A green approach towards simultaneous remediations of chromium(VI) and arsenic(III) in aqueous solution

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HIGHLIGHTS

- Simultaneous conversion of Cr(VI) and As(III) was achieved in glow plasma.
- The mechanism of redox interaction between Cr(VI) and As(III) was explored.
- Adding dicarboxylic acid improved Cr(VI) reduction but retarded As(III) oxidation.
- The effects of active species in the conversion of Cr(VI)/As(III) were quantified.

ARTICLE INFO

ABSTRACT

In this study, the applicability of glow discharge plasma for simultaneous redox transformations of Cr(VI) and As(III) was evaluated in aqueous solution. The results showed that there was a beneficially synergistic effect between Cr(VI) reduction and As(III) oxidation. The presence of Cr(VI) can significantly enhance As(III) oxidation, whereas a slight increase for Cr(VI) reduction mediated by As(III) was observed. The added ethanol or dicarboxylic acids can increase the Cr(VI) reduction with different mechanisms, but significantly retard As(III) oxidation. The conversions of both As(III) and Cr(VI) can also be effectively increased from 96% to 100% and 53% to 77%, respectively, by increasing the voltage input from 530 to 600 V. Cr(VI) reduction proceeded more rapidly, approximately 96% at pH 2.0, while As(III) oxidation was depressed under acidic conditions, only 70% at pH 2.0. And the optimal pH value for As(V) formation facilitated by Cr(VI) is 7.0. H_2O_2 generated in-situ in glow discharge plasma can reduce Cr(VI) and produce highly oxidizing $\cdot OH$ that was responsible for As(III) oxidation. Reaction between As(III) and $\cdot OH$ in turn partially avoided the re-oxidation of Cr(III) by $\cdot OH$ to Cr(VI), thus facilitating the net conversion of Cr(VI). Our study demonstrated the feasibility of GDP for the coconversion of As(III) and Cr(VI), holding a great promise for real-world wastewater remediation.

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1. Introduction

Arsenic and chromium are of particular environmental concern due to their toxicity and are challenging to remove from industrial wastewater. The concentrations of arsenic and chromium in natural waters, e.g., river water, lake water, seawater, and groundwater, vary at micromolar levels and they can coexist in mine drainage and many industrial wastewaters [1–3]. For example, the leaching concentrations of arsenic and chromium from the wood preservative wastewater are at the level of tens of milligrams per liter [4]. The redox species of arsenic and chromium greatly influence the mobility, toxicity, bioavailability, and environmental fates of these two inorganic elements [2]. It is known that As(III) and Cr(VI) are greater toxic and more mobile than their counterparts, namely As(V) and Cr(III) [5]. Therefore, the reduction of Cr(VI) to Cr(III) and the oxidation of As(III) to As(V) are considered highly desirable before the final removal of Cr(VI) and/or As(III) via traditional adsorption and coagulation techniques [6].

A variety of methods, such as advanced oxidation processes [7,8], traditional oxidation methods [9] and reduction methods with different reducing agents [10,11], have been applied for oxidizing As(III) to As(V) or reducing Cr(VI) to Cr(III). Despite of the

success in detoxification of individual Cr(VI) or As(III), it is a big challenge to simultaneously relieve the environmental hazard of these two constituents in contaminated wastewaters. Till now, the co-conversion of As(III) and Cr(VI) have been investigated by adding H_2O_2 [2], in the ice phase [5], iodide-mediated photolysis [12] or by *Bacillus firmus* [13]. To avoid the massive consumption of chemical reagents and the extreme conditions, it is urgently required to develop more efficient and widely practical technology towards the simultaneous conversion of As(III) and Cr(VI).

Over the past several years, interest in the utilization of electrical plasma technologies for wastewater remediation has increased enormously [14–16]. Glow discharge plasma (GDP) is sustained by glow discharges across a pointed electrode and the surface of the liquid electrolyte. GDP is characterized by its higher yields of reactive species including ·H, ·OH, H_2O_2 and hydrated electron ($e_{aq.}^-$) than those expected on the basis of Faraday's law [17]. Among these active species, ·OH is a strong oxidizing agent (E^0(·OH/H_2O) = 2.8 V_{NHE}). The formed H_2O_2 increases the collective oxidizability of the plasma and can be further transformed to ·OH via various reactions (e.g., dissociation, photolysis and metal-based catalytic reactions) [17]. Therefore, GDP has been intensively investigated as a promising tool for oxidative degradation of aqueous organic pollutants such as pesticides, dyestuffs, pharmaceuticals and phenolic compounds [17]. On the other hand, the formations of reductive species, such as $e_{aq.}^-$, ·H and H_2O_2 guarantee the feasibility of GDP for the reduction of metal ions with high valence [18,19]. Accordingly, we think it may be feasible for GDP to induce the simultaneous redox conversions of As(III) and Cr(VI) in aqueous solution. However, up till now, GDP has not been reported for simultaneous conversions of those two heavy metals in water.

Here, we explored the applicability of GDP for simultaneous Cr(VI) reduction and As(III) oxidation in aqueous solution. The effects of input energy, pH value and initial concentration on the redox transformations of Cr(VI) and As(III) were investigated, and the synergetic effect between Cr(VI) reduction and As(III) oxidation was also discussed.

2. Experimental section

2.1. Materials

All chemicals were obtained from commercial sources and are listed in the Supporting Information (Text S1). All reagents were used as received without further purification. UltraPure water (resistivity 18.2 MΩcm) was used for all experiments. A stock solution of As(III) (1000 mg/L) and Cr(VI) (1000 mg/L) were prepared by dissolving analytical grade $K_2Cr_2O_7$ and $NaAsO_2$ in deionized water.
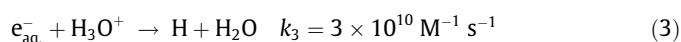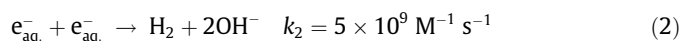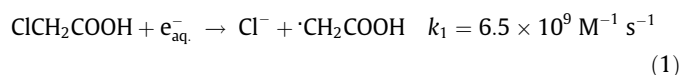
2.2. Experimental procedure

The experimental apparatus consisted of a direct current high voltage power supply and a reactor, as described in Fig. S1. All working solutions were freshly prepared before use by diluting the stock solution with deionized water, and the pH was adjusted to the desired values with concentrated solution of NaOH or H_2SO_4. Typically, 150 mL of argon-purged Na_2SO_4 solution (conductivity: 5 mS cm^{-1}) with 0.6 mM Cr(VI) and/or 1.0 mM As(III) was treated by GDP (580 V/120 mA). The initial pH value was adjusted to 3.0. All experiment were conducted at 298 ± 3 K by circulating cold water. The depth of the electrode immersed in the solution was carefully adjusted to stabilize the current and input voltage with deviation less than ±2%.

2.3. Analysis

The concentrations of Cr(VI), As(V)/total arsenic and H_2O_2 were measured spectrophotometrically using the modified diphenylcarbazide method, molybdene blue method and titanyl reagent, respectively [2,20]. A UV–visible spectrophotometer (UV-3000, MAPADA) was used to measure absorbance of solutions in a 1 cm quartz cell. Estimation of total chromium after GDP treatment was carried out using a high-resolution continuum source atomic absorption spectrometer (HR-CSAAS), ContrAA700, Analytik Jena AG (Jena, Germany). The conductivity and pH of the solution were determined by conductivity meter (DDS-307A) and pH meter (PHS-3C), respectively.

Hydrated electron ($e_{aq.}^-$) generated in GDP was estimated according to Goodman's method based on Eq. (1) [21]. 0.015, 0.1, 0.5 and 1.0 M of monochloroacetic acid were applied to scavenge $e_{aq.}^-$. The yield of Cl$^-$ within 3 min treatment was calculated according to standard curve of concentration vs. absorbance.

$$ClCH_2COOH + e_{aq.}^- \rightarrow Cl^- + ·CH_2COOH \quad k_1 = 6.5 \times 10^9 \, M^{-1} \, s^{-1} \tag{1}$$

$$e_{aq.}^- + e_{aq.}^- \rightarrow H_2 + 2OH^- \quad k_2 = 5 \times 10^9 \, M^{-1} \, s^{-1} \tag{2}$$

$$e_{aq.}^- + H_3O^+ \rightarrow H + H_2O \quad k_3 = 3 \times 10^{10} \, M^{-1} \, s^{-1} \tag{3}$$

Assuming that [$e_{aq.}^-$] is substantially constant in different experiments, G_{Cl^-} is determined simply by competition between reactions (Eqs. (1)–(3)), and the kinetics lead to the following expression:

$$\frac{1}{G_{Cl^-}} = \frac{1}{G_{e_{aq.}^-}} \frac{k_4[e_{aq.}^-] + k_5[H_3O^+]}{k_3[ClCH_2COOH]} + \frac{1}{G_{e_{aq.}^-}} \tag{4}$$

where G is defined as the ratio of the yield (mol per mol electron) observed to the yield (mol per mol electron) stipulated by Faraday's law.

A plot of $1/G_{Cl^-}$ versus $1/[ClCH_2COOH]$ gives a straight line with a y-intercept of $1/G_{e_{aq.}^-}$.

Based on Eq. (5), Coumarin fluorescence method was employed for probing and estimating ·OH in GDP [22]. The initial concentration of coumarin was 1.0 mM in each experiment. The fluorescence emission spectrum (excited at 332 nm) of the product 7-hydroxycoumarin was measured on a fluorescence spectrophotometer (F97PRO, Lengguang Tech.).

$$Coumarin + ·OH \rightarrow 7\text{-hydroxycoumain} \quad k_5 = 2 \times 10^9 \, M^{-1} \, s^{-1} \tag{5}$$
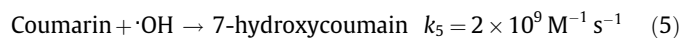
3. Results and discussion

3.1. Simultaneous conversion of Cr(VI) and As(III)

To examine the transformations of As(III) and Cr(VI) with GDP, As(V), Cr(VI) and H_2O_2 were simultaneously monitored as a function of reaction time (Fig. 1). In the presence of Cr(VI) alone or As(III) alone, 61% of 0.6 mM Cr(VI) was reduced or 56% of 1 mM As(III) was oxidized after 18 min GDP treatment. As(III) exists almost entirely as the nonionic H_3AsO_3 at pH 3.0 (Fig. S2), which was highly vulnerable to ·OH-induced oxidation with rate constant of $8.5 \times 10^9 \, M^{-1} \, s^{-1}$ in Eq. (6). One-electron oxidation of As(III) would involve the formation of the unstable As(IV) intermediate, which was further transformed to As(V) via As(IV) disproportionation or further oxidizing As(IV) by dissolved O_2 in Eqs. (7–10) [23].
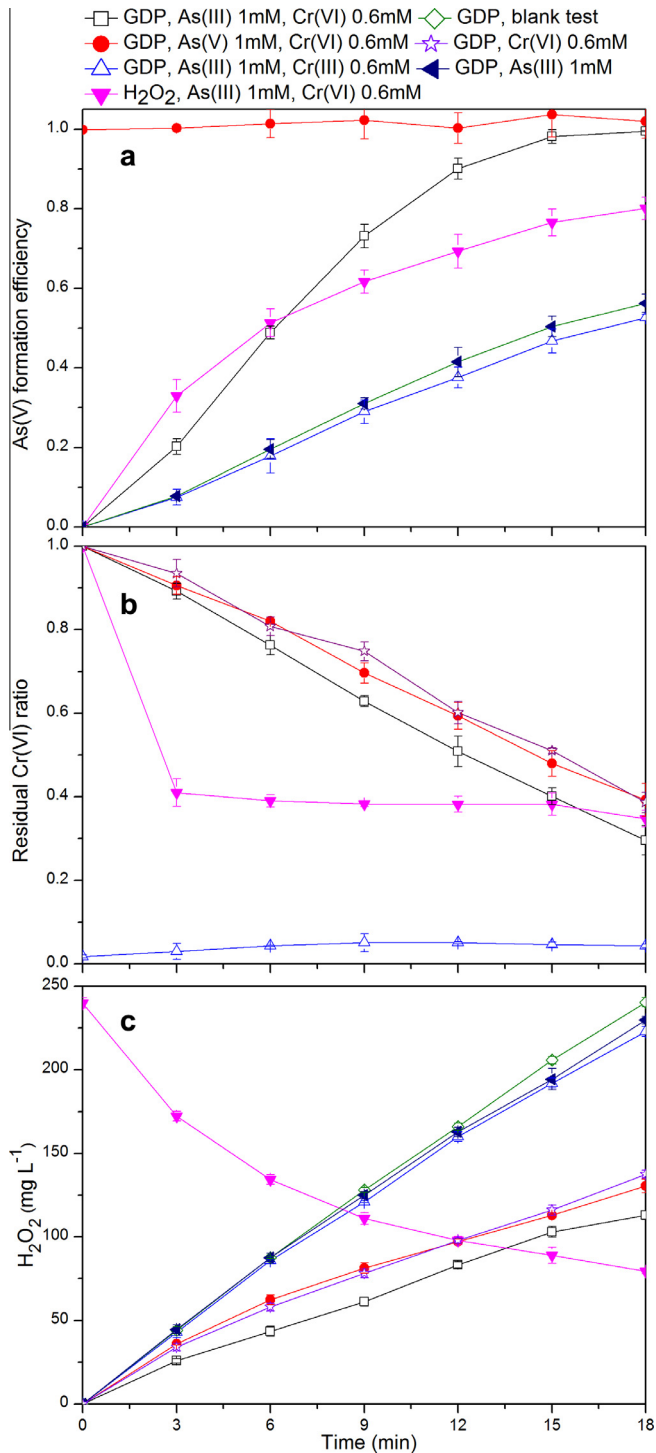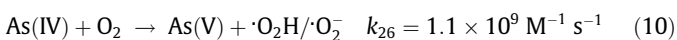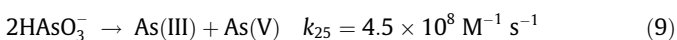
$$As(OH)_3 + ·OH \rightarrow H_2AsO_3 + H^+ + H_2O \quad k_6 = 8.5 \times 10^9 \, M^{-1} \, s^{-1} \tag{6}$$
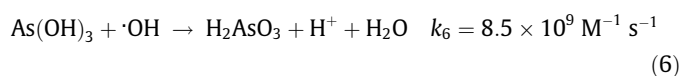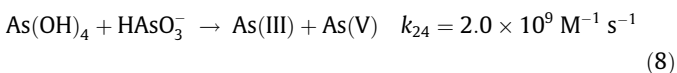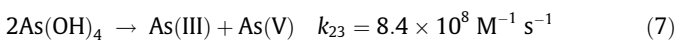
Fig. 1. As(III) oxidation (a), Cr(VI) reduction (b) and H_2O_2 variation (c) in the presence or absence of GDP (voltage: 580 V; current: 120 mA; solution volume: 150 mL; pH 3.0).
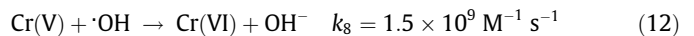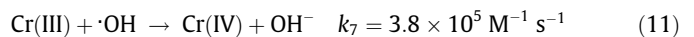
$$2As(OH)_4 \rightarrow As(III) + As(V) \quad k_{23} = 8.4 \times 10^8 \ M^{-1} \ s^{-1} \tag{7}$$

$$As(OH)_4 + HAsO_3^- \rightarrow As(III) + As(V) \quad k_{24} = 2.0 \times 10^9 \ M^{-1} \ s^{-1} \tag{8}$$

$$2HAsO_3^- \rightarrow As(III) + As(V) \quad k_{25} = 4.5 \times 10^8 \ M^{-1} \ s^{-1} \tag{9}$$

$$As(IV) + O_2 \rightarrow As(V) + \cdot O_2H/\cdot O_2^- \quad k_{26} = 1.1 \times 10^9 \ M^{-1} \ s^{-1} \tag{10}$$

In plasma generating process, the short-lived $\cdot OH$ (life time: 3.7×10^{-9} s) is abundant in the plasma zone [17]. Thus, H_2O_2, a long-lived plasma product, can be produced via the recombination of $\cdot OH$. Fig. 1(c) shows that approximately 242 mg L^{-1} H_2O_2 was produced after 18 min in aqueous solution. Although it was thermodynamically feasible ($\Delta G^0(H_3AsO_3 + H_2O_2) = -51.2$ kcal mol^{-1}), the direct oxidation of As(III) by H_2O_2 was negligible at pH 3.0 ($k(H_3AsO_3 + H_2O_2) = 5.5 \times 10^{-3}$ M^{-1} s^{-1}) [2]. Hence, H_2O_2 production was not influenced by the presence of As(III) (Fig. 1(c)).

In theory, H_2O_2 ($E^0(O_2/H_2O_2) = 0.68$ V$_{NHE}$) is known to serve as a reductant of Cr(VI) species ($E^0(HCrO_4^-/Cr^{3+}) = 1.35$ V$_{NHE}$). The consumption of H_2O_2 by Cr(VI) led to only 137 mg L^{-1} H_2O_2 measured in Cr(VI) involving GDP process. Besides, despite being transient species, very strong reducing agents, namely $e_{aq.}^-$ ($E^0(H_2O_2/e_{aq.}^-) = -2.77$ V$_{NHE}$) and $\cdot H$ ($E^0(H_2O/\cdot H) = -2.30$ V$_{NHE}$) were very likely to contribute to Cr(VI) reduction [19].

Now it is evident that H_2O_2 can efficiently reduce Cr(VI), but cannot oxidize As(III) at acidic pH. However, when H_2O_2, Cr(VI) and As(III) were mixed together, an evident conversion of As(III) and Cr(VI) was observed by Wang et al. [2], although the direct oxidation of As(III) by Cr(VI) was negligibly slow in dilute solution. Thus, it can be expected that GDP with producing large amount of H_2O_2 can provide a desirable condition for simultaneous redox reactions of As(III)/Cr(VI).

In Fig. 1(a), when Cr(VI)/As(III)-containing solution was exposed to GDP, As(III) was completely transformed to As(V) and meanwhile, approximately 9% more of Cr(VI) was reduced than that for Cr(VI) alone solution. For the solution of As(III)/Cr(III), only 53% of As(III) species was slowly oxidized to As(V) and a small amount of Cr(VI), approximately 1.5 mg L^{-1}, were produced. When As(V) and Cr(VI) initially coexisted in solution, approximately 61% of Cr(VI) reduction was achieved, without measurable decrease in As(V) concentration. This indicated that GDP can induce the reduction of Cr(VI) to Cr(III), but cannot lead to the conversion of As(V) to As(III).
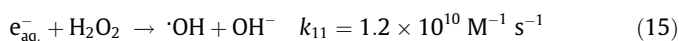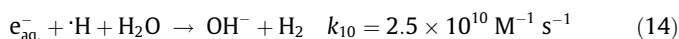
Fig. S3 indicates a significant enhancement of $\cdot OH$ generation at 9 min occurred in Cr(VI) solution in comparison to that in pure water solution. This suggested the enhanced in As(III) oxidation mediated by Cr(VI) should be ascribed to the formation of additional $\cdot OH$ via the reactions of Cr(VI) activating H_2O_2 [24]. In addition, the rate of Cr(VI) reduction also increased in As(III)/Cr(VI) system because As(III) was thought to alleviate Cr(III) re-oxidation to Cr(VI) by scavenging partial $\cdot OH$ (Eqs. (11) and (12)). In this process, ionic As(V) species ($H_2AsO_4^-$) and Cr(III) species (Cr^{3+} and $Cr(OH)^{2+}$) were simultaneously generated resulting in the rising solution conductivity from 5.0 to 5.46 mS cm^{-1} as shown in Fig. S4. Besides, in the case of As(III)/Cr(VI) solution, the removals of As(III) and Cr(VI) in GDP system drastically increased accompanied with equal amount of As(V) and Cr(III) productions (in Fig. S5).

$$Cr(III) + \cdot OH \rightarrow Cr(IV) + OH^- \quad k_7 = 3.8 \times 10^5 \ M^{-1} \ s^{-1} \tag{11}$$

$$Cr(V) + \cdot OH \rightarrow Cr(VI) + OH^- \quad k_8 = 1.5 \times 10^9 \ M^{-1} \ s^{-1} \tag{12}$$

To verify whether H_2O_2 was the only trigger for the simultaneous redox conversion of As(III) and Cr(VI), 242 mg L^{-1} H_2O_2 was added into As(III)/Cr(VI) solution without GDP. Fig. 1 shows initially rapid Cr(VI) reduction and gradual increasing As(V) generation were achieved in H_2O_2 solution. However, the conversion efficiencies of both species were lower at the cost of larger amount of H_2O_2 than these in GDP. Hence, H_2O_2 generated in GDP played a principal role on the redox reaction of As(III)/Cr(VI) but was definitely not a sole factor.

3.2. Effect of input energy

Figs. 2–4 show the effects of energy input on active species production and redox conversions of As(III)/Cr(VI) in GDP. In the light of the study of monochloroacetic acid as a scavenger of $e_{aq.}^-$, a decreasing $G_{e_{aq.}^-}$ from 3.66 to 2.90 mol (mol electrons)$^{-1}$ was obtained for increasing energy input from 530 V/80 mA to 600 V/140 mA, which correspondingly led to an enhancement for the yield of $e_{aq.}^-$ from 3.21 to 4.56×10^{-2} mol after 18 min treatment. The yields of $e_{aq.}^-$ were theoretically responsible for reduction of 1.07 to 1.52×10^{-2} mol Cr(VI) reduction. However, with considering the amount of Cr(VI) reduction in GDP in Fig. 4, $e_{aq.}^-$ actually contributed little to Cr(VI) reduction and this can be ascribed to its fast reactions with ·OH, ·H and H_2O_2 as follows [25]:

$$e_{aq.}^- + \cdot OH \rightarrow OH^- \quad k_9 = 3.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \tag{13}$$

$$e_{aq.}^- + \cdot H + H_2O \rightarrow OH^- + H_2 \quad k_{10} = 2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \tag{14}$$

$$e_{aq.}^- + H_2O_2 \rightarrow \cdot OH + OH^- \quad k_{11} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \tag{15}$$

Accompanied with $e_{aq.}^-$ formation, many other active radicals were also generated in GDP. Fig. 2 presents that the yield of ·OH was enhanced as a function of the energy input. According to

Fig. 3. Effect of the applied voltage and current on H_2O_2 formation rate and the mol H_2O_2 (mol electron)$^{-1}$ (As(III) concentration: 1 mM; Cr(VI) concentration: 0.6 mM; solution volume: 150 mL; pH 3.0).

Fig. 4. Effect of the applied voltage and current on As(III) oxidation and Cr(VI) reduction (As(III) concentration: 1 mM; Cr(VI) concentration: 0.6 mM; solution volume: 150 mL; pH 3.0).

Eq. (1), higher energy was also favorable for more ·H generation, which has been reported in the previous study [26]. However, a majority of ·H may be depleted with itself or ·OH forming H_2 or H_2O, respectively. Besides, as shown in Fig. 3, with increasing the energy from 530 V/80 mA to 600 V/140 mA, the formation rate of H_2O_2 increased from 9.9 to 15.6 mg L^{-1} min^{-1}, which averagely corresponded to 0.82 mol H_2O_2 (mol electron)$^{-1}$, much higher than that expected from Faraday's law (0.5 mol H_2O_2/mol electron).

Overall, higher input energy can induce higher active species production and therefore, led to faster As(III) oxidation and Cr(VI) reduction as presented in Fig. 4. For example, Cr(VI) reduction efficiency rose from 53% to 77% with increasing the voltage from 530 to 600 V. In these processes, a large portion of species were consumed which can be partially suggested by lower H_2O_2 formation rates and mol H_2O_2 (mol electron)$^{-1}$ (averagely 0.42) in comparison with blank tests in Fig. 3.

3.3. Effect of solution properties

The conversion efficiencies of As(III)/Cr(VI) at the pH range of 2.0 to 10.5 were compared. Fig. 5(a) shows that the As(V) formation increased significantly from 34% to 56% and 63% to 77% at
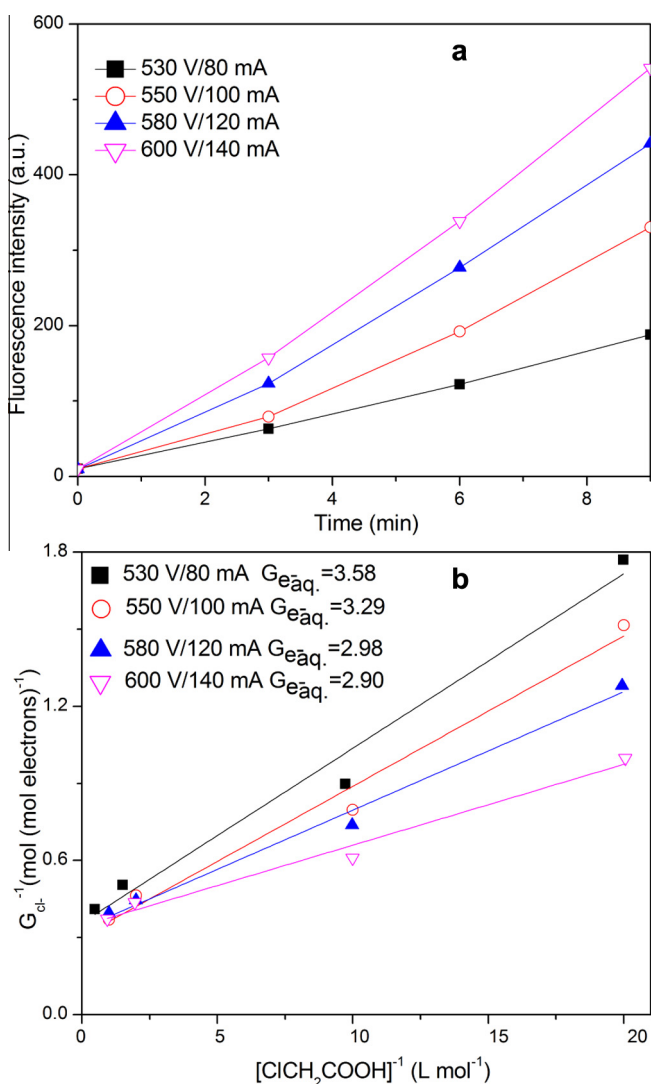

Fig. 2. Effect of the applied voltage and current on active species generation: (a) Fluorescence spectrum intensity; (b) Hydrated electron ($e_{aq.}^-$).
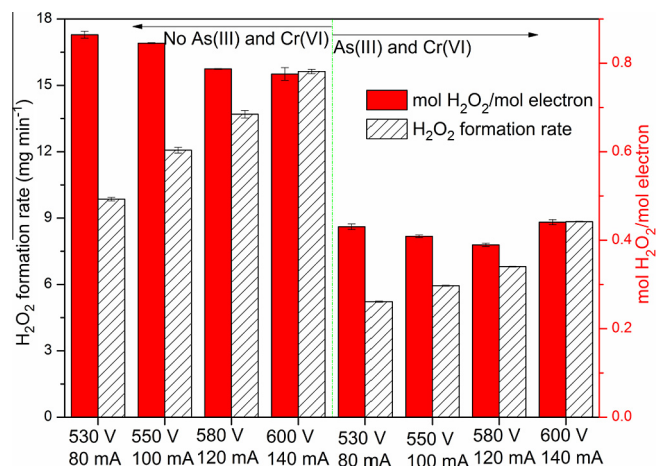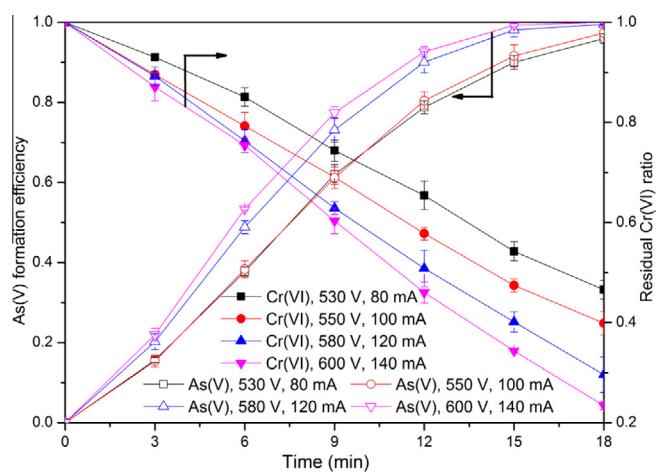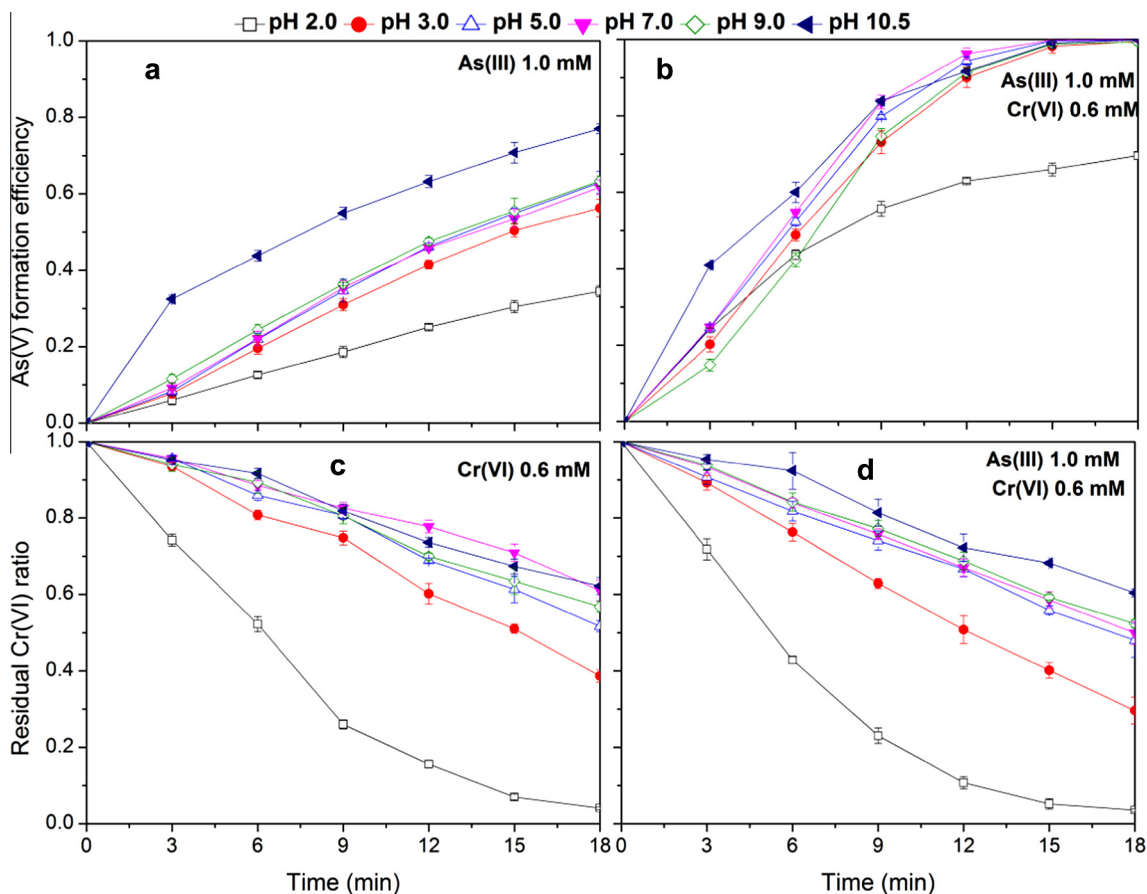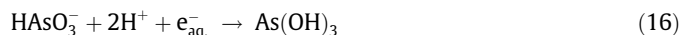
Fig. 5. Effect of solution pH on As(III) oxidation (a and b) and Cr(VI) reduction (c and d) (As(III) concentration: 1 mM; Cr(VI) concentration: 0.6 mM; voltage: 580 V; current: 120 mA; solution volume: 150 mL).

pH from 2.0 to 3.0 and 9.0 to 10.5, respectively, whereas only slight enhancement at pH 5.0–9.0. These results cannot be ascribed to the variation of ·OH concentration generated at different pH (Fig. 6). Partial reason may be the change in $E^0(As(IV)/As(III))$ with pH. As presented in Eqs. (16) and (17), $E^0(As(IV)/As(III))$ decreased as a function of pH resulting in larger difference between $E^0(·OH/H_2O)$ and $E^0(As(IV)/As(III))$, which was favorable for As(III) oxidation.

Fig. 6. Effect of solution pH on ·OH formation in blank solution and Cr(VI) mediated solution at 9 min (Cr(VI) concentration: 0.6 mM; voltage: 580 V; current: 120 mA; solution volume: 150 mL).

For example, the difference between $E^0(·OH/H_2O)$ and $E^0(As(IV)/As(III))$ was calculated to be 0.99 and 1.23 V_{NHE} at pH 5.0 and 7.0, respectively.

$$HAsO_3^- + 2H^+ + e_{aq.}^- \rightarrow As(OH)_3 \tag{16}$$

$$E^0(·OH\ /H_2O) - E^0(As(IV)/As(III))$$
$$= 0.4 + 0.0592 \log \frac{[As^{III}(OH)_3]}{[HAs^{IV}O_3]} + 0.1184pH \tag{17}$$

Transformation of As(III) to As(IV) was accompanied with proton production in Eq. (6) and this was in accord with the pH change in Fig. S4. Thus, the acidic pH did not favor the oxidation of As(III). As depicted in Fig. S2, an increase in the fractions of As(III) as $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} was present at pH > 9.0, which were expected to be stronger nucleophiles than As(OH)$_3$ [27]. In this case, H_2O_2 can be the primary reagent instead of ·OH for As(III) oxidation, whereas ionic As(III) species exerted negligible influence on As(V) formation at pH < 8.5, since fractions of these species are very small (<5×10^{-6}). The overall rate constant of As(III) oxidation with H_2O_2 can be presented as:

$$k = k_1' \alpha_{H_2AsO_3^-} + k_2' \alpha_{HAsO_3^{2-}} + k_3' \alpha_{AsO_3^{3-}} \tag{18}$$

where α_i is the molar fraction of As(III) species and k_i' is the rate constant of H_2O_2 reacting with corresponding As(III) species.

Pettine et al. gave the values: 42 ± 20, $(8 \pm 1) \times 10^4$ and $(72 \pm 18) \times 10^6$ M^{-1} min^{-1} for k_1', k_2' and k_3', respectively, in 0.01 M NaCl for the oxidation of 0.65 μM As(III) with 0.91 mM H_2O_2 at 25 °C [28].
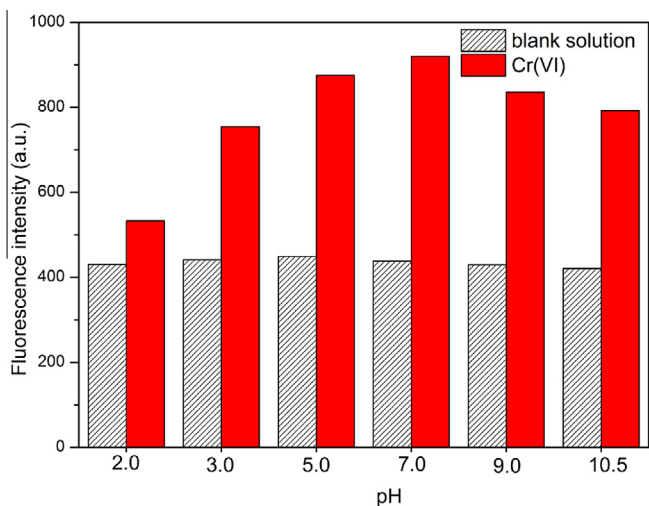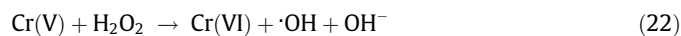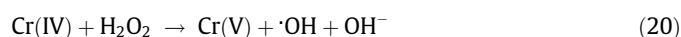
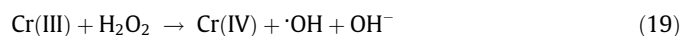With regard to Cr(VI) reduction, a maximum Cr(VI) reduction efficiency was obtained at strong acidic solution in Fig. 5(c and d). A significant increase of Cr(VI) reduction was obtained, e.g., from 61% to 96% and 70% to 96% in the absence and presence of As(III), respectively when pH reduced from 3.0 to 2.0. The reason argued by Wang et al. was that $Cr_2O_7^{2-}$ was predominant in acid media and the rate constant of its reaction with ·H was 2.0×10^{10} $M^{-1}\,s^{-1}$, which was larger than that of CrO_4^{2-} ($8.2 \times 10^9\,M^{-1}\,s^{-1}$), a predominant species in neutral or basic media [18]. Nevertheless, $Cr_2O_7^{2-}$ is predominantly present only when total Cr(VI) concentration is above the scale of 10^{-2} M at acid condition. In this study, $Cr_2O_7^{2-}$ accounted only approximately 4.4% in total Cr(VI) in Fig. S6, indicating higher reaction rate of $Cr_2O_7^{2-}$ and ·H may be not the main reason for rapid Cr(VI) reduction at pH 2.0. Cr(VI) can be also reduced by $e_{aq.}^-$, which also can be consumed by H_3O^+ at a rate comparable to that of the reaction of $e_{aq.}^-$ with CrO_4^{2-} ($3 \times 10^{10}\,M^{-1}\,s^{-1}$) [29]. At pH 2.0, Cr(VI) reduction by $e_{aq.}^-$ play a minor role in overall Cr(VI) transformation due to much higher proton concentration (1×10^{-2} M) than Cr(VI) concentration (6×10^{-4} M). A significant enhancement of Cr(VI) reduction with decreasing pH from 3.0 to 2.0 should be attributed to Cr(VI) reduction by H_2O_2. Fig. S6 depicts that the major Cr(VI) species at pH < 6.0 is $HCrO_4^-$, while CrO_4^{2-} is the major species at pH > 6.0, which is a much weaker oxidant than $HCrO_4^-$ [$E^0(CrO_4^{2-}/Cr(OH)_3) = 0.56\,V_{NHE}$ (pH = 7.0) vs $E^0(HCrO_4^-/Cr^{3+}) = 0.94\,V_{NHE}$ (pH = 3.0)]. Decreasing pH value from 3.0 to 2.0 significantly increased oxidation potential of Cr(VI), which was favorable for Cr(VI) reduction by H_2O_2. Since CrO_4^{2-} is less active than $HCrO_4^-$ for Cr(VI)-induced oxidative decomposition of H_2O_2 [24]. Thus, the reactive intermediate oxidants generated in situ in the course of Cr(VI) reduction could be favored at lower pH. It should be also mentioned that, Cr(III) species produced from Cr(VI) reduction at neutral and near-alkaline pH can also initiate similar catalytic reactions inducing ·OH generation as below [30]:
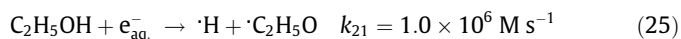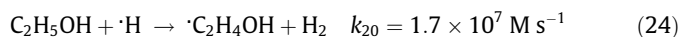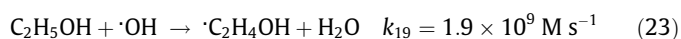
$$Cr(III) + H_2O_2 \rightarrow Cr(IV) + ·OH + OH^- \tag{19}$$

$$Cr(IV) + H_2O_2 \rightarrow Cr(V) + ·OH + OH^- \tag{20}$$

$$2Cr(IV) \rightarrow Cr(V) + Cr(III) \tag{21}$$

$$Cr(V) + H_2O_2 \rightarrow Cr(VI) + ·OH + OH^- \tag{22}$$

However, Cr(III) existed as inert hexaaquo complex $[Cr(H_2O)_6]^{3+}$ ($pK_a = 4$) at strong acid solution and Cr(III)-oligomers in strong alkaline condition, respectively, which unreactively activated H_2O_2 to efficiently generate ·OH [31]. Thus, the preferable oxidative capacity of the proposed Cr(III)/H_2O_2 system can be obtained over a pH wide range (5.0–11.0) [30]. As a result, ·OH concentration rose at the pH range of 2.0 to 10.5 in the processes mediated by Cr(VI) under GDP treatment in comparison with blank test in Fig. 6 and the largest amount of ·OH can be obtained at pH 7.0, which were coincident with the change of As(V) formation efficiency in Fig. 5(b).

Fig. S7 describes the effect of As(III)/Cr(VI) ratio on ΔAs(III)/ΔCr(VI) variation. GDP tended to induce faster reaction rate for As(III) oxidation than that for Cr(VI) reduction and this tendency was more remarkable in the case of higher As(III) concentration. For example, ΔAs(III)/ΔCr(VI) enhanced from 1.59 to 6.79 at 3 min and from 0.83 to 5.60 at 18 min with As(III) concentration increasing from 0.33 to 3 mM at Cr(VI) concentration of 0.6 mM. These results show that As(III) oxidation efficiency on the response of Cr(VI) concentration change was high sensitivity, whereas slight for Cr(VI) reduction efficiency. Increasing the concentration of Cr(VI) offered larger possibilities for additional ·OH formation and therefore, greatly accelerated As(V) formation.

3.4. Effect of hydroxyl radical scavenger

To investigate the role of ·OH in GDP-induced redox transformation, a radical scavenging experiment was conducted. Ethanol, a typical ·OH scavenger, was used to quench ·OH (Eq. (23)). Fluorescence intensity of 7-hydroxycoumarin (Fig. S8) was significantly reduced with the addition of ethanol, which resulted in decreasing H_2O_2 production in Fig. S9. Because of ethanol completing with As(III) species for ·OH, it finally retarded the As(V) generation in Fig. 7. This additionally validated that ·OH was the primary agent responsible for As(III) oxidation.

Fig. 7 also shows that ethanol addition was in favor of Cr(VI) reduction at the expense of less H_2O_2 and the optimal ethanol addition was 1.0 mL. However, in the H_2O_2/Cr(VI) solution, less Cr(VI) was reduced by consuming much more H_2O_2 in comparison with that in GDP. For example, with addition of 1.0 mL ethanol, approximately 1.45 mM H_2O_2 was consumed for 0.58 mM Cr(VI) reduction in GDP whereas only 0.18 mM Cr(VI) was reduced by depleting 3.23 mM H_2O_2 without GDP. This large difference can be interpreted by the fact that with scavenging ·OH, ethanol alleviated ·OH reoxidizing Cr(III) to Cr(IV) and meanwhile, weakened the reaction of ·OH with $e_{aq.}^-$ and ·H. However, with further addition of ethanol (>1.0 mL), the reduction of Cr(VI) diminished. Ethanol addition retarded the yield of H_2O_2 for Cr(VI) reduction as shown in Fig. S9. It is also likely that excessive ethanol can scavenge not only ·OH but also ·H and $e_{aq.}^-$ in Eqs. (24) and (25), which inhibited Cr(VI) reduction by ·H and $e_{aq.}^-$ [32].

$$C_2H_5OH + ·OH \rightarrow ·C_2H_4OH + H_2O \quad k_{19} = 1.9 \times 10^9\,M\,s^{-1} \tag{23}$$

$$C_2H_5OH + ·H \rightarrow ·C_2H_4OH + H_2 \quad k_{20} = 1.7 \times 10^7\,M\,s^{-1} \tag{24}$$

$$C_2H_5OH + e_{aq.}^- \rightarrow ·H + ·C_2H_5O \quad k_{21} = 1.0 \times 10^6\,M\,s^{-1} \tag{25}$$

GDP is very complicated since a large number of the short-lived active species, primary of which diffuse no further than 2000 nm into the bulk solution, e.g., approximately 6 nm for ·OH, 88–404 nm for ·H and 959–1981 nm for $e_{aq.}^-$, respectively [17]. Consequently, when adding ethanol with approximately 57 (0.5 mL ethanol) times As(III) concentration, no significant H_2O_2 decrease
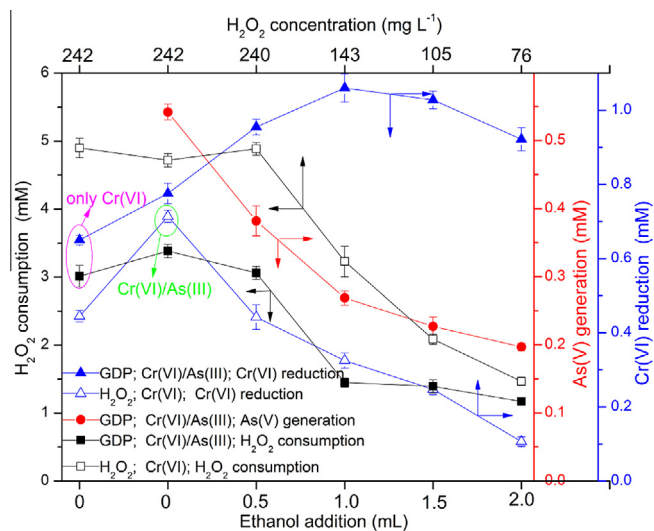

Fig. 7. Effect of ethanol addition in GDP and H_2O_2 concentration on Cr(VI) reduction, As(III) oxidation and H_2O_2 consumption with or without GDP (As(III) concentration: 1 mM; Cr(VI) concentration: 0.6 mM; H_2O_2 concentration: 242 mg L^{-1}; voltage: 580 V; current: 120 mA; solution volume: 150 mL; pH 3.0; time: 18 min).

was observed and only 7% of As(V) formation was reduced in As(III) alone solution, much less than approximately 30% in Cr(VI)/As(III) system in Fig. S10. These results indicated that As(III) species can be simultaneously oxidized in heterogeneous plasma zone and in homogeneous solution facilitated by Cr(VI) activating H_2O_2.

3.5. Effect of organics and metal ions

In practice, wastewaters often contain various organic matters and metal ions and these species may exert various influences on wastewater treatment efficiency. As demonstrated in Fig. 8(a), the presence of acetic acid did not pose evident effect on the redox of Cr(VI)/As(III) in comparison with equivalent ethanol due to its weaker radical scavenging capacity (k(·OH + acetic acid) = 1.5×10^7 M^{-1} s^{-1}) [33]. Interestingly, As(III) oxidation was greatly inhibited and Cr(VI) reduction was significantly enhanced in the presence of 0.5 mM oxalic acid or citric acid. These cannot be ascribed to their competing reactions against As(III) for ·OH, since oxalic acid and citric acid were less reactive toward ·OH with rate constants of 7.7×10^6 M^{-1} s^{-1} and 5×10^7 M^{-1} s^{-1}, respectively [34]. Taking oxalic acid as an example, oxalic acid can reversibly complex with Cr(V) (oxalato–Cr(V)) and H_2O_2 may not replace a coordinated ligand in oxalato–Cr(V) complex. Thus, the formation of the precursor for ·OH radical-tetraperoxochromate(V) was significantly inhibited leading to the negligible formation of additional ·OH and this can be proved by coumarin fluorescence intensity in Fig. 9. Then the formed oxalato-Cr(V) complex can quickly decompose to Cr(III) by inner-sphere electron transfer

[35]. Consequently, only 82% of As(III) was converted to As(V) after 18 min GDP treatment, while highlighted Cr(VI) reduction efficiency was approximately 92%. In the presence of equivalent phenol, As(III) oxidation were reasonably depressed owing to very high rate constant of 9×10^9 M^{-1} s^{-1} for its reaction with ·OH. Unexpectedly, phenol also drastically promoted Cr(VI) reduction, which can be ascribed to the direct reaction of Cr(VI) with phenol or its degradation intermediate products of dicarboxylic acids, such as maleic acid and oxalic acid in GDP [36]. All in all, the presence of organic matters in As(III)/Cr(VI) enhanced Cr(VI) reduction but retarded As(III) oxidation. To relieve the inhibition of As(III) oxidation owning to organic matters in wastewaters, the effective strategy was prolongating the plasma treatment time with much more active species generation.

The redox conversions of As(III)/Cr(VI) in the presences of Ni(II), Cu(II), Co(II) or Mn(II) are compared in Fig. 9. These metal ions did not significantly affect As(III) oxidation, whereas some of these ions enhanced Cr(VI) reduction. For example, Mn(II) can be oxidized by Cr(VI) and trap the intermediate chromium(IV), thus enhancing the conversion of Cr(VI) to Cr(III) [37].

Recently, to enhance the applicability of GDP in industry, adding iron ions can catalytically transform H_2O_2 to hydroxyl radicals via Fenton reactions [17]. However, this plasma-Fenton system are severely limited by the precipitation of Fe^{3+} ions at pH > 3.0, which limits the process to acidic conditions, requires large amount of ferrous salts and creates additional problem of iron sludge. Every year, large volumes of Cr-containing effluents are produced from industries such as metal finishing, leather tanning, dyeing, electroplating, and textile factories [38]. Traditional methods (e.g., ferrous sulfate or sulfur dioxide) for Cr(VI) reduction create additional pollution due to the excessive use of reducing chemicals and the production of toxic by-products. Our study presents that Cr(VI) can activate H_2O_2 into hydroxyl radical over a wide pH range and have successfully established the process viability by using GDP for simultaneous remediation of As(III)/Cr(VI)-contaminated wastewater. Thus, plasma-Cr(VI) process should be also ideally suited for organic pollutants contaminated wastewaters treatment. Although the deliberate addition of Cr(VI) into wastewaters would not be sensible, proposed plasma-Cr(VI) process provides an economical treatment method for wastewater containing Cr(VI) species remediation.
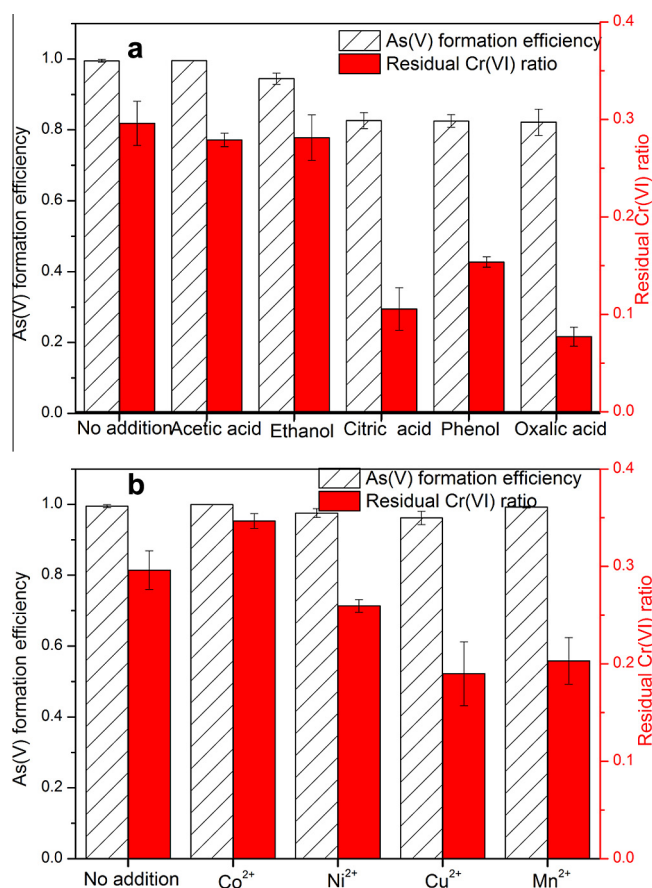

Fig. 8. Effect of organics (a) and metal ions (b) on As(III) oxidation and Cr(VI) reduction in GDP (As(III) concentration: 1 mM; Cr(VI) concentration: 0.6 mM; voltage: 580 V; current: 120 mA; solution volume: 150 mL; pH 3.0; time: 18 min; additive agent concentration 0.5 mM).
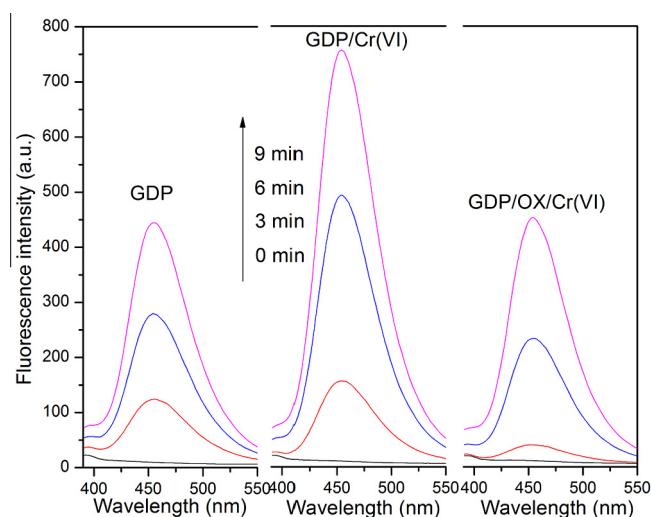

Fig. 9. Fluorescence spectrum intensity changes for different solution in GDP (Cr(VI) concentration: 0.6 mM; voltage: 580 V; current: 120 mA; solution volume: 150 mL; pH 3.0; time: 18 min; Ox concentration: 0.5 mM).

4. Conclusion

In summary, we have developed a strategy for simultaneous reduction of Cr(VI) to Cr(III) and the oxidation of As(III) to As(V) via glow discharge plasma. A beneficially synergistic effect is found between Cr(VI) and As(III). The presence of Cr(VI) can significantly enhance As(III) oxidation, whereas a slight increase for Cr(VI) reduction mediated by As(III) is observed. The added ethanol or dicarboxylic acids can increase the Cr(VI) reduction, but with different mechanisms. The conversions of both As(III) and Cr(VI) can also be effectively increased by increasing the energy input. GPD coupled with the synergetic effect between Cr(VI) reduction and As(III) oxidation lead to the effective conversion of Cr(VI) and As(III), holding a great promise for real-world heavy-metal water remediation.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2014.10.064.

References

[1] J. Kim, D. Kwon, K. Kim, M.R. Hoffmann, Electrochemical production of hydrogen coupled with the oxidation of arsenite, Environ. Sci. Technol. 48 (2014) 2059–2066.

[2] Z. Wang, R.T. Bush, L.A. Sullivan, J. Liu, Simultaneous redox conversion of chromium(VI) and arsenic(III) under acidic conditions, Environ. Sci. Technol. 47 (2013) 6486–6492.

[3] R. Aravindhan, B. Madhan, J.R. Rao, B.U. Nair, T. Ramasami, Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse, Environ. Sci. Technol. 38 (2003) 300–306.

[4] J.R. Jambeck, T. Townsend, H. Solo-Gabriele, Leaching of chromated copper arsenate (CCA)-treated wood in a simulated monofill and its potential impacts to landfill leachate, J. Hazard. Mater. 135 (2006) 21–31.

[5] K. Kim, W. Choi, Enhanced redox conversion of chromate and arsenite in ice, Environ. Sci. Technol. 45 (2011) 2202–2208.

[6] C.E. Barrera-Díaz, V. Lugo-Lugo, B. Bilyeu, A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction, J. Hazard. Mater. 223–224 (2012) 1–12.

[7] Y. Li, J.R. Liu, S.Y. Jia, J.W. Guo, J. Zhuo, P. Na, TiO₂ pillared montmorillonite as a photoactive adsorbent of arsenic under UV irradiation, Chem. Eng. J. 191 (2012) 66–74.

[8] J. Sánchez, B.L. Rivas, Arsenic extraction from aqueous solution: electrochemical oxidation combined with ultrafiltration membranes and water-soluble polymers, Chem. Eng. J. 165 (2010) 625–632.

[9] S. Sorlini, F. Gialdini, Conventional oxidation treatments for the removal of arsenic with chlorine dioxide, hypochlorite, potassium permanganate and monochloramine, Water Res. 44 (2010) 5653–5659.

[10] B. Hua, H. Xu, J. Terry, B. Deng, Kinetics of uranium(VI) reduction by hydrogen sulfide in anoxic aqueous systems, Environ. Sci. Technol. 40 (2006) 4666–4671.

[11] B. Sarkar, R. Naidu, G.S.R. Krishnamurti, M. Megharaj, Manganese(II)-catalyzed and clay-minerals-mediated reduction of chromium(VI) by citrate, Environ. Sci. Technol. 47 (2013) 13629–13636.

[12] J. Yeo, D.-H. Kim, A.D. Bokare, W. Choi, Photochemical removal of hexavalent chromium through iodide oxidation under 254 nm irradiation, Sep. Purif. Technol. 91 (2012) 18–22.

[13] S.P. Bachate, V.S. Nandre, N.S. Ghatpande, K.M. Kodam, Simultaneous reduction of Cr(VI) and oxidation of As(III) by *Bacillus firmus* TE7 isolated from tannery effluent, Chemosphere 90 (2013) 2273–2278.

[14] M. Tichonovas, E. Krugly, V. Racys, R. Hippler, V. Kauneliene, I. Stasiulaitiene, D. Martuzevicius, Degradation of various textile dyes as wastewater pollutants under dielectric barrier discharge plasma treatment, Chem. Eng. J. 229 (2013) 9–19.

[15] F. Huang, L. Chen, H. Wang, Z. Yan, Analysis of the degradation mechanism of methylene blue by atmospheric pressure dielectric barrier discharge plasma, Chem. Eng. J. 162 (2010) 250–256.

[16] P. Manoj Kumar Reddy, B. Rama Raju, J. Karuppiah, E. Linga Reddy, C. Subrahmanyam, Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor, Chem. Eng. J. 217 (2013) 41–47.

[17] B. Jiang, J. Zheng, S. Qiu, M. Wu, Q. Zhang, Z. Yan, Q. Xue, Review on electrical discharge plasma technology for wastewater remediation, Chem. Eng. J. 236 (2014) 348–368.

[18] L. Wang, X. Jiang, Plasma-induced reduction of chromium(VI) in an aqueous solution, Environ. Sci. Technol. 42 (2008) 8492–8497.

[19] Z. Ke, Q. Huang, H. Zhang, Z. Yu, Reduction and removal of aqueous Cr(VI) by glow discharge plasma at the gas–solution interface, Environ. Sci. Technol. 45 (2011) 7841–7847.

[20] G. Eisenberg, Colorimetric determination of hydrogen peroxide, Ind. Eng. Chem. Anal. Ed. 15 (1943) 327–328.

[21] J. Goodman, A. Hickling, B. Schofield, The yield of hydrated electrons in glow-discharge electrolysis, J. Electroanal. Chem. Interfacial Electrochem. 48 (1973) 319–322.

[22] K.-I. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, Detection of active oxidative species in TiO₂ photocatalysis using the fluorescence technique, Electrochem. Commun. 2 (2000) 207–210.

[23] U.K. Klaening, B.H.J. Bielski, K. Sehested, Arsenic(IV). A pulse-radiolysis study, Inorg. Chem. 28 (1989) 2717–2724.

[24] A.D. Bokare, W. Choi, Chromate-induced activation of hydrogen peroxide for oxidative degradation of aqueous organic pollutants, Environ. Sci. Technol. 44 (2010) 7232–7237.

[25] D.R. Grymonpré, W.C. Finney, B.R. Locke, Aqueous-phase pulsed streamer corona reactor using suspended activated carbon particles for phenol oxidation: model-data comparison, Chem. Eng. Sci. 54 (1999) 3095–3105.

[26] Y. Liu, B. Sun, L. Wang, D. Wang, Characteristics of light emission and radicals formed by contact glow discharge electrolysis of an aqueous solution, Plasma Chem. Plasma Process. 32 (2012) 359–368.

[27] M.C. Dodd, N.D. Vu, A. Ammann, V.C. Le, R. Kissner, H.V. Pham, T.H. Cao, M. Berg, U. von Gunten, Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: relevance to drinking water treatment, Environ. Sci. Technol. 40 (2006) 3285–3292.

[28] M. Pettine, L. Campanella, F.J. Millero, Arsenite oxidation by H₂O₂ in aqueous solutions, Geochim. Cosmochim. Acta 63 (1999) 2727–2735.

[29] L.M. Alrehaily, J.M. Joseph, A.Y. Musa, D.A. Guzonas, J.C. Wren, Gamma-radiation induced formation of chromium oxide nanoparticles from dissolved dichromate, Phys. Chem. Chem. Phys. 15 (2013) 98–107.

[30] A.D. Bokare, W. Choi, Advanced oxidation process based on the Cr(III)/Cr(VI) redox cycle, Environ. Sci. Technol. 45 (2011) 9332–9338.

[31] L. Rao, Z. Zhang, J.I. Friese, B. Ritherdon, S.B. Clark, N.J. Hess, D. Rai, Oligomerization of chromium(III) and its impact on the oxidation of chromium(III) by hydrogen peroxide in alkaline solutions, J. Chem. Soc. Dalton (2002) 267–274.

[32] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (˙OH/˙O⁻ in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886.

[33] J. Criquet, N.K.V. Leitner, Degradation of acetic acid with sulfate radical generated by persulfate ions photolysis, Chemosphere 77 (2009) 194–200.

[34] T. Zhang, J.-P. Croué, Catalytic ozonation not relying on hydroxyl radical oxidation: a selective and competitive reaction process related to metal–carboxylate complexes, Appl. Catal. B Environ. 144 (2014) 831–839.

[35] F. Hasan, J. Rocek, Three-electron oxidations. II. Chromium(VI) oxidation of oxalic acid, J. Am. Chem. Soc. 94 (1972) 9073–9081.

[36] J. Gao, Y. Liu, W. Yang, L. Pu, J. Yu, Q. Lu, Oxidative degradation of phenol in aqueous electrolyte induced by plasma from a direct glow discharge, Plasma Sources Sci. Technol. 12 (2003) 533.

[37] D. Kabir ud, K. Hartani, Z. Khan, Unusual rate inhibition of manganese(II) assisted oxidation of citric acid by chromium(VI) in the presence of ionic micelles, Transition Met. Chem. 25 (2000) 478–484.

[38] D.E. Kimbrough, Y. Cohen, A.M. Winer, L. Creelman, C. Mabuni, A critical assessment of chromium in the environment, Crit. Rev. Environ. Sci. Technol. 29 (1999) 1–46.