A collaborative strategy for enhanced reduction of Cr(VI) by Fe(0) in the presence of oxalate under sunlight: Performance and mechanism

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Abstract
Nanometer-size zero-valent iron (NZVI) is an efficient reducing agent, but its surface is easily passivated with an oxide layer, leading to reaction inefficiency. In our study, oxalate (OA) was introduced into this heterogeneous system of NZVI, which could form ferrioxalate complexes with the NZVI surface-bound Fe^{3+} and dissolved Fe^{3+} in the solution. Photolysis of ferrioxalate complexes can facilitate the generation of Fe^{2+} from Fe^{3+} and CO_2/C_15 radical, both species have strong reduction capacity. Hence, a “photo-oxalate-Fe(0)” system through sunlight induction was established, which not only prohibited the formation of a surface passivation layer, but also displayed a synergetic mechanism of ferrioxalate photolysis to enhance reduction, exhibiting remarkably higher degradation activity (several times faster) toward the model pollutant Cr(VI) than the mechanism with NZVI alone. Factor tests suggested that both NZVI dosage and OA content markedly affected the reduction rate. Low pH was beneficial to the reduction efficiency. Moreover, recyclability experiment showed that the reduction rate decreased from 0.21706 to 0.03977 min^{-1} after three cycles of reuse due to the NZVI losing reaction activity generally, but the system still maintained considerable reduction capacity. Finally, a mechanism was revealed whereby NZVI would transform to Fe oxides after the exhaustion of its reductive power, and the photolysis of ferrioxalate to promote the cycling of iron species played the predominant role in providing extra reduction ability. These features confirm that introduction of OA into Cr(VI) reduction by NZVI through sunlight induction is advantageous and promising.

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Introduction

Chromium-containing wastewater is widely discharged from industrial manufacturing processes, such as leather tanning, metallurgy, wood preservation, electroplating, etc. (Barreradiaz et al., 2012), which has posed great threat to the health of human beings (Aoudj et al., 2015). In particular, Cr(VI) is carcinogenic and teratogenic toward living cells and is 500–1000 times more harmful than Cr(III) (Costa, 2003). The need for detoxification of Cr(VI) in waterbodies is urgent, and has received wide attention. Cr(VI) mainly exists in the anionic forms of \( \text{Cr}_2\text{O}_7^{\text{2-}} \), \( \text{HCr}_2\text{O}_7^- \) and \( \text{CrO}_2\text{S}^{\text{4-}} \), which have high aqueous solubility, stability and mobility (Qian et al., 2019). Traditional water treatment technologies like coagulation and filtration have difficulty removing Cr(VI). Adsorption, ion exchange or membrane filtration methods (Gode and Pehlivan, 2005; Qi et al., 2016; Lei et al., 2017) have been validated as effective, but only result in phase transfer or concentration of the pollutant, so that its toxicity still exists and requires additional cost for post-treatment or disposal. As compared with Cr(VI), Cr(III) is less mobile and readily precipitates as \( \text{Cr(OH)}_3 \) and so is separated easily from water. Therefore, transformation of Cr(VI) to Cr(III) via a reduction approach has become the most extensively employed method to remove toxic Cr(VI).

Up to the present, a variety of techniques including chemical reduction (Petala et al., 2013), electrochemical methods (Zongo et al., 2009) and photochemical methods (Nan et al., 2010; Hu et al., 2019) have been developed for aqueous Cr(VI) detoxification, wherein chemical reduction is the most commonly used because of its cost effectiveness and efficiency. Zero-valent iron (ZVI) is a representative reductant for fast and effective removal of a variety of pollutants in wastewater (Westerhoff, 2003; Lin, 2015; Zhang et al., 2016). Due to its advantages of low toxicity, low price, easy operation and convenient magnetic separation, ZVI has received much attention for Cr(VI) removal in recent years. Its reduction mechanism involves Cr(VI) (standard redox potential \( E^0(\text{Cr}^6^+ / \text{Cr}^3^+) = 1.33 \text{ V} \)) direct reduction mediated by ZVI (\( E^0(\text{Fe}^3^+/\text{Fe}^2^+) = 0.44 \text{ V} \)) and indirect reduction induced by the corrosion products of ZVI oxidation under acidic conditions, e.g., Fe\(^{2+}\) (\( E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V} \)). However, ZVI always rapidly loses its reductive power as it donates electrons and becomes oxidized during reactive reactions. These oxidized metals may precipitate and cover the surface of ZVI to form a so-called “passivation layer”, preventing reaction between target pollutants and ZVI. In order to rejuvenate the reaction activity of ZVI, many regeneration treatments (e.g., acid-washing) are carried out before use, but these still have the disadvantages of being time consuming and requiring concentrated acids, restricting their practical application (Lin et al., 2017; Lin and Lin, 2016).

Oxalate (OA), which is naturally abundant in natural water bodies and can be found in various industrial wastewaters (Quitain et al., 2002; Clausen, 2004), exhibits high affinity towards oxidized iron to form ferrioxalate complexes on the surface, preventing the formation of a passivation layer. There have already been many reports proposing that the reductive reaction efficiency of zero-valent metal (ZVM) could be enhanced through the introduction of small amounts of oxalate (Bo et al., 2017; Lin and Lin, 2017). However, the reductive power always comes from the electrons provided by ZVM, without extra reduction capacity being obtained. It has also been recognized that soluble small organic molecules, such as oxalate or malonate, can form complexes with iron as organic ligands, which would be another kind of important photoactive species for the transformation from \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) (Wang, 2012). The organo–iron complexes differ from inorganic ones, exhibiting considerable photoinduced ligand-to-metal charge transfer (LMCT) absorption at longer wavelengths, even extending their light response in the visible spectrum. Under sunlight irradiation, the LMCT from the organic ligand to \( \text{Fe}^{3+} \) would lead to the reduction of \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) and the oxidation of the ligand to a reactive radical form (Mcknight et al., 1988; Behra and Sigg, 1990; Kieber et al., 2003). The promising applications of such ligands in environmental remediation have been explored in redox transformation of many important environmental pollutants (such as \( \text{SO}_3^{2-} / \text{SO}_2^{2-} \), \( \text{As(III)/As(V)} \), and \( \text{Cr(III)/Cr(VI)} \)), as well as the degradation of natural organic matter and anthropogenic contaminants (Chang et al., 2012; Finden et al., 1984; Wang et al., 2008; Xie et al., 2004). For instance, the complexation of \( \text{Fe}^{3+} \) with OA in aqueous solution yields a strongly absorbing chromophore that exhibits efficient LMCT to transform \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) and generates \( \text{CO}_2 \) radical via ligand oxidation (\( E^0(\text{CO}_2/\text{CO}_2^-) = -1.9 \text{ V} \)) (Thomas et al., 2016). Both the species have strong reduction ability. Moreover, this mechanism could occur on the heterogeneous surface of Fe substrates (Qing et al., 2008). Importantly, the complexes of \( \text{Fe}^{3+} \) with OA can absorb radiation of longer wavelengths and thus extend their light response in the visible spectrum (Balmer and Sulzberger, 1999). The application potential of such complexes under sunlight is great because no additional equipment is required.

In consideration of the core-shell structure of ZVI, a new concept was proposed to establish a “photo-oxalate-Fe(0)” system to innovatively overlay the photodissociation mechanism of ferrioxalate complexes onto the ZVI reduction process to enhance the reduction capacity, which could be activated under solar irradiation. In this study, nanoscale ZVI (NZVI) was adopted due to its smaller size (10–100 nm), larger specific surface area and higher reactivity by comparison to commercially available fine iron powder. It is anticipated that four beneficial effects would play a role in Cr(VI) reduction: (i) the self-reductive power of NZVI; (ii) preventing the formation of passivation layer via the coordination complexation of OA with surface bound Fe\(^{3+}\); (iii) the photolysis of ferrioxalate complexes to promote the redox cycle of Fe species and generation of active radical species; (iv) the presence of OA can markedly accelerate the unidirectional conversion of the coordination shell rearrangement from tetrahedral Cr(VI)/Cr(V) species to octahedral Cr(III)/Cr(IV) species via the affinity of oxalate to Cr(VI)/Cr(V) species. The influence of solution pH, NZVI dosage, OA content and Cr(VI) concentration on Cr(VI) reduction was investigated and the reaction mechanisms were also elucidated. Notably, the main raw materials used in this system are Fe and OA, which are inexpensive and widely available in nature, so this system is an attractive option for the treatment of inorganic oxyacid pollutants.
1. Materials and methods

1.1. Chemicals

Potassium chromate (K$_2$Cr$_2$O$_7$, >99%), diphenylcarbazide (98%), ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, >99.5%), sodium borohydride (NaBH$_4$, >99%), oxalic acid dihydrate (C$_3$H$_4$O$_4$·2H$_2$O, >99%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (C$_9$H$_{11}$NO, 99.9%), NaOH (>96%) and HCl (36%–38%) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All chemical reagents were used as received without further purification. All solutions were prepared with ultrapure water from a Millipore system.

1.2. Experimental procedures

Nanoscale zero-valent iron was prepared according to a previously reported method (Sushil Raj et al., 2005): 1.6 mol/L NaBH$_4$ aqueous solution was added dropwise into a Ar gas-purged 1 mol/L FeCl$_3$·6H$_2$O aqueous solution at ~25°C with magnetic stirring. The reduction reaction for ferric iron (Fe$^{3+}$) is shown as follows:

$$\text{Fe}^{3+} + 3\text{BH}_4^- + 3\text{H}_2\text{O} \rightarrow \text{Fe}^{0} + 3\text{B(OH)}_3 + 10.5\text{H}_2$$ (1)

The solution was stirred for 20 min and centrifuged at 6000 r/min for 3 min, then the solid was washed with acetone by a magnet and used for the next cycle directly.

Photoinduction experiments were performed in a batch photoreactor which consists of eight 50 mL quartz reaction tubes of 2 cm diameter placed around a xenon lamp at the same distance of 8.0 cm. The simulated sunlight source was provided by a 500 W xenon lamp placed in a double-walled tubes of 2 cm diameter placed around a xenon lamp at the same distance of 8.0 cm. The simulated sunlight source was provided by a 500 W xenon lamp placed in a double-walled reactor cooled by circulating water flowing through the jacket layer to maintain the reactor temperature. In a typical batch test, certain amounts of NZVI, OA, and Cr(VI) were placed in the reactor to achieve the predetermined dosage and concentration in a final solution volume of 40 mL, followed by adjusting the solution pH to 3. After illumination under stirring for specific time intervals, aliquots of the solutions were extracted and then filtered through a 0.45 μm membrane. The residual Cr(VI) concentration was measured. Each experiment was repeated two or three times and the average values and standard deviations are presented.

For the recyclability experiment, the NZVI was separated by a magnet and used for the next cycle directly.

1.3. Characterization

X-ray diffraction (XRD) patterns were measured on a D8-FOCUS powder diffraction system (D8-FOCUS, Bruker, Germany) with Cu Kα radiation operating at 40 kV and 40 mA. The microstructures of the samples were observed by transmission electron microscopy (TEM, Tecnai-12, Philip Apparatus Co., USA). The chemical composition of the catalysts before and after the reaction was detected by X-ray photoelectron spectroscopy (XPS, PHI-5000C, PerkinElmer, USA) using an Al Kα excitation source. The organic content (oxalic acid) in solution was monitored by using the total organic carbon content (TOC) using an Al Kα excitation source. The organic content (oxalic acid) in solution was monitored by using the total organic carbon content (TOC) using a LECO, USA). Radical detection was conducted using electron spin resonance (ESR) experiment on a X-band A200 spectrometer (Bruker, Germany) using dimethyl pyridine N-oxide (DMPO) as the spin-trapping agent.

1.4. Analytical methods

Solution pH was determined by a pH meter (PHS-3C, Rex Electric Chemical, China). The residual Cr(VI) concentration in the solution was analyzed using the 1,5-diphenylcarbazide colorimetric method. The method from Stookey and Lawrence (Balmer and Sulzberger, 1999) was adopted for Cr(VI) reduction, which is described as follows (Eq. (2)), and the corresponding half-life ($t_{1/2}$) is calculated by Eq. (3):

$$-\ln \frac{[\text{Cr(VI)}]_t}{[\text{Cr(VI)}]_0} = kt$$ (2)

$$t_{1/2} = \ln 2/k$$ (3)

where [Cr(VI)]$_0$ (mol/L) is the concentration at time $t = 0$ and [Cr(VI)]$_t$ (mol/L) is the concentration at time $t$. $k$ (min$^{-1}$) represents the rate constant.

2. Results and discussion

2.1. Cr(VI) reduction by NZVI in the presence of oxalate induced by sunlight

First, the enhanced ability for Cr(VI) reductive removal by NZVI in the presence of OA induced by sunlight was evaluated. As shown in Fig. 1, compared to commercial iron powder, NZVI exhibited better reduction efficiency. This confirms the much higher reaction activity of NZVI due to its smaller size. When OA was introduced during reductive reactions by NZVI, the decrease of Cr(VI) concentration was more rapid than reaction with NZVI alone. Moreover, in a reaction employing OA without NZVI to elucidate whether OA may act as a reductant to directly react with Cr(VI), it was observed that negligible decrease of Cr(VI) concentration occurred after a reaction time of 60 min. This showed that the effect of OA in enhancing Cr(VI) reduction should be attributed to the strong affinity of OA towards Fe$^{0}$ enabling the formation of a coordination complex, inhibiting the formation of passivation layer on the surface of NZVI so that the NZVI surface remained unpassivated.
highly reactive for reducing Cr(VI). What is more, it has been reported that the affinity of OA for Cr(VI)/Cr(V) species could facilitate the unidirectional conversion of Cr(VI) to Cr(III) by expansion of the Cr(VI)/Cr(V) coordination shell from tetrahedron to hexahedron, also accelerating the reduction rate of Cr(VI). Notably, on exposure of the system to sunlight (simulated), a sharp reduction in the amount of Cr(VI) was observed, such that the Cr(VI) was almost completely removed with 10 min at an initial concentration of 2 mmol/L, indicating that the light irradiation induced an additional mechanism for the improvement of the total removal capacity. The commercially available iron powder was also applied in the system, and as expected, the reduction rate was significantly less than that of NZVI because of its bigger particle size, but the significant enhancement effect on the reduction of Cr(VI) was also observed under photoinduction with iron powder, indicating that the photolysis mechanism of ferrioxalate could occur on the surface of the iron powder as well.

2.2. Factor analysis for Cr(VI) reduction

2.2.1. Effect of NZVI dosage
The influence of initial NZVI dosage on Cr(VI) reduction was investigated at four dosages (0.2, 0.5, 1.0, and 2.0 g/L), and the results are presented in Fig. 2a. The result shows that the reaction efficiency of Cr(VI) was remarkably improved with the increase of NZVI dosage. Apparently, the reduction efficiency of Cr(VI) increased from 56.76% to 94.51% as the initial NZVI dosage increased from 0.2 to 0.5 g/L at the reaction time of 60 min. Meanwhile, the reduction rate rose accordingly, and the complete removal of Cr(VI) could be achieved within 10 and 3 min with the NZVI dosage increased to 1.0 and 2.0 g/L respectively. Through kinetic model fitting of the data (Fig. 2b), we can also find that the corresponding rate constant values at NZVI dosages of 0.2, 0.5, 1.0 and 2.0 g/L are 0.01407, 0.04977, 0.23761 and 1.26095 min\(^{-1}\) respectively, showing a dramatic rise, and the corresponding half-life decreased from 49.26 to 0.55 min with increasing NZVI dosage from 0.2 to 2.0 g/L. With the extension of reaction time, the trend of Cr(VI) concentration continuously declined in all cases and until approximately complete removal was reached (complete removal was achieved with the dosages of 0.5, 1.0 and 2.0 g/L at 60 min, as shown in Fig. 2a). This indicates that the NZVI dosage is an important factor affecting the reaction rate, which could be explained by the fact that a higher amount of NZVI powder in solution would provide much larger reaction contact area for Cr(VI) and contribute more electrons per unit time.

2.2.2. Effect of initial OA and Cr(VI) concentrations
OA plays a key role in the “photo-oxalate-Fe(0)” dual mechanism system, which not only ensures the activity of Fe(0) particles, but also forms the photo-active species ferric oxalate on the surface. Under light induction, OA was consumed continuously in the reaction process. The reduction efficiency of Cr(VI) at different OA concentrations is shown in Fig. 3a. At constant Cr(VI) concentration, the increase of OA significantly improved the reduction rate of Cr(VI), and the reaction time for complete removal of Cr(VI) was shortened dramatically. It can also be found from Fig. 3b that there was a perfect linear correlation relation between the rate constant \(k\) and OA

![Fig. 1 – Comparison of reduction efficiency of Cr(VI) by iron powder and nanometer zero valent iron (NZVI) without light, with added oxalate (OA), and with light induction. Reduction conditions: 5 mmol/L OA, 2 mmol/L Cr(VI), pH 3, dosage 1 g/L. \(t\): reaction time.](image1)

![Fig. 2 – (a) Effect of NZVI dosage on Cr(VI) reduction efficiency and (b) reaction kinetics fitting of the reduction data, inset shows the kinetic constants \((k)\). Reaction conditions: 5 mmol/L OA, 2 mmol/L Cr(VI), pH 3. \([Cr(VI)]_0\): Cr(VI) concentration at time = 0; \([Cr(VI)]_t\): Cr(VI) concentration at time \(t\).](image2)
concentration. $k$ was 0.0289 min$^{-1}$ at 1 mmol/L OA, increasing to 0.12767 min$^{-1}$ at 3 mmol/L OA and 0.23761 min$^{-1}$ at 5 mmol/L OA, respectively. These kinetic comparisons revealed the key role of OA in tremendously expediting the reduction kinetics, hence implying that a second mechanism of photolysis by ferrioxalate complexes indeed existed in the reduction process to contribute to the reduction capacity, because the aforementioned results for the system of NZVI without the presence of OA only provided limited contribution to Cr(VI) reduction.

In addition, when increasing the initial Cr(VI) concentration, a significant decline in reaction efficiency was observed (Fig. 3c). As seen in Fig. 3d, the reaction rate constant $k$ showed a sharp decrease from 0.23761 min$^{-1}$ at 2 mmol/L Cr(VI) to 0.00498 min$^{-1}$ at 4 mmol/L Cr(VI), and then it remained almost unchanged on further increasing the Cr(VI) concentration from 4 to 6 mmol/L. This may be due to the high content of Cr(VI) in solution competing for the surface adsorption sites of NZVI, restricting the OA contact with the NZVI surface. Moreover, the Cr(VI) in solution may also associate with OA to form a complex, reducing the amount of ferrioxalate species in solution; therefore, the reaction process of Cr(VI) required much longer time.

2.2.3. Effect of solution pH

Reports suggest that solution pH would affect the formation of ferrioxalate species and the dissolution of NZVI, so it should be an important factor determining the reduction efficiency of Cr(VI). The effect of different initial pH values of 3, 5, 7 and 9, adjusted with dilute HCl and NaOH, on Cr(VI) reduction is depicted in Fig. 4a. It can be seen that the best reduction efficiency of Cr(VI) appeared at the low pH of 3 and gradually declined with the increase of initial pH. Moreover, as the reaction progressed, the final pH increased and reached a plateau approaching neutral pH for acidic conditions, while it was basically unchanged in an alkaline environment (pH = 9) (Fig. 4b), indicating that the Cr(VI) reduction by the “photo-oxalate-Fe(0)” system is a process of continuous consumption of H$^+$. Meanwhile, a significant reduction in the rate constant $k$ from 0.23761 to 0.03066 min$^{-1}$ was observed when the pH increased from 3 to 5, followed by a relatively small change of $k$ for pH continuously increasing to 9 (Fig. 4c). The fact that ideal treatment efficiency was observed under acidic conditions might be attributed to the following reasons: an acidic environment can promote dissolution of the surface oxide layer, allowing NZVI to maintain high reaction activity; also, the redox reaction between Fe(0) and Cr(VI) consumes a large amount of H$^+$, and low pH will speed up this reaction; moreover, the complexes of ferric trioxalate or ferric dioxalate with higher photoreactivity prefer to form in the acidic range, which should exist both on the NZVI surface with surface-bound Fe$^{3+}$ and in the homogeneous solution with dissolved Fe$^{3+}$, leading to a stronger photolysis effect to generate extra reductive species (Fe$^{2+}$ and CO$_2$). The data in Fig. 4d confirm that the dissolved Fe$^{3+}$ content was highest at pH 3, while the maximum consumption of OA also occurred at pH 3, then decreased substantially to be virtually absent at pH of 7.

Fig. 3 – Effects of (a) the OA content and (c) initial Cr(VI) concentration on Cr(VI) reduction efficiency; (b) and (d) show the reaction kinetics fittings of the reduction data (a) and (c), respectively. Inset shows the kinetic constants. Reduction conditions: 1 g/L NZVI, 2 mmol/L Cr(VI), and pH 3 for (a) and (b), and 1 g/L NZVI, 5 mmol/L OA, and pH 3 for (c) and (d).
2.2.4. Effect of coexisting organic matter and anions

Real wastewater usually has a complex composition, containing various co-existing anions and organic matter. In Fig. 5, the typical dye pollutant, Rhodamine B (RhB), with a concentration of 10 mg/L, was used to test the effect of co-existing organic matter in the reduction process of Cr(VI). RhB showed a weak decolorizing effect under the Xe lamp irradiation during the time of the experiment. In contrast, a very rapid complete decolorization took place within 6 min in the "photo-oxalate-Fe(0)" system, and the reduction efficiency of Cr(VI) was affected, implying that the oxidizing species formed in the system. In a previous report on photo/iron oxalate-assisted Fenton systems (Balmer and Sulzberger, 1999) it was revealed that $\text{H}_2\text{O}_2$ could be generated in the system, and photochemically produced Fe(II) catalyzing $\text{H}_2\text{O}_2$ is an important source of $\cdot\text{OH}$, which plays the role of oxidant. The reaction sequence in photo-Fenton systems is given below:

$$\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)^{3-} \rightarrow \text{hv} \rightarrow \text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)^{2-} + \text{C}_2\text{O}_4^{\cdot}$$

(4)

$$\text{C}_2\text{O}_4^{\cdot} \rightarrow \text{CO}_2 + \text{CO}_2^{\cdot}$$

(5)

$$\text{CO}_2^{\cdot} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2^{\cdot}$$

(6)

$$\text{O}_2^{\cdot} + \text{H}^+ \rightarrow \text{HO}_2^*$$

(7)

$$\text{HO}_2^{\cdot} + \text{O}_2^{\cdot} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$

(8)

$$\text{HO}_2^{\cdot} + \text{HO}_2^{\cdot} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$

(9)

$$\text{Fe(II)} + \text{O}_2^{\cdot} + 2\text{H}^+ \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2$$

(10)

$$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{HO}_2^* + \text{OH}^*$$

(11)

where $\text{hv}$ is the photon energy.

Therefore, a possible route in the "photo-oxalate-Fe(0)" system is the following: dissolved $\text{O}_2$ could adsorb on the surface of NZVI to obtain an electron and react with $\text{CO}_2^{\cdot}$ to produce $\cdot\text{O}_2^*$, then form $\text{H}_2\text{O}_2$ in an acidic environment, which...
could be catalyzed by iron species to yield oxidizing •OH radical. The results indicate that the system has great potential for simultaneous removal of Cr(VI) and organic pollution.

The effect of coexisting anions including sulfate (SO\textsubscript{4}\textsuperscript{2-}), nitrate (NO\textsubscript{3}-) and chloride (Cl\textsuperscript{-}) ions at equal concentrations (i.e., 2 mmol/L) on the removal of Cr(VI) is shown in Fig. 6. It can be seen in Fig. 6a that the system had almost no visible removal effect for the above-mentioned co-existing anions; meanwhile, the negative effect on Cr(VI) reduction efficiency was also almost negligible. However, when the reaction system was exposed to UV light (300 W high-pressure mercury lamp) (Fig. 6b), the reduction rate of Cr(VI) without co-existing anions showed obvious improvement, with the time for Cr(VI) complete removal shortened from 10 to 3 min. However, a different phenomenon was observed in the co-existing anion system: the NO\textsubscript{3} concentration decreased in the reaction process, while there was a weakening of the Cr(VI) reduction efficiency. It seems that the NO\textsubscript{3} consumed some of the reduction capacity for Cr(VI) reduction. This can be attributed to the different photolysis efficiency of ferrioxalate complexes under different light sources. Under sunlight, the photolysis degree is at a low level, so the amount of species of Fe\textsuperscript{2+} and CO\textsubscript{2} generated is small. Further, the strongly reducing CO\textsubscript{2} would be consumed via being captured by the dissolved O\textsubscript{2} to form O\textsubscript{2}\textsuperscript{-} (\(E^\circ(O_2/O_2^{-}) = -0.16\) V) and H\textsubscript{2}O\textsubscript{2} (\(E^\circ(O_2/H_2O_2) = 0.69\) V) or used to reduce Fe\textsuperscript{3+} to Fe\textsuperscript{2+}; these species could and should prefer to reduce Cr(VI) due to its standard oxidation potential being much higher than that of the co-existing anions. Thus, the reduction efficiency of Cr(VI) in the presence of co-existing anions was not significantly decreased. However, when exposed to UV light, more Fe\textsuperscript{2+} and CO\textsubscript{2} were produced per unit time, so that part of the CO\textsubscript{2} would be used to reduce NO\textsubscript{3} and some of the reduction capacity for Cr(VI) was lost.

2.3. Recyclability of NZVI in the presence of OA for photo-assisted Cr(VI) reduction

Recyclability is one of the most important aspects in evaluating the performance of an application system. Fig. 7a depicts the results for three reuse cycles of NZVI for the reduction of Cr(VI) in the “photo-oxalate-Fe(0)” system. In the first two cycles, a fast reduction rate was observed and complete removal was achieved within 10 min. However, by the third cycle, the reduction efficiency decreased drastically, with the reduction rate k declining from 0.21706 to 0.03977 min\textsuperscript{-1} (Fig. 7b). Furthermore, the recycling performance of NZVI alone was also tested and shown for comparison. As expected, NZVI showed a relatively lower reaction rate, which gradually diminished with the increase in reuse cycles. By the third cycle, NZVI had almost completely lost its capability for
reducing Cr(VI). This should be due to the reductive power of NZVI being gradually consumed in the repeated use cycles. However, there still remained a considerable reduction capacity in the third cycle for the “photo-oxalate-Fe(0)” system while NZVI alone exhibited a limited reduction ability, revealing that the additive effect of the photolysis mechanism of ferrioxalate could show activity even though the NZVI had transformed to Fe oxide. In other words, this also means that the photolysis mechanism of ferrioxalate could be implemented by using waste iron, iron scrap or metal oxide as an Fe substrate in the heterogeneous system so to achieve cost saving and follow the strategy of “waste control by waste”.

### 2.4. Reaction mechanism

The above experimental results have demonstrated the enhancement effect of ferrioxalate on the reduction ability of NZVI by an overlaid photolysis mechanism. Some characterization techniques were employed to validate the reaction process. The TEM images of NZVI before and after reaction are shown in Fig. 8a, showing that the morphology of the nanoparticles did not change much except for a reduction in particle size, which may be caused by the dissolution of NZVI. From the XRD patterns in Fig. 9a, it can be seen that the original sample mainly consisted of Fe(0). After use, some Fe

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**Fig. 8**  (a, b) Transmission electron microscopy (TEM) of NZVI before and after reaction and (c) electron spin resonance (EPR) free radical detection. Reaction conditions: 10 mmol/L OA, 1 g/L NZVI dosage, and pH 3. DMPO: dimethyl pyridine N-oxide.

**Fig. 9**  (a) X-ray diffraction (XRD) and (b–d) X-ray photoelectron spectroscopy (XPS) before and after reaction.
oxides (Fe₂O₃) were detected, revealing that the surface of the particles began to be oxidized due to losing some electrons of NZVI. At the third reuse cycle, the diffraction peak of Fe(0) almost disappeared while that of Fe₂O₃ was markedly enhanced, which proves that Fe(0) is constantly consumed in the reaction process until completely transforming to Fe oxide. XPS full peak analysis (Fig. 9b) found that Cr appeared on the surface of the material after the reaction, and the narrow peak fitting of the Cr spectrum in Fig. 9d indicates that it basically exists in the form of Cr(III). Fig. 9c shows that the iron species existing on the particle surface before reaction have valences of +3, +2 and zero, but the +2 and zero valence iron disappear after reaction, which indicates that FeOOH formed on the surface of NZVI in the Cr(VI) reduction process and the Cr(VI) was reduced to Cr(III), which deposited on the particle surface and converted into a passivation layer of ferrochromium hydroxide. The efficient photodissociation of the complex of Fe³⁺ with OA to give Fe²⁺ and CO₂⁻ anion radical is a well-known concept. However, according to an electron spin resonance (ESR) experiment (Fig. 8b), no visible radical signal was observed in the heterogeneous "photo-oxalate-Fe(0)" system; this should due to two aspects: (1) the amount of CO₂⁻ generated via photolysis of the iron oxalate complex on the particle surface is very limited. (2) the newly generated CO₂⁻ radicals are preferentially captured by the surface-bound Fe³⁺ in the passivation layer, so they were consumed completely.

In summary, the reaction path could be described as follows: Fe⁰ and the derived product, namely Fe²⁺, were proved to be the primary electron donors for Cr(VI) reduction. The enhancement of the Cr(VI) reduction rate by the addition of OA induced by sunlight was attributed to the strong affinity of OA for Fe³⁺, which can effectively prevent the formation of insoluble hydroxides on the NZVI surface and therefore increase its reactive activity. Moreover, the photolysis of the complex of OA with dissolved and surface-bound Fe³⁺ (Qing et al., 2008) could promote the cycling of iron species and yield CO₂⁻, which played the predominant role in the extra reduction ability. In addition, dissolved oxygen competed for the electrons of NZVI and CO₂⁻, then producing oxidizing •OH to degrade organic pollutants. The schematic diagram of the reaction path is shown in Fig. 10.

3. Conclusions

In this study, a strong "photo-oxalate-Fe(0)" reduction system was established for enhanced reduction of Cr(VI) by innovatively combining the mechanism of photolysis of ferrioxalate complexes and the reductive power of NZVI. A blank control experiment verified the enhancement effect, and the reduction capacity followed the order: NZVI + OA + sunlight > NZVI + OA > NZVI. This should be attributed to the presence of OA preventing the formation of an oxide passivation layer, therefore allowing NZVI to retain high activity for the reduction of Cr(VI). Further, when illuminated by sunlight, the photodissociation of ferrioxalate would be induced. According to the ESR experiment and XPS analysis, the transformation of iron species but not the CO₂⁻ radical should play the predominant role in Cr(VI) reduction due to the low energy intensity of sunlight. The reduction of Cr(VI) was significantly influenced by the dosage of NZVI, initial OA concentration and initial pH, and the Cr(VI) reduction rate increased with the increase of NZVI dosage, but decreased with the increase of initial pH. An increase in the initial OA concentration could improve the reduction capacity. The reduction of 2 mmol/L Cr(VI) reached more than 99% within 10 min under the condition of NZVI = 1 g/L, initial OA concentration = 5 mmol/L and initial pH = 3. Moreover, the Fe(0) can be easily separated from water by a magnetic field for repeated use, but due to the loss of reaction activity of Fe(0), the Cr(VI) reduction efficiency decreases significantly with repeated reuse; however, the mechanism of photolysis of ferrioxalate could be maintained. This system can be expanded to use iron scrap as an Fe substrate to meet the "waste control by waste" strategy. Therefore, this study provided a new perspective on the role of OA to enhance the reduction capacity of Fe(0) under solar irradiation with the advantages of simplicity, speed, non-toxicity...
and low cost, holding significant promise for the detoxification of Cr(VI).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES


