

# Synergetic Transformations of Multiple Pollutants Driven by Cr(VI)–Sulfite Reactions

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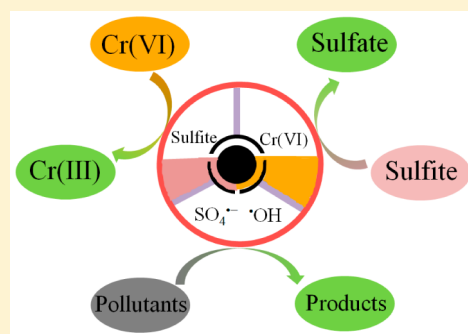
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## Supporting Information

**ABSTRACT:** Reduction of Cr(VI) is often deemed necessary to detoxify chromium contaminants; however, few investigations utilized this reaction for the purpose of treating other industrial wastewaters. Here a widely used Cr(VI)–sulfite reaction system was upgraded to simultaneously transform multiple pollutants, namely, the reduction of Cr(VI) and oxidation of sulfite and other organic/inorganic pollutants in an acidic solution. As(III) was selected as a probe pollutant to examine the oxidation capacity of a Cr(VI)–sulfite system. Both  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  were considered as the primary oxidants for As(III) oxidation, based on the results of electron spin resonance, fluorescence spectroscopy, and specific radicals quenching. As(III)-scavenging, oxidative radicals greatly accelerated Cr(VI) reduction and simultaneously consumed less sulfite. In comparison with a Cr(VI)– $\text{H}_2\text{O}_2$  system with  $50\ \mu\text{M}$  Cr(VI), Cr(VI), the sulfite system had excellent performance for both As(III) oxidation and Cr(VI) reduction at pH 3.5. Moreover, in this escalated process, less sulfite was required to reduce Cr(VI) than the traditional Cr(VI) reduction by sulfite process. This effectively improves the environmental compatibility of this Cr(VI) detoxification process, alleviating the potential for  $\text{SO}_2$  release and sulfate ion production in water. Generally, this study provides an excellent example of a “waste control by waste” strategy for the detoxification of multiple industrial pollutants.

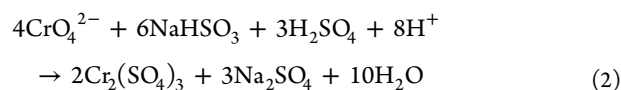
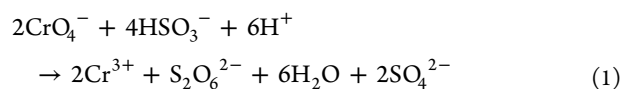


## INTRODUCTION

Hexavalent chromium (Cr(VI)) is extensively used in various industrial processes, such as electroplating, pigments, and leather tanning.<sup>1</sup> However, Cr(VI), an U.S. Environmental Protection Agency “priority pollutant”, is known to be toxic and carcinogenic and is highly mobile in many soils and waters.<sup>2</sup> Hence, disposal of Cr(VI)-bearing waste is a significant and well-recognized environmental issue.<sup>2</sup> In contrast to Cr(VI), Cr(III) is less toxic and can be readily precipitated out of solution in the form of  $\text{Cr}(\text{OH})_3$ . Consequently, the reduction of Cr(VI) to nontoxic Cr(III) is of great interest for engineered waste management systems.

To date, a variety of methods have been developed for aqueous Cr(VI) detoxification including conventional methods (e.g., chemical reduction and precipitation) and advanced processes (e.g.,  $\text{TiO}_2$ -based photocatalysis, glow plasma processes, and photochemical methods mediated by organic acids).<sup>1–7</sup> In spite of the success in detoxification of Cr(VI) species, these processes consume a large number of chemical reagents or energy input and are therefore not cost-effective. Notably, Bokare et al.<sup>8</sup> and Wang et al.<sup>9</sup> recently reported the novel application of Cr(VI) reduction by  $\text{H}_2\text{O}_2$  to generate highly reactive  $\cdot\text{OH}$  toward pollutant oxidation in situ. For example,  $100\ \mu\text{M}$  4-chlorophenol was completely oxidized at

solution pH 3.0–7.0 within 360 min in a Cr(VI)– $\text{H}_2\text{O}_2$  reaction system ( $[\text{Cr(VI)}]_0 = 2.0\ \text{mM}$ ,  $[\text{H}_2\text{O}_2]_0 = 20\ \text{mM}$ ). Although this reaction system gained some economic benefits, it cannot efficiently relieve the environmental hazard of Cr(VI) and thus still required additional processes to detoxify Cr(VI) in the wastewater.



An alternative to  $\text{H}_2\text{O}_2$ , sulfite, a common industrial contaminant in wastewaters or in exhaust gas, is a typical reducing agent and has been widely utilized for reductive detoxification of chromate-containing wastewaters or remediation of contaminated sites in many emergency cases.<sup>2,10–12</sup> The reaction between Cr(VI) and sulfite can be described by

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reaction 1 in the presence of an excess of sulfite, whereas the theoretical stoichiometry of Cr(VI)/sulfite is 2:3 for excessive Cr(VI), reaction 2.<sup>11</sup> Until now, the literature has primarily focused on kinetic or equilibrium models to study the reaction of sulfite reducing Cr(VI) in an acid solution with excess sulfite.<sup>11–14</sup> For example, Beukes et al.<sup>12</sup> investigated Cr(VI) reduction by sulfite as a function of pH in wastewater and reported that for a 26 mg L<sup>-1</sup> Cr(VI) solution, a sulfite concentration of at least 5 times the initial Cr(VI) concentration was required for complete reduction within the pH range of 2.0–5.0.

Moreover, the significant role of sulfite as an efficient source of active radicals via the reaction of an iron–sulfite–oxygen complex under light irradiation has been reported.<sup>13–16</sup> For example, Zhang et al.<sup>15</sup> reported that 84% of Orange II (10 mg L<sup>-1</sup>) can be efficiently decolorized within 60 min in an Fe(II)/sulfite-based photochemical system using a xenon lamp (350 W), whereas less efficiency (15%) was achieved without irradiation. Application of industrially available sulfite as a new source of sulfate radicals, instead of using expensive persulfate reagents (ca. \$1300/t), seems very promising in the practice of advanced oxidation technologies (AOTs).<sup>14</sup>

Compared with Fe(III), Cr(VI) may be found more abundant in some industrial wastewaters, is soluble over a larger pH range, and has a higher standard oxidation potential ( $E^0(\text{HCrO}_4^-/\text{Cr}^{3+}) = 1.35 \text{ V}_{\text{NHE}}$ ).<sup>8</sup> Thus, aqueous Cr(VI) species may be an alternative activator for transforming sulfite to active radical species. However, although Cr(VI) reduction by sulfite is a common process for Cr(VI) detoxification throughout the world,<sup>11,12</sup> there are few reports describing a sulfite-mediated generation of active radicals in Cr(VI) reduction processes.

This study investigated the reactions occurring in a Cr(VI)–sulfite reaction system and examined the feasibility of upgrading this reaction system for the oxidation of other inorganic/organic contaminants. The changes in concentrations of various reagents were measured over reaction time, with different dosages of Cr(VI) and sulfite. The effects of pH, additions of other metal ions, and scavenging radicals were examined to probe the underlying reaction mechanisms. This work provides a new route for the oxidation of organic/inorganic pollutants, co-occurring with sulfite oxidation and Cr(VI) reduction.

## EXPERIMENTAL SECTION

**Chemicals.** Sodium arsenite (NaAsO<sub>2</sub>, 97%) and sodium arsenate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, 99%) were supplied by Xiya Reagent and Jiangxi Qianhua Industry Co., Ltd., respectively. Methyl orange (MO), methylene blue (MB), rhodamine B (RB), anhydrous sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>, >97%), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, >99%), potassium chromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, >99%), diphenylcarbazide (98%), sodium pyrosulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, >96%), sodium hydrosulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, >86%), ammoniummolybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, >99%), ethanol (EtOH, 73.0%–75.0%), 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB, >99%), ethylenediaminetetraacetic acid (EDTA, >99.5%), antimony potassium tartrate (K(SbO)·C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·0.5H<sub>2</sub>O, >99%), L-ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, >99.7%), chromium nitrate (Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, >99%), copper sulfate (CuSO<sub>4</sub>·5H<sub>2</sub>O, >99%), cobaltous sulfate (CoSO<sub>4</sub>·5H<sub>2</sub>O, >99.5%), manganese sulfate (MnSO<sub>4</sub>, >99%), aluminum sulfate hydrate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O, 98%), ferrous sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O, >99%), ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, >99%), coumarin (C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>), *tert*-butyl alcohol (TBA, >98%), H<sub>2</sub>SO<sub>4</sub>

(73.0%–75.0%), H<sub>3</sub>PO<sub>4</sub> (>98.5%), NaOH (>96%), HCl (36%–38%), and H<sub>2</sub>O<sub>2</sub> were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All chemical reagents were used without further purification. UltraPure water was used for all experiments.

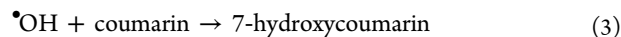
**Reaction Procedures.** All experiments were conducted in an open, 150 mL, cylindrical glass tube, magnetically stirred, and maintained at a temperature of 20 ± 1 °C in a circulating water jacket. Stock solutions of 1000 mg L<sup>-1</sup> Cr(VI) and As(III) were prepared by dissolving analytical grade K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and NaAsO<sub>2</sub> in pure water. All working solutions were freshly prepared before use by diluting the stock solution with pure water. The pH was adjusted to the desired values with concentrated H<sub>2</sub>SO<sub>4</sub> or NaOH solution. Cr(VI) and As(III) were premixed, and sulfite was added to initiate the experiment. For the experiments using a volumetric flask (250 mL) as the reaction vessel in the presence of argon or oxygen (gas velocity, 0.6 L min<sup>-1</sup>), the solution was purged with the corresponding gas for 10 min prior to initiating the reaction. The samples were withdrawn at various time intervals and immediately measured.

**Analytical Methods.** The pH of the solution was determined by pH meter (PHS-3C). As(V) concentration was determined using a modified molybdenum-blue method.<sup>17</sup> Briefly, for each 2.0 mL quenched aliquot (1 mL of sample +1 mL of methanol), 0.5 mL of the 2% HCl acidifying solution and 0.3 mL of the color reagent were mixed sequentially. For total As determination, 0.5 mL of the 2% HCl containing 2 mmol L<sup>-1</sup> KIO<sub>3</sub> was used instead of 2% HCl solution. The absorbance at 880 nm was determined within 30 min using an 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 acid with Cr(VI) determination. The absorbance of sample solutions was detected at 540 nm after full color development (>15 min).<sup>7,9</sup>

The concentration of S(IV) was determined using a modified colorimetric procedure with DTNB.<sup>18</sup> Briefly, 1 mL of sample was added into a cuvette containing a mixture with 1 mL of EDTA (1 mM), 2 mL of DTNB (1 mM), and 5 mL of Na<sub>2</sub>HPO<sub>4</sub>/KH<sub>2</sub>PO<sub>4</sub> buffer (pH = 7). The color was allowed to develop for 15 min, and the sample solutions were detected at 412 nm with an UV–vis spectrophotometer.

Electron spin resonance (ESR) experiments were performed using DMPO as a spin-trapping agent, whose detailed parameters and procedure are shown in Text S1. A UV–visible spectrophotometer (UV-3000, MAPADA) was employed to measure the concentrations of MO, MB, and RhB at wavelengths of 505, 663, and 554 nm, respectively.

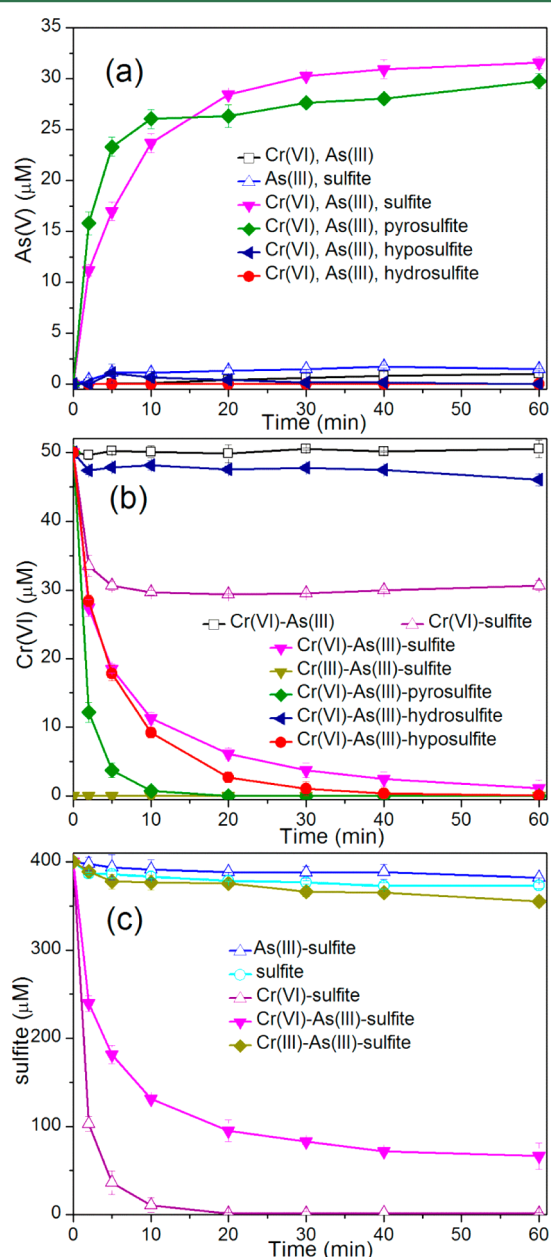
Coumarin (1 mM) was employed as a chemical probe for •OH. 7-Hydroxycoumarin, reaction 3, was measured by monitoring the fluorescence emission at 460 nm under excitation at 332 nm using a spectrofluorometer (F97PRO, Lenggung Tech.).<sup>19</sup>



## RESULTS AND DISCUSSION

**Oxidation of Pollutants by Cr(VI)–Sulfite Reactions.** In this study, toxic As(III) was selected as a model pollutant. Its oxidation kinetics have been extensively studied and can be

easily characterized by measuring the oxidation product—As(V).<sup>7,20–22</sup> Figure 1a compares the extent of As(III)



**Figure 1.** (a) Oxidation of As(III), (b) reduction of Cr(VI), and (c) consumption of sulfite under varying experimental conditions ( $[\text{As(III)}]_0 = 50 \mu\text{M}$ ,  $[\text{Cr(III)}]_0$  or  $[\text{Cr(VI)}]_0 = 50 \mu\text{M}$ ,  $[\text{sulfite}]_0 = 400 \mu\text{M}$ ,  $[\text{pyrosulfite}]_0 = 400 \mu\text{M}$ ,  $[\text{hydrosulfite}]_0 = 400 \mu\text{M}$ ,  $[\text{hydrosulfite}]_0 = 400 \mu\text{M}$ ,  $\text{pH}_{\text{ini}} = 3.5$ ).

oxidation under the different experimental conditions. In the reaction system of Cr(VI)–sulfite, approximately 400 μM sulfite was depleted for only 20 μM Cr(VI) reduced with a  $[\text{sulfite}]_{\text{consumption}}/[\text{Cr(VI)}]_{\text{reduction}}$  stoichiometric ratio of 20 in Figure 1b,c (no significant sulfite removal due to the oxidation of air or the complexation of Cr(III) in Figure 1c). In contrast, when adding 50 μM As(III), as an electron donor, into a Cr(VI)–sulfite solution, much more Cr(VI) (approximately 49 μM) was rapidly reduced, consuming only 330 μM sulfite ( $[\text{sulfite}]_{\text{consumption}}/[\text{Cr(VI)}]_{\text{reduction}} \approx 6.7$ ). Accordingly, approximately 32 μM of As(III) was gradually transformed to

As(V) in this process. As shown in Figure 1a, neither sulfite nor Cr(VI) nor Cr(III)–sulfite can individually lead to measurable As(V) formation. Consequently, the oxidative conversion of As(III) can be attributed to interactions between As(III), Cr(VI), and sulfite. Similarly, rapid decoloration of MO, MB, and RB within tens of seconds can be achieved (Figures S1–S3), in contrast to the oxidation performance of Fe(II)/sulfite-based photochemical systems with reaction times in tens of minutes.<sup>13–16</sup> This indicates the strong oxidation capacity of Cr(VI)–sulfite reaction system toward oxidation of both inorganic arsenite and organic pollutants.

To examine the role of sulfite in simultaneous conversions of Cr(VI) and As(III), hydrosulfite ( $\text{S}_2\text{O}_4^{2-}$ ), pyrosulfite ( $\text{S}_2\text{O}_5^{2-}$ ), and hydrosulfite ( $\text{S}_2\text{O}_3^{2-}$ ) were chosen as alternative, reducing sulfur sources. The results in Figure 1 show that although pyrosulfite and hydrosulfite can effectively reduce Cr(VI) to Cr(III), only pyrosulfite can simultaneously trigger As(III) oxidation to As(V). Since a pyrosulfite molecule can be easily transformed to two sulfites through a hydrolysis reaction (Figure S4),<sup>23</sup> sulfite is expected to play a critical role in the synergetic conversion of Cr(VI) and As(III). As for hydrosulfite, no obvious conversion of As(III) or Cr(VI) was observed at pH 3.5 after 60 min. The importance of free inorganic sulfite was further demonstrated by a formaldehyde addition experiment (see more details in Figure S5). In conclusion, although many reducing sulfur reagents can transform Cr(VI) to Cr(III), only free inorganic sulfite species result in As(III) oxidation.

**Effect of Initial Reagent Concentration.** To investigate the effects of initial reagent concentrations on the oxidation capacity of a Cr(VI)–sulfite system, batch experiments were carried out in aqueous solution by varying their initial concentrations at pH 3.5. Figure S6 shows that for 50 μM Cr(VI) reduction, the addition of As(III) resulted in the reduction of more Cr(VI) to Cr(III) and consumed less sulfite than a Cr(VI)–sulfite system without As(III). Therefore, the ratio of  $[\text{sulfite}]_{\text{consumption}}/[\text{Cr(VI)}]_{\text{reduction}}$  (5–10) was lower in the Cr(VI)–sulfite–As(III) systems. The reason may be that As(III), acting as an active radicals scavenger, can alleviate the consumption of sulfite, another electron donor in the systems.

The optimal As(III) oxidation (approximately 32 μM) observed was achieved at a sulfite concentration of 400 μM (Figure S7). Further increasing sulfite concentration (>400 μM) retarded As(V) formation. This could be explained by excess sulfite causing rapid Cr(VI) reduction, increasing competition with As(III) for reactive oxidants. Higher concentrations of As(III) may counter this effect, increasing the ionic activity of As(III) in the system, leading to more As(V) formation and a higher ratio of  $[\text{As(III)}]_{\text{oxidation}}/[\text{Cr(VI)}]_{\text{reduction}}$  (Table 1). Although an increase of Cr(VI) (25–100 μM) greatly enhanced the oxidation of As(III) to As(V), the ratio of  $[\text{As(III)}]_{\text{oxidation}}/[\text{Cr(VI)}]_{\text{reduction}}$  reduced from 0.82 to 0.55 ( $[\text{As(III)}]_0 = 50 \mu\text{M}$ ,  $[\text{sulfite}]_0 = 400 \mu\text{M}$ ). Moreover, even though  $[\text{sulfite}]_0$  was optimized for As(V) formation at  $[\text{Cr(VI)}]_0$  of 400 μM, a downtrend of  $[\text{As(III)}]_{\text{oxidation}}/[\text{Cr(VI)}]_{\text{reduction}}$  was observed under the conditions of Cr(VI) ranging from 50 to 400 μM with the  $[\text{Cr(VI)}]_0/[\text{As(III)}]_0$  ratio of 1:1 (Table 1). These results indicated that the reaction of sulfite reducing Cr(VI) for radicals generation was inhibited at high Cr(VI) concentrations, implying that the reduction mechanism of Cr(VI) may depend on the Cr(VI) levels in Cr(VI)–sulfite systems.

Table 1. Effect of Reagents' Concentrations on the Transformations of As(III) and Cr(VI) and Sulfite within 60 min ( $\text{pH}_{\text{ini}} = 3.5$ )

Cr(VI) ( $\mu\text{M}$ )	25	50	75	100	100	50	50	50	50	100	200	400	400	400	400	400	400	400	400
As(III) ( $\mu\text{M}$ )	50	50	50	50	400	400	400	400	400	400	200	200	200	400	400	400	400	400	400
sulfite ( $\mu\text{M}$ )	400	400	400	400	63.6	44.6	49.6	49.6	49.6	100	200	1600	1600	1600	2400	3200	399.9	400	3200
Cr(VI) reduction	2.5	48.9	63.6	69.6	38.4	44.6	38.4	49.3	49.3	200	200	380.8	380.8	380.8	399.8	399.9	84.6	400	75.4
As(III) oxidation	20.5	31.6	35.0	38.4	388.0	381.8	316.6	301.2	47.3	59.3	73.6	124.5	124.5	182.5	130.7	1055.5	1181.8	0.21	0.19
sulfite consumption	220.5	336.1	388.0	396.0	0.55	0.52	0.78	0.95	0.59	0.37	0.20	0.30	0.30	0.48	0.33	0.32	0.34	0.21	0.19
$[\text{As(III)}]_{\text{oxidation}}/[\text{Cr(VI)}]_{\text{reduction}}$	0.82	0.65	0.55	0.55	0.52	0.52	0.16	0.16	0.15	0.20	0.30	0.30	0.30	0.48	0.33	0.32	0.34	0.21	0.19
$[\text{Cr(VI)}]_{\text{reduction}}/[\text{sulfite}]_{\text{consumption}}$	0.11	0.15	0.16	0.18	0.12	0.12	0.16	0.16	0.15	0.20	0.30	0.30	0.30	0.48	0.33	0.32	0.34	0.21	0.19

**Effect of Initial pH.** The pH was a potentially critical variable for As(III) oxidation in this Cr(VI)–sulfite reaction system, because of its effect on the speciation and redox potentials of Cr(VI) and sulfite. Figure S8 demonstrates that  $\text{SO}_2\cdot\text{H}_2\text{O}$  and  $\text{HSO}_3^-$  were prominent species at lower pH values ( $\text{pH} < 7.0$ ). Figure S9 depicts that the major Cr(VI) species at  $\text{pH} < 6.0$  is  $\text{HCrO}_4^-$ , while  $\text{CrO}_4^{2-}$  is the major species at  $\text{pH} > 6.0$ . Since  $\text{CrO}_4^{2-}$  is a much weaker oxidant than  $\text{HCrO}_4^-$  ( $E^0(\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_3) = 0.56 \text{ V}_{\text{NHE}}$  at  $\text{pH} 7.0$  vs  $E^0(\text{HCrO}_4^-/\text{Cr}^{3+}) = 0.94 \text{ V}_{\text{NHE}}$  at  $\text{pH} 3.0$ ),  $\text{CrO}_4^{2-}$  is less active than  $\text{HCrO}_4^-$  for the Cr(VI)-induced oxidation of sulfite.<sup>8</sup> Therefore, a faster reduction of Cr(VI) is expected, with enhanced oxidation of As(III) at more acidic pH, as shown in Figures 2 and S10. Again, the pH dependence of As(III) oxidation demonstrates the driving role of Cr(VI) in the transformations of sulfite and As(III).

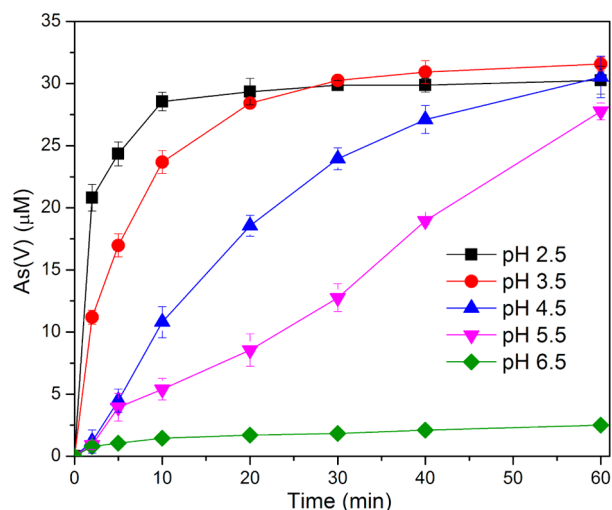
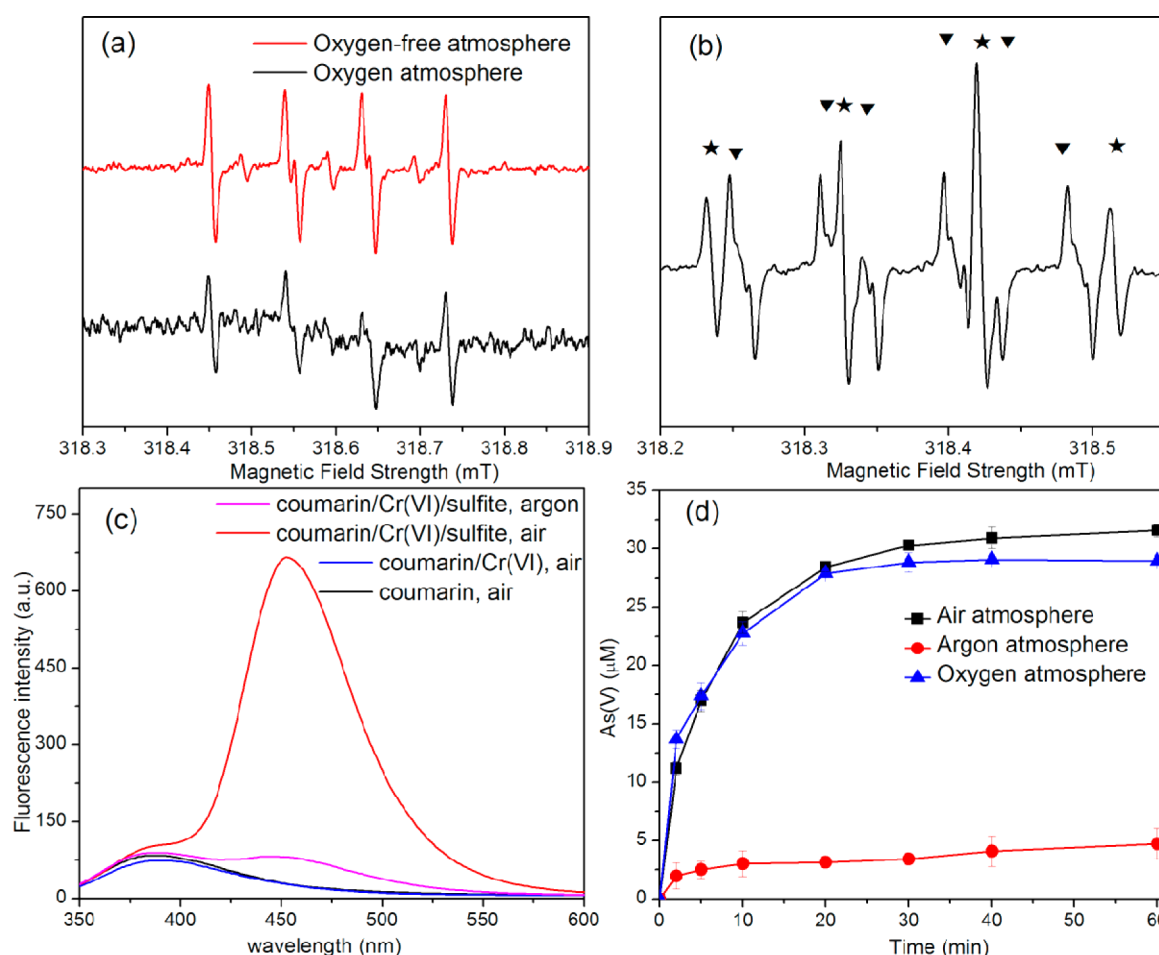


Figure 2. Effect of solution pH on the oxidation of As(III) ( $[\text{As(III)}]_0 = 50 \mu\text{M}$ ,  $[\text{Cr(VI)}]_0 = 50 \mu\text{M}$ ,  $[\text{sulfite}]_0 = 400 \mu\text{M}$ ).

**Identification of the Reactive Oxidants.** The rapid oxidation of As(III) at acidic pH suggests that it might be a radical-involved process initiated by the oxidative activation of sulfite with Cr(VI). To gain direct evidence for the involvement of radicals, fluorescence measurement and electron paramagnetic resonance (ESR) were employed. In oxygen or an oxygen-free atmosphere, the characteristic signal of the sulfite anion radical ( $\text{SO}_3^{\bullet-}$ ) ( $a^N = 14.7 \text{ G}$ ,  $a^H = 15.9 \text{ G}$ ) from Cr(VI)-initiated oxidation of sulfite was observed by spin-trapping ESR in Figure 3a.<sup>24</sup> Signal intensity of  $\text{DMPO}/\text{SO}_3^{\bullet-}$  adduct became stronger in the deoxygenated solution than the oxygenated solution. Other radicals were not observed perhaps because excess DMPO (100 mM) trapped all of the  $\text{SO}_3^{\bullet-}$  and terminated any subsequent radical propagation reactions.

In order to trap secondary radicals formed from the sulfite chain reactions, the concentration of DMPO was decreased to 25 mM, enhancing the reaction of the primary  $\text{SO}_3^{\bullet-}$  with  $\text{O}_2$ . As presented in Figure 3b, typical  $\text{DMPO}\cdot\text{OH}$  adducts ( $a^N = 1.49 \text{ mT}$ ,  $a^H = 1.49 \text{ mT}$ ) and  $\text{DMPO}\cdot\text{SO}_4^{\bullet-}$  adducts ( $a^N = 1.38 \text{ mT}$ ,  $a^H = 1.02 \text{ mT}$ ,  $a^H = 0.14 \text{ mT}$ ,  $a^H = 0.08 \text{ mT}$ ) signals can be confirmed based on the previous literature,<sup>25</sup> indicating the generation of  $\text{SO}_4^{\bullet-}$  and  $\cdot\text{OH}$  in the Cr(VI)–sulfite reaction system. Coumarin was used as a chemical probe for  $\cdot\text{OH}$ , reaction 3,<sup>26</sup> to compare the formation of  $\cdot\text{OH}$  in the Cr(VI)–sulfite system under various gas atmospheres. As



**Figure 3.** ESR spectrum of sulfite radical (a) (100 mM DMPO,  $[\text{Cr(VI)}]_0 = 0.3 \text{ mM}$ ,  $[\text{sulfite}]_0 = 1.8 \text{ mM}$ ,  $\text{pH}_{\text{ini}} = 3.5$ ), ESR spectrum of sulfate and hydroxyl radicals (b) (25 mM DMPO,  $[\text{Cr(VI)}]_0 = 0.3 \text{ mM}$ ,  $[\text{sulfite}]_0 = 1.8 \text{ mM}$ ,  $\text{pH}_{\text{ini}} = 3.5$ , initiating reaction in argon atmosphere and then in an oxygenating condition, ★ represents  $\text{DMPO}\text{-}\cdot\text{OH}$  adduct and ▼ represents  $\text{DMPO}\text{-}\text{SO}_4^{\cdot-}$  adduct), determination of hydroxyl radical using fluorescence spectrometry (c), and the formation of As(V) (d) in Cr(VI)–sulfite system under various gas atmospheres ( $[\text{coumarin}]_0 = 1 \text{ mM}$ ,  $[\text{Cr(VI)}]_0 = 50 \text{ }\mu\text{M}$ ,  $[\text{As(III)}]_0 = 50 \text{ }\mu\text{M}$ ,  $[\text{sulfite}]_0 = 400 \text{ }\mu\text{M}$ ,  $\text{pH}_{\text{ini}} = 3.5$ ).

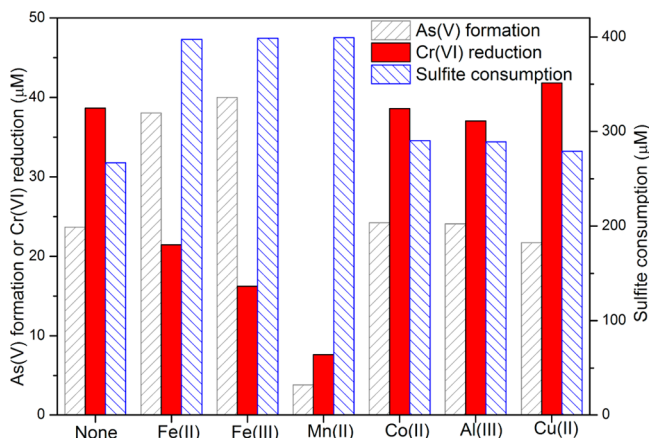
shown in Figure 3c, the production of 7-hydroxycoumarin ( $\cdot\text{OH} + \text{coumarin}$ ) was determined in an air atmosphere; however, it was greatly inhibited in an argon atmosphere. These results confirm the participation of oxygen for  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  generation in the Cr(VI)–sulfite system. Thus, explaining the small quantity of As(III) oxidized in an argon atmosphere, the observed oxidation may be attributed to remnants of oxygen dissolved in the reaction mixture. Significant amounts of As(V) were formed in air and oxygen atmospheres, respectively, in Figure 3c. Besides, oxidation of sulfite by oxygen and its derived reactive radicals accounted for the enhanced depletion of sulfite, which led to the inferior reduction of Cr(VI) in air and oxygen atmospheres to that in an argon atmosphere (Figure S11).

To quantitatively differentiate the roles of various active species in As(III) oxidation, radicals scavenging experiments for As(V) formation were performed by adding EtOH and TBA with 400:1 molar ratio of the alcohols versus sulfite. Previous works<sup>14,27–32</sup> have shown that EtOH can effectively scavenge  $\text{HO}\cdot$  and  $\text{SO}_4^{\cdot-}$  at a rate of  $(1.2\text{--}2.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $(1.6\text{--}7.7) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. As for the alcohols without  $\alpha$ -hydrogen, the rate constant of TBA reacting with  $\text{HO}\cdot$  was  $(3.8\text{--}7.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , approximately 3 orders of magnitude greater than that with sulfate radicals  $((4.0\text{--}9.1) \times 10^5 \text{ M}^{-1}$

$\text{s}^{-1}$ ). Other radicals, e.g.,  $\text{SO}_5^{\cdot-}$  and  $\text{SO}_3^{\cdot-}$ , generated in this system are fairly inert toward alcohols ( $k \leq 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ). Table S1 indicates that As(V) generation in the Cr(VI)–sulfite system was greatly affected by the presence of EtOH, implying that  $\text{HO}\cdot$  and  $\text{SO}_4^{\cdot-}$  were primarily responsible for As(III) oxidation, approximately 89% at 10 min and 91% at 60 min, respectively. Although  $\text{SO}_3^{\cdot-}$  and  $\text{SO}_5^{\cdot-}$  were produced in this system, they cannot efficiently oxidize As(III) to As(V) ( $E(\text{SO}_3^{\cdot-}/\text{SO}_3^{2-}) = 0.72 \text{ V}_{\text{NHE}}$ ,  $E(\text{SO}_5^{\cdot-}/\text{SO}_5^{2-}) = 1.1 \text{ V}_{\text{NHE}}$ ),<sup>33</sup> only accounting for the remaining 11.0% and 9.2% of As(V) formation within 10 and 60 min, respectively. As for adding TBA in solution, the transformation of the As(III) decreased by 31.2% and 31.6% within 10 and 60 min, respectively. In the Cr(VI) sulfite system,  $\text{SO}_4^{\cdot-}$  contributed much more to As(III) oxidation, e.g., 57.8% and 59.2% within 10 and 60 min, respectively, than  $\text{HO}\cdot$ .

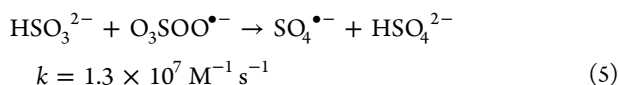
**Effect of Metal Ions.** Divalent/trivalent metals are often abundant and coexist with Cr(VI) species in many wastewaters, e.g., acid mine drainage and electroplating effluent. Sulfite preferentially forms complexes with Fe(III) over Cr(VI).<sup>11</sup> It is well understood that iron ions are very active for the catalytic oxidation of sulfite via the formation of a “generalized” sulfite-complex of Fe(III).<sup>34</sup> In this case, the fast intramolecular redox decomposition of Fe(III)–sulfite to Fe(II) and the sulfite

radical ( $\text{SO}_3^{\bullet-}$ ) can lead to the production of active radicals such as  $\text{SO}_4^{\bullet-}$ ,  $\text{HO}^\bullet$ , and  $\text{SO}_5^{\bullet-}$ , responsible for the enhanced oxidation of As(III)/sulfite and significantly retarding the reduction of Cr(VI) in As(III)–Fe(II)/Fe(III)–sulfite–Cr(VI) systems (Figure 4 and Figure S12).<sup>13</sup> Similarly, the formation of



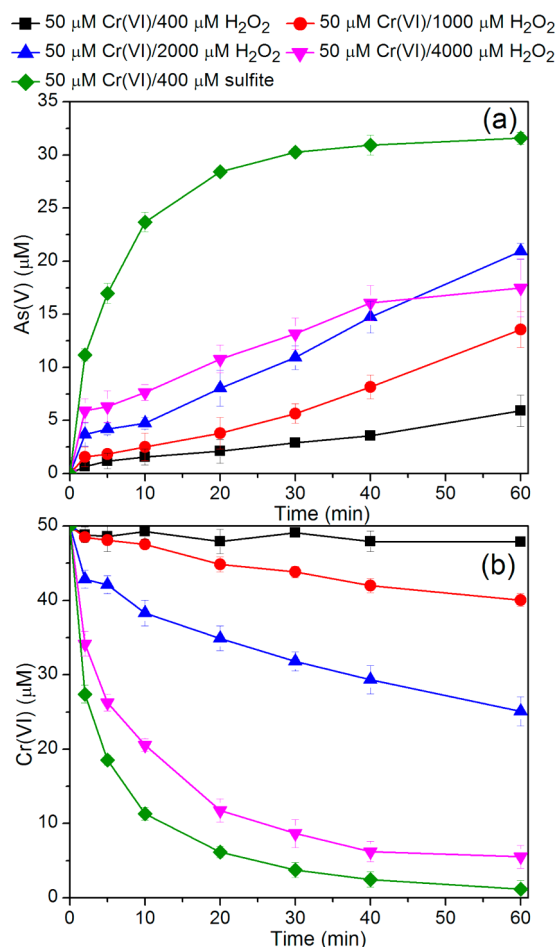
**Figure 4.** Effects of coexisting metal ions on simultaneous transformations of As(III), Cr(VI), and sulfite in Cr(VI)–sulfite systems ( $[\text{As(III)}]_0 = 50 \mu\text{M}$ ,  $[\text{Cr(VI)}]_0 = 50 \mu\text{M}$ ,  $[\text{sulfite}]_0 = 400 \mu\text{M}$ ,  $[\text{metal ions}] = 50 \mu\text{M}$ ,  $\text{pH}_{\text{init.}} = 3.5$ ).

$\text{SO}_3^{\bullet-}$  is also involved in the Mn(II)–sulfite reaction system, but the addition of Mn(II) depletes sulfite, at an even greater rate (Figure S12), greatly suppressing conversions of As(III) and Cr(VI) in Figure 4.<sup>35</sup> The exceptional activity of Mn(II) can be explained by the fact that the rate constant of Mn(III) oxidizing sulfite is ca.  $5 \times 10^3$  times larger than that for the reaction between Fe(III) and sulfite. Rapid reaction between  $\text{SO}_3^{\bullet-}$  and Mn(II) ( $\approx 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) regenerates Mn(III), blocking the reaction pathways for the generation of highly active radicals, reactions 4 and 5.<sup>35</sup> Moreover, in the Cr(VI)–As(III)–sulfite system, the active radicals produced, i.e.,  $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$ , can oxidize Mn(II) to Mn(III) at a rate of  $3 \times 10^7$  and  $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, further driving sulfite consumption.<sup>31,32</sup> In contrast, Cu(II), Co(II), and Al(III) did not cause any significant change in the coconversion of As(III) and Cr(VI).



### ■ COMPARISON WITH THE Cr(VI)–H<sub>2</sub>O<sub>2</sub> SYSTEM

Cr(VI) species are known to activate H<sub>2</sub>O<sub>2</sub> to generate  $\text{HO}^\bullet$  for oxidation of organic compounds in water.<sup>8,36</sup> Thus, a comparison is made of As(III) oxidation in two Cr(VI)-related oxidation systems, i.e., Cr(VI)–sulfite and Cr(VI)–H<sub>2</sub>O<sub>2</sub>. Figure 5 shows that although Cr(VI) readily reduces with high concentrations of H<sub>2</sub>O<sub>2</sub>, the transformation of As(III) to As(V) is low within 60 min. In contrast, relatively low sulfite concentrations were required for complete Cr(VI) reduction and resulted in more As(III) oxidation within 60 min in the Cr(VI)–H<sub>2</sub>O<sub>2</sub> system. In addition, the Cr(VI)–sulfite system required no additional chemical reagents because sulfite and Cr(VI) themselves are common industrial contaminants, while

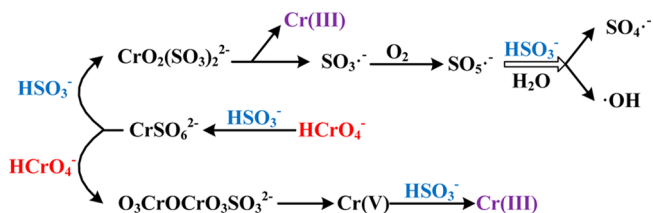


**Figure 5.** Comparisons of oxidation capacity for As(III) (a) and Cr(VI) reduction capacity (b) between the Cr(VI)–sulfite system and Cr(VI)–H<sub>2</sub>O<sub>2</sub> system ( $[\text{As(III)}]_0 = 50 \mu\text{M}$ ,  $[\text{Cr(VI)}]_0 = 50 \mu\text{M}$ ,  $\text{pH}_{\text{init.}} = 3.5$ ).

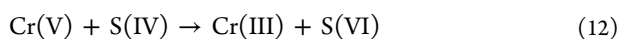
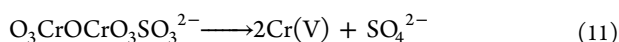
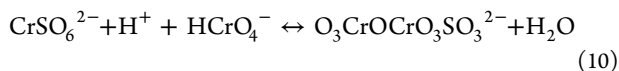
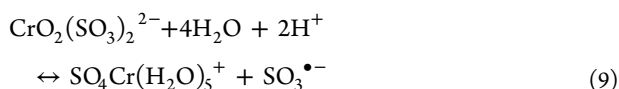
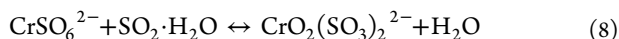
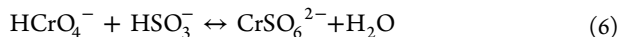
expensive, large volumes of H<sub>2</sub>O<sub>2</sub> (\$1520/t) are required to drive the oxidation of As(III) in a Cr(VI)–H<sub>2</sub>O<sub>2</sub> system. It is well-known that the peroxochromate(V) complex in Cr(VI)–H<sub>2</sub>O<sub>2</sub> systems is potentially the most significant intermediate for  $\bullet\text{OH}$  formation.<sup>36,37</sup> However, the mechanisms of active radicals formation in Cr(VI)–sulfite reaction systems are not well understood.

**Mechanism Discussion.** The studies on Cr(VI) reduction by organic and inorganic acids are well documented. The reaction begins with the formation of chromium(VI) esters followed by either a redox reaction or a unimolecular redox reaction.<sup>38–40</sup> Thus, as seen in Scheme 1, it is reasonably proposed that the mechanism of sulfite oxidation by Cr(VI)

**Scheme 1.** Proposed Pathways for the Reduction of Cr(VI) and the Formation of Active Species, i.e.,  $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$ , in the Cr(VI)/Sulfite System

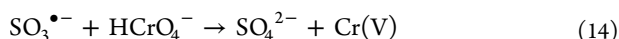


involves the sequent condensation of  $\text{HSO}_3^-$  with  $\text{HCrO}_4^-$  to give activated complexes, i.e.,  $\text{CrSO}_6^{2-}$  and  $\text{CrO}_2(\text{SO}_3)_2^{2-}$ , reactions 6–8.<sup>41</sup> Specifically, one-step, spontaneous decomposition of  $\text{CrO}_2(\text{SO}_3)_2^{2-}$  to give Cr(III)-bound  $\text{SO}_4^{\bullet-}$  and  $\text{SO}_3^{\bullet-}$  in reaction 9 was confirmed by a spin-trapping technique (Figure 3a), which leads to Cr(VI) reduction via an intramolecular electron transfer reaction.

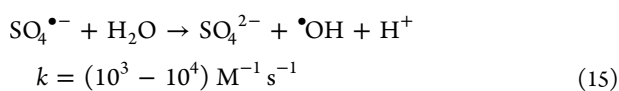


Increasing the concentration of Cr(VI) in aqueous solution, Cr(VI) reduction was accelerated, with less sulfite consumption (shown in Table 1). Cr(VI) species probably participates with  $\text{CrSO}_6^{2-}$  in the formation of the complex ( $\text{O}_3\text{CrOCrO}_3\text{SO}_3^{2-}$ ), which then decomposes into Cr(V) and sulfate ions (see reactions 10 and 11). The formed Cr(V) is probably directly bound to sulfite, leading to the direct reduction to Cr(III) in reaction 12, bypassing the highly energetic intermediates Cr(IV).<sup>41</sup> Reactions 10 and 11 should compete with reaction 8 and therefore block the one-step, three-electron reaction of Cr(VI) and  $\text{SO}_3^{\bullet-}$  production in reaction 9. Thus, this step can account for relatively less generation of active radicals and a higher ratio of  $[\text{Cr(VI)}]_{\text{reduction}}/[\text{sulfite}]_{\text{consumption}}$  at high  $[\text{Cr(VI)}]_0$  (Table 1). The two fates of  $\text{CrSO}_6^{2-}$  in reactions 8 and 10 were demonstrated by Haight et al.<sup>41</sup> to account for the variation in stoichiometric values of  $[\text{sulfite}]_{\text{consumption}}/[\text{Cr(VI)}]_{\text{reduction}}$ , i.e., 3/2 and 2/1 (see reactions 1 and 2). Reactions 7, 9, and 10 consume protons, which can explain the acidity dependence of Cr(VI)–sulfite reactions.

In an Ar-saturated solution, the transformation of  $\text{SO}_3^{\bullet-}$  proceeds via reactions 13 and 14, which would terminate the radical propagation processes. As a consequence, a negligibly measurable  $\bullet\text{OH}$  signal was observed in the fluorescence spectrum, and oxidation of As(III) was significantly inhibited in this anaerobic environment (see Figure 3c).



However, when Cr(VI)–sulfite reaction is exposed to an oxygen atmosphere, the unstable  $\text{SO}_3^{\bullet-}$  is prone to being oxidized by oxygen and then gives rise to the formation of the oxygen-centered peroxymonosulfate ( $\text{O}_3\text{SOO}^{\bullet-}$ ) and sulfate ( $\text{SO}_4^{\bullet-}$ ) anion radicals through chain propagation steps shown in reactions 4 and 5:<sup>23,42</sup>



In this scenario,  $\text{SO}_4^{\bullet-}$  can oxidize almost any biomolecular  $\text{H}_2\text{O}$  for  $\bullet\text{OH}$  production, reaction 15.<sup>31</sup> Although, in a Cr(VI)–sulfite reaction system, the radicals of  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  are very strong oxidants, they may not lead to the reoxidation of Cr(III) to Cr(VI) ( $E(\text{HCrO}_4^-/\text{Cr}^{3+}) = 1.35 \text{ V}_{\text{NHE}}$ ) due to the excess of sulfite ( $E(\text{SO}_4^{2-}/\text{SO}_2) = 0.158 \text{ V}_{\text{NHE}}$ ). Thus, scavenging the radicals of  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  by free sulfite can be responsible for deviant stoichiometric consumption of sulfite ( $k_{\bullet\text{OH}/\text{sulfite}} = 4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{SO}_4^{\bullet-}/\text{sulfite}} > 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). This is verified by a greater production of sulfate ions than in the argon atmosphere, Cr(VI)–sulfite reaction system, as shown in Figure S13a,b. These findings also explain the requirement of excess sulfite for complete Cr(VI) reduction in acidic solutions in previous studies.<sup>2,10–12</sup>

However, when As(III) is present in a Cr(VI)–sulfite system, it can scavenge highly active radicals such as  $\bullet\text{OH}$  ( $k_{\bullet\text{OH}/\text{As(III)}} = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and  $\text{SO}_4^{\bullet-}$  ( $k_{\text{SO}_4^{\bullet-}/\text{As(III)}} > 8.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>31</sup> As a consequence, sulfite oxidation, mediated by active radicals, can be interrupted with oxidative transformation of As(III) to As(V), which in turn accelerates the reduction of Cr(VI). Thus, compared with a Cr(VI)–sulfite reaction in an air atmosphere, much less sulfate was produced in a Cr(VI)–sulfite–As(III) reaction system (Figure S13c). Generally, in a Cr(VI)–sulfite system, the presence of other organic/inorganic pollutants decreases the amount of sulfite required for Cr(VI) reduction and therefore the sulfate concentration in the resulting wastewater.

**Environmental Implications.** In the present study, we shed light on the involvement of  $\text{SO}_4^{\bullet-}$  (2.5–3.1  $\text{V}_{\text{NHE}}$ ) and  $\bullet\text{OH}$  (1.8–2.7  $\text{V}_{\text{NHE}}$ , pH dependent) in Cr(VI)–sulfite system, which can be potentially utilized for the oxidation of other pollutants with rates of  $10^4$ – $10^{10}$  and  $10^7$ – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively.<sup>31,32</sup> To evaluate the industrial flexibility of this proposed process, real concentrated Cr(VI) electroplating effluent from the electroplating industrial park of Qingdao Development Zone ( $[\text{Cr(VI)}] = 162.7 \text{ mg L}^{-1}$ ,  $[\text{Fe}] = 79 \text{ }\mu\text{M}$ , pH = 2.23) was utilized to examine organic pollutant removal in an air atmosphere. For example, 40  $\mu\text{M}$  rhodamine B (100 mL, pH = 3.0), a common contaminant, can be quickly bleached with the addition of a portion of initiator (1.6 mL real Cr(VI) electroplating effluent and 1.2 mM sulfite). Approximately 24% TOC was diminished after adding a second portion of initiator. This result validates that the traditional Cr(VI) reducing process can be potentially and economically upgraded for the treatment of Cr(VI) and other inorganic/organic pollutants mixed wastewaters (e.g., chromate-containing textile wastewater and tannery wastewater) with externally added sulfite as the reductant or the synergetic transformations of multiple pollutants, such as Cr(VI) reduction, sulfite oxidation, and the oxidation of other inorganic/organic pollutants if mixing their relevant wastewaters is cost-effective.

There is an environmental risk that a sulfite process can cause the toxic release of  $\text{SO}_2$  in an acidic environment (pH  $\leq$  3.5 in Figure S8) and high concentrations of sulfate will remain in the wastewater. In spite of these, compared with the traditional sulfite reducing Cr(VI) process, the upgraded process, utilizing  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  for the oxidation of other inorganic/organic pollutants in acidic solutions (pH  $\leq$  4.5) with a  $[\text{sulfite}]_0/[\text{Cr(VI)}]_0$  ratio of 3.0–8.0, requires less sulfite addition for more Cr(VI) reduction. Thus, it effectively alleviates the environmental risks, making the process of sulfite reducing Cr(VI) more environmentally favorable. As such, the

Cr(VI)–sulfite system is a new cost-effective technology for the treatment of various industrial wastewaters.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03275.

Additional experimental evidence (PDF)

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### Notes

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