



# Highly reductive radical $\text{CO}_2^{\cdot-}$ deriving from a system with $\text{SO}_4^{\cdot-}$ and formate anion: Implication for reduction of Cr(VI) from wastewater

Hejun Ren<sup>a</sup>, Zhimin Hou<sup>a</sup>, Xiao Han<sup>b</sup>, Rui Zhou<sup>a,c,\*</sup>

<sup>a</sup>Key Laboratory of Groundwater Resources and Environment of the Ministry of Education, College of Environment and Resources, Jilin University, 2519 Jiefang Road, Changchun 130021, People's Republic of, China

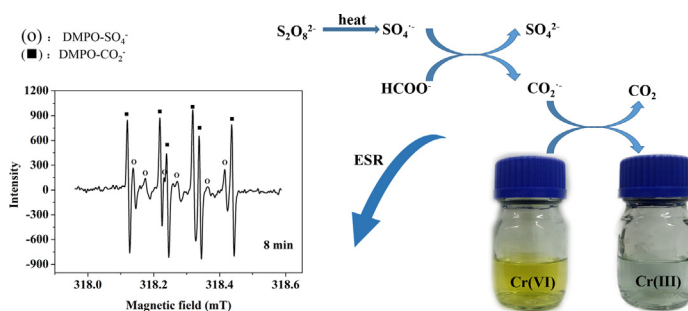
<sup>b</sup>College of Mathematics, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of, China

<sup>c</sup>Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

## HIGHLIGHTS

- An advanced reduction process based on  $\text{CO}_2^{\cdot-}$  was used to reduce Cr(VI).
- The reduction mechanism and the effects on Cr(VI) reduction was studied.
- This study provided a nontoxic and highly efficient process for Cr(VI) reduction.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 24 June 2016

Received in revised form 16 October 2016

Accepted 17 October 2016

Available online 18 October 2016

### Keywords:

Carbon dioxide anion radical

Advanced reduction process

Cr(VI) reduction

Mechanism

Persulfate

Formate

## ABSTRACT

An advanced reduction process (ARP) was established for the highly reductive radical  $\text{CO}_2^{\cdot-}$  produced by thermally activated persulfate (TAP) system in the presence of formate anions (FA). A series of control tests suggested that FA converted a strong oxidative condition into a reductive one, with  $\text{CO}_2^{\cdot-}$  as the pre-dominant radical for Cr(VI) reduction initiated by  $\text{SO}_4^{\cdot-}$  in the presence of FA. This mechanism was confirmed by electron spin resonance experiment. The ability of the system to reduce Cr(VI) mainly depended on the dosage ratio of FA and persulfate (PS), and the system maintained a strong reductive condition at ratios of FA to PS equal to or higher than one. Moreover, the rate of reaction increased with increasing PS dosage and reaction temperature, but decreased with increasing pH. The reduction efficiency of Cr(VI) reached more than 99% within 240 min for an initial Cr(VI) concentration of  $50 \text{ mg}\cdot\text{L}^{-1}$  under the condition of  $[\text{FA}]_0 = 30 \text{ mM}$ ,  $[\text{PS}]_0 = 30 \text{ mM}$ ,  $T = 70 \text{ }^\circ\text{C}$ , and unadjusted pH.

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## 1. Introduction

Chromium contamination of water has received increased attention because of its severe impact on public health. With its carcinogenicity, toxicity, and high aqueous solubility, Cr(VI) is

\* Corresponding author at: Key Laboratory of Groundwater Resources and Environment of the Ministry of Education, College of Environment and Resources, Jilin University, 2519 Jiefang Road, Changchun 130021, People's Republic of, China.

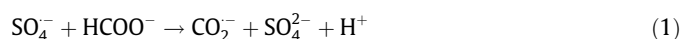
E-mail address: [zhour@jlu.edu.cn](mailto:zhour@jlu.edu.cn) (R. Zhou).

500–1000 times more harmful to living cells than Cr(III) [1]. The reduction of Cr(VI) to Cr(III) is beneficial because the trivalent form is less mobile and toxic. As such, a number of treatment processes have been developed to reduce Cr(VI) to Cr(III). These techniques include chemical reduction [2,3], electrochemical method [4], photochemical method [5], and bioremediation [6,7]; of which, chemical reduction is the most commonly used because of its cost effectiveness and efficiency. Nanoscale zero-valent iron (nZVI) is a representative reductant for Cr(VI). The direct reduction mechanism is that  $\text{E}^0 (\text{Fe}^{2+}/\text{Fe}^0) (-0.44 \text{ V})$ ,  $\text{E}^0 (\text{Fe}^{3+}/\text{Fe}^0) (-0.04 \text{ V})$ , and  $\text{E}^0$

( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) (0.77 V) are all lower than  $E^0(\text{Cr}^{6+}/\text{Cr}^{3+})$  (1.33 V) under acidic conditions. However, under this mechanism, nZVI particles tend to rapidly agglomerate and the co-precipitates cover the particle surface, thereby preventing subsequent Cr(VI) reduction [2] and causing rapid loss of reduction reactivity.

This study reports an instance of Cr(VI) reduction using a carbon dioxide anion radical ( $\text{CO}_2^-$ ) from a viewpoint of environmental remediation, with a low redox potential ( $-1.9$  V [8]), and can rapidly transfer an electron to several organic and inorganic compounds [9]. Several researchers reported that  $\text{CO}_2^-$  is an effective electron donor and can reductively transform different kinds of organic compounds, such as substituted benzenes [10], methyl viologen [11], Trichloroacetic acid [12,13], maleate [14], fumarate [14], and 4-nitroaniline [15]. This radical has also been used to reduce inorganic metal ions, such as  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Tl}^+$  [16], and  $\text{Hg}^{2+}$  [17,18].

Harbour et al. reported that addition of formate anions (FA) to a solution containing  $\text{SO}_4^-$  and  $\text{HO}^\cdot$  can transform the oxidizing condition of the solution into a reductive one [12,18,19] and generate  $\text{CO}_2^-$ . The transformation reactions occurring in the system are shown in Eqs. (1) and (2).



Hence, it is essential that an advanced reduction process (ARP) be established to transform the oxidative atmosphere into a reductive one by adding formate to an advanced oxidation process. Berkovic et al. employed laser flash photolysis with Ar-saturated persulfate (PS) solutions in the presence of formic acid to produce the  $\text{CO}_2^-$  [18]. Rosso et al. used vacuum ultraviolet (172 nm) irradiation to generate  $\text{CO}_2^-$  from  $\text{N}_2$ -saturated solutions containing formate [10]. Schutz and Meyerstein produced  $\text{CO}_2^-$  through ionizing radiation in neutral He- and  $\text{N}_2\text{O}$ -saturated solutions [14]. Nevertheless, the operational costs of these technologies are very expensive and impractical for large-scale applications. Alternatively, a thermally activated persulfate (TAP) system in the presence of formate is a highly effective and clean method, which only releases  $\text{CO}_2$  and leaves no toxic residues [12,17].

To the best of our knowledge, a few studies have reported Cr(VI) reduction by  $\text{CO}_2^-$ , and the underlying mechanism remains unclear. Therefore, the current study aims to establish ARP by adding formate anion to a TAP system to reduce Cr(VI). Control experiments were performed to elucidate Cr(VI) reduction performance and mechanism. The dominant free radicals in the ARP system were studied by electron spin resonance (ESR) experiment. Furthermore, factors affecting reduction were then conducted to gain insights into the reductive ability of Cr(VI), including initial FA dosage, initial PS dosage, initial pH, reaction temperature, and the presence of other coexisting small-molecule organic compounds.

## 2. Materials and methods

### 2.1. Chemicals

The following analytical-grade chemical reagents were purchased from Sinopharm Chemical Reagent Co., China:  $\text{K}_2\text{Cr}_2\text{O}_7$  ( $\geq 99.8\%$ ),  $\text{Na}_2\text{S}_2\text{O}_8$  (99%),  $\text{NaCOOH}$  ( $\geq 99.5\%$ ),  $\text{NaHCO}_3$  ( $\geq 99.5\%$ ),  $\text{KI}$  ( $\geq 99.0\%$ ), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) ( $\text{C}_6\text{H}_{11}\text{NO}$ , 99.9%),  $\text{CH}_3\text{CH}_2\text{OH}$  (99.8%),  $\text{HCHO}$  (37%–40%),  $\text{CH}_3\text{COOH}$  (98.0%), diphenylcarbazine (DPCI) ( $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$ , 99.9%),  $\text{H}_2\text{SO}_4$  (98%),  $\text{H}_3\text{PO}_4$  ( $\geq 85.0\%$ ), and  $\text{NaOH}$  (99.5%). All solutions were prepared with ultrapure water from a Millipore system.

### 2.2. Experimental procedure

Batch tests were conducted in a series of 100 mL closed vials placed in a water bath-stirring reactor at a constant temperature under 150 rpm for 4 h. Appropriate volumes of Cr(VI), FA, and PS were sequentially placed in the reactor to achieve the optimal reactant ratio at a final solution volume of 50 mL. Aliquots of the samples were obtained at specific time intervals and then immediately filtered through a 0.45  $\mu\text{m}$  membrane into containers flooding in an ice bath ( $\sim 4^\circ\text{C}$ ) to quench the reaction by chilling for at least 5 min [20–22]. The residual Cr(VI) and PS concentrations of the samples were determined. All experiments were conducted in triplicate, and the average values and standard deviations were presented. The initial pH in all experiments was unadjusted; however, pH was adjusted by adding 0.1 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{NaOH}$  in experiments to investigate the influence of initial pH [23]. The effects of four temperature levels ( $T = 50^\circ\text{C}$ ,  $60^\circ\text{C}$ ,  $70^\circ\text{C}$ , and  $80^\circ\text{C}$ ), five pH levels (pH = 3.0, 5.0, 7.0, 9.0, and 11.0), and coexisting small-molecule organic compounds (ethanol, formaldehyde, and acetic acid) on reduction efficiency were also assessed.

### 2.3. Analytical methods

Residual Cr(VI) concentration was analyzed using the 1,5-diphenylcarbazine colorimetric method [24–26] at wavelength of 540 nm (GB 7466–87, Standards of China) [5] with a 7200 visible spectrophotometer. Residual PS concentration was determined according to the method proposed by Liang et al. [27]. Solution pH was measured using a pH meter (YSI EcoSense pH100). Radical measurement was conducted through an ESR experiment (Supplementary Material Text S1 and Table S1). The reduction efficiency of Cr(VI) is defined as below:

$$\text{Reduction efficiency} = ([\text{Cr(VI)}]_0 - [\text{Cr(VI)}]) / [\text{Cr(VI)}]_0$$

## 3. Results and discussion

### 3.1. Reduction of Cr(VI) in the system with $\text{SO}_4^-$ and FA

A series of control experiments was conducted to establish an ARP system and distinguish which substance suitable for Cr(VI) reduction. Fig. 1(a) shows the performances of Cr(VI) reduction in PS or FA solution alone and in PS coupled with FA with or without heating. The results represented that Cr(VI) was not reduced without PS or FA and minimally reduced at room temperature. By contrast, Cr(VI) concentration rapidly decreased in the heat-treated system added with PS and FA. Hence, Cr(VI) reduction occurred in the presence of PS, FA, and heat at the same time and was not affected by FA or PS alone. Although TAP can induce  $\text{SO}_4^-$  and sequentially  $\text{HO}^\cdot$  [21], these strong oxidizing radicals cannot react with the highest valence state of chromium. Moreover, Cr(VI) is difficult to reduce in systems containing heated FA or unheated PS coupled with FA without  $\text{SO}_4^-$ , indicating the critical function of  $\text{SO}_4^-$ . According to Eqs. (1) and (2), FA can react with both radicals [12,18]; hence, the resulting radicals,  $\text{CO}_2^-$ , may be preliminary inferred to reduce Cr(VI).

Parallel to Cr(VI) reduction, PS consumption was also observed in the systems, as illustrated in Fig. 1(b). PS showed a high consumption efficiency of more than 72% in all the systems, with consumption rates of  $0.0825 \text{ mM}\cdot\text{min}^{-1}$  for heat/PS/FA/Cr,  $0.0665 \text{ mM}\cdot\text{min}^{-1}$  for heat/PS/Cr, and  $0.0183 \text{ mM}\cdot\text{min}^{-1}$  for PS/FA/Cr, in 30 min. The highest decomposition efficiency of PS (91.03%) was observed in the system of heat/PS/FA/Cr at 240 min. This result indicates that PS concentration rapidly decreased within the first 30 min but maintained a relatively high consump-

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