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Effect of synergistic sorption of Cr(VI) and Mn(II) in aqueous solution using magnetic nanoparticles

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ABSTRACT

In this study, the effect of synergistic sorption of Cr(VI) and Mn(II) in aqueous solution removal by synthetic magnetic nanoparticles (Fe_3O_4) was investigated. The results showed that individual removal of Cr(VI) and Mn(II) by Fe_3O_4 nanoparticles was evidently dependent on pH, and the optimum removal condition for Cr(VI) and Mn(II) was at pH 4 and pH 8, respectively. The removal of Cr(VI) with the pre-treated method was slightly higher than simultaneous method at pH 4. However, the removal of Cr(VI) with simultaneous method was significantly higher than pre-treated method at pH 8 of which the removal percentages were 84.9 and 21.5, respectively. At the same time, for the pre-treated and simultaneous method at pH 8, the equilibrium capacity of Mn(II) on Fe_3O_4 nanoparticles was changed from 36.8 to 49.7 $mg\,g^{-1} Fe_3O_4$. The XRD patterns after sorption indicated that there is some hematite formation on the Fe_3O_4 surfaces. Therefore, a redox process could happen in the Cr (VI) sorption on the Fe_3O_4 nanoparticles.

Keywords: Cr(VI); Mn(II); Fe_3O_4; Synergistic sorption

1. Introduction

Chromium is widely used in various industrial processes such as metal electroplating, corrosion protection, and leather tanning due to its unique properties. With its commonly used in industry, it is also one of the most toxic pollutants in soil, groundwater, and surface water. Chromium in the environment primarily exists in two valence states: Cr(VI) and Cr(III) [1–3]. Compared with Cr(III), Cr(VI) is highly mobile in aqueous environment and exerts more toxic effects on biological systems [4,5]. Highly exposed in Cr(VI) could cause some diseases, such as bronchogenic carcinoma, asthma, pneumonitis, and dermatitis [6]. The discharge of Cr(VI) to surface water is regulated below $0.05\,mg\,L^{-1}$ by the US EPA, and total Cr including Cr (III), Cr(VI) as well as its other forms is regulated below 2 mg/L [7]. Many conventional methods such as chemical precipitation [8], membrane separation [9], and adsorption [10] have been employed to remove Cr (VI) in industrial wastewater. Manganese, the second abundant metal in nature, is commonly used in ceramics, dry battery cells, and alloys. It is an essential metal for human system and many enzymes are activated by

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manganese [11]. However, manganese pollution in our environment has attracted more attention in the recent years because of its harmful effects to ecosystems and human beings [12,13]. Due to the uncontrolled disposal and untreated discharge of manganese into waters, some countries like China, Vietnam, and Cambodia are facing serious manganese contamination. There is a "manganese triangle" in the southeast of China where the manganese concentration is excessive to the standard regulation from ten to hundred times in water systems. Conventional treatment for manganese removal generally requires the use of strong oxidizing agents, such as potassium permanganate, chlorine, hypochlorite, chlorine dioxide, or ozone [14].

Sorption as an economical and readily available method could provide an effective treatment to remove heavy metals from aqueous solution. Some materials, such as zeolites, chitosan, activated carbon, iron oxide, and clay are being considered as low-cost adsorbents [15,16]. In the recent years, magnetic nanoparticles (Fe_3O_4) have attracted more attention as the effective adsorbents for the removal of heavy metals due to their large surface area, easy separation, and low-cost [17–19]. Cr(VI) sorption with Fe_3O_4 focus on optimal conditions, such as pH, temperature, and ratio of sorbent. Or some modification of magnetic nanoparticles to obtain desired functional group to remove Cr(VI) [20–22]. Some different metal ions effect in sorption focus on competitive effect such as Zn(II) and As(V) [23]. However, little is known regarding the effect of Mn(II) on the sorption process of Cr(VI) on magnetic nanoparticles. In this study, in order to investigate the presence of Mn(II) on the removal of Cr(VI) by magnetic nanoparticles and the mechanisms involved in the process, two different sorption patterns, namely the pre-treated sorption and the simultaneous sorption were designed, and compared with the individual sorption of Mn(II) or Cr (VI). TEM and XPS characterization of Fe_3O_4 before and after the treatment of Cr(VI) and Mn(II) was also conducted, and then possible mechanisms involved in these processes were discussed.

2. Materials and methods

2.1. Chemicals

Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous chloride ($FeCl_2{\cdot}4H_2O$), sodium hydroxide (NaOH), potassium bichromate ($K_2Cr_2O_7$), and manganese chloride ($MnCl_2{\cdot}4H_2O$) were of analytical grade and purchased from Tianjin Chemical Reagent Co. Ltd. All other chemicals were the analytic grade reagents commercially available and used without further purification. All solutions were prepared with distilled water.

2.2. Preparation of Fe_3O_4 nanoparticles

The preparation of Fe_3O_4 nanoparticles was described in our previous work [24]. In a typical synthesis, 10 mL of solution containing 1.22 g of $FeCl_3{\cdot}6H_2O$ and 0.5 g of $FeCl_2{\cdot}4H_2O$ was drop-wise added to 25 mL of degassed NaOH solution (1.3 M). During the experiment, the nitrogen gas was kept passing through the solution to prevent the oxidation of Fe^{2+} in the system. After kept at the room temperature for 8 h, the produced black solid powders were separated by a magnet, and washed with distilled water and ethanol thrice, respectively. The final products were dried in vacuum atmosphere at 60℃ for 10 h.

2.3. Kinetic experiments

A 0.3 g of Fe_3O_4 nanoparticles was added in 50 mL 0.1 M NaCl solution at desired pH values for 8 h to reach equilibrium before the addition of Cr(VI) and/or Mn(II). In order to investigate the effect of Mn(II) on the removal of Cr(VI), three kinetic experiments were designed and conducted as followed:

(i) Individual sorption of Cr(VI) or Mn(II) by Fe_3O_4 nanoparticles: 50 mL Fe_3O_4 nanoparticles suspension was mixed thoroughly with 100 mL of 0.15 g/L Cr(VI) or Mn(II) in 0.1 M NaCl solution, which had the same pH values as the Fe_3O_4 nanoparticles suspension. The mixtures were then placed on a shaker at 130 rpm at room temperature, and liquid solution samples (1.5 mL from each flask) were collected at regular intervals and analyzed for residual concentrations of Cr(VI).

(ii) Pre-treated sorption procedure: 50 mL Mn(II) solution of different concentration, 0.15, 0.3, and 0.6 g/L, at pH 4 or pH 8 was mixed with 50 mL Fe_3O_4 nanoparticles suspension with the same pH value for 12 h on a shaker at room temperature. Afterward, 50 mL of 0.3 g/L Cr(VI) solution with the same pH value was added subsequently into the mixture an d placed again on the shaker with the same operational conditions as mentioned above. The final ratios of Mn (II) to Cr(VI) were 1:2, 1:1, and 2:1.

(iii) Simultaneous sorption procedure: 50 mL Mn(II) solution of different concentration, 0.15, 0.3, and 0.6 g/L, at pH 4 or pH 8 was mixed with 50 mL of 0.3 g/L Cr(VI) solution rapidly, and pH value was adjusted to 4 or 8. The final ratios of Mn(II) to Cr(VI) were 1:2, 1:1, and 2:1. After adjustment, Cr(VI) and Mn(II) solution was mixed thoroughly with 50 mL Fe_3O_4 nanoparticles suspension with the same pH value. The mixtures were then placed on a shaker with the same operational conditions as mentioned above.

2.4. Characterization and analysis

XRD and TEM were performed on a type of D8 FOCUS diffractometer (BRUKER Co. Switzerland) with Cu ($K\alpha\lambda = 1.5406$ Å) radiation, and scanning range from 10° to 90° and transmission electron microscope (FEI, Tecnai G2 F20) with an accelerating voltage of 200 kV. The magnetization curve of the Fe_3O_4 nanoparticles was measured on a VSM 6900-1 (LDJ Electronics Co. US) at room temperature. Surface area measurement was taken with a Brunauer-Emmett-Teller (BET) analyzer (Gemini V, Micrometrics Co. US) at liquid nitrogen temperature using conventional gas sorption apparatus. Cr(VI) in liquid solution was determined according to the standard method described by Clesceri method [25]. The absorbance of the purple complex formed from reacting Cr(VI) with 1,5-diphenylcarbohydrazide was measured at $\lambda = 540$ nm by a UV spectrophotometer (Shimadzu, UV-1201). Mn(II) and total Cr(VI) concentration was determined by atomic absorption spectroscopy (Shimadzu, AA-6501).

3. Results and discussion

3.1. Characterization of Fe_3O_4 nanoparticles

The XRD pattern of Fe_3O_4 nanoparticles was shown in Fig. 1. There had six characteristic peaks for Fe_3O_4 ($2\theta = 30°, 36°, 43°, 53°, 57°$, and $62°$), marked by their indices ((2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0)). These peaks were consistent with the database in the JCPDS file (PDF standard cards, JCPDS 88–0315). The TEM image shown in Fig. 2 indicates that the Fe_3O_4 nanoparticles with a mean diameter of 10 nm. Fig. 3 shows magnetization curves of Fe_3O_4 nanoparticles as-prepared. As shown in Fig. 3, the magnetization curves revealed the magnetic nanoparticles were superparamagnetic at room temperature. The magnetization saturation values were measured to be 80.7 emu g^{-1}. It could be concluded that Fe_3O_4 nanoparticles could be separated easily with magnetic field. BET analysis revealed the surface area for the Fe_3O_4 nanoparticles was 105 m^2/g.

3.2. Individual sorption of Cr(VI) by Fe_3O_4 nanoparticles

The kinetics of Cr(VI) sorption by Fe_3O_4 nanoparticles was studied under the different pH value. It could be seen that a rapid removal of Cr(VI) took place in the first 1 h, and the rate became level off thereafter (Fig. 4). The equilibrium time was about 10 h. As seen from Fig. 4, the effect of pH value on the Cr(VI) sorption process was significant. Compared with the high pH value, low pH value could enhance the Cr(VI) removal percentages. At initial pH 4, 6, 7, and 8, the Cr(VI) removal percentages were 55.1, 45.1, 36.8, and 27.2%, respectively. Previous results also reported that the pH value had a significant effect on Cr(VI) removal under the experimental conditions [26]. As demonstrated in

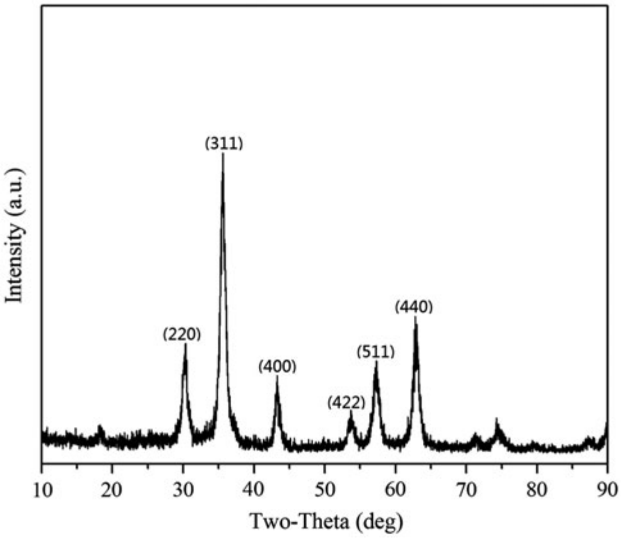

Fig. 1. XRD pattern of Fe_3O_4 nanoparticles.

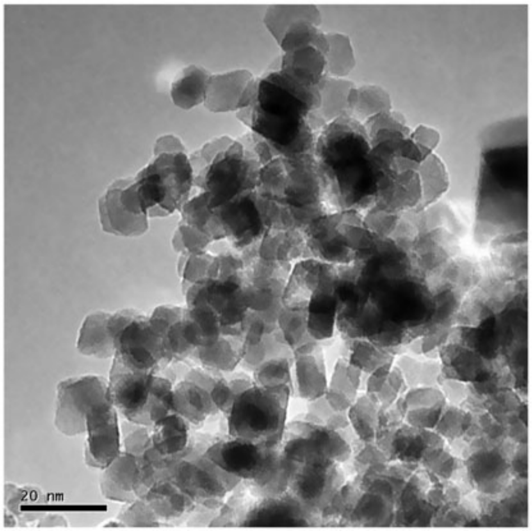

Fig. 2. TEM image of Fe_3O_4 nanoparticles.

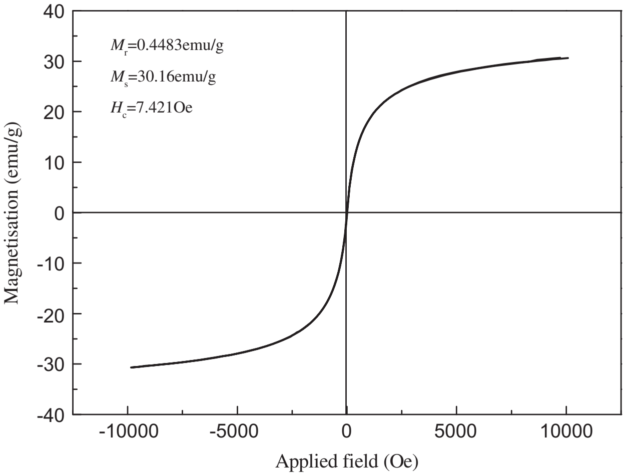

Fig. 3. Hysteresis loop of Fe_3O_4 nanoparticles at room temperature.

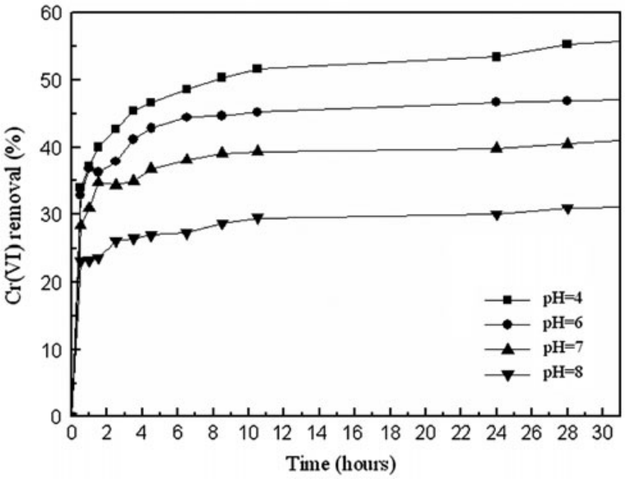

Fig. 4. Kinetic study of Cr(VI) absorption under different pH values. Initial concentrations of Cr(VI) and Fe_3O_4 nanoparticles were 100 mg/L and 2 g/L, respectively.

Fig. 5, Cr(III) appeared gradually with the removal of Cr(VI), indicating that the Cr(VI) adsorbed on the Fe_3O_4 nanoparticles reduced to Cr(III). The amount of Cr(VI) removed from the solution was more than the amounts of Cr(III) detected, suggesting that not all of the absorbed Cr(VI) was reduced to Cr(III), some of the reduced Cr(III) was released into the solution while some adsorbed on the Fe_3O_4 nanoparticles. The FTIR and XRD of Fe_3O_4 nanoparticles after adsorption are shown in Fig. 6. As seen from Fig. 6(a), FT-IR spectrum of magnetic nanoparticles after adsorption exhibit the presence of remarkable Fe_3O_4 (574.23 cm^{-1}, 3423.48 cm^{-1}) [27]. While the band at 632.02 cm^{-1} was attributed to the Cr–O–Cr group [28]. The bands at 1086.07 cm^{-1} and 1,250–1,700 cm^{-1} are associated with stretching of the CrO_4^{2-} and $Cr(OH)_3$ [29]. As shown in Fig. 6(b), after Cr(VI) adsorption process, there some hematite (Fe_2O_3) peaks occurred on the magnetic nanoparticles. These results indicated the formation of hematite on Fe_3O_4 surfaces. Therefore, there is a redox process happen in the Cr(VI) sorption on the Fe_3O_4 nanoparticles. Similar results are also reported in previous studies [30,31].

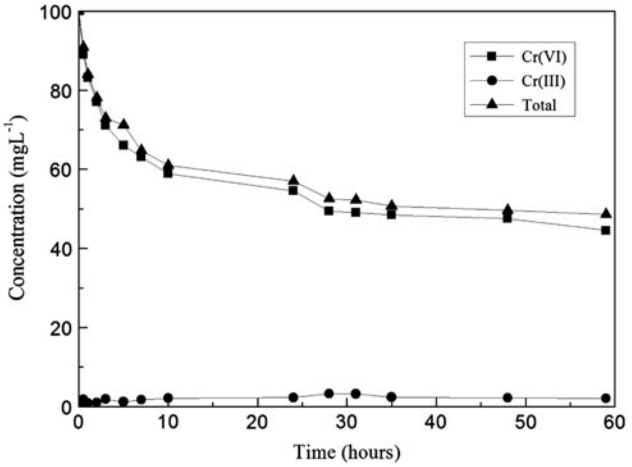

Fig. 5. Cr species and distribution in solution during the process of Cr(VI) removal. Initial concentrations of Cr(VI) and Fe_3O_4 nanoparticles were 100 mg/L and 2 g/L, respectively.

3.3. Individual sorption of Mn(II) by Fe_3O_4 nanoparticles

The kinetics of Mn(II) sorption by Fe_3O_4 nanoparticles was studied under different pH values. The sorption capacity is shown in Fig. 7. During the first 2 h, Mn(II) in solution was adsorbed on Fe_3O_4 nanoparticles surface rapidly. The equilibrium time at the different pH value was about 3 h, which was shorter than Cr(VI) sorption. Similar to Cr(VI) sorption, pH value has a significant effect on the Mn(II) sorption process. However, the effect trend was contrary, which indicated that the high pH value had a better Mn(II) sorption capacity. At initial pH 4, 6, and 8, the Mn(II) sorption capacity were 8.5, 14.6, and 36.8 mg. g^{-1} Fe_3O_4, respectively.

3.4. Cr(VI) sorption by pre-treated method with Fe_3O_4 nanoparticles

In order to investigate the effect of pH on Cr(VI) sorption with pre-treated method by Fe_3O_4 nanoparticles, two levels of pH 4 and pH 8 were studied. Fig. 8 shows the removal of Cr(VI) under different ratio of

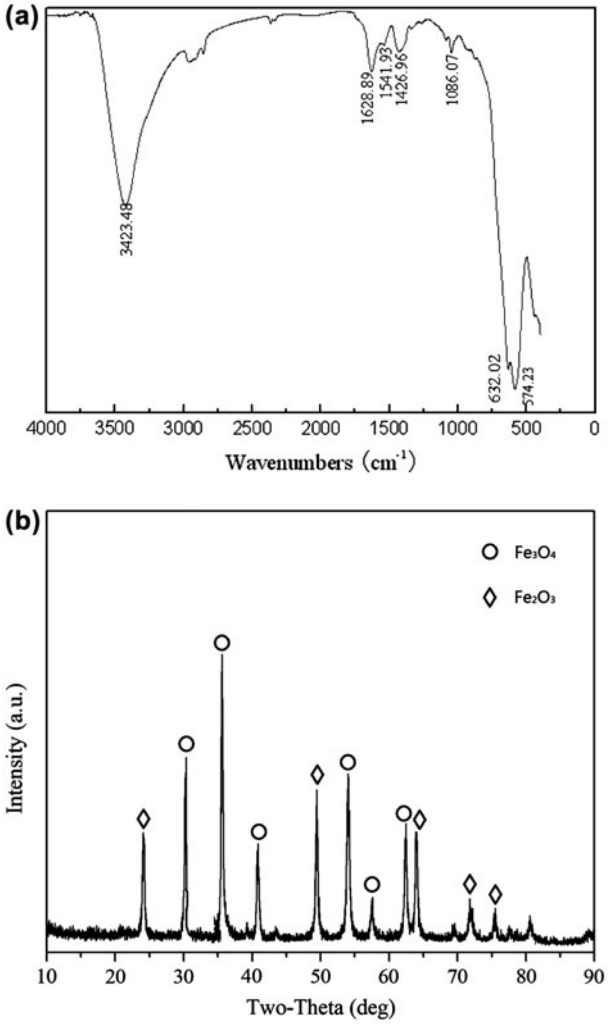

Fig. 6. Infra-red spectra (a) and XRD (b) of Fe_3O_4 nanoparticles after Cr(VI) adsorption.

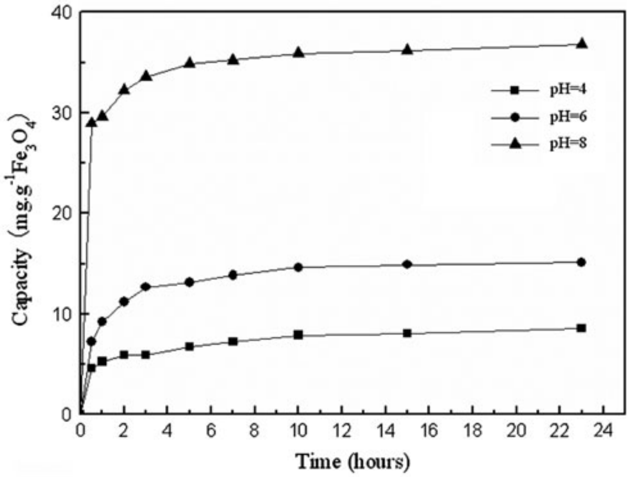

Fig. 7. Kinetic study of Mn(II) absorption under different pH values. Initial concentrations of Mn(II) and Fe_3O_4 nanoparticles were 100 mg/L and 2 g/L.

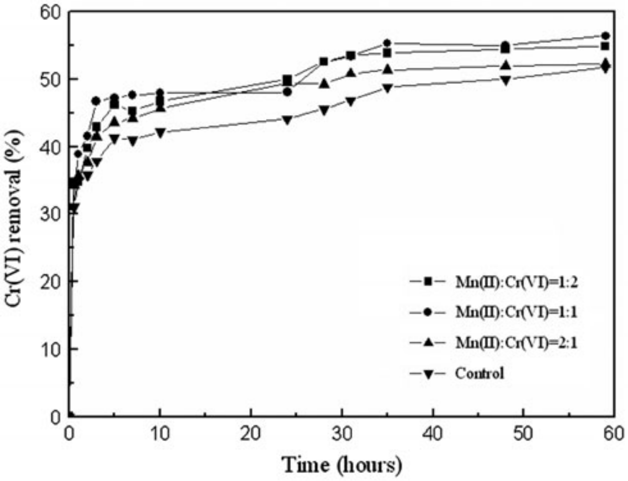

Fig. 8. pH = 4, kinetic study of Cr(VI) removal with pretreated method under different ratio of Mn(II) and Cr(VI).

Mn(II) and Cr(VI) with pH 4. It was found that the removal of Cr(VI) was slightly higher than the control under the experimental conditions. The removal percentage were at 54.3, 55.1, 48.7, and 47.5% under the ratio of Mn(II) and Cr(VI) 1:2, 1:1, 2:1 with the control, respectively. Fig. 9 shows the removal of Cr(VI) under the different molar ratio of Mn(II) and Cr(VI) with the control at pH 8. As seen from Fig. 9, the removal of Cr(VI) was slightly lower than the control under the experimental conditions. The removal percentage were at 13.8, 21.3, 21.5, and 24.3 under the ratio of Mn(II) and Cr(VI) 1:2, 1:1, 2:1 with the control, respectively. Cr(VI) forms $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, $HCr_2O_7^-$ and H_2CrO_4 in solution, and the relative proportion of each species depends on both pH and Cr(VI) concentration [6]. At pH 4, $HCrO_4^-$ should be the dominant Cr(VI) species in solution. Mn^{2+} mainly exists as a positive ion in the solution and Mn^{2+} pre-adsorbed on Fe_3O_4 nanoparticles is favorable for Cr(VI) due to the electrostatic attraction between Mn^{2+} and $HCrO_4^-$. While at pH 8, there is too much amount of Mn^{2+} pre-absorbed compared with pH 4. The absorbed Mn^{2+} took place at the most sorption sites and hence the effect of Cr(VI) removal decreased. Similar results are reported in previous research [32].

3.5. Cr(VI) sorption by simultaneous method with Fe_3O_4 nanoparticles

To investigate the effect of pH on Cr(VI) sorption with Fe_3O_4 nanoparticles by simultaneous sorption method, acidic condition of pH 4 and basic condition of

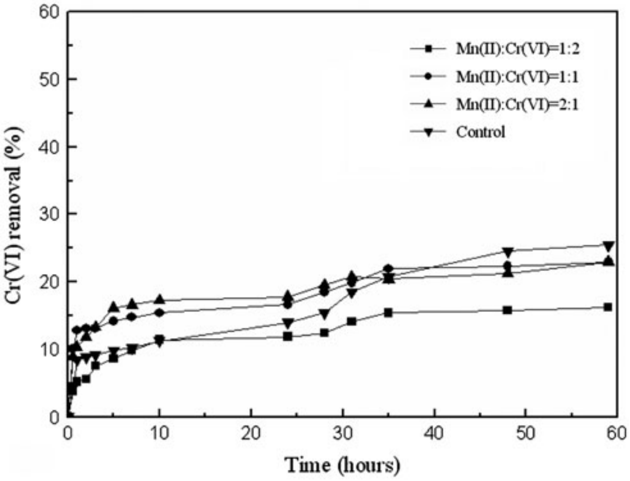

Fig. 9. pH = 8, kinetic study of Cr(VI) removal with pre-treated method under different ratio of Mn(II) and Cr(VI).

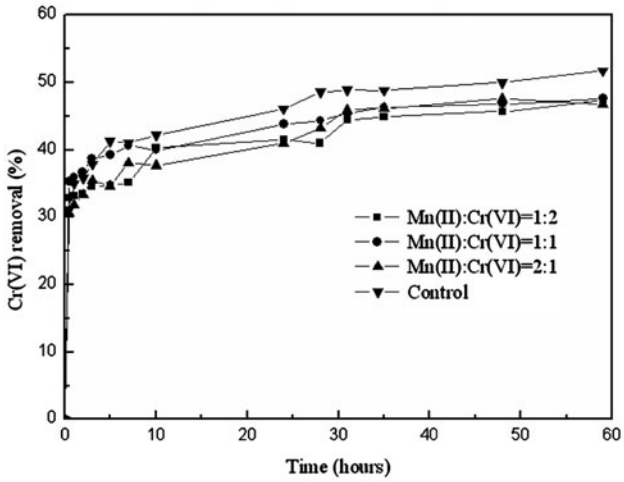

Fig. 10. pH = 4, kinetic study of Cr(VI) removal with simultaneous method under different ratio of Mn(II) and Cr(VI).

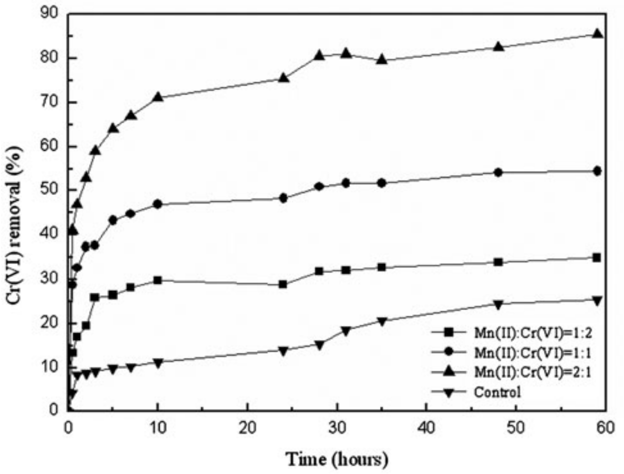

Fig. 11. pH = 8, kinetic study of Cr(VI) removal with simultaneous method under different ratioes of Mn(II) and Cr(VI).

pH 8 were studied. Figs. 10 and 11 shows the removal of Cr(VI) under the different ratio of Mn(II) and Cr(VI) with the control at pH 4 and pH 8. As seen from Fig. 10, the Cr(VI) removal percentage were 44.3, 44.9, 44.1, and 47.5 at the ratio of Mn(II) and Cr(VI) 1:2, 1:1, 2:1 with the control, respectively. The removal of Cr(VI) was slightly lower than the control under the experimental conditions, similar to the pre-treated method sorption at pH 8. However, under the simultaneous method at pH 8, the Cr(VI) removal was significantly higher than the control. The removal percentages of Cr(VI) in the simultaneous sorption method were 31.3, 49.8, and 84.9% at the ratio of Mn(II) and Cr(VI) 1:2, 1:1, and 2:1, respectively. Compared with the control, the removal percentages increased by 28.8, 104.5, and 249.4% at the ratio of Mn(II) and Cr(VI) 1:2, 1:1, and 2:1, respectively. At the same time, it could be seen that the simultaneous method at pH 8 had the maximum Mn(II) q_e of 49.75 mg g^{-1}Fe$_3$O$_4$ from Table 1. The interesting results indicated that the presence of Mn(II) could contribute to the increased Cr(VI) removal in the solution due to more positive charges on the surfaces of Fe$_3$O$_4$ nanoparticles. Different cations have significant effects on the sorption process. Two cations with different charges were added into iron hydroxides solution could increase sorption percentage obviously in some pH condition. Grâfe et al. observed that Zn^{2+} increased the sorption of As(V) on goethite at pH 4.0 and 7.0. Masue et al. demonstrated that Ca^{2+} enhanced As(V) retention on iron hydroxides only at pH > 5 [23,33]. It could be, therefore, explained that more positive charges carried by Mn(II) on Fe$_3$O$_4$ nanoparticles at higher pH contributed to the increased sorption of the anionic Cr(VI).

Table 1
Fe$_3$O$_4$ nanoparticles equilibrium sorption capacity of Mn(II) under different sorption methods and pH values

	Pre-treated method q_e(mg g^{-1} Fe$_3$O$_4$)	Simultaneous method q_e(mg g^{-1} Fe$_3$O$_4$)	Control q_e(mg g^{-1} Fe$_3$O$_4$)
pH = 4	10.58	9.72	8.55
pH = 8	42.37	49.75	36.81

4. Conclusions

The present study revealed that Mn(II) had an important effect on Cr(VI) removal by magnetic nanoparticles under the different pH conditions. The individual sorption study indicated that magnetic nanoparticles as-prepared had a good sorption ability on both Cr(VI) and Mn(II). At the same time, solution pHs significantly affected the removal of Cr(VI) and Mn(II). On the other hand, our results suggested that the magnetic nanoparticles had a better sorption effect on Cr(VI) and Mn(II) by simultaneous method at basic condition than acidic condition. The method herein introduced could provide a potential application for the removal of Cr(VI) and Mn(II) or other heavy metal ions in aqueous environments.

Acknowledgments

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