



## Research paper

# Mn<sup>2+</sup> promoted Cr(VI) reduction with oxalic acid: The indispensable role of In-situ generated Mn<sup>3+</sup>



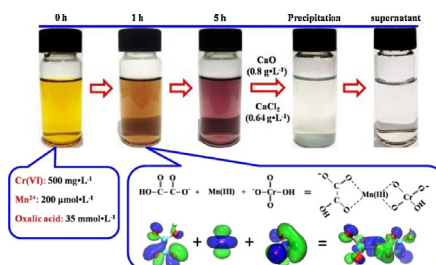
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## HIGHLIGHTS

- Mn<sup>2+</sup> can greatly promote the Cr(VI) reduction by oxalic acid at pH < 5.
- The reduction of Cr(VI) had an induction period followed by an auto-acceleration period.
- The in situ generated Mn<sup>3+</sup> might complex with oxalate and Cr(VI) to produce a ternary complex.
- The ternary complex of oxalate and Cr(VI) can automatically accelerate the Cr(VI) reduction process.
- This study provides an efficient way to remediate Cr(VI)-containing acid wastewater.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, we demonstrate that Mn<sup>2+</sup> can greatly promote the Cr(VI) reduction by oxalic acid at pH < 5 via an induction period and a subsequent auto-acceleration process. The Cr(VI) reduction rate constant during the late auto-acceleration process was about 10 times that of the initial induction period. Characterization results revealed that this interesting two-step Cr(VI) reduction phenomenon was attributed to the in-situ generated Mn<sup>3+</sup> by the oxidation of Mn<sup>2+</sup> with Cr(VI) in the presence of oxalic acid during the induction period. The in-situ generated Mn<sup>3+</sup> might complex with oxalate and Cr(VI) to produce a ternary complex, thus facilitating the electron transfer from oxalate to Cr(VI) to automatically accelerate the Cr(VI) reduction process. These findings shed insight into the possible roles of widely existed Mn ions (Mn<sup>2+</sup> and Mn<sup>3+</sup>) and oxalic acid in the transformation of Cr(VI) in natural aquatic environment, and also provided an efficient way to remediate Cr(VI)-containing acid wastewater.

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## 1. Introduction

Chromium is widely used in many industrial processes and more than 40.8 million tons of chromium-containing waste is released

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annually [1]. Chromium mainly exists in two valence states in the environment, namely hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Cr(VI) is extremely toxic even at very low concentrations [2]. Long term exposure to the Cr(VI) pollution environment will cause a considerable health problem to human beings, as Cr(VI) can cross cell membranes, and convert to reactive Cr(V) and Cr(IV) species, which can suppress cellular receptors involved in the immune response and activate cell cycle-related and proapoptosis genes [3,4]. So Cr(VI) pollution has been ranked

the third among the top ten worst toxic pollution problems in the world. On contrast, Cr(III) is essential in trace quantities for sugar and lipid metabolism in humans [5]. The most common approach to remediate Cr(VI) pollution is to reduce Cr(VI) into relatively less toxic Cr(III). The typical Cr(VI)-contaminated water treatment methods are based on the reduction of Cr(VI) to Cr(III) by sulfite or ferrous compounds [6], followed by precipitation with alkali. Although these methods are often effective, the use of ferrous compounds may cause secondary pollution of iron sludge and sulfite itself is a typical industrial pollutant. Therefore, it is imperative to find an efficient, cost-effective and environmentally benign reductant to reduce Cr(VI).

Oxalic acid, mainly from the decomposition of organic matter and plant root exudates, is one of most widely natural existed organic acids [7]. It is widely used as an industrial cleansing agent [8], and also extensively applied to reduce Cr(VI) because of its environmentally friendly nature and low cost [9–12]. Although the oxalic acid could direct reduce Cr(VI) via expansion of Cr(VI)/Cr(V) coordination number from tetrahedron to hexahedron and the direct Cr(VI) reduction by oxalic acid is thermodynamically feasible [13], the reduction process is very slow. For example, no Cr(VI) ( $20 \mu\text{mol L}^{-1}$ ) reduction was observed in  $200 \mu\text{mol L}^{-1}$  oxalic acid solution even after 400 days [12]. Many methods have been proposed to speed up the Cr(VI) reduction by oxalic acids. For example, Deng and Stone found that  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{FeOOH}$  could catalyze the Cr(VI) reduction by oxalic acid in the pH range from 3 to 7, and thus shortened the Cr(VI) reduction time from hundreds of days down to hundreds of hours [12]. Hug and Laubscher found that Fe(III) could catalyze photochemical reduction of Cr(VI) by oxalate in aqueous solutions to realize the 95% Cr(VI) reduction within 40 min [14]. Unfortunately, these oxalic acid based methods are still not feasible for the practical application, especially in the case of groundwater remediation. Thus, the development of efficient and facile oxalic acid based Cr(VI) methods is of great significance for the Cr(VI) pollution remediation.

$\text{Mn}^{2+}$  is abundant in natural environment. In 1976, Huber and Haight reported that the Cr(VI) reduction by oxalic acid could be accelerated by adding trace amount of  $\text{Mn}^{2+}$  to the reaction system, and attributed this accelerated Cr(VI) reduction to the formation of  $\text{Mn}^{2+}$ -oxalate complex, as  $\text{Mn}^{2+}$  could not reduce Cr(VI) alone [15]. Till now, the catalysis mechanisms of  $\text{Mn}^{2+}$  remain controversial. For example, Kabir-ud-Din et al. thought that  $\text{Mn}^{2+}$  could complex with oxalic acid to form Mn(II)-oxalate complex, which was responsible for the formation of an ester-like species with Cr(VI), and then the reduction of Cr(VI) to Cr(III) occurred in a single-step three-electron redox transfer without generating Cr(V)/Cr(IV) intermediates [16]. However, Perez-Benito and Arias suggested that oxalic acid acted as a stabilizing ligand for  $\text{Mn}^{3+}$ , which would lower the energy required to form the transition state for the subsequent one-electron oxidation of  $\text{Mn}^{2+}$  by Cr(VI), and thus facilitate the Cr(VI) reduction in  $\text{Mn}^{2+}$ /oxalic acid system [17]. Recently, Kazimierz et al. proposed a mechanism that involved a one-electron transfer from  $\text{Mn}^{2+}$ /bis-oxalate complex to Cr(VI) by reducing  $\text{Cr}=\text{O}$  to  $\text{Cr}-\text{OH}$  [18]. Obviously, these controversial mechanisms of  $\text{Mn}^{2+}$  catalyzed Cr(VI) reduction by oxalic acid are detrimental to the treatment of Cr(VI)-containing wastewater with  $\text{Mn}^{2+}$  and oxalic acid based methods of cost-effective and environmentally benign characteristics.

In this study, we systemically investigate the kinetics of Cr(VI) reduction by oxalic acid in the presence of  $\text{Mn}^{2+}$ , aiming to deeply understand the catalytic role of  $\text{Mn}^{2+}$  on Cr(VI) reduction by oxalic acid. On the basis of experimental and theoretical results, we intend to propose a credible mechanism to explain  $\text{Mn}^{2+}$  promoted Cr(VI) reduction by oxalic acid. The intermediate of Cr(VI) reduction and the final reduction products are measured and analyzed carefully. More importantly, we also extend this method to reme-

diate wastewater containing Cr(VI) of concentration as high as  $500 \text{ mg L}^{-1}$  ( $9.62 \text{ mmol L}^{-1}$ ).

## 2. Experimental section

### 2.1. Chemicals

Manganese(II) chloride tetrahydrate ( $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$ ), oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), chromium chloride ( $\text{CrCl}_3$ ), sodium hydroxide ( $\text{NaOH}$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were purchased from National Medicines Corporation Ltd., China. 1, 5-diphenylcarbazide was obtained from Alfa-Aesar. All of the chemicals were of analytical grade and used as received. Deionized water was used throughout the experiments.

### 2.2. Cr(VI) removal experiments

All of the removal experiments were performed in 250 mL three-neck flask. Stock solutions of  $1000 \text{ mg L}^{-1}$  ( $19.23 \text{ mmol L}^{-1}$ ) Cr(VI),  $30 \text{ mmol L}^{-1}$  oxalic acid and  $20 \text{ mmol L}^{-1}$   $\text{Mn}^{2+}$  were prepared by dissolving analytical grade  $\text{K}_2\text{Cr}_2\text{O}_7$ , oxalic acid and  $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$  in deionized water. All working solutions were prepared by diluting the stock solution with deionized water. Cr(VI) and oxalic acid were premixed, more deionized water was added into the resulting solution until the volume reached 99 mL. 1 mL of  $\text{Mn}^{2+}$  stock solution was then added into the above solution to make the final volume of 100 mL and trigger the Cr(VI) reduction process. The flask was then transferred into a shaker with a speed of 200 rpm to initiate the Cr(VI) reduction immediately. The initial pH of the solution was 2.50. The temperature was kept at  $30^\circ\text{C}$  during the removal process. The temporal pH values were measured as a function of time during the Cr(VI) reduction. 0.2 mL of solution was sampled for measurement at regular intervals. For comparison, oxalic acid was replaced with other organic acids (citric acid, malonic acid, tartaric acid, glycolic acid, sorbic acid and cinnamic acid) for the Cr(VI) reduction reaction. The effects of other metal ions ( $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$ ) on the Cr(VI) reduction by oxalic acid were also investigated. The initial pH values were adjusting to 2.50 with  $\text{HCl}$  ( $1 \text{ mol L}^{-1}$ ) and  $\text{NaOH}$  ( $1 \text{ mol L}^{-1}$ ) solutions where necessary.

### 2.3. Analysis method

The concentration of Cr(VI) and oxalate ion were measured by using the 1, 5-diphenylcarbazide spectrophotometric method and ion chromatographer (Dionex ICS-900, Thermo, USA) equipped with Ion Pac AS14A Anion-Exchange Column respectively (SI). As  $\text{Mn}^{2+}$  is a EPR-active metal specie, the quantitative information of  $\text{Mn}^{2+}$  was obtained with electron paramagnetic resonance (EPR) spectra (Bruker A300) during the Cr(VI) reduction in  $\text{Mn}^{2+}$ /oxalic acid system [19].

### 2.4. Theory calculations

Density functional theory (DFT) calculations were carried out with using the Gaussian 09 software package (SI) [20]. In this method, the interaction between the two fragments A and B is partitioned into three terms as follows.

The charge donation  $d_i$  from A to B defined as:

$$d_i = \sum_k^{occ,A} \sum_n^{vac,B} m_i c_{ki} c_{ni} \langle \Phi_k | \Phi_n \rangle \quad (1)$$

The back-donation  $b_i$  from B to A defined as:

$$b_i = \sum_l^{occ,B} \sum_n^{vac,A} m_i c_{li} c_{mi} \langle \Phi_l | \Phi_m \rangle \quad (2)$$

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