Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1006259

57 (2016) 5592–5600
March

Taylor & Francis
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Removal of hexavalent chromium from wastewater by acid-washed zero-valent aluminum

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Received 6 August 2014; Accepted 22 December 2014

ABSTRACT

This paper deals with the treatment of hexavalent chromium (Cr(VI)) and its removal mechanism using acid-washed zero-valent aluminum (ZVAl). The acid-washed ZVAl before and after reaction was characterized by scanning electron microscope, X-ray diffraction, and X-ray photoelectron spectroscopy. The influence factors such as ZVAl loading, acid washing time, and pH values on Cr(VI) removal were studied. Cr(VI) removal by acid-washed ZVAl was also evaluated under different humic acid and Fe^{2+} concentrations. The removal of Cr(VI) was accelerated with increasing acid-washed ZVAl loadings and decreasing initial pH. The addition of humic acid inhibited the Cr(VI) removal, while Fe^{2+} significantly accelerated the Cr(VI) removal. More than 98% Cr(VI) was removed from synthetic wastewater containing 20.0 mg/L Cr(VI) in 180 min by 0.4 g/L acid-washed ZVAl at initial pH 2.0. Cr(VI) removal by acid-washed ZVAl is proved by reduction, not by adsorption. The remarkable capacity of acid-washed ZVAl in removing Cr(VI) from wastewater displays its potential application in the treatment of wastewater-containing Cr(VI).

Keywords: Cr(VI); Wastewater; Zero-valent aluminum; Removal; Humic acid; Fe(II)

1. Introduction

Chromium (Cr) is the 21st most abundant element in the earth's crust [1]. It is considered as a priority pollutant by the US Environmental Protection Agency, discharged from electroplating, metallurgy, leather tanning, textile dying, wood-preserving industries, and preparation of Cr chemicals [2,3]. The most common Cr species are hexavalent [Cr(VI)] and trivalent [Cr(III)]. Among them, Cr(VI) is tremendously toxic and a confirmed carcinogen, and its toxicity is 100 times greater than that of Cr(III). Furthermore, Cr(VI) is more water-soluble and mobile than Cr(III) in surface water and groundwater [4]. The maximum permissible limit of Cr(VI) in inland surface water is 0.1 mg/L and in domestic water supplies 0.05 mg/L set by the World Health Organization [5].

Therefore, it is imperative to adopt effective methods to remove Cr(VI) from wastewater before its discharging into water bodies. Pioneering works have been studied for the removal of Cr(VI) including chemical reduction [6–8], adsorption [9–11], and ion exchange [12,13], etc. By adsorption and ion exchange methods, Cr keeps its toxic hexavalent state. Chemical reduction of Cr(VI) to less toxic Cr(III) is a more effective remediation strategy which does not use or

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discharge any perilous chemicals. The successful chemical reduction of Cr(VI) depends on the reductants. The common reductants include zero-valent iron [14,15], $Na_2SO_3/FeSO_4$ [16], hydrogen sulfide [17], steel wool [18], pyrrhotite [19], and sulfite [20], etc. Among these reductants, zero-valent iron (ZVI) and its derivant technology including nanoscale zero-valent iron (nZVI) are most used and studied. For example, a combination of pillared bentonite with ZVI was studied in column experiments to enhance Cr(VI) removal and improve the longevity of Fe^0-based permeable reactive barriers [21]. Shi et al. [22] synthesized bentonite-supported nZVI to remove Cr(VI) from wastewater and found bentonite-nZVI could remediate electroplating wastewater with the removal efficiencies for Cr, Pb, and Cu > 90%. Němeček et al. [7] studied the ability of injection of nZVI to reduce Cr (VI) *in situ* conditions at the contaminated site of Kortan in Hradek nad Nisou, Czech Republic. They found the injection of nZVI resulted in a rapid decrease in concentrations of Cr(VI) and total Cr in the groundwater without any substantial effect on the chemical properties of the groundwater.

ZVI with higher efficiency of reducing Cr(VI) depends crucially on the easy transfer of electrons to Cr(VI). In this regard, zero-valent aluminum (ZVAl) can provide a far greater thermodynamic driving force for electron transfer compared to ZVI (Eqs. (1) and (2)).

$$Al^{3+} + 3e^- \rightarrow Al^0 (E^0 = -1.667\ \mathrm{V}) \quad (1)$$

$$Fe^{2+} + 2e^- \rightarrow Fe^0 (E^0 = -0.44\ \mathrm{V}) \quad (2)$$

Aluminum is the third most abundant element on earth and the most abundant metallic element. The electron-transfer capacity of ZVAl has already been exploited for the reductive conversion of nitrate to ammonia [23] and oxidative degradation of aquatic organic contaminants [24]. Though aluminum is an effective electron donor, the quick formation of aluminum oxides under neutral conditions limits its application as a reactive medium. Many studies focused on the reactivity enhancement methods; currently, acid washing for ZVAl is one of the method applied [25,26]. It has proved that the commercial ZVAl under acidic conditions demonstrated an excellent capacity to remove aqueous organic compounds [25,27] and perchlorate [26]. For example, Zhang et al. [25] demonstrated that ZVAl/H^+/air system under pH < 3.5 possessed a high capacity in removing aqueous acetaminophen. Lien et al. [26] studied the removal of perchlorate using acid-washed ZVAl in batch reactors and found approximately 90–95% of perchlorate was removed within 24 h in the presence of 35 g/L ZVAl at acidic pH (4.5 ± 0.2).

Previous studies focused on the application of ZVAl in organic contaminants degradation [24,25,27] and perchlorate removal [26]. In this study, the acid-washed ZVAl was employed to remove Cr(VI) from wastewater under ambient conditions. The main objective of this study is to evaluate the influence factors on Cr(VI) removal by acid-washed ZVAl under various operational conditions such as ZVAl loading, pH, humic acid, and Fe^{2+} concentrations. The optimal reaction conditions were discovered and reaction mechanism was also studied.

2. Experimental methods

2.1. Materials

The chemicals and reagents used in this study including ZVAl powders (99% purity, 20 μm, specific surface area 1.63 m^2/g), potassium dichromate, and humic acid (HA, fulvic acid ≥ 90%, Aladdin) were all of analytical grade. All solutions were prepared using distilled water. The glassware was acid-washed and rinsed before use. The Cr(VI)-containing simulated wastewater was prepared using potassium dichromate. All solutions were prepared using distilled water. Acid-washed ZVAl was prepared by soaking the Al metal in sulfuric acid solution with initial pH of 1.9 for 2 h.

2.2. Cr(VI) removal by acid-washed ZVAl

After acid washing, 100 mL of 40.0 mg/L stock solutions of Cr(VI) were added to the flasks containing acid-washed ZVAl to obtain a nominal initial concentration of 20.0 mg/L of Cr(VI). All reactions were carried out in 500-mL glass flasks with a total suspension volume of 200 mL under air conditions. Unless otherwise noted, temperature was fixed at 25 ± 2°C. The initial pH (pH_0) of the solutions was adjusted to the designated value with 1.0 M H_2SO_4 or NaOH solution. Reaction mixtures were constantly shaken in a thermostatic mechanical shaker at 175 rpm. Aliquots of 3.0 mL sample were periodically withdrawn. The samples were centrifuged and then determined the residual Cr(VI) concentration. Specific treatments including the effect of Fe^{2+} and HA on the Cr(VI) removal were evaluated. All the experiments were carried out in triplicates, and the average values along with one standard deviation were presented.

2.3. Analytical methods

The specific surface area of the ZVAl and acid-washed ZVAl was assessed by surface area analyzer (Gemini V2380, Micromeritics Co., USA). The morphology of the metal particles was observed under a scanning electron microscope (SEM S-3400 N, Hitachi Co., Japan), using an operating voltage of 15.0 kV. X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer (Siemens D5000) in a scanning range of 10–700 with a copper target tube radiation (Cu Ka) producing X-rays with a wavelength of 1.54056 Å. The surface composition of ZVI was detected by X-ray photoelectron spectroscopy (XPS, Amicus, Shimadzu Co., Japan). The oxidation reduction potential (ORP) was monitored with an ORP sensor connected to a pHS-3C pH meter. Cr(VI) concentration was quantified spectrophotometrically at 540 nm using 1,5-diphenylcarbazide in acid solution as the complexing agent for Cr(VI) [28]. pH values were measured with PHS-3C pH meter (Shanghai, China).

3. Results and discussion

3.1. Characterization of ZVAl, acid-washed ZVAl, and ZVAl after reaction with Cr(VI)

3.1.1. SEM

The morphology of ZVAl, acid-washed ZVAl, and acid-washed ZVAl after reaction with Cr(VI) was analyzed using SEM (Fig. 1). From the figure, the particles of the original ZVAl and acid-washed ZVAl were microscale. After acid washing, the ZVAl particles become slightly smaller, which can also be reflected from the increase in the specific area from original 1.63 to 2.50 m^2/g. After reaction with Cr(VI), the particles of acid-washed ZVAl were partly aggregated.

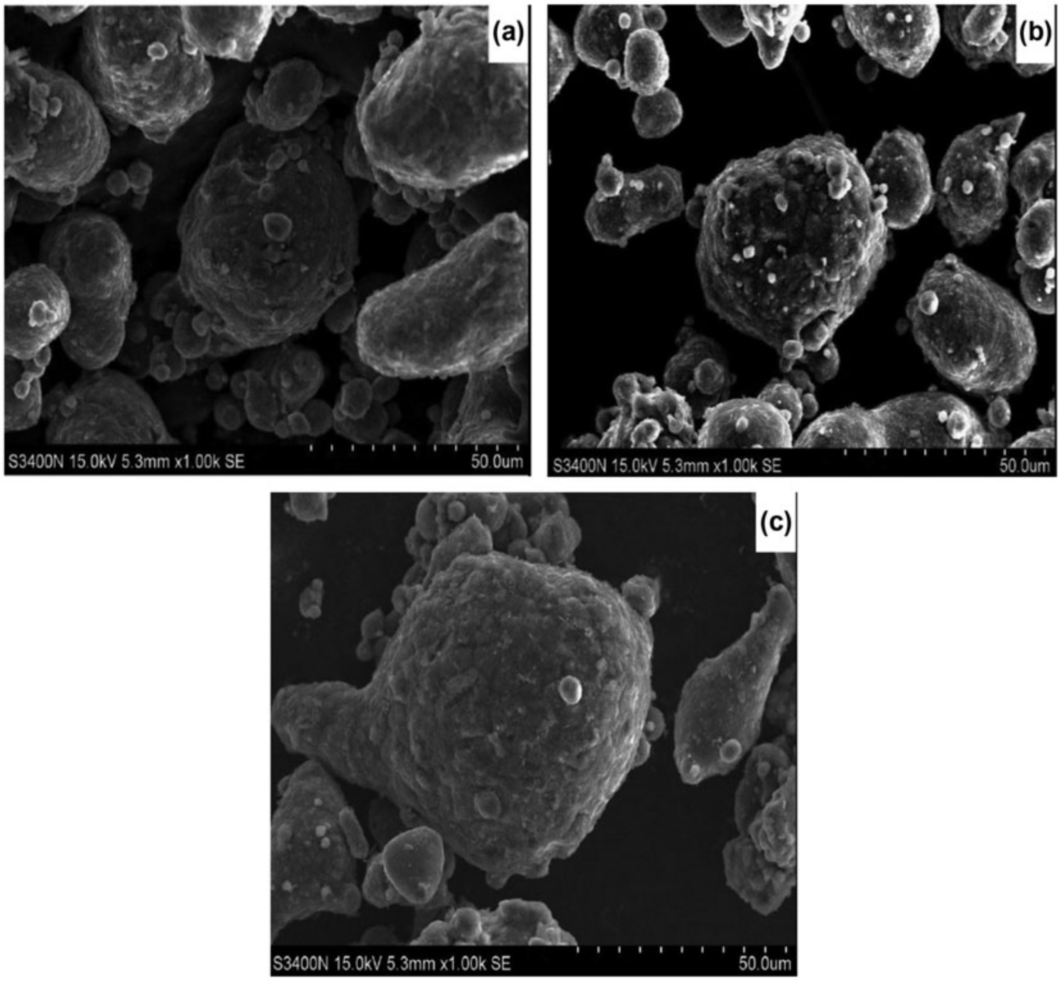

Fig. 1. SEM of (a) ZVAl, (b) acid-washed ZVAl, and (c) ZVAl after reaction with Cr(VI).

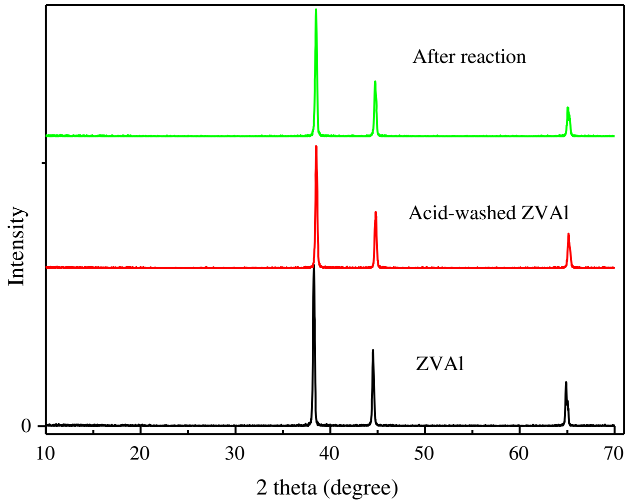

Fig. 2. XRD patterns of ZVAl, acid-washed ZVAl and ZVAl after reaction with Cr(VI).

3.1.2. XRD

The XRD patterns of the three particles are shown in Fig. 2. The characteristic peaks of aluminum appear at the diffraction angle (2θ) of 38.6, 44.9, and 65.2° where the main diffraction peak is located at 38.6°. Al patterns in ZVAl, acid-washed ZVAl, and acid-washed ZVAl after reaction were nearly same, which illustrated that the crystal phase of Al was stable in the whole reaction process. Due to the limitation of XRD technique to detect the phase below 2% volume fraction, other elements could not be detected.

3.1.3. XPS

The chemical composition of original ZVAl, acid-washed ZVAl, and acid-washed ZVAl after reaction was investigated by XPS. The atomic ratios of the three materials are summarized in Table 1. The XPS analysis of original ZVAl showed the presence of Al, O, and C on its surface. The surfaces of acid-washed ZVAl and after reaction were mainly covered by Al, O, and C, with relatively smaller amounts of N and S.

The characteristic peak of Cr(VI) located at 580 eV reported in the literatures [29] cannot be observed, indicating that there was no residual Cr(VI) existing on ZVAl surface. There is also no peak of Cr(III) because in the acid condition, there was no Cr(III) precipitates formed on ZVAl surface. So, the Cr element exists in the form of Cr(III) ions in solution. The XPS of Al 2p (Fig. 3) showed two peaks at the binding energies of 71.3 and 74.3 eV. According to the literature [30], the peak at low binding energy (71.3 eV) is assigned to the metallic contribution of aluminum, where the peak at higher binding energy (74.3 eV) was assigned to aluminum oxide structure (Al_2O_3). For the original ZVAl, there was nearly no metal aluminum observed, indicating the surface of ZVAl was covered by oxides. After acid washing, the peak of metal aluminum was found, but the intensity and peak area of the peak corresponding to Al metal were much lower than that of the Al_2O_3. So, the surface of acid-washed ZVAl was also covered partly by an aluminum oxide film.

3.2. Kinetics of Cr(VI) removal by acid-washed ZVAl

A pseudo-first-order kinetic model described as Eq. (3) was employed to determine the removal rate of Cr(VI) removal by acid-washed ZVAl.

$$C_t = C_0 \exp(-k_{obs}t) \tag{3}$$

where C_0 and C_t are the initial Cr(VI) concentration and Cr(VI) concentration at time t, respectively; k_{obs} is the observed rate constant of pseudo-first-order reaction (min^{-1}); and t is the time of reaction (min).

3.2.1. Effect of acid-washed ZVAl loading

Fig. 4 shows the influence of acid-washed ZVAl loading on the removal of Cr(VI). From the figure, Cr (VI) removal increased with acid-washed ZVAl loading. The reduction of Cr(VI) by acid-washed ZVAl is a surface-mediated reaction; hence, the enrichment of ZVAl loading can increase the total available surface area and improve Cr(VI) removal. For example, the

Table 1
Changes of atomic ratios collected from original ZVAl, acid-washed ZVAl, and acid-washed ZVAl after reaction with Cr(VI)

	Al 2p (%)	O 1s (%)	C 1s (%)	N 1s (%)	S 2p (%)
ZVAl	15.10	55.05	29.85	–	–
Acid-washed ZVAL	14.78	55.43	28.37	0.93	0.49
ZVAl reacted with Cr(VI)	14.50	54.39	28.38	0.61	2.12

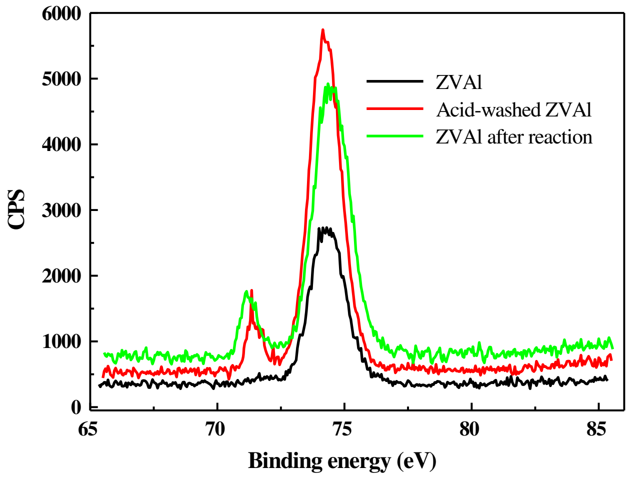

Fig. 3. XPS analyses of Al 2p of three materials.

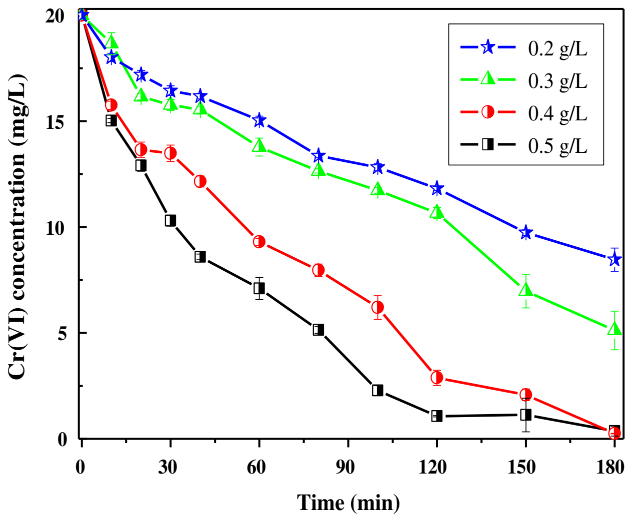

Fig. 4. Effect of acid-washed ZVAl loading on Cr(VI) removal from solution containing 20.0 mg/L Cr(VI) at initial pH 2.0.

residual concentration of Cr(VI) at 120 min decreased from 11.82 mg/L by 0.2 g/L acid-washed ZVAl to 0.37 mg/L by 0.5 g/L acid-washed ZVAl. The enhanced Cr(VI) removal with higher ZVAl loading was obviously due to the increase in the total surface area of ZVAl. Table 2 listed the kinetic parameters of Cr(VI) by acid-washed ZVAl. From the table, the rate constants increased remarkably from 0.0048 to 0.0204 min^{-1} with the increase in acid-washed ZVAl concentration from 0.2 to 0.5 g/L, which was consistent with Cr(VI) removal. The most high values of the correlation coefficient (R^2) indicated that the removal of Cr(VI) by acid-washed ZVAl followed pseudo-first-order kinetics. Because the final residual Cr(VI) concentration is nearly same by 0.4 and 0.5 g/L acid-washed ZVAl, the optimal acid-washed ZVAl concentration was selected as 0.4 g/L.

Table 2
Effect of different factors on the kinetics of Cr(VI) removal

Factors	Values	Kobs (min^{-1})	R^2
ZVI conc. (g/L)	0.2	0.0048	0.9722
	0.3	0.0063	0.9604
	0.4	0.0137	0.9687
	0.5	0.0204	0.9861
Initial pH	1.5	0.0200	0.9863
	2.0	0.0138	0.9681
	2.5	0.0019	0.3462
	3.0	0.0010	0.3195
Acid washing time (h)	0	0.0042	0.9643
	0.5	0.0057	0.9495
	1.0	0.0078	0.9461
	1.5	0.0108	0.9720
	2.0	0.0139	0.9777
	2.5	0.0104	0.9788
HA conc. (mg/L)	0	0.0138	0.9681
	10.0	0.0123	0.9269
	30.0	0.0104	0.8838
	50.0	0.0045	0.8792
Fe^{2+} (mM)	0.5	0.0185	0.4832
	0.75	0.1018	0.9346
	1.0	0.1889	0.9732

3.2.2. *Effect of initial pH*

Commercial ZVAl powder inherently contains aluminum oxides layer on its surface. To favor the intrinsic electron transfer of the metal aluminum, the dissolution of oxides in acid condition is essential. Just as the oxidative capacity of zero-valent metal toward organic compounds [31,32] or reductive capacity of zero-valent metal toward heavy metal [33,34] were pH dependent, Cr(VI) removal by acid-washed ZVAl was found to be pH dependent. Residual Cr(VI) concentration decreased with decreasing pH (Fig. 5), indicating that the acidic conditions facilitated Cr(VI) removal. For example, Cr(VI) concentration after reaction for 180 min increased from 0.07 mg/L for solution at pH 1.5 to 16.87 mg/L for solution at pH 3.0. From Eq. (4), strong acid conditions favor the redox reaction between ZVAl and Cr(VI).

$$2\text{Al} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 2\text{Al}^{3+} + 7\text{H}_2\text{O} \tag{4}$$

$$2\text{Al} + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\uparrow \tag{5}$$

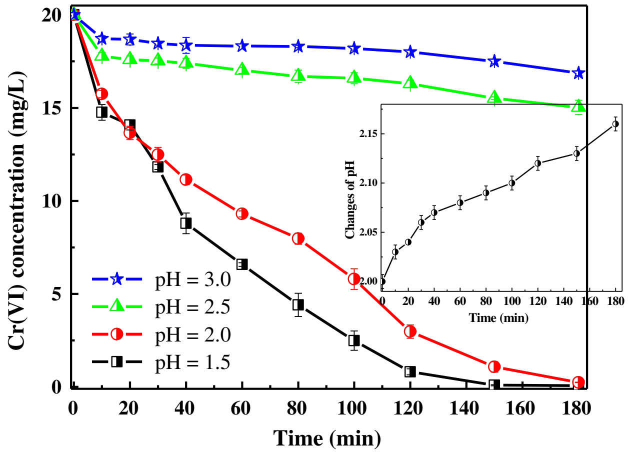

Fig. 5. Effect of initial pH values on Cr(VI) removal from solution containing 20.0 mg/L Cr(VI) by 0.4 g/L acid-washed ZVAl.

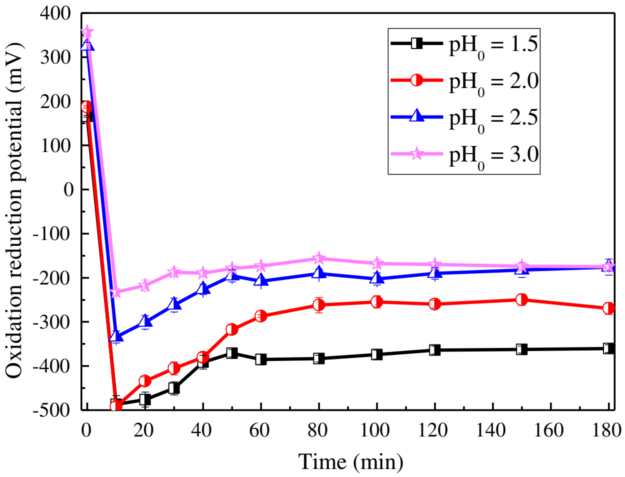

Fig. 6. Changes of ORP values during the reaction process.

In fact, in this study, the reaction of aluminum with Cr(VI) (Eq. (4)) and the dissolution of aluminum both depleted H^+ (Eq. (5)), which led to an increase in pH over time. The pH of the reaction solution increased as the reaction proceeded, which in turn gradually hindered the reaction. For example, after 180 min of reaction, pH increased from initial 2.0 to 2.2 (Inset of Fig. 5). The changes of rate constants with pH were also shown in Table 2. Apparently, pH has an obvious effect on the rate constants. The rate constants decreased from 0.0200 to 0.0010 min^{-1} as initial pH increased from 1.5 to 3.0.

The changes of redox potential at different pH values were investigated as the reaction proceeded. As shown in Fig. 6, the initial ORP values of Cr(VI) solution with initial pH 1.5, 2.0, 2.5, and 3.0 varied from +166.0 to +357.7 mV, and after acid-washed ZVAl particles were added into Cr(VI) solution, the ORP rapidly reduced at first 10 min. This occurred because Al has a very strong reductive capacity. Then, the ORP values gradually increased to −383.3, −262.0, −190.3, and −156.0 mV at 80 min and then nearly unchanged. Comparing the changes of ORP and the variation of Cr(VI) concentration, it was concluded that the decrease in ORP was necessary for Cr(VI) removal by acid-washed ZVAl and the variation in ORP values was indicative of the progress of the reaction between Cr(VI) and acid-washed ZVAl.

3.2.3. Acid washing time on Cr(VI) removal

In the absence of acid washing, less Cr(VI) removal was observed in the solution during the reaction. However, more than 98.7% of Cr(VI) was removed in 180 min by 0.4 g/L acid-washed ZVAl at initial pH 2.0 (Fig. 7). The use of acid washing to treat aluminum is to activate its reducing power by dissolving the passive oxide layer from ZVAl surface and to increase the ZVAl surface area from 1.63 to 2.50 m^2/g by acid etching and pitting. It should be noted that the Cr(VI) removal increased with the increase in acid washing time from 0 to 120 min, but decreased from 120 min to 150 min. With the increase in acid washing time, the aluminum oxides on the surface of ZVAl can be removed and the surface area increased, which was favorable for Cr(VI) removal. Due to this long acid washing time (150 min), much aluminum will dissolve into Al^{3+} in acid condition and hence the aluminum reacting with Cr(VI) is not enough. Also from Table 2,

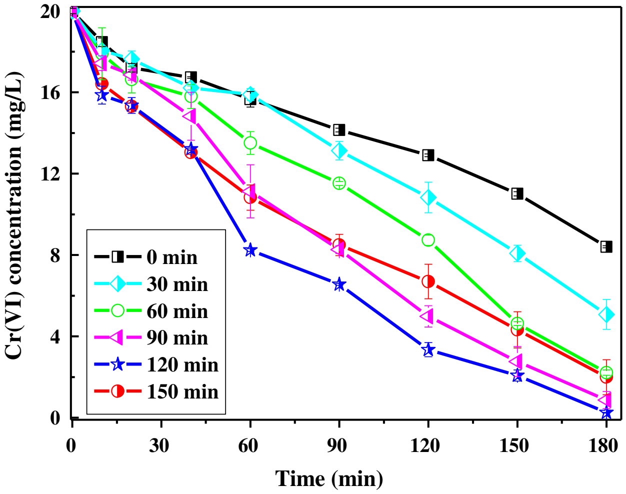

Fig. 7. Effect of acid washing time on Cr(VI) removal from solution containing 20.0 mg/L Cr(VI) by 0.4 g/L acid-washed ZVAl at initial pH 2.0.

the rate constants increased with the increase in acid washing time from 0 to 120 min, and then the rate constants decreased from 120 to 150 min. So, acid washing time of 120 min is the optimal. Compared with the removal of bisphenol A by acid-washed ZVAl [31], higher removal efficiency of Cr(VI) (98.7%) vs. bisphenol A (75%) was observed for initial concentration of Cr(VI) 20.0 vs. 2.0 mg/L bisphenol A, with less time 3 vs. 12 h, and in the presence of 0.4 g/L acid-washed ZVAl vs. 4 g/L, at pH 2.0 vs. pH 1.5. So, it can be concluded that Cr(VI) is more easily removed than bisphenol A by acid-washed ZVAl.

3.2.4. Effect of HA concentration

HA, a dissolved organic matter commonly found in natural and wastewater, is another factor that may influence the removal of Cr(VI) by acid-washed ZVAl. In order to evaluate the effect of HA on the Cr(VI) removal, the concentration of HA was designed at 10, 30, and 50 mg/L, respectively, corresponding to a low, moderate, and high HA level. HA demonstrated an obvious inhibitory effect on Cr(VI) removal (Fig. 8). For example, the residual Cr(VI) concentration was 0.2 mg/L in 180 min for the reaction without HA, while the residual Cr(VI) concentrations were 3.2, 5.3, and 10.1 mg/L in the presence of 10.0, 30.0, and 50.0 mg/L HA addition, respectively. Also from Table 2, the rate constants decreased from 0.0138 to 0.0045 min^{-1} with the increase in HA concentration from 0 to 50.0 mg/L.

From the literatures [25,35], HA has an obvious inhibitory effect on contaminants removal by zero-valent metal, which was ascribed to the competition for reactive sites between HA and the target contaminants. In this study, HA also had an obvious inhibitory effect on the Cr(VI) removal by acid-washed ZVAl. The inhibition might be due to the fact that when the HA concentration increased, the HA adsorbed on the acid-washed ZVAl also increased, which made the active reaction sites of the ZVAl with Cr(VI) become less.

3.2.5. Effect of Fe^{2+} concentration

Fe^{2+} was added to Cr(VI) solution to improve the Cr(VI) removal by lowering the acid-washed ZVAl loading (0.2 g/L ZVAl). From Fig. 9, it can be seen that with the addition of Fe^{2+}, the concentrations of Cr(VI) can sharply decrease in the first 10 min because Fe^{2+} can also reduce Cr(VI) according to Eq. (6). The concentration of Cr(VI) both decreased to below 1.0 mg/L in 120 min in the presence of 0.75 and 1.0 mM Fe^{2+} by 0.2 g/L acid-washed ZVAl. The contrasted experiments for Cr(VI) removal only in the presence of Fe^{2+} were conducted (Fig. 9). Cr(VI) removal also mainly occurred in the first 10 min, and then the Cr(VI) concentration was unchanged after 10 min. So, it can be concluded that the reaction of Cr(VI) with Fe^{2+} is very fast. This report is similar to the study by Zhang et al. [25] who reported Fe^{2+} dramatically accelerated the removal of acetaminophen in ZVAl/H^+/air system. Besides, Fe^{2+} can dramatically enhance Se(VI) removal [36] and nitrate reduction [37] in the presence of ZVI.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad (6)$$

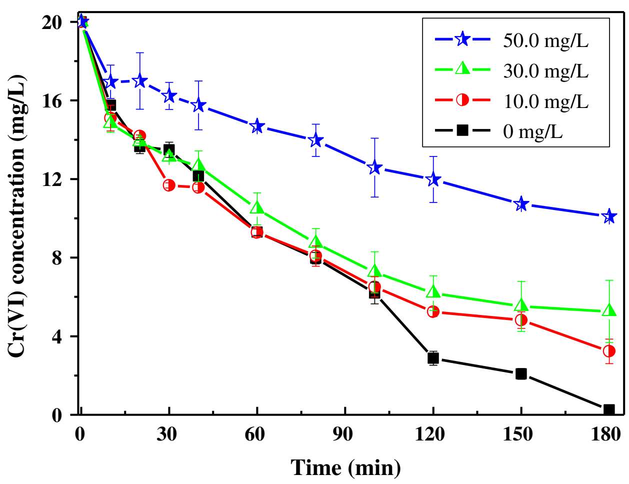

Fig. 8. Effect of HA concentration on Cr(VI) removal from solution containing 20.0 mg/L Cr(VI) by 0.4 g/L acid-washed ZVAl at initial pH 2.0.

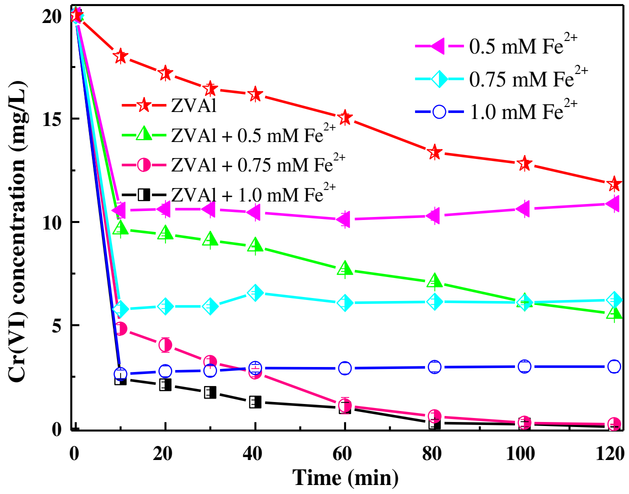

Fig. 9. Effect of Fe^{2+} on Cr(VI) removal from solution containing 20.0 mg/L Cr(VI) by 0.2 g/L acid-washed ZVAl at pH 2.0.

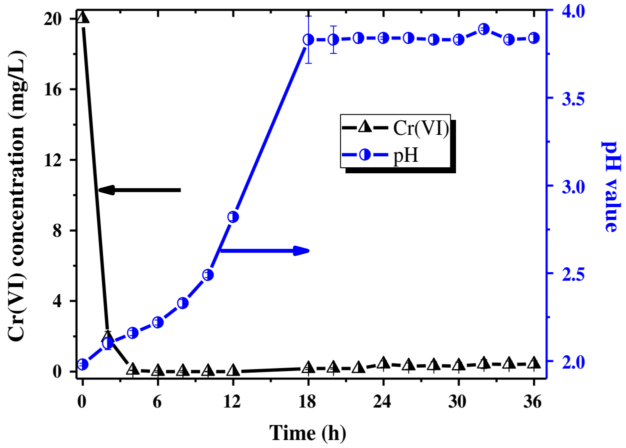

Fig. 10. Adsorption and desorption of Cr(VI) in the removal of Cr(VI) by acid-washed ZVAl and changes of pH values with time.

3.2.6. Adsorption and desorption of Cr(VI) in the removal of Cr(VI) by acid-washed ZVA1

The adsorption at the ZVA1 surface is another possible process to explain the Cr(VI) removal. To verify whether the disappearance of Cr(VI) is a consequence of surface adsorption on ZVA1, desorption experiments were performed. The addition of 240 mg/L SO_4^{2-} was carried out when the entirely disappearance of Cr(VI) was achieved at 4 h. It was found that no Cr(VI) desorption was observed in the aqueous solution in the following 32 h (Fig. 10). No Cr(VI) desorption indicated that Cr(VI) removal attributed to the chemical reduction of Cr(VI) by acid-washed ZVA1, not by adsorption. Also from the figure, the pH increased with time. For example, initial pH 2.0 at 0 h increased to pH 3.83 at 18 h, and then nearly unchanged. The increased pH is attributed to the fact that both the dissolution of native oxide layer and corrosion of aluminum led to H^+ depletion. From 18 to 36 h, there is no increase in pH, which may be attributed to the fact that oxide layer and metal aluminum nearly dissolved in the solution.

4. Conclusions

This study investigated the use of acid-washed zero-valent aluminum (ZVAl) as a new method to remove Cr(VI) from wastewater. Results demonstrated that Cr(VI) removal by acid-washing ZVAl were affected by ZVAl loading, initial pH, acid washing time, humic acid concentration, and Fe^{2+} concentration. Cr(VI) removal increased with acid-washed ZVAl loading and decreased with pH values. HA has an obvious inhibitory effect on contaminants removal, while Fe^{2+} can improve the Cr(VI) removal. The removal of Cr(VI) is through reduction by ZVAl, not by adsorption. And it may be a cheap and effective method for treating Cr(VI) wastewater if the released Al^{3+} and Cr^{3+} are well disposed of and do not cause environmental problems.

Acknowledgments

This research was supported by National Natural Science Foundation of China (No. 51008084), Guangzhou Pearl River Nova Program (No. 2012J2200097) and Training Program for Outstanding Young Teachers in Guangdong Province (No. Yq2013055).

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