



# Dual enhancement-inhibition roles of polycarboxylates in Cr(VI) reduction and organic pollutant oxidation in electrical plasma system



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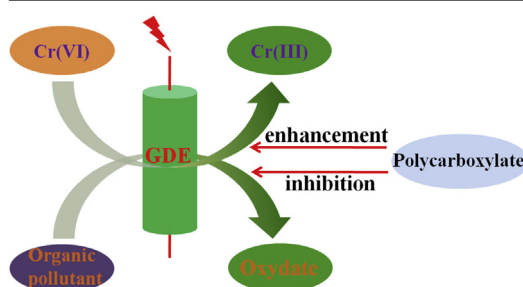
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## HIGHLIGHTS

- Polycarboxylate was found as a catalyst for enhancing Cr(VI) reduction in GDE.
- The synergistic effect in  $\cdot\text{OH}$  production was observed in GDE/Cr(VI) system.
- The formation of  $\cdot\text{OH}$  via Cr(V) activating  $\text{H}_2\text{O}_2$  was inhibited by polycarboxylate.
- Polycarboxylates expand Cr(V) coordination number from tetrahedron to octahedron.
- Real concentrated Cr(VI) effluent can be successfully detoxified in GDE.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, the roles of polycarboxylates in synergistic Cr(VI) reduction and organic pollutant oxidation are investigated in glow discharge electrolysis (GDE).  $\text{H}_2\text{O}_2$  generated in GDE plays a primary role for Cr(VI) reduction, and the presence of polycarboxylates can significantly enhance the reduction of Cr(VI) to Cr(III) with less value of  $[\text{H}_2\text{O}_2]_{\text{consumption}}/[\text{Cr(VI)}]_{\text{reduction}}$ . Simultaneously, polycarboxylates inhibit the production of  $\cdot\text{OH}$  via chromium-based Fenton-like reaction, leading to the retarded oxidation of other pollutant oxidation, i.e., RhB. The formation of peroxochromate(V) is a requisite both for Cr(VI) reduction to Cr(III) and  $\cdot\text{OH}$  formation via Fenton-like reaction. Polycarboxylates can form complexes with peroxochromate(V), which can transform to Cr(III) spontaneously, thereby interrupting the pathway for additional  $\cdot\text{OH}$  production. These influences induced by polycarboxylate were found closely relative to the number and position of  $-\text{OH}$  group in polycarboxylates. Besides,  $162.7 \text{ mg L}^{-1}$  Cr(VI) in actual electroplating effluent can be rapidly and almost completely reduced in GDE with introducing polycarboxylate containing nickel electroplating effluent. Generally, the present study provides a versatile strategy for Cr(VI) reduction, exhibiting a bright application future for real wastewater treatment.

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## 1. Introduction

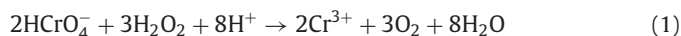
Due to its unique chemical and technical properties, hexavalent chromium (Cr(VI)) is widely utilized in a wide range of industrial applications, such as electroplating, pigments, leather tanning and wood preservation (Owlad et al., 2009). In contrast to the

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other stable chromium species, i.e., Cr(III), Cr(VI), listed among the top 20 contaminants on Superfund Priority List of Hazardous Substances, is known to be highly toxic and carcinogenic to human and animals, and its maximum allowable level is 0.05 mg L<sup>-1</sup> regulated by United States Environmental Protection Agency (USEPA) (Saha et al., 2011; Barrera-Díaz et al., 2012). Consequently, disposal of Cr(VI)-contaminated wastewaters is a seriously environmental concern, and its reduction to Cr(III) attracts significant attention (Barrera-Díaz et al., 2012).



Notwithstanding successes made in detoxification of Cr(VI), traditional chemical methods require a continuous feed of excess chemical reagents (FeSO<sub>4</sub>, NaHSO<sub>3</sub> or FeCl<sub>2</sub>) and produce considerable amounts of sludge or secondary pollution (Barrera-Díaz et al., 2012). H<sub>2</sub>O<sub>2</sub>, an environmental friendly reagent, has been reported as a reductant for Cr(VI) pollutant with the productions of green products, i.e., H<sub>2</sub>O and O<sub>2</sub> (Eq. (1)) (Pettine et al., 2002). In this reaction process, H<sub>2</sub>O<sub>2</sub>-mediated Cr(VI) reduction is accompanied by the catalytic generation of •OH via Fenton-like reaction (Shi, 1999). On the basis of this, Choi et al. (Bokare and Choi, 2010) exploited the oxidation performance of H<sub>2</sub>O<sub>2</sub>/Cr(VI) on aquatic organic pollutant removal. The complete oxidation of 4-chlorophenol (100 μM) was successfully achieved at pH = 5.0 within 60 min in H<sub>2</sub>O<sub>2</sub>/Cr(VI) solution ([Cr(VI)]<sub>0</sub> = 2 mM, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 20 mM). However, this process cannot provide the best of both worlds: an effective detoxification of Cr(VI) and preferable yield of •OH. Furthermore, although H<sub>2</sub>O<sub>2</sub> is an alternative source for •OH, it is scarcely used as the industrially desirable reductant for Cr(VI) pollutant due to its hazardousness, inconvenient storage and requirement for large quantities.

Owing to active oxidative species (e.g., •OH) and reductive species (e.g., H<sub>2</sub>O<sub>2</sub> and •H) substantially generated in-situ, glow discharge electrolysis (GDE), as a nonthermal plasma technology, is an attractive strategy for simultaneous organic and Cr(VI) pollutants treatment (Ke et al., 2011; Rong and Sun, 2015). Although the produced H<sub>2</sub>O<sub>2</sub> is impotent to the oxidation of most organic compounds due to its relatively low oxidation potential of 1.77 V<sub>NHE</sub> (E<sup>0</sup>(H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O)), GDE provides a much more desirable condition for Cr(VI) catalytically activating H<sub>2</sub>O<sub>2</sub> to •OH, resulting in the enhancement of •OH production. Thus, this strategy can provide an excellent example of “waste control by waste” strategy in detoxification of toxic Cr(VI) and other industrial pollutants.

Notably, polycarboxylates are frequently detected as intermediates or final products in abiotic degradation of high molecular-weight organic wastes and also found abundantly in many industrial processes. Some polycarboxylates, such as oxalic acid, malic acid and citric acid, can also act as the effective sacrificial electron donors for Cr(VI) reduction catalyzed by some homogeneous/heterogeneous transition metal ions with or without light irradiation (Das et al., 2005; Sun et al., 2009; Gherbi et al., 2011; Dozzi et al., 2012; Li et al., 2015). For example, Wang et al. (Wu et al., 2015) experimentally demonstrated oxalic acid showed enhanced performance for the photocatalytic Cr(VI) reduction by CeO<sub>2</sub> nanotubes under UV light irradiation at room temperature. In this system, oxalic acid can form a surface complex with CeO<sub>2</sub> nanotube and the surface adsorbed oxalic acid, as an electron donor, can transform to more reductive species, i.e., C<sub>2</sub>O<sub>4</sub><sup>2-</sup>•, via a ligand to-metal charge-transfer pathway, resulting in the enhanced photoreduction of Cr(VI). However, till now, it is yet unknown whether and how the existence and accumulation of polycarboxylates in wastewaters affect the treatment performance of Cr(VI) pollutant and environmental utilization of Cr(VI) pollutant in GDE or H<sub>2</sub>O<sub>2</sub> reaction system.

For above reasons, the present study sought to inspect the roles of polycarboxylates in Cr(VI) reduction and organic pollutant ox-

idation in GDE. Fluorescence spectrometry and electron spin resonance (ESR) were utilized to detect the active radicals and the chromium intermediates formed in Cr(VI) reduction process to clarify the underlying mechanisms.

## 2. Materials and methods

### 2.1. Experimental procedures

All chemical reagents were of analytical grade and supplied in Text S1. The experimental apparatus consisted of a direct current high voltage power supply and a reactor, as described in Fig. S1. Stock solution of 20 mM Cr(VI) was prepared by dissolving analytical grade K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in deionized water. All working solutions were freshly prepared before use by diluting the stock solution with deionized water, and the pH of solution was adjusted to the desired values with concentrated H<sub>2</sub>SO<sub>4</sub> or NaOH solution. Typically, 150 mL of argon-purged Na<sub>2</sub>SO<sub>4</sub> solution (conductivity: 3.0 mS cm<sup>-1</sup>) with 0.6 mM Cr(VI) was treated in GDE (550 V/100 mA). All experiments were carried out at 298 ± 3 K by circulating cold water. In H<sub>2</sub>O<sub>2</sub> reaction solution, the addition of concentrated H<sub>2</sub>O<sub>2</sub> was used to initiate an experiment. The samples were withdrawn at a fixed time interval and followed by immediate measurements. Experiments were repeatedly conducted, with relative errors less than 3%.

### 2.2. Analysis methods

H<sub>2</sub>O<sub>2</sub> formed in the solution was determined by a spectrophotometrical method using titanyl reagent (Eisenberg, 1943). 0.3 mL water sample and 6 mL titanium potassium oxalate (4 mM in 0.25 M sulfuric acid) were mixed together. Then the absorbance of above solution was obtained at 400 nm on the UV-vis spectrophotometer (UV-3000, MAPADA). The concentration of Cr(VI) remaining in the solution was measured by a diphenylcarbazide method. The concentrated acids (H<sub>3</sub>PO<sub>4</sub>:H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O = 1:1:2, v:v:v) were 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) (Wang et al., 2013). The concentrations of Cr(VI) and H<sub>2</sub>O<sub>2</sub> can be calculated according to their standard concentration curve (C<sub>Cr(VI)</sub> = 19.73788 × A<sub>Cr(VI)</sub> + 0.53134, C<sub>H2O2</sub> = 631.447 × A<sub>H2O2</sub> + 0.539). The concentration of rhodamine B (RhB) was monitored at 557 nm using a UV-visible spectrophotometer. Mineralization of the organics in solution was monitored by measuring the total organic content carbon (TOC) using an Elementar Germany Liqui TOCII analyzer. Electron spin resonance (ESR) experiments were performed to detect the carboxyl radical and Cr(V), whose detailed parameters and analysis procedure were shown in Text S2.

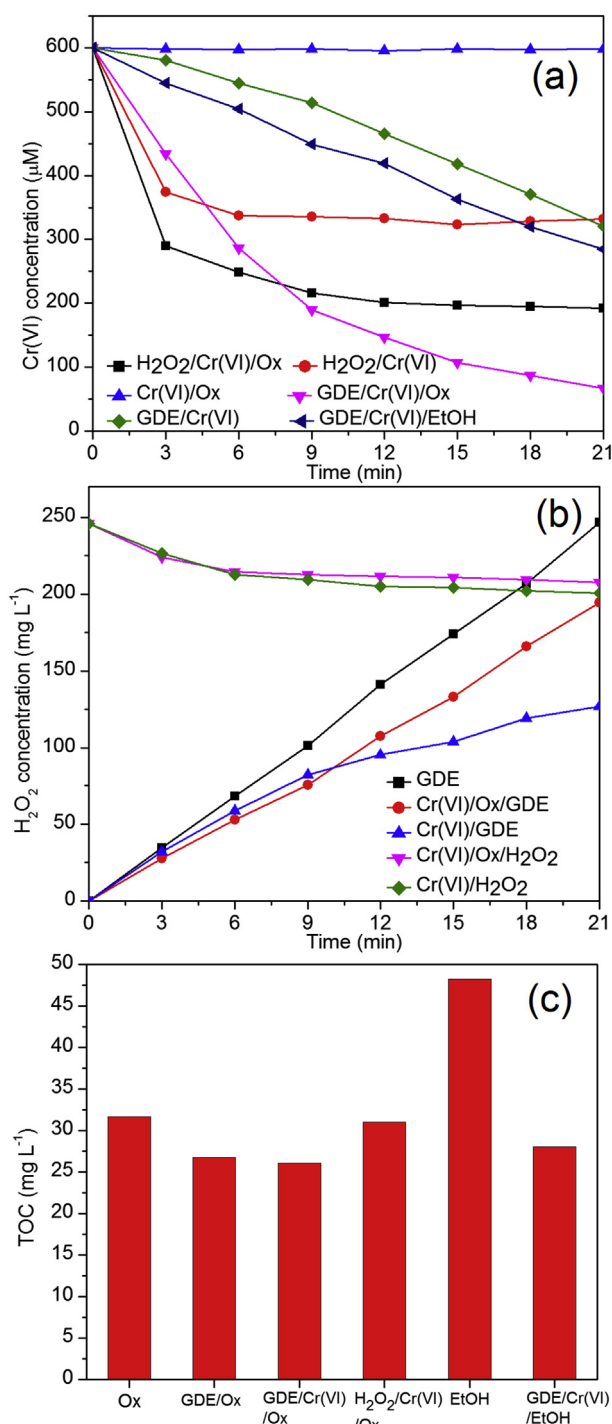
Besides, 1.0 mM coumarin (COU) was employed as a chemical probe for •OH (see Eq. (2)). 7-hydroxycoumarin (1 mL sample + 2.5 mL water) was measured by monitoring the fluorescence emission at 460 nm under excitation at 332 nm using a spectrofluorometer (F97PRO, Lengguang Tech.) (Kim et al., 2014).



## 3. Results and discussion

### 3.1. Enhancement of Cr(VI) reduction induced by Ox in GDE

To investigate the effects of polycarboxylates on Cr(VI) reduction, oxalic acid (Ox) was selected as a typical polycarboxylate with considering them being the typical frequent polycarboxylates in natural environment. Fig. 1 compares the extents



**Fig. 1.** The reduction of Cr(VI) (a), H<sub>2</sub>O<sub>2</sub> concentration (b) and TOC consumption (c) in various reaction systems (voltage 550 V, current 100 mA, [Cr(VI)]<sub>0</sub> = 600 μM, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 247 mg L<sup>-1</sup>, pH<sub>ini</sub> = 4.0, [Ox] = 1.0 mM, [EtOH] = 2 mM).

of Cr(VI) reduction and H<sub>2</sub>O<sub>2</sub> concentration variation under the different conditions. Fig. 1(a) shows that approximately 280 μM Cr(VI) was reductively transformed to Cr(III) after 21 min in GDE, whereas the amount of Cr(VI) reduction was substantially enhanced up to 533 μM with the presence of Ox (see Fig. S2), in which no evident Cr(VI) reduction was induced by Ox (see Fig. 1(a)). As shown in Fig. 1(b), 247 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> was produced in blank solution by GDE within 21 min. Approximately 120 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> was consumed in GDE/Cr(VI) with a stoichiometric ratio R

([H<sub>2</sub>O<sub>2</sub>]<sub>consumption</sub>/[Cr(VI)]<sub>reduction</sub>) of approximately 12.6. Compared with GDE/Cr(VI), only 53 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> was consumed for 253 μM more Cr(VI) reduction in GDE/Cr(VI)/Ox with R value of 2.9.

To inspect the importance of H<sub>2</sub>O<sub>2</sub> in the conversion of Cr(VI) to Cr(III), 247 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> was added into Cr(VI) or Cr(VI)/Ox solution without GDE. Fig. 1(a) shows initially rapid Cr(VI) reduction (approximately 268 μM) was observed in H<sub>2</sub>O<sub>2</sub>/Cr(VI) solution, which was less than 407 μM Cr(VI) reduction in H<sub>2</sub>O<sub>2</sub>/Cr(VI)/Ox solution. Based on above results, H<sub>2</sub>O<sub>2</sub> can be considered as a predominant reductant for Cr(VI) reduction in GDE.

It is well known that •OH (E<sup>0</sup>(•OH/H<sub>2</sub>O) = 2.8 V<sub>NHE</sub>) can be generated in GDE and is capable of re-oxidizing low valent chromium to Cr(VI) (E<sup>0</sup>(HCrO<sub>4</sub><sup>-</sup>/Cr<sup>3+</sup>) = 1.35 V<sub>NHE</sub>). Thus, the presence of organics can reasonably inhibit the regeneration of low valent chromium to Cr(VI) induced by •OH (Liu, 2009; Dai et al., 2010). This can be evidenced by the result in Fig. 1(c) that approximately 35 μM more Cr(VI) was reduced at the cost of approximately 20 mg L<sup>-1</sup> TOC with the presence of 2 mM ethanol (EtOH), a widely used scavenger for •OH, in GDE. However, as for Ox, it is less reactive towards •OH with rate constant of 7.7 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> than 9 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> of EtOH (Zhang and Croué, 2014). Thus, TOC held at the almost same level (approximately 16% abatement) after 21 min in GDE with or without Cr(VI) and negligible TOC consumption was observed in H<sub>2</sub>O<sub>2</sub>/Cr(VI)/Ox solution. Therefore, in spite of a small number of Ox mineralized in GDE, the possibility of Ox acting as a sacrificial electron donor or •OH scavenger for the enhanced reduction of Cr(VI) can be ruled out.

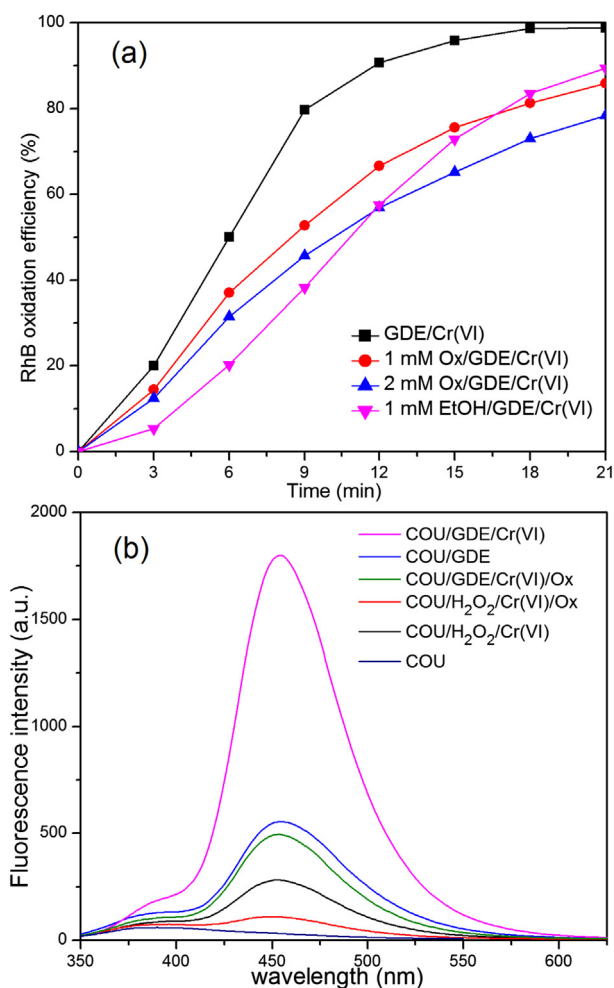
### 3.2. Effect of solution pH value

The pH value of solution was potentially a critical variable for Cr(VI) reduction because of its effect on the speciation distribution of Cr(VI) (Fig. S3). Due to the superior oxidation capacity of HCrO<sub>4</sub><sup>-</sup> (E<sup>0</sup>(HCrO<sub>4</sub><sup>-</sup>/Cr<sup>3+</sup>) = 1.35 V<sub>NHE</sub>) over CrO<sub>4</sub><sup>2-</sup> (E<sup>0</sup>(CrO<sub>4</sub><sup>2-</sup>/Cr(OH)<sub>3</sub>) = -0.13 V<sub>NHE</sub>), HCrO<sub>4</sub><sup>-</sup> (dominant at pH < 6.5) is more reactive towards H<sub>2</sub>O<sub>2</sub> than CrO<sub>4</sub><sup>2-</sup> (dominant at pH > 6.5) (Bokare and Choi, 2010). Thus, decreasing acidity is unfavorable for Cr(VI)-induced oxidative decomposition of H<sub>2</sub>O<sub>2</sub> and therefore inhibits the reduction of Cr(VI) mediated by H<sub>2</sub>O<sub>2</sub>. Consequently, as shown in Fig. S4(a), at all pH values (2.3–8.0) examined, the transformation of Cr(VI) to Cr(III) increased with the decreasing pH value of Cr(VI)/Ox solution. For example, at pH = 2.3, 600 μM Cr(VI) almost completely reduced to Cr(III) within 6 min, whereas only 336 μM Cr(VI) was reduced at pH = 8.0 after 21 min. Although similar variation tendency of Cr(VI) reduction can also be obtained in GDE without adding Ox, the reduction amount of Cr(VI) is much less than that in GDE/Ox (Fig. S4(b)).

### 3.3. Inhibition of organic pollutant oxidation by Ox in GDE/Cr(VI)

To evaluate the oxidation performance of various systems, RhB (40 mg L<sup>-1</sup>) was selected as a model pollutant and its oxidation efficiency is shown in Fig. 2(a). RhB oxidation efficiency gradually increased to approximately 51% after 21 min of GDE treatment. This oxidation efficiency was greatly promoted up to 100% in GDE/Cr(VI) treatment system, and this enhancement can be also observed in other glow plasma systems (see Table S1). However, the presence of Ox inhibited RhB oxidation in GDE/Cr(VI) as shown in Fig. 2(a). In spite of this, there was still synergistic effect in oxidation capacity, leading to more preferable RhB oxidation efficiency.

As shown in Fig. 2, approximately 16% Ox was mineralized by •OH, which may retard RhB oxidation via its outcompeting RhB for •OH. However, compared with the case of adding EtOH as •OH scavenger in GDE/Cr(VI) system, a very different kinetic behavior of inhibited RhB oxidation in GDE/Cr(VI)/Ox system was

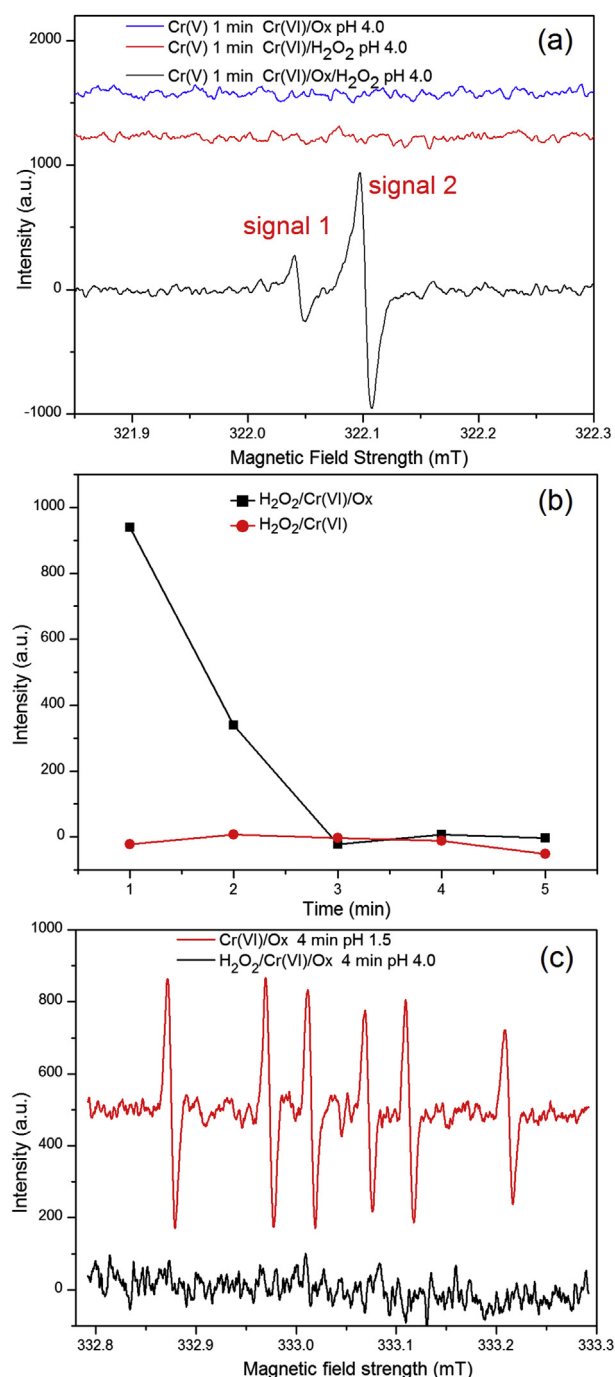


**Fig. 2.** Effect of Ox on the oxidation of RhB in GDE (a) and the detection of •OH using fluorescence spectrometry in various reaction systems (b) (voltage 550 V, current 100 mA,  $[\text{Cr(VI)}]_0 = 600 \mu\text{M}$ ,  $\text{pH}_{\text{ini}} = 4.0$ ,  $[\text{RhB}] = 40 \text{ mg L}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 247 \text{ mg L}^{-1}$ ).

observed, which, to a certain extent, suggests that besides capturing •OH, other role of Ox may participate in the oxidation of RhB. As shown in Fig. 2(b), the fluorescence intensity of 7-hydroxycoumarin (coumarin + •OH) was significantly improved in GDE/Cr(VI) whereas the presence of Ox in GDE/Cr(VI) and H<sub>2</sub>O<sub>2</sub>/Cr(VI) retarded the formation of •OH, which were identical to the changes of RhB oxidation. Based on the negligible Ox consumption in H<sub>2</sub>O<sub>2</sub>/Cr(VI) solution (see Fig. 1(c)) and the distinct magnitude difference in reaction rate constant of EtOH ( $9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and Ox ( $7.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) with •OH, Ox probably induced the inhibitory effect on the formation of additional •OH derived from the reaction between H<sub>2</sub>O<sub>2</sub> and Cr(VI).

### 3.4. Cr(V) formation and evolved radicals

The paths through which Cr(VI) is reduced to Cr(III) by electron donors have been the key subject of discussion, and here ESR technique is used to obtain more information of Cr intermediates (Wang et al., 2008). The involvement of Cr(V) in the reaction of Cr(VI) with H<sub>2</sub>O<sub>2</sub> or Ox has been previously validated by ESR spectroscopy and the ESR signal intensity of Cr(V) is dependent on solution pH and reagent concentrations (Zhang and Lay, 1998). In present H<sub>2</sub>O<sub>2</sub>/Cr(VI) solution, no evidence of Cr(V)-aquo species could be recorded; thus, if formed, Cr(V)-aquo species probably at-



**Fig. 3.** The ESR signals of Cr(V) (a), Cr(V) ESR intensity variation (b) and carboxyl radical (c) in H<sub>2</sub>O<sub>2</sub>/Cr(VI)/Ox and H<sub>2</sub>O<sub>2</sub>/Cr(VI) solutions ( $[\text{Cr(VI)}]_0 = 1200 \mu\text{M}$ ,  $[\text{H}_2\text{O}_2]_0 = 494 \text{ mg L}^{-1}$ ,  $\text{pH}_{\text{ini}} = 4.0$ ,  $[\text{Ox}] = 2.0 \text{ mM}$ ; For Cr(VI)/Ox solution in (c),  $[\text{Cr(VI)}]_0 = 2000 \mu\text{M}$ ,  $[\text{Ox}] = 20.0 \text{ mM}$ ).

tain a considerably low concentration, making these species undetectable by ESR (Fig. 3(a)). Besides, no Cr(V) signal was observed in Cr(VI)/Ox, which is concordant with no direct Cr(VI) reduction by Ox in Fig. 1. However, when Ox was present in H<sub>2</sub>O<sub>2</sub>/Cr(VI) solution, two major ESR signals ( $g_1 = 2.00942$ ,  $g_2 = 2.00906$ ) of Cr(V) were observed, which can be not attributed to the Cr(V)-oxalate or Cr(V)-peroxo complexes because of mismatching  $g$  values according to the previous studies (Farrell et al., 1998; Zhang and Lay, 1998). Thus, in this case, peroxo and Ox mixed-ligands Cr(V) complexes probably formed, which is analogous to

the Cr(V)/glutathione/peroxo complex and Cr(V)/ascorbate/peroxo complex in previous literature (Aiyar et al., 1990; Zhang and Lay, 1996). Fig. 3(b) shows the major Cr(V) signal intensity (signal 2) as a function of reaction time in H<sub>2</sub>O<sub>2</sub> solution. The maximal intensity of Cr(V) signal within 1 min indicates that Cr(V) complexes stabilized by carboxylato ligand was rapidly accumulated upon the mixing of Ox, Cr(VI) and H<sub>2</sub>O<sub>2</sub>. Once these mixed-ligand Cr(V) complexes were formed, they immediately vanished resulting in the fast decay of Cr(V) ESR signal within 3 min. This observation is similar with the results reported by Zhang (Zhang and Lay, 1996), that an ESR signal at  $g = 1.9818$  was assigned to a highly reactive Cr(V)/ascorbate/peroxo complex and this complex is detected to quickly decay.

It has been reported that carboxyl radical can be produced in the reduction of Cr(VI) by Ox at extremely acidic solution as indicated by the ESR spectra in Fig. 3(c) (Farrell et al., 1998). However, no ESR signal of carboxyl radical was detected in H<sub>2</sub>O<sub>2</sub>/Cr(VI)/Ox solution at pH = 4.0. These results suggest that in spite of Ox involving in the reaction between Cr(VI) and H<sub>2</sub>O<sub>2</sub>, no decomposition of Ox into carboxyl radical happened accompanied with the reduction of Cr(VI), which was coincident with the TOC data in Fig. 1(c).

### 3.5. Effects of various polycarboxylates on Cr(VI) reduction and RhB oxidation

The effects of various polycarboxylates on Cr(VI) reduction and RhB oxidation were also examined as given in Table 1. With comparing TOC consumption and Cr(VI) reduction between the cases of ethanol and various polycarboxylates in Table 1, it can be concluded that not only Ox, but also other polycarboxylates can significantly enhance the conversion of Cr(VI) to Cr(III). It should be pointed out that acetic acid negligibly influenced the reduction of Cr(VI), because monocarboxylate cannot participate in the reac-

tion of Cr(VI) reduction due to its poor complexation capacity with chromium species. Besides, as shown in Table 1 and Fig. S5, these polycarboxylates had an inhibitory action on the oxidation of RhB with different degrees. The biggest inhibitory effect on RhB oxidation was observed with the presence of tartaric acid and Ox, and 84–86% of RhB was oxidized in GDE/Cr(VI) within 21 min. Citric acid and malic acid showed almost the same inhibition on RhB oxidation, and a little more than 90% of RhB was oxidized. Malonic acid showed the lowest inhibitory action on RhB oxidation, RhB was almost completely bleached after 21 min.


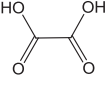
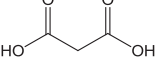
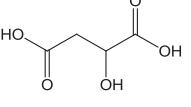
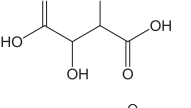
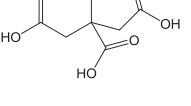

The enhanced reduction of Cr(VI) and inhibited oxidation of RhB in GDE/Cr(VI)/polycarboxylate are found closely relative to the number and position of –OH group in polycarboxylate. The more  $\alpha$ -OH group with respect to one carboxylic acid group in polycarboxylate, the higher complexation capacity with chromium species will have, which are in agreement with the enhancement of Cr(VI) reduction and inhibition of  $\bullet$ OH formation in GDE/Cr(VI)/polycarboxylate.

### 3.6. Mechanism discussion

In GDE, many primary free radicals including  $\bullet$ H,  $\bullet$ OH and hydrated electron are produced from the bombardment of water molecules by the energetic H<sub>2</sub>O<sup>+</sup> ions at the plasma/solution interface or the dissociation of H<sub>2</sub>O vapor molecules within the plasma zone around the anode (Wang et al., 2012). Due to their short life-spans (e.g.,  $3.7 \times 10^{-9}$  s for  $\bullet$ OH,  $1.2 \times 10^{-6}$  s for H $\bullet$  and  $1.0 \times 10^{-6}$  s for hydrated electron), these active species are mainly confined to the tiny plasma zone and immediately consumed via dimerization or interaction with their precursors, inducing the formation of H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, etc. (Jiang et al., 2014). The stable H<sub>2</sub>O<sub>2</sub> can diffuse into the bulk solution and, as a reductant, can react with aqueous Cr(VI) species. As for organic pollutant in aqueous solution, its oxidation primarily initiated by  $\bullet$ OH near the plasma zone.

**Table 1**

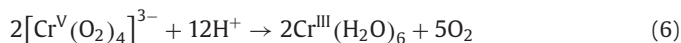
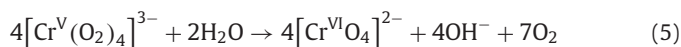
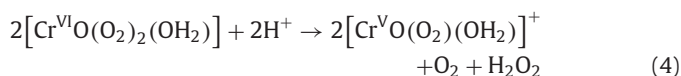
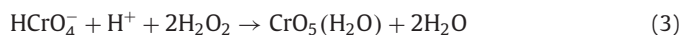
Effects of different polycarboxylates on Cr(VI) reduction, TOC consumption and RhB oxidation (Cr(VI) reduction in GDE, RhB oxidation in GDE/Cr(VI), TOC consumption experiments without RhB; voltage 550 V, current 100 mA, [Cr(VI)]<sub>0</sub> = 600  $\mu$ M, pH<sub>ini</sub> = 4.0, [polycarboxylate] = 1.0 mM, [RhB] = 40 mg L<sup>−1</sup>).

Carboxylates	Structural formula	Cr(VI) reduction ( $\mu$ M)	TOC consumption (mg L <sup>−1</sup> )		RhB oxidation (%)
			GDE	GDE/Cr(VI)	
None		280	–	–	100
Acetic acid		283	6.61	10.97	99
Oxalic acid		553	4.95	5.66	86
Malonic acid		393	3.71	4.87	99
Malic acid		538	8.8	17.59	92
Tartaric acid		564	5.55	20.01	84
Citric acid		568	4.46	19.31	93

When Cr(VI) and organic pollutant coexist in solution, the synergistic enhancements of Cr(VI) reduction and organic pollutant oxidation can be obtained in GDE. The added polycarboxylates can further increase the reduction capability of Cr(VI), nevertheless, it hinders the oxidation of organic pollutant. Therefore, the resolution of overall reaction pathways in GDE/Cr(VI) with or without polycarboxylates (Ox as an example) should be clarified.

#### (1) Cr(VI) reduction mechanism

Based on the experimental results in Fig. 1, the produced  $\text{H}_2\text{O}_2$  is primarily responsible for Cr(VI) reduction in GDE. This reaction is initiated by forming monoperoxy species  $\text{CrO}_5(\text{H}_2\text{O})$  (Eq. (3)), which then can react with another molecule of  $\text{H}_2\text{O}_2$  forming diperoxy-chromium derivative ( $\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2(\text{OH}_2)$ ). Subsequently, an intramolecular one-electron redox reaction occurs between a coordinated peroxy group and the central Cr(VI) in  $\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2(\text{OH}_2)$ , leading to the formation of monoperoxo-chromate(V) complex in Eq. (4) (Pettine et al., 2002). The multi-peroxochromate(V) species can be produced via sequential peroxy groups substituting oxo ligands of peroxochromate(V) complex, which easily undergo the spontaneous disproportionation reaction with regenerating Cr(VI) or being directly reduced to Cr(III), taking tetrahedral tetrakis( $\eta^2$ -peroxy)chromate(V) as an example in Eqs. (5) and (6) (Pettine et al., 2002). Reactions in Eqs. (3), (4) and (6) are probably facilitated by protonation, which can explain the acidity dependence of Cr(VI) reduction in GDE system.

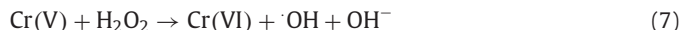


It has been reported that Ox is capable of binding to Cr(V) intermediate during many Cr(VI) reduction processes (Testa et al., 2004; Wang et al., 2008). Therefore, when Ox was present in  $\text{H}_2\text{O}_2$ /Cr(VI) solution, a mixed-ligands Cr(V) complexes are formed between Ox and peroxochromium(V) via ligand substitution reactions. And these assumption can be confirmed by the results of ESR analysis in Fig. 3.

It is known that in the reduction of Cr(VI) to Cr(III), the rearrangement of coordination shell from tetrahedron for Cr(VI)/Cr(V) to octahedron for Cr(III)/Cr(IV) is considered as the rate-limiting step (Beattie et al., 1972). It is proposed that the affinity of Ox to peroxochromate(V) species probably induces the expansion of Cr(V) coordination number by the coordination of water molecules to Cr(V), which is preferred by product Cr(III) with octahedral structure. This change in the coordination number of Cr(V) induced by Ox in previous literature also support this standpoint (Bramley et al., 1990; Farrell et al., 1998). For example, the coordination number of Cr(V) complexes (five- or six-coordinate) has been determined by Lay et al. (Barr-David et al., 1995) using EPR spectroscopy in the reaction of Cr(VI) with Ox. Consequently, the formed activated mixed-ligands Cr(V) complexes can easily and quickly reduce to Cr(III) via an intramolecular two-electron redox reaction between Cr(V) and peroxy ligand. This reaction mechanism can reasonably account for the negligible mineralization of Ox in Cr(VI) reduction process and relatively low R value with the presence of Ox in GDE.

#### (2) Hydroxyl radical generation mechanism

Besides  $\bullet\text{OH}$  produced by GDE, additional  $\bullet\text{OH}$  can be also formed through the Fenton-like reaction in Eq. (7).



As a result, an enhanced generation of  $\bullet\text{OH}$  is achieved in GDE/Cr(VI), which significantly accelerates the oxidation rate of organic pollutant, e.g., almost 100% oxidation of RhB within 15 min (see Fig. 2).

In this process, the peroxochromate(V) complex in Cr(VI)- $\text{H}_2\text{O}_2$  system is known as the most significant intermediate for  $\bullet\text{OH}$  formation (Shi and Dalal, 1994). However, as discussed above, due to the affinity of Ox to Cr(V), Ox presented in GDE/Cr(VI) can lead to rapid reduction of Cr(VI) to Cr(III), which inevitably retards the Fenton-like reaction between Cr(V) with  $\text{H}_2\text{O}_2$ . Therefore, the inhibition of  $\bullet\text{OH}$  formation by Ox leads to the abatement of organic pollutant oxidation. However, it should be noted that although organics oxidation is more or less inhibited by polycarboxylates, GDE/Cr(VI)/polycarboxylate still exhibits superior oxidation capacity over sole GDE.

#### 3.7. Environmental applications

In this process, the deliberate addition of polycarboxylates to Cr(VI) wastewater for enhancing Cr(VI) detoxification is not advisable in the area of environmental remediation. It is known that polycarboxylates are the main products in aerobic degradation of organic pollutants and ubiquitous in organic wastewaters. Thus, it is viable to introduce organic wastes into Cr(VI) treatment system for achieving preferable Cr(VI) detoxification performance accompanied by the removal of organic wastes. Specifically, many polycarboxylates, e.g., citric acid and malic acid, are widely used as complexing agents for nickel ion in the electroless nickel bath (Cui et al., 2005). Here, real concentrated Cr(VI) electroplating effluent can be successfully detoxified with introducing polycarboxylates containing nickel electroplating effluent (Fig. S6) in air atmosphere, which are both collected from electroplating industrial park of Qingdao Development Zone. In this case,  $162.7 \text{ mg L}^{-1}$  Cr(VI) (150 mL) can be rapidly and almost completely reduced within 15 min with adding 15 mL nickel electroplating effluent, in which approximately  $258 \pm 20 \text{ mg L}^{-1}$  chemical oxygen demand (COD) was diminished.

#### 4. Conclusion

In this study, an environmental benign process GDE employed in this study can efficiently reduce Cr(VI) to Cr(III), which can be further and significantly enhanced with the presence of polycarboxylates. The enhancement of Cr(VI) reduction was much more favorable in lower pH solution. In this process, the presence of polycarboxylates simultaneously inhibited the yield of  $\bullet\text{OH}$  derived from chromium species catalytically activating  $\text{H}_2\text{O}_2$ . In spite of this, the synergistic effect in  $\bullet\text{OH}$  production in GDE/Cr(VI) system guarantees the relatively high performance in organic pollutant treatment. In a word, GDE strategy in this work is a practical and effective strategy for treating actual Cr(VI)-contaminated wastewaters with introducing polycarboxylates-containing effluents.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.10.018>.

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