ > SO₄²⁻ > Cl⁻. Cr(VI) adsorption on both FOAE and anion exchanger followed pseudo first order kinetic. Because the Freundlich isotherm could describe the adsorption of Cr(VI) on FOAE more adequately, it can be deduced that heterogeneous adsorption occurred on FOAE.

Key words:

Cr(VI) removal, adsorption, nanosized ferric oxyhydroxide, anion exchanger

Introduction

Heavy metal pollution has attracted increasing interests all over the world for its toxicity and environmental hazard. Chromium is one of the most dangerous heavy metals in water and soil that mainly originates from the emissions of industries such as tanning, metallurgy, plating and metal finishing.¹ Chromium exists mainly in two stable oxidation states, Cr(III) and Cr(VI) in the ecosystem. Hexavalence is considered the most toxic state of chromium for its carcinogenicity, toxicity and high mobility.² Recently, chromium pollution attracts serious concerns because of its high toxicity to human health even at low concentrations.¹ Commonly used techniques for Cr(VI) removal include reduction and precipitation, ion exchange, as well as reverse osmosis.^{3–5} Most of these methods are not widely applied due to their shortcomings such as insufficient removal of pollutants, high capital costs, high reagents and/or energy requirements, and disposal of toxic sludge or other waste products, etc.⁶ Adsorption is a promising method that can be applied as an economically feasible alternative for Cr(VI) removal.¹ Some novel and inexpensive adsorbents were developed to achieve higher efficiency and lower operating cost.^{1,7}

Recently, it has been proved that ferric oxides act as an effective and environmentally benign sorbent for anionic pollutants removal, such as the removal of arsenite/arsenate,⁸ selenite,⁹ phosphate¹⁰ and chromate¹¹

from contaminated waters. However, ferric oxides cannot be used directly in a continuous flow system due to excessive pressure drops caused by their ultra-fine particle sizes. To solve this problem, various new adsorbents were developed by loading ferric oxides onto conventional porous adsorbents including activated carbon,¹⁰ bead cellulose,¹² alginate beads,¹³ sand,¹⁴ and polymeric adsorbents.¹⁵ The combination of ferric oxides and their carriers simultaneously showed specific affinity of ferric oxides toward the targeted anion pollutants as well as excellent supporting and flow characteristics. However, most of the related studies were focused on the supporting of carriers and little attention was paid to the surface chemical characteristics that affected the performance of hybrid adsorbents.

In the last few years, novel hybrid adsorbents have been fabricated by loading ferric oxides on ion exchange resin to remove anionic pollutants including arsenite/arsenate and phosphate.^{15,16} Sengupta *et al.* have developed the hybrid adsorbent HAIX loaded ferric oxyhydroxide on anion exchanger according to the Donnan membrane principle for arsenic removal.^{15,17} Pan *et al.* have developed a similar hybrid adsorbent for enhanced removal of anionic pollutants from waters.⁹ It had been proved that arsenite, arsenate and phosphate can be efficiently removed over a wide range of concentrations.^{15,16} However, little knowledge has been obtained on ion-exchanger-based ferric oxides hybrid adsorbents used for the removal of chromium ions.

In the present study, the adsorption and desorption properties of Cr(VI) on hybrid adsorbent

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made of anion exchanger-based nanosized ferric oxyhydroxide were investigated. The applicability of hybrid adsorbent for the removal of Cr(VI) was evaluated in view of the effects of initial Cr(VI) concentration, pH, temperature and competing anion on adsorption efficiencies in batch adsorption experiments. In order to gain a better understanding of the process and mechanisms of adsorption, the adsorption equilibrium data were applied to elucidate the kinetic parameters and isotherm models.

Materials and methods

Preparation of hybrid adsorbent and solution

The hybrid adsorbent was prepared by loading nanosized ferric oxyhydroxide onto macroporous anion exchanger beads (D201) with diameter of 0.4–0.7 mm. The specific gravity and bulking density were 0.65–0.73 and 1.05–1.10 g mL⁻¹, respectively. Traditionally, Fe³⁺ cannot be ion-exchanged onto an anion exchanger due to the electrostatic repulsion. A novel method had been developed to overcome the electrostatic repulsion and load the FO onto the anion exchanger. Chemical precipitation combined with a thermal technique was applied to prepare the FOAE according to the following steps. Fe(III) was first adsorbed onto the macroporous anion exchanger resin. 100 mL mixed solution of Fe(NO₃)₃·NaCl-HCl (mole ratio of 1:3:1) was flown through a column filled with 15 g anion exchanger beads. Then, the resulting FeCl₄⁻ in solution was decomposed and precipitated onto the inner surface of anion exchanger by rinsing the anion exchanger with NH₄Cl-NH₃·H₂O solution (mole ratio of 1:1). Finally, thermal treatment was performed (313 K) for 8 hours to obtain the anion exchanger based ferric oxyhydroxide adsorbent (FOAE).

Cr(VI) solution was prepared by dissolving analytical grade potassium dichromate (K₂Cr₂O₇) in double distilled water. The pH was adjusted by 0.1 mol L⁻¹ HCl and 0.1 mol L⁻¹ NaOH.

Adsorption and desorption experiments in batch system

Adsorption and desorption tests were performed using a traditional batch test method to determine the equilibrium concentration of Cr(VI) in aqueous solution. Adsorption experiments were carried out in 100 mL solution with different initial Cr(VI) concentrations ($\gamma_i = 20, 40, 60, 80, 100, 120$ and 150 mg L⁻¹) prepared in 250 mL flasks placed in a temperature-controlled shaker. 0.025 g adsorbent beads were added into the solutions at a predetermined agitation speed (160 rpm) and temperatures (from 298 K to 328 K as noted) for 24 hours. Desorption experiments were carried out by agitat-

ing Cr(VI)-adsorbed adsorbents in mixed solution of 5 % NaCl and 5 % NaOH (200 mL) at 298 K for 24 h. Samples were then filtered through 0.45- μ m filter for Cr(VI) measurement.

Analyses and calculation

The concentrations of Cr(VI) in the filtered liquid samples were determined by an ICP-AES (ICP-optima 2001DV, Perkin-Elmer, USA). The amount of Fe(III) loaded within FOAE was analyzed by the ICP-AES after being extracted by strong acid solution. FOAE samples were porphyriized and loaded on a copper grid coated with a thin layer of diluted magnetic particle suspension for transmission electron microscopy (TEM, ECNAI G²F-20, FEI Inc., USA) measurement. The elemental contents of adsorbent surface were analyzed by energy dispersive X-ray (EDAX) equipped on TEM. The mineralogy of ferric oxyhydroxide on the surface of the FOAE was determined by X-ray diffraction (XRD; D/MAX 2500, Rigaku, Japan) with Cu K α radiation and semiconductor detector, operated at 40 kV and 25 mA with $2\theta = 10$ –90°.

The experimental equilibrium adsorption capacity (Q_e , mg g⁻¹) was calculated as:

$$Q_e = \frac{(\gamma_i - \gamma_e) \cdot V}{m} \quad (1)$$

where γ_i and γ_e were initial concentration and equilibrium concentration of Cr(VI), V was the volume of solution, and m was the mass of FOAE.

Results and discussion

Characterization of FOAE

After the coating procedure, deep brown spherical adsorbent beads were developed by ferric oxyhydroxide coating, the content of ferric atoms on hybrid adsorbent was about 8.6 %. As shown in TEM photographs (Fig. 1), nanosized ferric oxyhydroxide particles were apparently spread over the surface of the anion exchanger. The elemental microprobe analysis using TEM/EDAX showed that only C, O, S and Cl were the principal elements on the uncoated anion exchanger. After surface ferric oxyhydroxide precipitation, Fe appeared as another principal element (Fig. 2), providing the direct evidence of ferric oxyhydroxide coating on the carrier. The results of XRD spectra indicated that the ferric oxide prepared by coating procedure was amorphous state (Fig. 3).

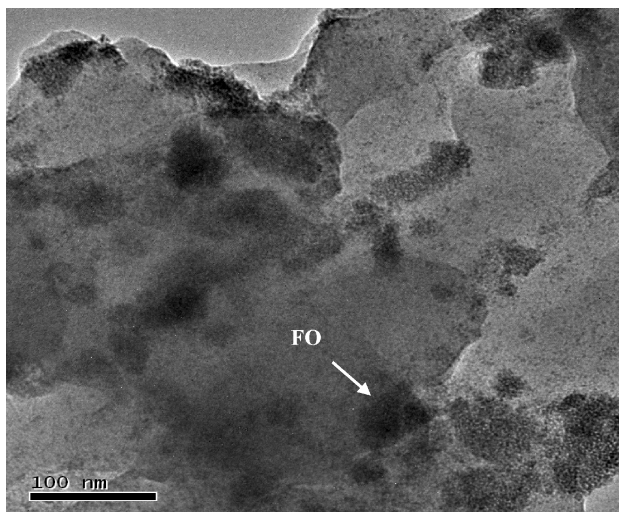


Fig. 1 – TEM micrograph of the FOAE adsorbent

Effect of initial Cr(VI) concentration

Equilibrium concentrations γ_e increased from 0.6 to 119.4 mg L⁻¹ with initial Cr(VI) concentrations varied from 20 to 150 mg L⁻¹, while the removal efficiency of Cr(VI) exhibited a reverse trend from 97±2 to 20±1 %. As shown in Fig. 4, the Q_e increased from 77±2 to 123±5.2 mg g⁻¹ with the initial concentration of Cr(VI) increased from 20 to 100 mg L⁻¹. Though initial concentrations of Cr(VI) higher than 100 mg L⁻¹ provided higher driving force to overcome the mass transfer resistances of the Cr(VI) migration from the aqueous to the solid phase, the Q_e reached a plateau with a maximum of 123 mg Cr(VI) g⁻¹ adsorbents at the point of initial Cr(VI) concentration of 100 mg L⁻¹, indicating that the adsorbent was saturated.

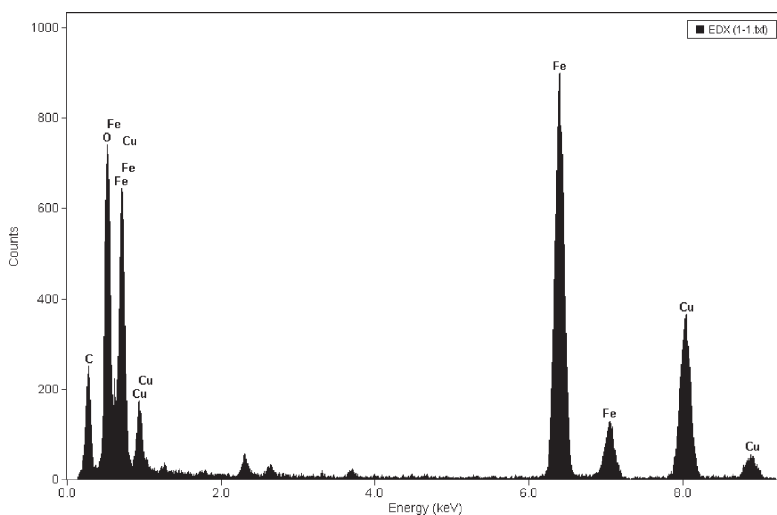


Fig. 2 – EDAX spectrum of the FOAE adsorbent

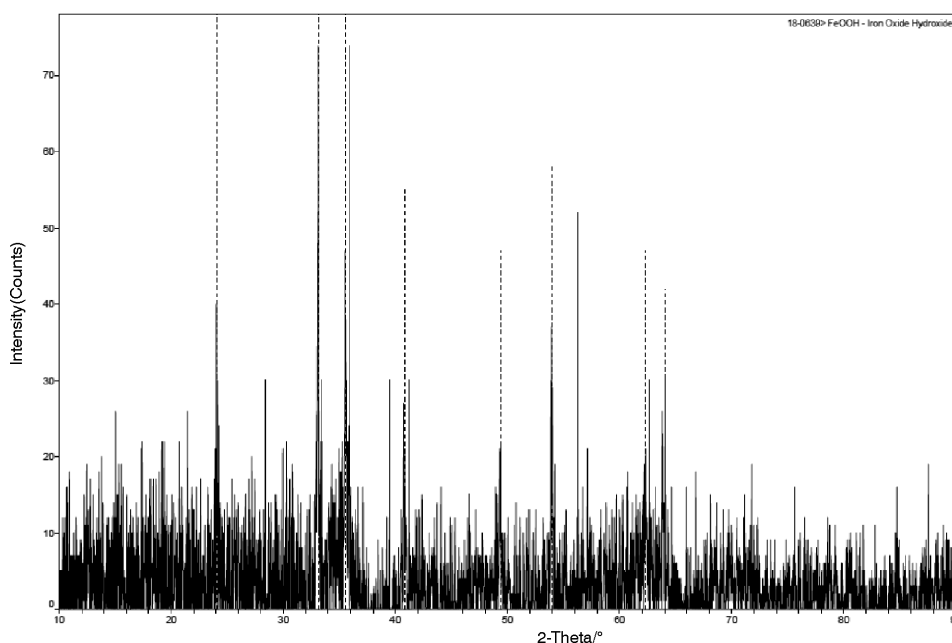


Fig. 3 – XRD spectra of the FOAE adsorbent

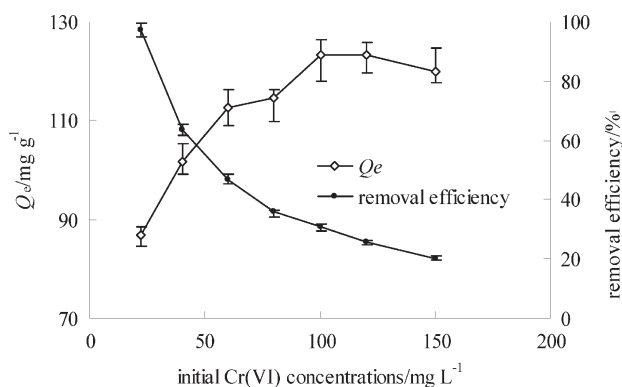


Fig. 4 – Effect of initial Cr(VI) concentration on adsorption (FOAE = 0.025 g, $T = 298$ K)

Desorption experiments were performed using 5 % NaOH and 5 % NaCl mixture as regenerant on FOAE (Cr(VI) adsorbed). Comparison of the total amounts of Cr(VI) in solution before adsorption and after desorption at each initial Cr(VI) concentration mentioned above (20, 40, 60, 80, 100, 120 and 150 mg L⁻¹), indicated that the Cr(VI) desorption efficiency was above 97 %. The Q_e and adsorption efficiency of FOAE on Cr(VI) were not remarkably attenuated in 5 cycles.

Effect of pH

In order to illuminate the effect of pH on the adsorption of Cr(VI), batch experiments of adsorption were operated individually at different pH values of 2, 4, 6, 7, 8, 10 and 12 by adding 0.025 g adsorbent into solution with the same initial Cr(VI) concentration of 50 mg L⁻¹ at 298 K. The removal efficiency was negatively related with initial solution pH from 2 to 12, indicating that low pH was propitious to the adsorption of Cr(VI) (Fig. 5). Similar results were obtained by Malkoc *et al.*,¹⁸ Garg *et al.*¹⁹ and Kiran *et al.*²⁰ when the effect of pH on the adsorption of chromium ions from wastewaters using different adsorbents were investigated. Cr(VI) exists in various species of anions such as H₂CrO₄, HCrO₄⁻, CrO₄²⁻, HCr₂O₇⁻, and Cr₂O₇²⁻ depending

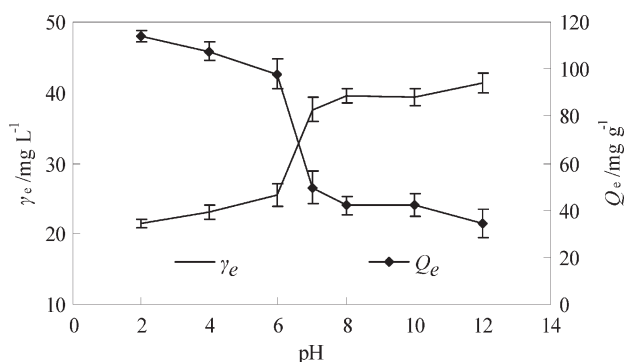


Fig. 5 – Effect of pH on adsorption (FOAE = 0.025 g, $T = 298$ K, $\gamma_i = 50$ mg L⁻¹)

upon the pH and the concentration of Cr(VI) in solution. In the neutral solution of low concentration, Cr(VI) will be present in the forms of HCrO₄⁻ and CrO₄²⁻, while HCrO₄⁻ is the predominant Cr(VI) species in the acidic aqueous phase. At pH 2, the active sites on the hybrid adsorbent positively charged due to the excess amount of H⁺ ions within the aqueous solutions, resulted in the highest Q_e value of the FOAE.^{21,22} The Q_e of Cr(VI) adsorbed by hybrid adsorbents smoothly decreased over a pH ranged from 2–6 and 7–12 mainly due to the change of Cr(VI) species in solution. However, a sharp decrease on Q_e (from 97.8±6 to 49.7±6.8 mg g⁻¹) was observed when pH increased from 6 to 7. This can be explained by the abrupt change of dominant chromium from HCrO₄⁻ to CrO₄²⁻ when the pH slightly increased from 6 to 7 as previously reported.²³ At pH values greater than 7.0, adsorbent surface is negatively charged, and less adsorption of Cr(VI) occurs may be due to the competition between the CrO₄²⁻ and OH⁻ anions to be adsorbed on the surface of the adsorbent. During the adsorption experiments at different pH, no ferric ions had been detected in the solution, which confirmed that the FOAE was stable in experimental pH range (data not shown).

Effect of temperature

Temperature is a key parameter affecting the reaction kinetics and performance of adsorption. The effect of temperature on the adsorption of Cr(VI) was investigated by adding 0.025 g of adsorbents into solutions with different initial Cr(VI) concentrations (20, 40, 60, 80 and 100 mg L⁻¹) at the temperatures of 298, 313 and 328 K (pH 2.0), respectively. As shown in Fig. 6, when the initial Cr(VI) concentration was 20 mg L⁻¹, more than 90 % of Cr(VI) in solution had been adsorbed by FOAE in batch experiments at 298, 313 and 328 K. The removal efficiency strongly depended on the

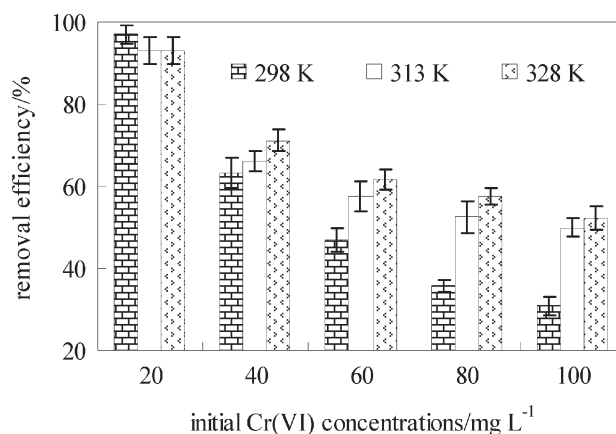


Fig. 6 – Effect of temperature on adsorption of Cr(VI) on FOAE (FOAE = 0.025 g, pH = 2)

temperature with the increase of initial Cr(VI) concentrations. Due to the anion exchange process being a typical endothermic process, an increase in temperature resulted in the increase of both adsorption efficiency and Q_e . When the initial concentration of Cr(VI) was 100 mg L^{-1} , the highest Cr(VI) removal rate of $52.2 \pm 3 \%$ was obtained at 328 K ($30.8 \pm 2.3 \%$ at 298 K; $49.9 \pm 2.2 \%$ at 313 K). Highest removal rates of 71.2 ± 2.8 , 61.6 ± 2.6 and $57.5 \pm 1.9 \%$ were also observed at the same temperature when initial Cr(VI) concentrations were 40, 60 and 80 mg L^{-1} . In contrast, the lowest Cr(VI) removal rates of $63.3 \pm 3.7 \%$ ($\gamma_i = 40 \text{ mg L}^{-1}$), $46.7 \pm 2.8 \%$ ($\gamma_i = 60 \text{ mg L}^{-1}$) and $35.8 \pm 1.5 \%$ ($\gamma_i = 80 \text{ mg L}^{-1}$) were obtained at 298 K respectively. It was clearly shown that there was slight enhancement on the Cr(VI) removal efficiency when the temperature further increased from 313 to 328 K. Thus, it was much more applicable and stable to use FOAE at 313 K ($Q_e = 200 \text{ mg g}^{-1}$) since the suggested operating maximum temperature of the strong basic anion exchanger was below 333 K.

Competing effect of other anions

Some soluble anions, called competing anions, usually coexist with Cr(VI) in water, which may affect the removal of Cr(VI) by adsorbents. The competing effect of coexisting anions investigated here included SO_4^{2-} , PO_4^{3-} and Cl^- at six concentration levels (5, 10, 20, 40, 60 and 80 mg L^{-1}) by adding Na_2SO_4 , NaH_2PO_4 and NaCl with the initial Cr(VI) concentration of 50 mg L^{-1} (Fig. 7). The pH of solution was adjusted to 7.0 for adsorption experiments. The Q_e of Cr(VI) in the presence of PO_4^{3-} , SO_4^{2-} and Cl^- were 84.9 ± 3.2 , 88.3 ± 3.8 and $100.8 \pm 2.9 \text{ mg g}^{-1}$ respectively when the concentration of competing anions was 5 mg L^{-1} . At a relatively higher competing anion concentration of 80 mg L^{-1} , the Q_e of Cr(VI) decreased to 16.8 ± 3.6 , 35.9 ± 2.4 , and $45.4 \pm 3.9 \text{ mg g}^{-1}$, respectively. It

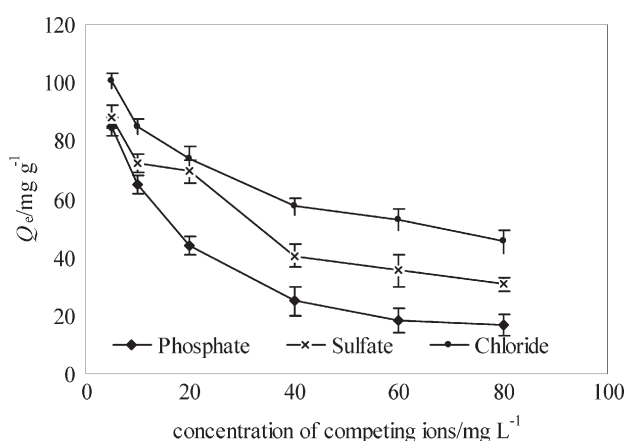


Fig. 7 – Effect of competing anions on adsorption of Cr(VI) on FOAE

was clearly shown that both the species of anions and their concentrations affected the adsorption of Cr(VI) on FOAE. Of all the three anions investigated, PO_4^{3-} exhibits the largest competing effect followed by SO_4^{2-} , while Cl^- had the least effect due to the different configuration between CrO_4^{2-} and Cl^- . It had been proved that the adsorption of both CrO_4^{2-} and PO_4^{3-} onto ferric oxyhydroxide occurred via the formation of inner-sphere surface complexes,²⁴ whereas SO_4^{2-} was usually adsorbed as both inner- and outer-sphere surface complexes.²⁵ Therefore, higher competition occurred between CrO_4^{2-} and PO_4^{3-} .

Adsorption kinetics

In order to further investigate the mechanism of adsorption process, the pseudo first order and pseudo second order kinetic models were employed to describe the adsorption kinetics. The pseudo first order model according to the Lagergren equation is presented as follows:²⁶

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303} \quad (2)$$

where Q_e and Q_t are the amounts of Cr(VI) adsorbed at equilibrium and at time t (min) respectively, k_1 is the first order adsorption rate constant. The pseudo second order model can be expressed as:²⁷

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

where k_2 is the second order adsorption rate constant. As expected, the maximum adsorption rate of 9.2 and 6.3 mg h^{-1} were obtained during the initial 90 minutes of the adsorption processes for both FOAE and anion exchanger, which was mainly due to the abundant active sites on clean adsorbents (Fig. 8a). However, the adsorption rates decreased with time due to the coverage of the active sites by the Cr(VI). Adsorption process of FOAE was almost complete within 210 minutes and no significant change was observed after that, while the anion exchanger needed 300 minutes to achieve the same equilibrium. This clearly showed that the maximum adsorption rates of FOAE were 46 % higher than those of anion exchanger, indicating that the immobilization of ferric oxyhydroxide on anion exchanger substantially enhanced the adsorption process. Kinetics of Cr(VI) adsorption on both adsorbents determined by the pseudo first order and pseudo second order models are shown in Fig. 8b and Fig. 8c. The values of kinetic parameters were then calculated from the slopes, as listed in Table 1. The theoretical values of Q_e of FOAE and anion exchanger calculated by pseudo first order model

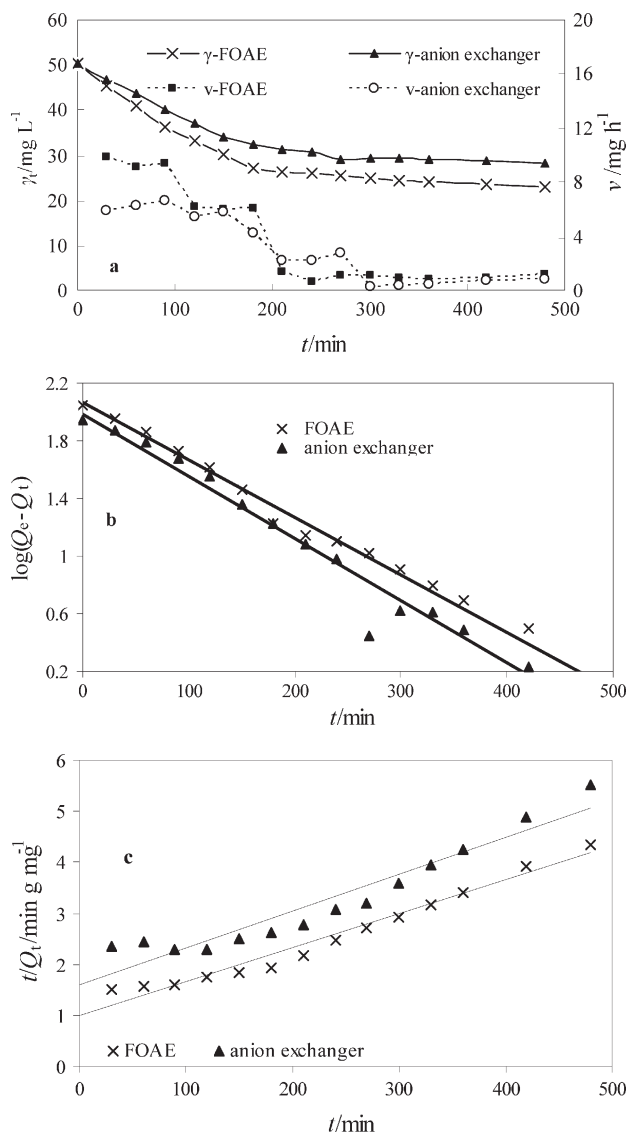


Fig. 8 – Adsorption kinetics (a) in which γ_t was the Cr(VI) concentration at time t and v was adsorption rate of Cr(VI), Pseudo first order adsorption (b), and Pseudo second order adsorption (c) of Cr(VI) on FOAE

were much closer to the experimental values as well as higher R^2 than those calculated by pseudo second order model, showing that the adsorption processes of both FOAE and anion exchanger can be described better by the model of pseudo first order.

Adsorption isotherm

The Langmuir and Freundlich adsorption isotherms were used to characterize the adsorption models. The Langmuir adsorption isotherm is

$$Q_e = \frac{Q_0 K_L \gamma_e}{1 + K_L \gamma_e} \quad (4)$$

where Q_0 and K_L are the Langmuir isotherm constants related to maximum adsorption capacity and adsorption net enthalpy. Linearized form of Langmuir isotherm is expressed as:

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \left(\frac{1}{K_L Q_0} \cdot \frac{1}{\gamma_e} \right) \quad (5)$$

The Freundlich adsorption isotherm is

$$Q_e = K_F \gamma_e^{1/n} \quad (6)$$

where K_F and $1/n$ are the Freundlich isotherm constants depend on temperature and adsorption characteristics. The adsorption isotherm results of Cr(VI) adsorption on FOAE at 298 K, 313 K and 328 K are shown in Fig. 9a and Fig. 9b. Based on Langmuir constants, Freundlich constants and R^2 given in Table 2, the Freundlich isotherm represented the adsorption of Cr(VI) on FOAE at 298, 313 and 328 K more adequately. Generally, the Langmuir isotherm assumes that the adsorption occurs on a homogeneous surface by monolayer adsorption, whereas the Freundlich isotherm is especially good for fitting data from highly heterogeneous adsorbent systems. Data analysis showed that heterogeneous adsorption possibly occurred on FOAE for Cr(VI) adsorption.

Conclusions

A hybrid adsorbent of FOAE prepared by loading ferric oxyhydroxide on anion exchanger was proven to be an applicable adsorbent for Cr(VI) removal due to its high Cr(VI) removal efficiency and favorable regeneration performance. It was found in

Table 1 – Kinetic parameters of FOAE and anion exchanger calculated by pseudo first and pseudo second order models

Adsorbents	Model	Rate constant	Q_e (mg g ⁻¹)		R^2
			experimental	modeling	
FOAE	Pseudo first order	$9.2 \cdot 10^{-3}$	110.2	116.1	0.9859
	Pseudo second order	$4.6 \cdot 10^{-5}$		149.3	0.9689
Anion exchanger	Pseudo first order	$9.9 \cdot 10^{-3}$	87.6	97.5	0.9677
	Pseudo second order	$3.2 \cdot 10^{-5}$		138.9	0.9111

Table 2 – Adsorption isotherm constants of Langmuir and Freundlich models

	Langmuir isotherm constant			Freundlich isotherm constant		
	Q_0 (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	$1/n$	K_F (mg L ^{1/n} g ⁻¹ mg ^{-1/n})	R^2
298 K	113.6	3.52	0.906	0.0934	80.77	0.9866
313 K	161.3	0.579	0.870	0.2602	65.15	0.9573
328 K	169.5	0.551	0.868	0.2854	64.08	0.9555

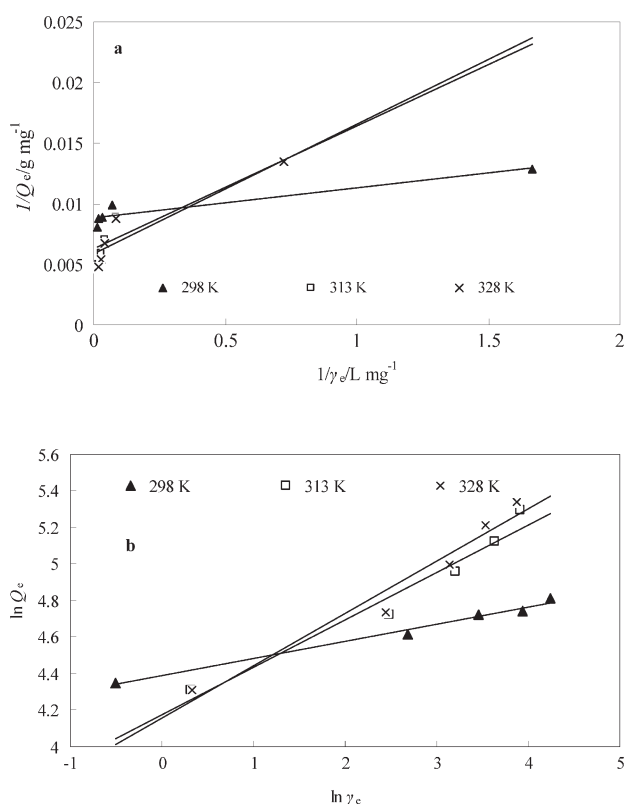


Fig. 9 – Application of the Langmuir adsorption isotherm (a) and Freundlich adsorption isotherm (b) to the experimental data obtained at different temperatures

batch experiments that the removal of Cr(VI) greatly depended on initial Cr(VI) concentration, pH and temperature. Q_e of Cr(VI) increased with the initial concentrations of Cr(VI) varying in the range from 20 to 100 mg L⁻¹ when 0.025 g FOAE was added. Considering both the stability and the adsorption performance of FOAE, the optimum conditions for Cr(VI) adsorption were determined at 313 K and pH 2 ($Q_e = 200$ mg g⁻¹). The adsorption kinetics and equilibrium isotherms revealed that the adsorption process obeyed pseudo first order kinetics model and agreed well with the Freundlich adsorption model, which suggested that the adsorption of Cr(VI) on FOAE was assumed as a heterogeneous adsorption.

ACKNOWLEDGEMENT

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List of symbols

- Q_e – amount of solute adsorbed at equilibrium, mg g⁻¹
- Q_t – amount of solute adsorbed at time t , mg g⁻¹
- γ_i – initial concentration of solute, mg L⁻¹
- γ_e – equilibrium concentration of solute, mg L⁻¹
- m – mass of adsorbent, g
- V – volume of solution, L
- k_1 – first order adsorption rate constant
- k_2 – second order adsorption rate constant
- v – adsorption rate of Cr(VI), mg h⁻¹
- K_F – Freundlich isotherm constant, mg L^{1/n} g⁻¹ mg^{-1/n}
- $1/n$ – Freundlich isotherm constant
- K_L – Langmuir isotherm constants, L mg⁻¹
- Q_0 – adsorption capacity of adsorbent, mg g⁻¹
- R^2 – correlation coefficient

List of abbreviations

- FOAE – ferric oxyhydroxide on anion exchanger
- EBPR – enhanced biological phosphorus removal
- ICP-AES – Inductively coupled plasma atomic emission spectroscopy
- TEM – transmission electron microscopy
- EDAX – energy dispersive X-ray
- XRD – X-ray diffraction

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