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Removal of Cr(VI) from wastewater by FeOOH supported on Amberlite IR120 resin

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ABSTRACT

Resin-supported FeOOH (R-FeOOH) was synthesized by the chemical reaction of Fe^{3+}-exchange resin with H_2O_2. R-FeOOH was characterized with scanning electron microscopy and X-ray powder diffraction. The optimum R-FeOOH was synthesized in the presence of 0.5 mol/L Fe^{3+} and 0.09 mol/L H_2O_2. Then, R-FeOOH was employed to remove Cr(VI) from aqueous solutions under different conditions. The results indicated that the removal efficiencies of Cr(VI) were all over 98% for initial Cr(VI) concentration of 20.0 mg/L at initial pH of 2.0, 3.0, 5.0, and 7.0, with R-FeOOH dose of 15.0 g/L after reaction for 120 min. The Cr(VI) removal efficiency can attain 100% at pH 3.0 after reaction for 90 min. Besides, a test on the reuse of the R-FeOOH was conducted. The removal of Cr(VI) by R-FeOOH was through adsorption, ion exchange, and reduction. R-FeOOH can be an effective agent for Cr(VI) removal from wastewater.

Keywords: Cr(VI) wastewater; Resin; FeOOH; Supported; R-FeOOH; Removal efficiency

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1. Introduction

Chromium is released into the environment mainly from the industries such as mining, leather tanning, dye, electroplating, steel, metal alloys, photographic material, and metal corrosion inhibition [1]. Chromium usually exists in both hexavalent (Cr(VI)) and trivalent (Cr(III)) forms in aqueous system. Cr(VI), existing in chromate (CrO_4^{2-} and $HCrO_4^-$), is particularly concerned because of its acute toxicity and carcinogenic effect on biological systems [2–4]. The permissible limit of Cr(VI) in inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L [3,5]. In contrast, Cr(III) is less toxic and could be a nutrient for the proper functioning of humans at low concentrations [3,6].

Removal of Cr(VI) from wastewater is studied by many researchers. Available methods for the removal of Cr(VI) from wastewater are reduction followed by precipitation [7], adsorption [8], electrocoagulation [9], membrane separation processes [10], and bioremediation [6]. Among the various treatment techniques, adsorption is considered as one of the most attractive methods [11]. The selection of an ideal adsorbent plays an important role in the removal of Cr(VI) from wastewater. Various adsorption materials have been reported to remove Cr(VI) from wastewater, such as

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modified biosorbent [12], nanoscale zero-valent iron [13], and iron oxides [14]. In recent years, the iron oxides have attracted attention due to their unique applications in adsorption [11,15,16].

FeOOH is a type of iron oxy-hydroxide [17]. FeOOH nanomaterials have been widely used as sorbents [18–21] and catalysts [22–24]. However, FeOOH is always present as fine or ultrafine particles, which cannot be appropriately employed in practical use. In addition, the hydroxyl groups on the surface of the FeOOH nanoparticles are easy to attract one another through hydrogen bonds and thus they get agglomerated [19]. These drawbacks have hindered the reaction of the FeOOH nanoparticles with other compounds. In order to overcome the problems of agglomeration, the nanoparticles are usually supported on activated carbon [24], fly ash [25], graphene [26], and resin [27,28]. Wang et al. [27] reported the preparation of FeOOH nanoparticles supported on macroporous acid resins and found that the resulting nanocomposites possessed high catalytic activity in hydroxylation of phenol with H_2O_2. Besides, Zhao et al. [28] synthesized the FeOOH supported on resin and explored its catalytic activity for the degradation of 17β-estradiol in the presence of H_2O_2 under relatively weak irradiation. However, FeOOH supported on resin to treat heavy metal wastewater is rarely reported.

In this paper, FeOOH supported on a cation-exchange sulfonated polystyrene resin was synthesized and used to remove Cr(VI). Amberlite IR120 was selected as the model of cation-exchange resin. Amberlite IR120 resin-supported FeOOH was prepared through the chemical reaction of Fe^{3+} ions which were ion exchanged into the resin, with H_2O_2. Resin-supported FeOOH was shortened as R-FeOOH in this paper. The feasibility of removal of Cr(VI) from aqueous solutions by R-FeOOH was examined in batch experiments. The effects of Fe^{3+} concentration, H_2O_2 concentration on the synthesis of R-FeOOH, and initial pH and resin dosage on Cr(VI) removal were investigated. The recycling and reuse of R-FeOOH was also evaluated.

2. Materials and methods

2.1. Materials

All chemical regents were of analytical regent grade and were used without further purification. All solutions were prepared using the distilled water. A stock solution of chromium was prepared by dissolving $K_2Cr_2O_7$ to a final concentration of 1.0 g/L of chromium. Solutions used during the experiment were prepared by diluting the stock solution to the desired concentration daily.

The resin obtained from Tianjin Beilian Fine Chemicals Development Co., Ltd is a strong acid cation-exchange resin composed of sulfonated polystyrene marked by Amberlite IR120. Its structure parameters were as follows: shape, bead; size, 0.3–1.2 mm; exchange capacity, 4.4 mmol/L; water content, 45–55%; ionic forms available, Na^+. The fresh resins were transformed from Na^+ ions into H^+ ions after treatment with 1.5 mol/L HCl and then washed with distilled water before use.

2.2. Synthesis of R-FeOOH

R-FeOOH was prepared according to the adapt method in the literature [27]. Five grams of resin was placed in a 250-ml wide-mouth bottle. The resin was mixed with 50 mL of 0.5 M $FeCl_3$ solution. The mixtures were shaken by a water-bathing constant temperature vibrator (SHA-B, Changzhou) for 40 min to obtain desired ion-exchange amounts for ferric ion and the resin. Then, the exchanged resin was washed with distilled water three times to remove the residual Fe^{3+} ions. Fifty milliliters of a certain concentration of H_2O_2 was added subsequently and the mixtures were shaken for 1.0 h. Finally, the synthesized R-FeOOH was obtained by filtration, rinsed with distilled water, and dried in a desiccator for future use.

2.3. Batch experiments

The batch experiments for the removal of Cr(VI) were performed in flasks at room temperature. R-FeOOH particles were added to the flasks containing 200 mL of 20.0 mg/L Cr(VI) aqueous solution. The reaction solutions were stirred at 130 rpm by a water-bathing constant temperature vibrator for 120 min. The solutions were periodically sampled. The influence factors in the synthesis of R-FeOOH, and the effects of resin amount and pH values on Cr(VI) removal were evaluated. During the reaction, the pH was not controlled. All the experiments were conducted at least in triplicate, and average values along with one standard deviation were presented.

The reuse of R-FeOOH was evaluated as follows: after R-FeOOH reacted with Cr(VI) solution for 120 min, filtration was performed to obtain solid–liquid separation. The used R-FeOOH was washed with distilled water for three times, and then it was reused to remove Cr(VI).

2.4. Analytical methods

The morphology of the as-prepared samples were observed under a scanning electron microscope (S-3400 N, Hitachi Co., Japan), using an operating voltage of 15.0 kV. X-ray diffraction (XRD) patterns of the samples were performed using an X-ray powder diffractometer (XD-2, Purkinje General Instrument Co., Ltd, Beijing, China) that employed Cu Kα radiation. The accelerating voltage and applied current were 36 kV and 20 mA, respectively. Cr(VI) concentration was determined with 1,5-diphenylcarbazide at 540 nm, using a UV-2400 spectrophotometer (Shanghai, China). Fe^{2+} concentration in solutions was determined using 1,10-phenanthroline method [29]. pH values were measured using a PHS-3C pH meter (Shanghai, China).

3. Results and discussion

3.1. Preparation and characterization of R-FeOOH

The resin used in this study is a strong acid sulfonated polystyrene cation-exchange resin. There are a lot of $-SO_3H$ functional groups in the pore walls. The resin can ion exchange with Fe^{3+} and form $(R\text{-}SO_3)_3Fe$ (Eq. (1)). Then, the Fe^{3+} ions in resin can react with H_2O_2 and thus the R-FeOOH formed (Eq. (2)):

$$3R\text{-}SO_3H + Fe^{3+} \rightarrow (R\text{-}SO_3^-)_3Fe^{3+} + 3H^+ \quad (1)$$

$$\begin{aligned}(R\text{-}SO_3^-)_3Fe^{3+} + 6H_2O_2 &\rightarrow 4H_2O + 3O_2 + 3H^+ \\ &+ \left(R\text{-}SO_3^-\right)_3{-}FeOOH \text{ (marked as R-FeOOH)}\end{aligned} \quad (2)$$

Fig. 1 shows the scanning electron microscopy (SEM) images of the (a) original resin, (b) R-FeOOH, (c) R-FeOOH before reaction, and (d) after reaction. From this figure, it can be seen that an appreciable amount of protuberance sprang up on the preformed smooth surfaces (Fig. 1(b) and (c)). The protuberance may be attributed to the fact that the FeOOH was supported on the surface of the resin. After R-FeOOH reaction with Cr(VI), the rough surface with holes becomes more caked (Fig. 1(d)), indicating that the FeOOH particles might be bonded by chromate ions.

The XRD patterns of R-FeOOH and R-FeOOH after reaction with Cr(VI) were also performed in the study. Based on the XRD results, no distinct XRD diffraction peaks of FeOOH were observed, which was presumably due to its amorphous structure. In addition, the peaks of chromium could hardly be observed, possibly because the amount of chromium in the resin was small.

3.2. Cr(VI) removal by R-FeOOH

It has been proposed that the FeOOH can be used as adsorbents because of its adsorption ability for contaminants. The removal of Cr(VI) by R-FeOOH is shown in Fig. 2. According to the references [20,21,28], the R-FeOOH surface can be protonated ($-OH_2^+$) under acid solutions (Eq. (3)), and the negatively charged $Cr_2O_7^{2-}$ or $HCrO_4^-$ ion can come to the R-FeOOH surface due to electronic attraction. So, the enriched $Cr_2O_7^{2-}/HCrO_4^-$ ion would exchange with the hydroxyl groups (Eq. (4)) on the surface of R-FeOOH and promote the adsorption process [20].

$$R\text{-}FeOOH + H^+ \rightarrow R\text{-}FeOOH_2^+ \quad (3)$$

$$R\text{-}FeOOH_2^+ + HCrO_4^- \rightarrow R\text{-}FeO(HCrO_4) + H_2O \quad (4)$$

Besides, according to the previous studies by Abdel-Samad and Watson [30], and Otte et al. [31], the FeOOH contained some Fe^{2+} ions at least in the surface layer. To confirm the Fe^{2+} ions existing in the synthesized R-FeOOH, the possible leaching of Fe^{2+} ions from R-FeOOH was determined with 1.5 g of R-FeOOH soaked in 100 ml of distilled water at pH 3.0. After soaked for 1.0 h, the Fe^{2+} concentration was about 12 mg/L. So, the prepared R-FeOOH contains some Fe^{2+} ions. Fe^{2+} ions can reduce Cr(VI) through Eq. (5):

$$3Fe^{2+} + HCrO_4^- + 7H^+ \rightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O \quad (5)$$

So, three mechanisms play roles in the Cr(VI) removal by R-FeOOH, that is, R-FeOOH removed Cr(VI) from wastewater by adsorption, ion exchange, and reduction.

3.2.1. Influence factors in the synthesis of R-FeOOH on the removal of Cr(VI)

3.2.1.1. Effect of Fe^{3+} concentration. Fe^{3+} concentration is an important factor that influences the synthesis of R-FeOOH. So, the effect of Fe^{3+} concentration in the synthesis of R-FeOOH on Cr(VI) removal was examined and the results are shown in Fig. 3. It was clear that the Cr(VI) removal efficiencies increased with the increasing Fe^{3+} concentration. A Fe^{3+} concentration of 0.3 mol/L was associated with Cr(VI) removal efficiency of 93.6%. When Fe^{3+} concentrations increased to 0.5 mol/L, the Cr(VI) removal efficiencies were above 98% after the reaction for 90 min. With an

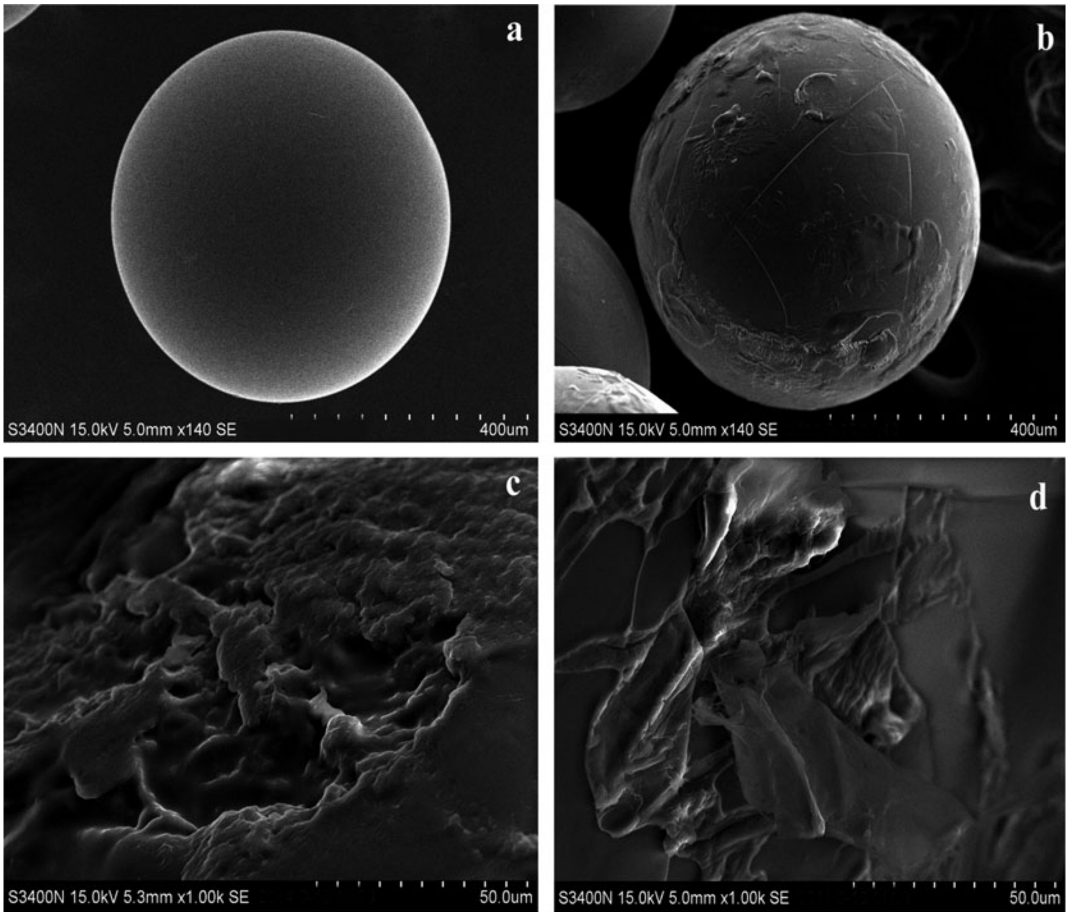

Fig. 1. SEM images of: (a) Resin (×140), (b) R-FeOOH (×140), (c) R-FeOOH (×1,000), and (d) R-FeOOH after reaction with Cr(VI) solution (×1,000).

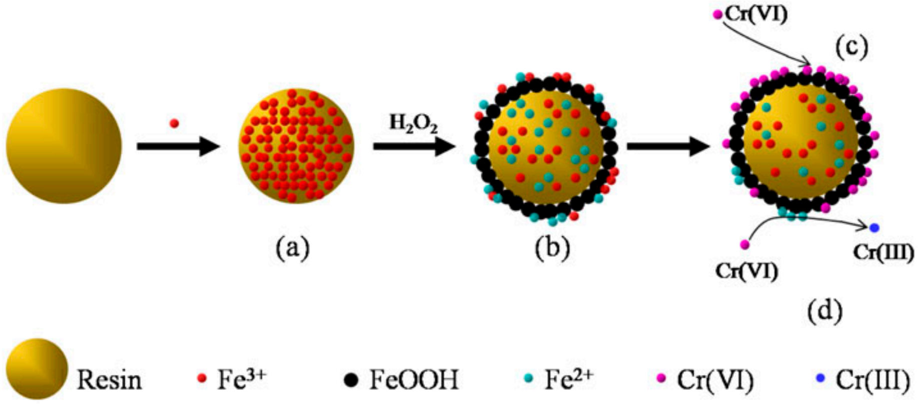

Fig. 2. Schematic of the synthesis of R-FeOOH and Cr(VI) removal mechanism by R-FeOOH: (a) resin was ion exchanged with Fe^{3+}, (b) resin–Fe^{3+} reacted with H_2O_2 and formed R-FeOOH, (c) Cr(VI) can be adsorbed and ion exchanged on the surface of R-FeOOH, and (d) Cr(VI) was reduced according to the equation: $3Fe^{2+} + HCrO_4^- + 7H^+ \rightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O$.

increase in the Fe^{3+} concentration, more FeOOH can support on the resin, so there are more reaction active sites for Cr(VI) with R-FeOOH. Hence, the Cr(VI) removal efficiencies increased with increasing Fe^{3+} concentration. In the following experiment, the optimum Fe^{3+} concentration was selected as 0.5 mol/L.

3.2.1.2. Effect of H_2O_2 concentration. The Fe^{3+} ions exchanged on the resin can react with H_2O_2 and form FeOOH particles. The effect of H_2O_2 concentration in the synthesis of R-FeOOH on Cr(VI) removal efficiency is shown in Fig. 4. The Cr(VI) removal efficiency increased significantly with an increase in the H_2O_2 concentration. With the H_2O_2 concentration increasing from 0.05 to 0.09 mol/L, the removal efficiency of Cr(VI) increased significantly from 46.8 to 97.8%. The result indicated that the concentration of H_2O_2 was proportional to the Cr(VI) removal. So the optimal H_2O_2 concentration was selected for 0.09 mol/L.

3.2.2. Influence factors on the Cr(VI) removal by R-FeOOH

3.2.2.1. Effect of initial pH on the removal of Cr(VI). The effect of solution pH on Cr(VI) removal was investigated and the results are shown in Fig. 5. At initial pH values of 2.0, 3.0, 5.0, and 7.0, the Cr(VI) removal efficiencies were all over 98% after 120 min, but the lower solution pH value was beneficial for Cr(VI) removal. At 90 min, the Cr(VI) removal efficiency can attain 100% at pH 3.0. With the variation in pH, the surface of R-FeOOH changed and formed $-OH_2^+$, $-OH$, or $-O^-$ [28,32], and the surface functional group $FeO\text{-}OH_2^+$ was more efficient than $FeO\text{-}O^-$ to adsorb Cr(VI) [21]. At low pH value, hydroxyl groups existing on the surface of R-FeOOH can be protonated and formed $-OH_2^+$ (Eq. (3)), which favored the electrostatic attraction force with negatively charged $HCrO_4^-$ (Eq. (4)). So, the ion exchange between the hydroxyl groups and Cr(VI) was promoted. Besides, acid conditions favored the reduction of Cr(VI) to Cr(III) by Fe^{2+} (Eq. (5)), and hence favored the Cr(VI) removal. With an increase in the pH, the surface of R-FeOOH became negatively charged, which hindered Cr(VI) access to the surface of R-FeOOH, and hence prevented the sorption of Cr(VI). From the above results, the optimal removal of Cr(VI) was selected at pH 3.0.

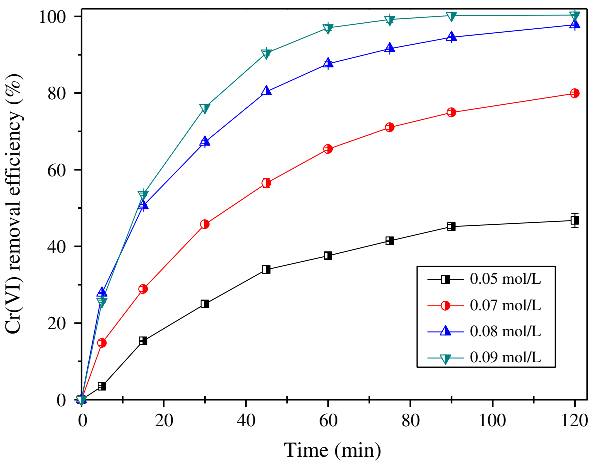

Fig. 4. Effect of H_2O_2 concentration on the Cr(VI) removal efficiency ($[Cr(VI)]_0 = 20.0$ mg/L, $[Fe^{3+}]_0 = 0.5$ mol/L, $[R\text{-}FeOOH]_0 = 15.0$ g/L, mixing rate = 130 rpm, $T = 25 \pm 2$°C at $pH_0 = 3.0$).

3.2.2.2. Effect of resin dose on removal of Cr(VI). Fig. 6 presents the effect of resin dosage ranging from 10.0 to 20.0 g/L on Cr(VI) removal. It was apparent that

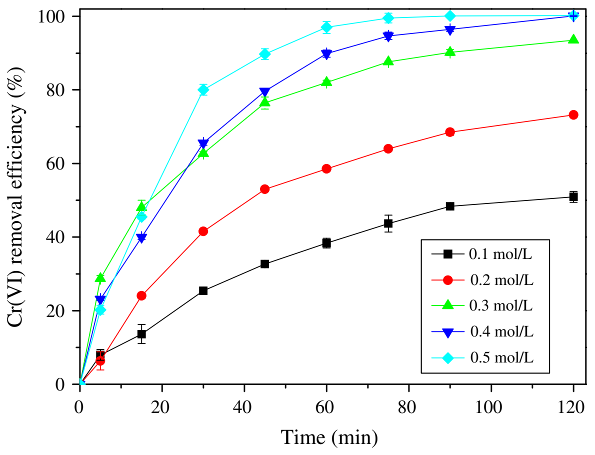

Fig. 3. Effect of Fe^{3+} concentration on the Cr(VI) removal efficiency by R-FeOOH ($[Cr(VI)]_0 = 20.0$ mg/L, $[H_2O_2]_0 = 0.09$ mol/L, $[R\text{-}FeOOH]_0 = 15.0$ g/L, mixing rate = 130 rpm, $T = 25 \pm 2$°C at $pH_0 = 3.0$).

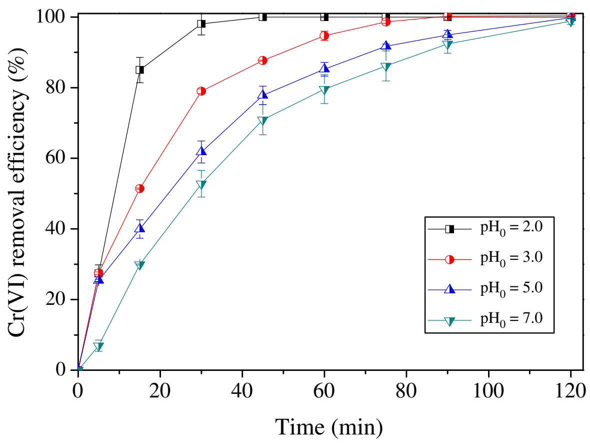

Fig. 5. Effect of initial pH on the Cr(VI) removal efficiency ($[Cr(VI)]_0 = 20.0$ mg/L, $[Fe^{3+}]_0 = 0.5$ mol/L, $[H_2O_2]_0 = 0.09$ mol/L, $[R\text{-}FeOOH]_0 = 15.0$ g/L, mixing rate = 130 rpm, $T = 25 \pm 2$°C).

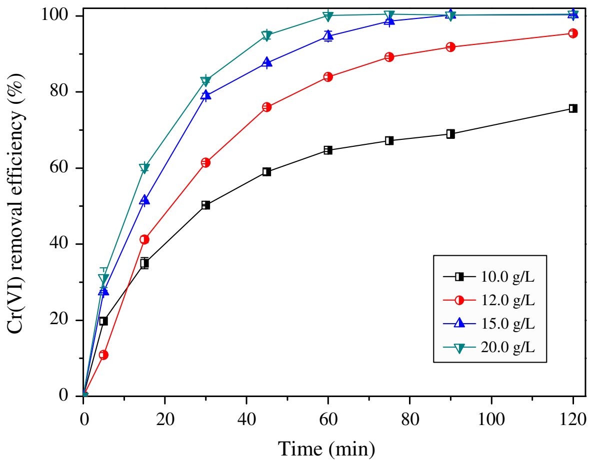

Fig. 6. Effect of resin dosage on the removal efficiency ($[Cr(VI)]_0 = 20.0$ mg/L, $[Fe^{3+}]_0 = 0.5$ mol/L, $[H_2O_2]_0 = 0.09$ mol/L, mixing rate = 130 rpm, $T = 25 \pm 2$℃ at $pH_0 = 3.0$).

the Cr(VI) removal increased with an increase in the resin dose. At higher R-FeOOH dosage, higher Cr(VI) removal efficiency was observed. Increasing the resin concentration from 10.0 to 12.0 g/L, the removal efficiency of Cr(VI) increased from 75.7 to 95.4%. When the resin dosage was 15.0 g/L, the Cr(VI) removal efficiency can attain 100%. It may be attributed that higher dosage of R-FeOOH with high resin dosage could provide more active sites for Cr(VI) removal. Considering the Cr(VI) removal efficiency and resin dosage, an optimum resin dosage of 15.0 g/L was required.

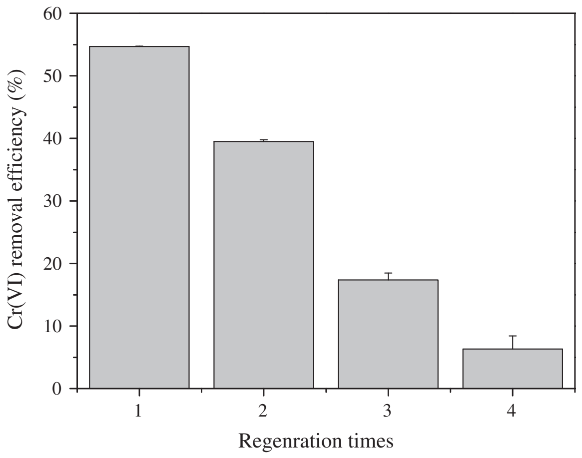

Fig. 7. Removal efficiencies of Cr(VI) by the recycled R-FeOOH ($[Cr(VI)]_0 = 20.0$ mg/L, $[R\text{-}FeOOH]_0 = 15.0$ g/L, $T = 25 \pm 2$℃ at $pH_0 = 3.0$).

3.3. Regeneration times

The effectiveness of R-FeOOH is strongly influenced by the reaction active sites on the surface of R-FeOOH. In this study, after the removal of Cr(VI), some of the active sites were occupied, which were adverse to the transport of Cr(VI) ions and decrease Cr(VI) removal during the second use of the R-FeOOH. To evaluate the reuse of R-FeOOH in Cr(VI) removal, R-FeOOH was repeatedly used for four times. The Cr(VI) removal efficiency by the reused R-FeOOH is shown in Fig. 7. After being reused 1, 2, 3, and 4 times, the Cr(VI) removal efficiencies were 54.7, 39.5, 17.4, and 6.3%, respectively. The R-FeOOH can be reused directly, but the removal efficiency decreased successively, which was attributed to the loss of some of the active sites of R-FeOOH and thus resulting in the decrease in Cr(VI) removal.

4. Conclusions

FeOOH can be successfully supported onto the surface of the Amberlite IR120 resin. The R-FeOOH can be used as an adsorbent for Cr(VI) removal, and it can be easily separated and collected after loading pollutants. The Fe^{3+} concentration and H_2O_2 concentration in the synthesis of R-FeOOH affected the Cr(VI) removal efficiencies significantly. Besides, the Cr(VI) removal efficiencies were obviously influenced by the initial pH and resin dosage. After reaction for 120 min, the removal efficiencies of Cr(VI) were all over 98% for initial Cr(VI) concentration of 20.0 mg/L at initial pH values of 2.0, 3.0, 5.0, and 7.0. Cr(VI) removal by R-FeOOH is through adsorption, ion exchange, and reduction. R-FeOOH may be an effective agent for the removal of Cr(VI) from contaminated water.

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