



Dramatically enhanced aerobic Cr(VI) reduction with scrap zero-valent aluminum induced by oxalate

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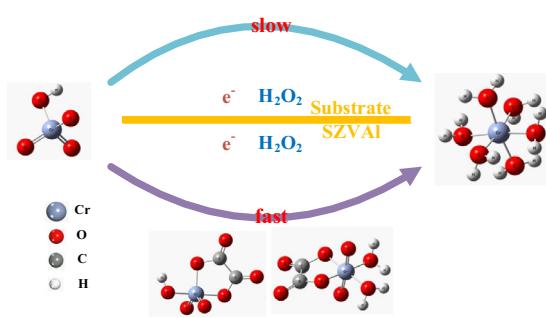
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HIGHLIGHTS

- Scrap zero-valent aluminum can be utilized for Cr(VI) reduction.
- Adding oxalate can significantly enhance the reduction of Cr(VI).
- The enhanced Cr(VI) reduction was induced by the affinity of oxalate to Cr(VI).
- Real Cr(VI) effluent can be successfully detoxified in SZVAI/oxalate system.
- An excellent example of “waste control by waste” strategy was provided.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, the flexibility of utilizing scrap zero-valent aluminum (SZVAI) for Cr(VI) reduction mediated by oxalate was evaluated. Results show that the produced H_2O_2 and the reactive electrons releasing from metal aluminum were the primary electron donors for the preferable Cr(VI) reduction in anaerobic SZVAI/Cr(VI)/oxalate system. The reduction rate of Cr(VI) decreased with the increase of both initial pH value of 1.5–4.5 and Cr(VI) initial concentration of 50–300 μM , increased with oxalate concentration from 0 to 4.0 mM, and markedly retarded under anaerobic condition due to the completely inhibited H_2O_2 production. Notably, the accelerated Cr(VI) reduction induced by oxalate can be ascribed to the fact that the affinity of oxalate to Cr(VI)/Cr(V) species resulted in the expansion of Cr(VI)/Cr(V) coordination from tetrahedron to hexahedron, which was preferred for hexahedral Cr(III) species. Consequently, the presence of oxalate can significantly accelerate Cr(VI) reduction rate, and acted as an alternative electron donor simultaneously for Cr(VI) reduction through intramolecular electron transfer reaction. As compared with zero-valent aluminum (ZVAI), SZVAI exhibited superior reducing capacity for Cr(VI) reduction due to the presence of numerous galvanic cells in SZVAI corrosion process. The appreciable treatment efficiency of real chrome electroplating effluent indicates SZVAI/oxalate system presents as a preferable case of “waste control by waste” strategy. Moreover, the present study provided a new perspective on the role of oxalate in Cr(VI) reduction, which was significant in the detoxification of Cr(VI) process.

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1. Introduction

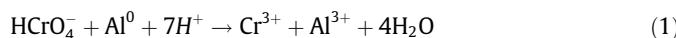
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Chromium is commonly used in a variety of industrial processes including leather tanning, metallurgy, wood preserving and elec-

troplating, etc.[1]. Thus, improper disposal of chromium waste and accidental leakages of industrial chromium-containing effluents causes severe chromium contamination in natural environment. In contrast to Cr(III), Cr(VI) is known to be hypertoxic and carcinogenic to human and animals and thus listed as a priority pollutant [2]. Moreover, as compared with Cr(VI), Cr(III) is less soluble and readily precipitates as Cr(OH)₃ via simple adjusting the solution pH [1]. In view of this, transformation of Cr(VI) to Cr(III) is known as the most extensively employed approach to remove the toxicity of Cr(VI) contaminant [1].

Up to present, a variety of advanced processes (e.g., photocatalysis, electrical discharge plasma and photochemical method) have been developed for aqueous Cr(VI) detoxification [1,3,4]. Despite preferable efficiency in Cr(VI) detoxification, most of these approaches require a large number of chemicals addition or energy input and thereby their industrial applications are restricted by their relatively high costs. Over the recent decades, a great deal of effort has been devoted to develop and improve the strategies of using zero-valent iron (ZVI) for Cr(VI) detoxification [5]. In a ZVI/H₂O system, Cr(VI) detoxification by ZVI can be accomplished via direct reduction mediated by ZVI and indirect reduction induced by the corrosion products (e.g., Fe(II)) of ZVI oxidation. However, dissolved oxygen inevitably competed with Cr(VI) adsorbed for the electrons of ZVI and ferrous ions. As a result, in an aerobic ZVI solution, the presence of oxygen inevitably poses negative impact on the reduction of Cr(VI) [5].



The zero-valent aluminum (ZVAL) is a strong reducing agent that has a more negative standard reduction potential ($E^\circ(\text{Al}^{3+}/\text{Al}) = -1.662 \text{ V}_{\text{NHE}}$) than that of ZVI ($E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.43 \text{ V}_{\text{NHE}}$). In this regard, ZVAL can reasonably provide a far greater thermodynamic driving force for electron transfer compared to ZVI [6]. Furthermore, as depicted in Eq. (1), when ZVAL is used as a reductant for Cr(VI), a less reaction stoichiometry of ZVAL is required for reducing the same amount of Cr(VI) than that of ZVI and Fe(II), leading to less sludge production. Thus, increasing attention has been paid to enhancing the reactivity of ZVAL for the reductive decontamination of Cr(VI) [7]. For example, polyoxometalate (HNa₂PW₁₂O₄₀), owning higher Brønsted acidity than usual inorganic acids (e.g., H₂SO₄ and HCl), was used to enhance Cr(VI) reduction by ZVAL [7]. In this reaction system, polyoxometalate could rapidly remove the aluminum oxides on ZVAL, and also act as a shuttle for electron transfer from ZVAL to Cr(VI). With adding polyoxometalate (0.1 mM), the reduction efficiency of Cr(VI) by uncleaned ZVAL increased greatly from insignificant amount to 0.192 mM after 240 min at pH = 1.0 in oxygen atmosphere [7].

It is widely known that oxalate is ubiquitously found in natural water and many industrial processes (e.g., metallurgy, decontamination of nuclear plants, wood preservation) [8,9]. Recently, as an environmental friendly reagent, oxalate has been demonstrated to be the electron donor for Cr(VI) conversion to Cr(III) in Cr(VI)-contaminated waters when exposed to catalysis by homogeneous and heterogeneous iron or manganese ions with or without light irradiation [10,11]. However, until now, it is still unknown whether and how the introduction or accumulation of oxalate in Cr(VI)-containing waters influence the reduction of Cr(VI) by ZVAL. Besides, scrap aluminum beverage cans (SZVAL) mainly consists of metal aluminum and therefore, utilization of SZVAL could be an attractive alternative to commercial ZVAL for pollutant removal [12]. However, reports on the utilization of SZVAL for Cr(VI) reduction are scarce.

In this study, the feasibility of applying SZVAL for Cr(VI) reduction is evaluated with the presence of oxalate. And the new concept of reducing Cr(VI) by SZVAL mediated by oxalate is proposed

and justified. The effects of solution pH, oxalate dosage, Cr(VI) concentration and gas atmosphere on Cr(VI) reduction were also investigated. In addition, the contributing factors for Cr(VI) reduction is identified to elucidate the reaction mechanisms. Ultimately, the effectiveness of this proposed process for the actually concentrated chrome plating effluent was estimated. In general, present study shows an excellent example of “waste control by waste” strategy in detoxification of industrial pollutants.

2. Materials and methods

2.1. Experimental procedures

Potassium chromate (K₂Cr₂O₇, >99%), diphenylcarbazide (98%), aluminum sulfatehydrate (Al₂(SO₄)₃·H₂O, 98%), oxalic acid (H₂C₂O₄, >99%), H₂SO₄ (73.0–75.0%), H₃PO₄ (>98.5%), NaOH (>96%), HCl (36–38%) and H₂O₂ were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All chemical reagents were used without further purification. UltraPure water (18.2 MΩ cm) was used for all experiments.

The used scrap aluminum beverage cans (Coca Cola[®]) were collected and abraded with fine emery paper, rinsed with distilled water, and finally exposure to air for a week. The obtained scrap aluminum (SZVAL) and aluminum foil (ZVAL) were cut into pieces with average dimensions of 3 mm × 3 mm. The experiments were conducted in an open cylindrical glass tube with 150 mL capacity under magnetic stirring and cooled by circulating water with the temperature maintained at 20 ± 1 °C. All working solutions were freshly prepared before use by diluting the stock solution with deionized water, and solution pH was adjusted to the desired values with concentrated H₂SO₄ or NaOH solution. For the experiments using a volumetric flask (250 mL) as the reaction vessel in the presence of argon (gas velocity, 0.6 L min⁻¹), the solution was purged with argon gas for 10 min prior to initiating the reaction. The samples were withdrawn at various time intervals, and followed by immediate measurements. Most of the batch experiments were conducted in duplicate, and the relative error was less than 3%.

2.2. Analysis

The pH of the solution was determined by pH meter (PHS-3C). The concentration of Cr(VI) remaining in the solution was measured by a diphenylcarbazide method. The concentrated acids (H₃PO₄:H₂SO₄:H₂O = 1:1:2, v:v:v) should be premixed with diphenylcarbazide reagent to minimize the interference of acidification with Cr(VI) determination. The absorbance of sample solutions was detected at 540 nm after full color development (>15 min) [3]. H₂O₂ formed in the solution was determined by a spectrophotometrical method using titanyl reagent [3]. Briefly, 2 mL reaction mixture and 1.0 mL of titanium potassium oxalate (4 mM in 0.25 M sulfuric acid) were mixed together. Then the absorbance of the resulting solution was measured at 400 nm on the UV-vis spectrophotometer. The interferences of other species (e.g., Cr(III) and Cr(VI)) in absorbance value were eliminated using the chromogenic agent-free mixture as the blank sample in each measurement. To analyze the compositions of ZVAL and SZVAL, these two materials with 0.2 g were separately dissolved in 2 mol L⁻¹ H₂SO₄ (100 mL) solution. The concentrations of Al, Mn, Mg, Fe and Cu ions were determined using inductively coupled plasma spectrometer (ICP). Mineralization of the organics in solution was monitored by measuring the total organic content carbon (TOC) using an Elementar Germany Liqui TocII analyzer. For Cr(V) species detection, the electron spin resonance (ESR) experiments were performed on the ESR spectrometer (Bruker A200) under

the following conditions: center field, 323.300 mT; sweep width, 5 mT; microwave frequency, 9.056 GHz; microwave power, 0.998 mW; temperature, 295.0 K.

Cr(VI) reduction behavior could be described by first-order kinetics with good correlation coefficient values (>0.90):

$$\ln(1 - \eta) = -kt \quad (2)$$

where η (%) is Cr(VI) reduction efficiency, k (min^{-1}) is the reaction rate constant and t (min) is the reaction time.

3. Results and discussion

3.1. SZVAL induced Cr(VI) reduction mediated by oxalate

It was known that the equilibrium constant of redox reaction dependent on the potential difference value can reflect the spontaneity of the reaction ($K > 1$ indicates spontaneous reaction according to Eq. (3)) [13]. At pH 2.5 the value of the K is approximately 10^{140} , so it is thermodynamically feasible for the direct reduction of Cr(VI) by ZVAL.

$$K = 10^{(n(E'_{\text{ox}} - E'_{\text{red}}))/0.06} \quad (3)$$

where n is the number of the transferred electron between reductant and oxidant, E'_{ox} and E'_{red} are standard electrode potentials of Cr(VI) and metal aluminum, respectively.

However, as shown in Fig. 1, with ZVAL, approximately 24 μM decrease but no significant in Cr(VI) concentration was observed when 100 μM Cr(VI) was reacted with ZVAL (6.4 g L^{-1}) under the air saturation. This can be attributed to the shielding effect of oxide layer on the surface of ZVAL, which completely interrupted the interaction between metal aluminum and Cr(VI). Despite relatively preferable Cr(VI) reduction performance obtained in Cr(VI)/SZVAL (4.0 g L^{-1}) system (same surface area of 4.0 g L^{-1} SZVAL to 6.4 g L^{-1} ZVAL), there was still approximately 56 μM Cr(VI) residual after 150 min. Interestingly, the reduction rate of Cr(VI) by SZVAL can be essentially accelerated with the addition of 1.0 mM oxalate. Specifically, 100 μM Cr(VI) can be completely removed after 150 min in Cr(VI)/SZVAL/oxalate system. In addition, the enhanced reduction efficiency of Cr(VI) can be also observed in Cr(VI)/ZVAL system with the presence of oxalate. In spite of this, the reduction efficiency of Cr(VI) in ZVAL/oxalate system was lower as compared with that SZVAL/oxalate system. After 150 min, much more Al(III) ion (approximately 252 μM) can be detected in SZVAL/Cr(VI)/oxalate system than 163 μM in ZVAL/Cr(VI)/oxalate system. These experimental evidences suggest that metal aluminum was probably the electron donor for Cr(VI) reduction. As compared with SZVAL/oxalate system, the cleaned SZVAL/oxalate system exhibits superior reduction rate of Cr(VI) with complete reduction of 100 μM Cr(VI) within 120 min. This can be ascribed to the fact that the oxide layer of SZVAL can be previously peeled off by 0.2 M H_2SO_4 , leading to the exposure of much more reactive reaction sites on the SZVAL surface.

Considering that oxalate may act as a reductant to directly react with Cr(VI) [14], preliminary experiment on reduction of Cr(VI) by oxalate without SZVAL was conducted. Negligible decrease of Cr(VI) concentration was observed after a reaction time of 150 min (see Fig. 1). Besides, influence of Al(III) ion on Cr(VI) reduction was also ruled out because the total Cr(VI) concentrations remained nearly constant during the reaction processes of Cr(VI)/Al(III)/oxalate reaction system.

Fig. 2a shows that increasing oxalate concentration was proportional to the enhancement of Cr(VI) reduction. For example, Cr(VI) reduction increased from 44 μM to 100 μM with increasing oxalate concentration from 0 to 4.0 mM within 150 min. But Cr(VI) reduction was negatively influenced by increasing initial concentration of Cr(VI) (see Fig. 2b). It was found that 50 μM Cr(VI) was completed reduced within 90 min, whereas as for 300 μM Cr(VI), approximately 270 min was required for complete reduction of Cr(VI). The decrease in Cr(VI) reduction efficiency with increasing initial Cr(VI) concentration is presumably ascribed to the insufficient reactive surface sites of SZVAL for Cr(VI) reduction.

3.2. Validation of contributing factors for Cr(VI) reduction

Chromium (VI) reduction by zero valent metals or metal oxide mediated by some polycarboxylates is a well-known concept and has been extensively reported in a large number of literatures [14]. In these cases, the affinity of polycarboxylates to dissolved and surface-bound metal ions is mostly proposed as the prerequisite process for Cr(VI) reduction. For example, in the case of zero valent iron, Fe^0 and derived product, namely $\text{Fe}(\text{II})$, were proved to be the primary electron donors for Cr(VI) reduction. The rate enhancement of Cr(VI) reduction induced by polycarboxylates was attributed to their strong affinity to $\text{Fe}(\text{III})$, which can effectively prevent the insoluble hydroxides formation on Fe^0 surface and therefore decrease the passivation of Fe^0 surface [15]. However, in SZVAL/Cr(VI) system, the generated Al(III) can exist as a soluble form in solution at solution pH 2.5 (see Fig. S1), which does not pose the negative influence on the reactivity of SZVAL. In addition, the aforementioned results of the controlled Al(III)/oxalate/Cr(VI) reaction system excluded the direct contribution of Al(III)-oxalate complex formation for Cr(VI) reduction. In spite of this, adding oxalate in SZVAL/Cr(VI) reaction system can greatly improve the reduction of Cr(VI). Therefore, the resolution of the contributing factors for Cr(VI) reduction requires a thorough inspection of interactions among Cr(VI), oxalate, SZVAL and the produced products.

3.2.1. Reaction between Cr(VI) and H_2O_2 mediated by oxalate

The reduction potential of ZVAL ($E^0(\text{Al}^{3+}/\text{Al}^0) = -1.667 \text{ V}_{\text{NHE}}$) is higher than oxygen ($E^0(\text{O}_2/\text{H}_2\text{O}_2) = 0.68 \text{ V}_{\text{NHE}}$). Therefore, H_2O_2 can be generated in situ in the aerobic SZVAL system, which should be initiated by the corrosive dissolution of metal aluminum and concurrent reduction of oxygen via reactions (4) and (5) [6]. The rapid disproportionation of HO_2 radical results in the production of H_2O_2 (see reaction (6)). Thus, the overall reaction between Al^0 and O_2 for H_2O_2 production can be described in reaction (7).

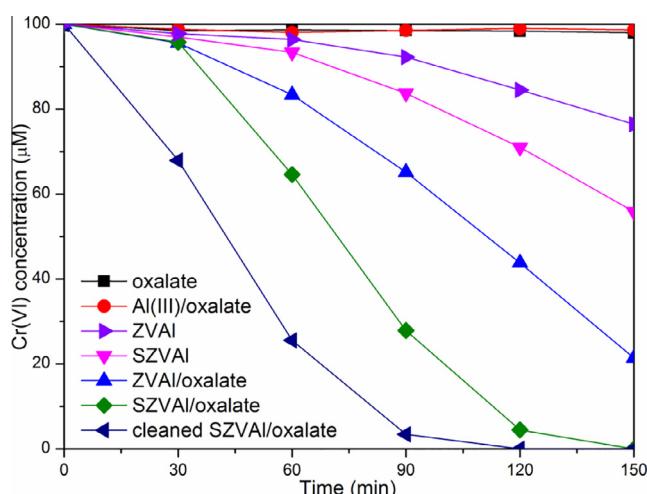


Fig. 1. Reduction of Cr(VI) by an excess of ZVAL or SZVAL in the presence and absence of oxalate under aerobic condition. ([Cr(VI)] = 100 μM , pH = 2.5, [oxalate] = 1.0 mM, [ZVAL] = 4.0 g L^{-1} , [SZVAL] = 6.4 g L^{-1}).

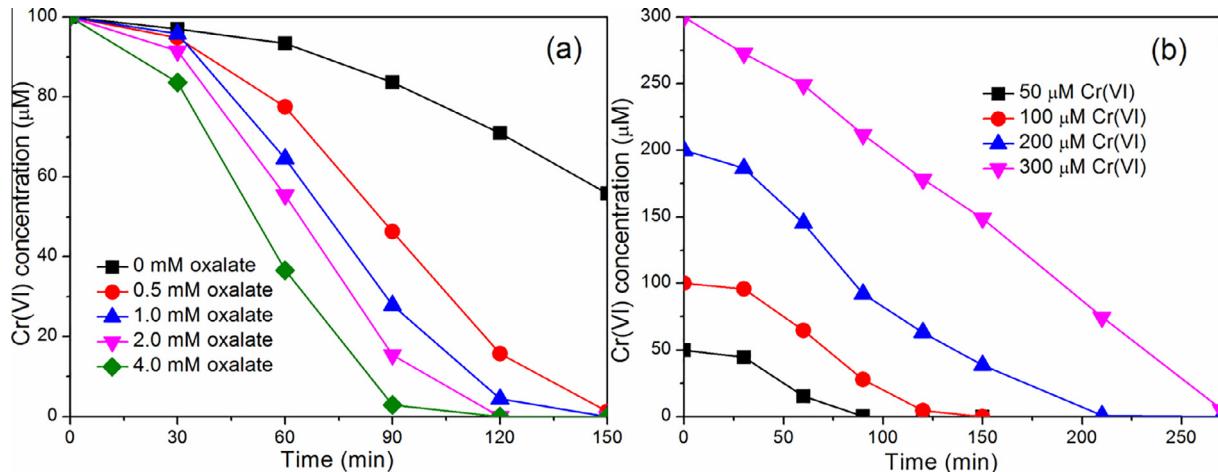
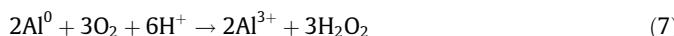


Fig. 2. Effects of oxalate concentration (a) and Cr(VI) concentration (b) on the reduction of Cr(VI) in SZVAI/oxalate reaction systems. (a: [Cr(VI)] = 100 μM, pH = 2.5, [SZVAI] = 4.0 g L⁻¹; b: pH = 2.5, [oxalate] = 1.0 mM, [SZVAI] = 4.0 g L⁻¹).



As shown in Fig. 3a and Table 1, the concentration of H₂O₂ can be accumulated to 194 μM and 219 μM with corresponding production of 185 μM and 263 μM Al(III) ion in SZVAI system and SZVAI/oxalate system, respectively. Theoretically, H₂O₂ ($E^0(O_2/H_2O_2) = 0.68 V_{NHE}$) can serve as a reductant of Cr(VI) ($E^0(HCrO_4^-/Cr^{3+}) = 1.14 V_{NHE}$ at pH 2.5) [3]. Thus, inhibited Cr(VI) reduction can be reasonably expected under oxygen-free condition. And this can be confirmed by the results in Fig. 3 that the reduction of Cr(VI)

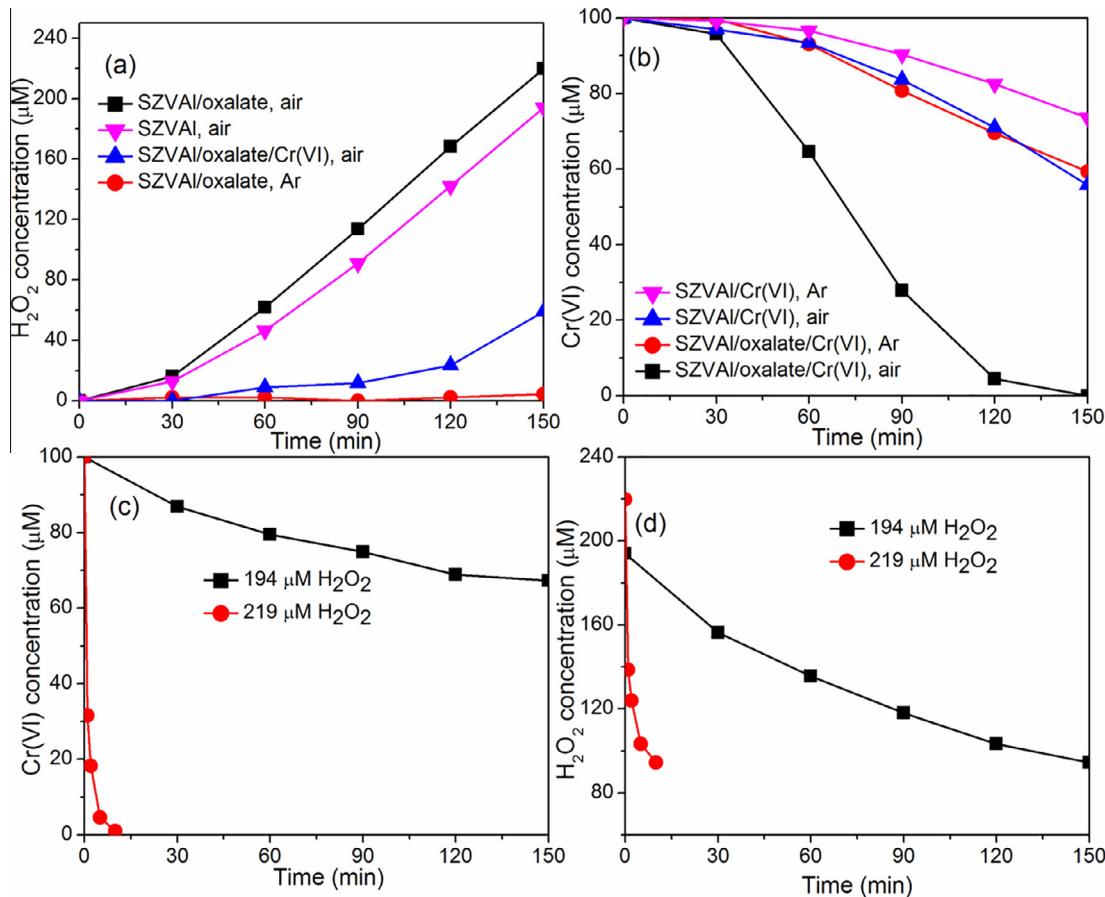


Fig. 3. The effect of gas atmosphere on H₂O₂ formation (a) and Cr(VI) reduction (b) in SZVAI/Cr(VI) and SZVAI/oxalate/Cr(VI) systems; the concentration of Cr(VI) (c) and H₂O₂ (d) in H₂O₂/Cr(VI) and H₂O₂/oxalate/Cr(VI) systems ([Cr(VI)] = 100 μM, [SZVAI] = 4 g L⁻¹, pH = 2.5, [oxalate] = 1.0 mM).

Table 1

The concentration of Al(III) ion after 150 min reaction in various reaction systems ($[Cr(VI)] = 100 \mu M$, $[SZVAl] = 4 g L^{-1}$, $[ZVAl] = 6.4 g L^{-1}$, pH = 2.5, [oxalate] = 1.0 mM).

Reaction system	SZVAl/Cr(VI)/oxalate, air	ZVAl/Cr(VI)/oxalate, air	SZVAl, air
Al(III) concentration (μM)	252	163	185
Reaction system	SZVAl, Ar	SZVAl/oxalate, Ar	ZVAl, air
Al(III) concentration (μM)	85	111	100

was evidently retarded in SZVAl/Ar system regardless of with or without oxalate. For example, only $41 \mu M$ Cr(VI) was reduced within 150 min in SZVAl/Cr(VI)/oxalate/Ar system, which was inferior to that of SZVAl/Cr(VI)/oxalate/air system. Besides, in aerobic SZVAl/Cr(VI)/oxalate system, negligible H_2O_2 was detected within 120 min, whereas the concentration of H_2O_2 accumulated considerably in the reaction process after 120 min. This abrupt change of H_2O_2 production can be obtained only when a majority of Cr(VI) was depleted in aerobic reaction system, which definitely confirms the produced H_2O_2 accounting for the reduction of Cr(VI).

To inspect the influence of oxalate on the reaction between H_2O_2 and Cr(VI), H_2O_2 with the concentration of $194 \mu M$ and $219 \mu M$, equivalent to the corresponding H_2O_2 yield in SZVAl and SZVAl/oxalate system, was added into Cr(VI) or Cr(VI)/oxalate solution. Fig. 3c shows Cr(VI) was gradually reduced in Cr(VI)/ H_2O_2 solution, accompanied with the consumption of H_2O_2 . As shown in Fig. 3c and d, after 150 min, approximately $33 \mu M$ Cr(VI) was reduced at the cost of $100 \mu M$ H_2O_2 and the calculated stoichiometric ratio of $[Cr(VI)]_{reduction}/[H_2O_2]_{consumption}$ was 0.33. However, $100 \mu M$ Cr(VI) can be completely reduced to Cr(III) within 10 min with higher $[Cr(VI)]_{reduction}/[H_2O_2]_{consumption}$ ratio (approximately 0.8) in Cr(VI)/oxalate/ H_2O_2 solution than that in Cr(VI)/ H_2O_2 solution. Hence, H_2O_2 generated in aerobic SZVAl system played a crucial role in the conversion of Cr(VI) to Cr(III), and this can be accelerated and enhanced with the presence of oxalate.

It has been reported that reduction of Cr(VI) to Cr(III) probably involves the formation of Cr intermediates (i.e., Cr(IV) or Cr(V)) via multiple electron transfer reaction steps [14]. In addition, redox reaction between oxalate and Cr(VI) can occur at extremely acidic solution, in which the formations of various Cr(V)-oxalate species normally involved [14]. However, as shown in Fig. 4a, no evident Cr(V) signal can be recorded in present Cr(VI)/oxalate reaction system, probably due to the relatively low concentrations of reactants (i.e., protons, Cr(VI) and oxalate), which suggests no Cr(VI) reduc-

tion induced by oxalate [14]. This result is consistent with the insignificant reduction of Cr(VI) in Fig. 1. It is well known that in $H_2O_2/Cr(VI)$ reaction system, peroxychromate(V) complex can be produced via the intramolecular electron redox reactions and sequential ligand substitution reactions between H_2O_2 and Cr(VI) species [16]. But, in present Cr(VI)/ H_2O_2 solution, no evidence of Cr(V) species was recorded within 1 min. This was probably due to the considerably low concentration or rapid decay of Cr(V) species, making these species undetectable by ESR spectroscopy. Oxalate has been demonstrated to be an effective organic ligand for Cr(V) during many Cr(VI) reduction processes [17]. And an ESR signal of Cr(V) was detected in oxalate/Cr(VI)/ H_2O_2 solution, which indicates the rapid accumulation of Cr(V) species stabilized by carboxylato ligand, i.e., oxalate, upon the mixing of Cr(VI), oxalate and H_2O_2 . Besides, the recorded ESR signal immediately decayed within 3 min, indicating the fast depletion of Cr(V)-oxalate complexes. This observation confirms that oxalate involved in the reaction between Cr(VI) and H_2O_2 .

During the course of Cr(VI) reduction to Cr(III), the coordination shell rearrangement from tetrahedral Cr(VI)/Cr(V) species to octahedral Cr(III)/Cr(IV) species is taken to be the rate-limiting step [18]. However, the aforementioned results show that the presence of oxalate can markedly accelerate the reduction of Cr(VI) to Cr(III). This can be explained by the expansion of Cr(VI)/Cr(V) coordination shell from tetrahedron to hexahedron via the affinity of oxalate to Cr(VI)/Cr(V) species, which facilitates the unidirectional conversion of Cr(VI) to Cr(III). Some previous literatures can also validate this viewpoint [14,19]. In the above reaction system, the formed Cr(V) and Cr(IV) intermediates were probably further reduced by oxalate through intramolecular electron transfer reaction, which played as an alternative electron donor to H_2O_2 and the electron releasing from the corrosion of metal aluminum [14,20]. Thus, in SZVAl/Cr(VI)/oxalate reaction solution, the increased mineralization of oxalate was observed as compared with the those in Cr(VI)/oxalate, $H_2O_2/Cr(VI)/oxalate$ and SZVAl/oxalate reaction systems at pH = 2.5 (see Fig. 4b).

3.2.2. Reaction between Cr(VI) and metal aluminum mediated by oxalate

In present reaction system, the initial concentration of Cr(VI) ($100 \mu M$) is less than the aqueous solubility of O_2 (1.25 mM) at room temperature [21]. In spite of this, the standard oxidation potential of Cr(VI) ($E^0(Cr(VI)/Cr(III)) = 1.14 V_{NHE}$ at pH 2.5) is much higher than that of O_2 with production of H_2O_2 ($E^0(O_2/H_2O_2) = 0.68 V_{NHE}$). Thus, in aerobic SZVAl/Cr(VI)/oxalate system, the released electron via the corrosion of metal aluminum can be con-

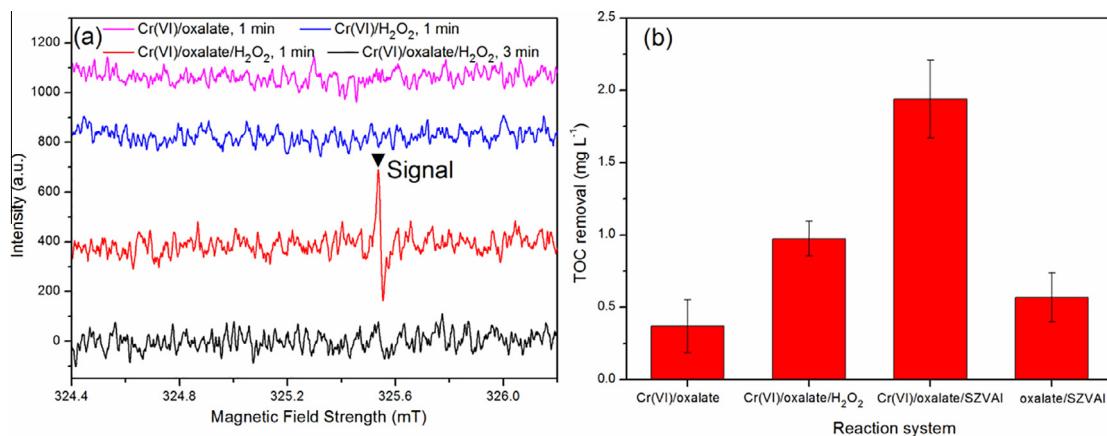


Fig. 4. The detection of Cr(V) species (a) and the consumption of oxalate (b) in various reaction system (a: $[Cr(VI)] = 2.0 \text{ mM}$, pH = 2.5, [oxalate] = 20.0 mM , $[H_2O_2] = 4.0 \text{ mM}$; b: $[Cr(VI)] = 100 \mu M$, $[SZVAl] = 4 g L^{-1}$, pH = 2.5, [oxalate] = 1.0 mM , $[H_2O_2] = 219 \mu M$).

sumed for direct reduction of Cr(VI), instead of the production of H₂O₂. This statement can be solidly supported by the results in Fig. 5a that there was still approximately 26 μM Cr(VI) reduced in SZVAL/Ar reaction system. As a result, the direct redox reaction between Cr(VI) and metal aluminum undoubtedly resulted in the decreased production of H₂O₂ in SZVAL/Cr(VI)/oxalate system, which can be reflected by the contribution efficiency difference of H₂O₂ for Cr(VI) reduction in Fig. 3b and c.

In addition, as shown in Fig. 5a, an evident increase in Cr(VI) reduction rate was also observed with increasing oxalate concentration. Specifically, when adding 1.0 mM and 4.0 mM oxalate, the reduction of Cr(VI) increases from 26 μM to 41 μM and 63 μM, respectively, within 150 min. And this enhanced performance was also significant when using cleaned SZVAL as the reductant. Besides, as for uncleaned SZVAL system, the relatively low rate constants of Cr(VI) reduction was observed as compared with the those in the case of the cleaned ZVAL system Fig. 5b. These phenomena were probably due to the presence of oxidized layer on the surface of SZVAL. In cleaned ZVAL system, the rate of Cr(VI) reduction increased significantly from 0.00513 to 0.00781 and 0.0142 min⁻¹ with increasing oxalate concentration from 0 to 1 and 4 mM, respectively, under Ar atmosphere. The enhanced Cr(VI) reduction was probably induced by the coordination expansion of Cr(VI)/Cr(V) from tetrahedron to hexahedron through the affinity of oxalate to Cr(VI)/Cr(V) [14,22]. And this enhancement tendency was more obvious with the addition of much higher dosage of oxalate.

3.2.3. Contribution of hetero-ions in SZVAL

The XRD patterns of ZVAL and SZVAL are depicted in Fig. S2. The characteristic peaks of aluminum appear at the diffraction angle (2θ) of 38°, 45°, and 65°, which indicate that metal aluminum is the main component in ZVAL and SZVAL. The morphology of SZVAL was analyzed using SEM (see Fig. S3). And energy dispersive spectrometer (EDS) analysis suggests that in addition to metal aluminum, SZVAL also contains many hetero-metals. ICP technique was applied to detect other elements and the atomic ratios of the two materials are summarized in Table S1. As compared with those in ZVAL, relatively high concentrations of Mg ($E^0(Mg^{2+}/Mg) = -2.36 V_{NHE}$), Fe ($E^0(Fe^{2+}/Fe) = -0.44 V_{NHE}$), Mn ($E^0(Mn^{2+}/Mn) = -1.182 V_{NHE}$) and Cu ($E^0(Cu^{2+}/Cu) = 0.518 V_{NHE}$) are detected in SZVAL [23]. Consequently, approximately 0.04 mg/L Mn ion, 0.03 mg/L Fe ion, 0.04 mg/L Cu ion and 0.2 mg/L Mg ion were detected after the reaction time of 150 min in SZVAL/Cr(VI)/oxalate system. Although Fe, Mn and Cu ions have been demonstrated as the effective catalysts for the reduction of Cr(VI) induced by

organic acids, tiny amounts of these hetero-metals negligibly affect the reduction of Cr(VI) (see Fig. S4) [24,25]. Thus, the evident difference of Cr(VI) reduction rate between SZVAL and ZVAL reaction systems cannot be ascribed to the production of Fe, Mn, Mg and Cu ions via the corrosion of these impure metals. In contrast, the galvanic cell theory probably explains these experimental results [26]. The bimetallic particles in SZVAL can act as galvanic cells during reaction, and the galvanic corrosion favorably facilitated the electron releasing with larger yield of Al(III) ion in SZVAL/oxalate solution than that in ZVAL/oxalate solution (see Table 1). Consequently, as shown in Figs. 1 and S5, appreciable Cr(VI) reduction and H₂O₂ production can be observed in SZVAL/oxalate reaction system. For example, the metal iron has a higher electrode potential ($E^0(Fe^{2+}/Fe) = -0.43 V_{NHE}$) than Al ($E^0(Al^{3+}/Al) = -1.662 V_{NHE}$), leading to formations of numerous galvanic cells on the Fe/Al bimetallic particles, in which iron acts as anode and aluminum as cathode [23]. Thus, the electrons can rapidly transfer from aluminum atom to iron atom (not only on the accessible surface but also inside of the Fe and Al particles). As a result, Cr(VI) and oxygen as electron acceptors can be preferably reduced to Cr(III) and H₂O₂, respectively on the surface of SZVAL.

3.3. Dependence of Cr(VI) reduction on solution pH

Just as the oxidative capacity of zero-valent metal toward organic compounds [6], solution pH probably also determines the reducing capacity of SZVAL toward Cr(VI), which was thus studied here. As shown in Fig. 6, in acidic conditions ($pH \leq 5$), the reduction of Cr(VI) decreased with increasing solution pH, and almost complete interruption was observed at pH 4.5. This can be attributed to the stable surface aluminum oxide layer on SZVAL in the pH range of 4.0–9.0, which would hinder the release of electrons via the corrosion of metal aluminum [27].

This inhibition of aluminum oxides can be effectively relieved via stripping this layer off in strongly acidic solution. As seen in Fig. 6b, the reduction of Cr(VI) can be evidently accelerated in cleaned SZVAL reaction system. For example, the reduction of Cr(VI) can gradually proceed with reduction amount of approximately 26 μM within 150 min in cleaned SZVAL/oxalate/Cr(VI) system at initial solution pH 4.5.

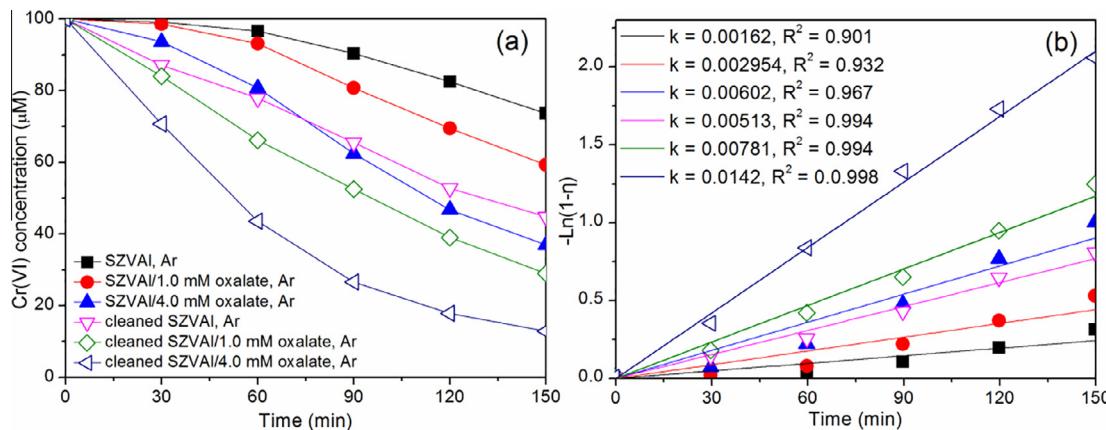


Fig. 5. The reduction of Cr(VI) and reaction kinetics fitted to the reduction data of Cr(VI) in various reaction systems under argon atmosphere ([Cr(VI)] = 100 μM, [SZVAL] = 4 g L⁻¹, pH = 2.5).

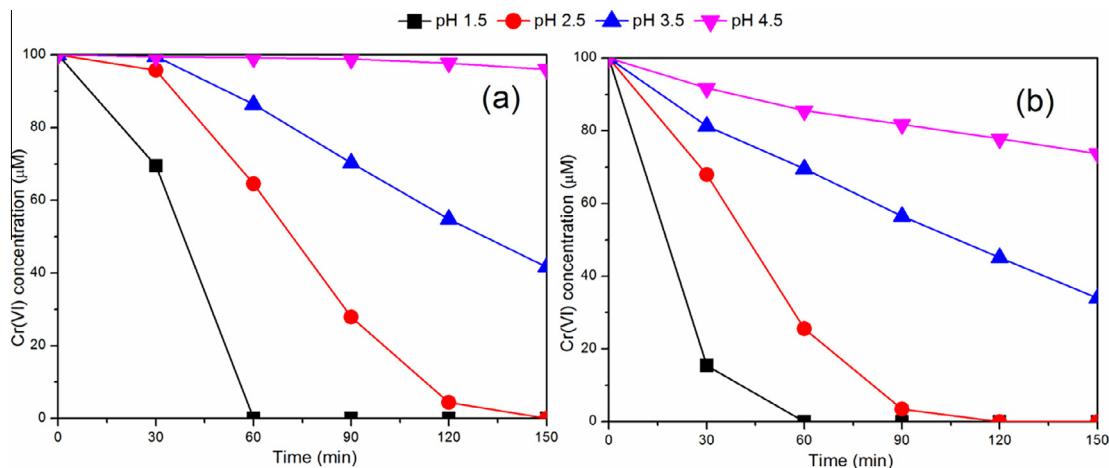


Fig. 6. The effect of initial solution pH on Cr(VI) reduction in SZVAI/oxalate/Cr(VI) (a) and cleaned SZVAI/oxalate/Cr(VI) reaction (b) systems in air atmosphere ($[Cr(VI)] = 100 \mu M$, $[SZVAI] = 4 g L^{-1}$, $[oxalate] = 1.0 mM$).

During the course of the SZVAI/oxalate/Cr(VI)/O₂ reaction, the reaction of aluminum with Cr(VI) (reaction (1)), the corrosion of aluminum generates Al(III) and H₂ (reaction (8)), and the dissolution of native oxide layer all depleted H⁺ (reaction (9)), inevitably leading to an increase in pH over time. For example, the 150 min reaction of SZVAI with 100 μM Cr(VI) mediated by 1.0 mM oxalate increased the pH as follows: (a) pH_{initial} 1.5, pH_{final} 1.54, (b) pH_{initial} 2.5, pH_{final} 2.60, (c) pH_{initial} 3.5, pH_{final} 3.77 and (d) pH_{initial} 4.5, pH_{final} 4.79. As depicted in Fig. S1a, at low pH_{initial} values, alumina is readily soluble and aluminum hydroxides will not form immediately after the start of the experiments. Nevertheless, the pH of the reaction solution increased as the reaction proceeded, which in turn gradually hindered the reaction. Especially, in case of pH ≥ 4.0, the formation of insoluble aluminum hydroxides inevitably interrupted the dissolution of metal alumina thus minimized the reduction rate of Cr(VI). However, the presence of oxalate can form soluble complexes with the produced Al(III) ion at pH ≤ 7.0 (see Fig. S1b). Consequently, this reaction can inhibit precipitates formation and decrease the passivation of aluminum surface, guaranteeing the durative corrosion of metal aluminum for Cr(VI) reduction at a relatively large range of solution pH.

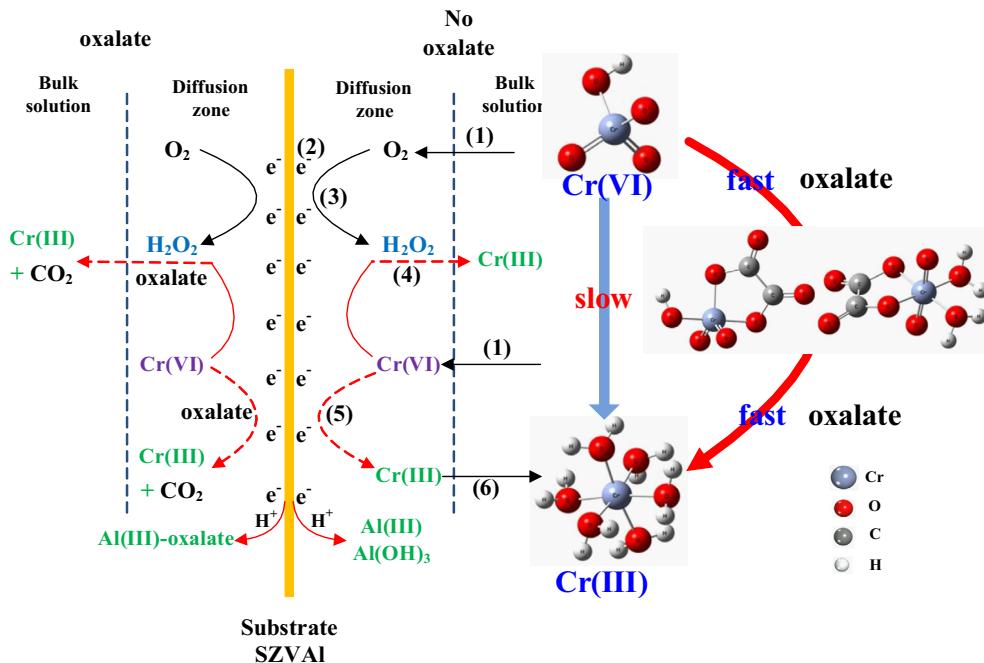
3.4. The proposed conceptual model

A conceptual model of Cr(VI) reduction by SZVAI is illustrated in Scheme 1 according to the aforementioned results. In SZVAI/Cr(VI) reaction system, the process for the Cr(VI) reduction by SZVAI can be presented as follows: (1) generation of electrons via the corrosion of metal aluminum, (2) diffusion of O₂ and Cr(VI) from the solution to the interface between SZVAI and solution, (3) formation of H₂O₂ via the reduction of O₂ by reactive electrons, (4) the formed H₂O₂ homogeneous or heterogeneous reducing Cr(VI), (5) reduction of Cr(VI) to Cr(III) by reactive electrons on the surface reactive sites, and (6) dissolving of produced Cr(III) into the solution. In above reaction process, upon reactive sites on the surface of SZVAI exposed to the solution, Cr(VI) and O₂ competed with proton ions for reactive electrons. Meanwhile, Cr(VI) and O₂ obtained the electrons released from metal aluminum probably via an inner-sphere or outer-sphere complex pathway because electron has never existed in solutions [28]. Thus, diffusion of soluble O₂ and Cr(VI) to SZVAI reactive sites and the corrosion of metal aluminum interfered with the reduction of Cr(VI). Besides, it should be noted that under strongly acidic solution, the reaction (7) certainly competed with the reactions of H₂O₂ production and Cr(VI) reduction for reactive electrons.

As mentioned above, owing to the dramatic decrease in Al(III) solubility with increasing solution pH, deposition of aluminum hydroxide onto the surface reactive sites of SZVAI (step 6) at relatively high pH could block the interaction between metal aluminum and electron acceptors (i.e., Cr(VI) and O₂). As a result of oxalate present in SZVAI/Cr(VI) system, the sustained desorption of Al(III) species from surface reactive sites (step 6) can be attained via the soluble complex formation between Al(III) and oxalate. In addition, it should be noted that when oxalate was added into SZVAI/Cr(VI) reaction system, oxalate can assist the expansion of Cr(VI) coordination shell involving the formation of oxalic acid-chromium complex, which is preferred for Cr(VI) conversion to Cr(III). Thanks to this role of oxalate, the reductants (i.e., reactive electrons releasing from metal aluminum and H₂O₂) can be more efficiently utilized for Cr(VI) reduction.

3.5. Implications for real Cr(VI) wastewater remediation

It is well known that the residual Al(III) ion in the treated water is a problematic for the practical application of metal aluminum-based treatment process due to its toxicity toward natural organisms and humans [29]. It is known that the aqueous Al(III) ion can be transformed to aluminum hydroxide precipitation via pH adjustment (pH > 4.0, see Fig. S1). In this regard, toxic Al(III) ion can be synchronously precipitated with Cr(III) species via adjusting solution pH. In present SZVAI/oxalate/Cr(VI) reaction system, the total Al(III) ion concentration in SZVAI/oxalate/Cr(VI) reaction system was detected 252 μM after 150 min reaction ($[SZVAI] = 4.0 g/L$, pH = 2.5, $[oxalate] = 1.0 mM$). After adjusting the pH to approximately 6.0, Al(III) concentration level was reduced to <0.01 mg/L detected by ICP technique (maximum contaminant level in drinking water is 0.2 mg/L) due to the precipitation of insoluble aluminum hydroxide. Further adjusting solution pH to approximately 10.0 can make the precipitation of Cr(III) as chromic hydroxide with residual Cr(III) concentration below 0.05 mg/L. Thus, a simple adjusting pH to basic values can completely wipe off the threat of aluminum and chromium contamination. Besides, it should be noted that only 25.2 μM metal aluminum was consumed for 10 μM Cr(VI) reduction in each recycle and thus a portion of SZVAI (0.4 g) can be theoretically used for 588 L chromium wastewater (100 μM Cr(VI)) under the fixed reaction condition. Thus, this proposed process obviously exhibit superior capacity for Cr(VI) reduction over many alternative energy consumption processes (e.g., photocatalysis, electrical discharge plasma and photochemical method) with considering the



Scheme 1. Proposed pathways for the reduction of Cr(VI) in SZVAI system with the presence or absence of oxalate.

economic and environmentally friendly aspects [1,3,30]. Although it is also cost-effective to utilize ZVI for Cr(VI) pollutant treatment, this process inevitably produces much more sludge production due to the significantly easy corrosion of ZVI under the acidic solution, which potentially poses threat to environmental safety. Consequently, the recycling of spent aluminum beverage cans for Cr(VI) pollutant removal is an cost-effective strategy by reducing waste, saving energy and lessening use of municipal landfills.

As mentioned above, adjusting solution pH within appropriate acidic pH range may be a prerequisite to attain the appreciable activity of metal aluminum for reductive removal of Cr(VI). Coincidentally, the chromate wastewaters are usually very acidic, within a typical pH range of 1.5–3.5, which thus provided a much more desirable condition for the proposed SZVAI + Cr(VI) + oxalate reaction [31]. Here, to examine the flexibility of employing SZVAI for real Cr(VI)-containing wastewater treatment, chrome electroplating effluent with approximately 160 mg L⁻¹ Cr(VI) is collected from electroplating industrial park of Qingdao Development Zone. In this case, Cr(VI) can be rapidly and almost completely reduced within 120 min with adding 2.0 mL oxalate (100 mM) and 5 g/L SZVAI (see Fig. 7).

In above process, the deliberate addition of oxalate chemical to Cr(VI) wastewater for enhancing Cr(VI) detoxification induced by SZVAI is not advisable in the area of environmental remediation. However, oxalate is the main product in aerobic degradation of organic pollutants and ubiquitous in organic wastewaters. Specifically, oxalic acid and Cr(VI) are jointly used in many industries, such as electroplating industry and wood preservative processing [32,33]. Thus, it is economical and practical to introduce oxalate waste into Cr(VI) treatment system for achieving preferable Cr(VI) detoxification performance.

4. Conclusion

This study proposed and justified a new concept of reducing aqueous Cr(VI) pollutant by SZVAI mediated by oxalate. It is found that the presence of oxalate can significantly enhance the reduction of Cr(VI) due to its affinity to Cr(VI)/Cr(V) species. Metal aluminum

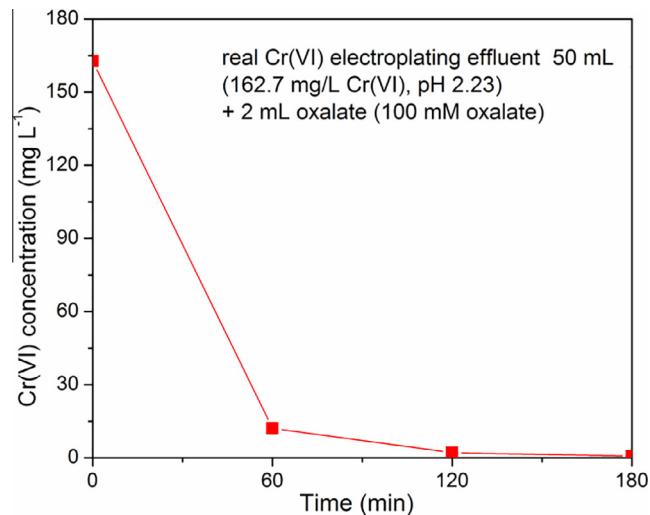


Fig. 7. The reduction of Cr(VI) in real chromium electroplating effluent in SZVAI/oxalate reaction system ($[\text{SZVAI}] = 5 \text{ g L}^{-1}$).

and the produced H_2O_2 was validated as the predominant species contributing to Cr(VI) reduction. H_2O_2 production was completely interrupted under anaerobic condition, leading to the evident inhibition of Cr(VI) reduction. In addition, Cr(VI) reduction was enhanced with decreasing solution pH. Moreover, the metals with minor contents in SZVAI can form numerous galvanic cells with metal aluminum and thus facilitated the removal of Cr(VI). Overall, the scrap zero-valent aluminum is highly active and stable for the fast removal of Cr(VI) and presents a promising solution for such environmental application in practice.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.09.098>.

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