



Short Communication

Improved electrochemical Cr(VI) detoxification by integrating the direct and indirect pathways

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ABSTRACT

Cr(VI) is classified as one of the 17 chemicals posing greatest threat towards humans, therefore considerable efforts have been made to reduce the Cr(VI) pollution. In this study, a novel integrated direct and indirect electrochemical Cr(VI) reduction was first reported for the highly efficient Cr(VI) detoxification. Through the controllable oxygen reduction reaction (ORR), the H₂O₂ was readily generated and employed as a mediator to synergistically improve the direct Cr(VI) reduction. A significant degradation enhancement was achieved from 37% to 100% within a fast 40 min treatment. Besides, there is an optimum pH condition for Cr(VI) reduction due to the competition between the mechanistic and kinetic consideration. This novel intensification approach provides new insight on the application of electrocatalysis in environmental remediation.

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1. Introduction

Over recent decades, increasing toxic heavy metal effluents are released and accumulated in the aquatic environment [1,2]. Among these heavy metal contaminants, chromium discharged from steel making, electroplating and catalysis processes, is one of the most hazardous [3,4]. The industrial Cr(VI) processing sources usually involve highly acidic solutions, and there are two drastically different oxidation states of chromium, i.e. Cr(III) and Cr(VI) [5,6]. Cr(III) is demonstrated to be relatively harmless, while Cr(VI) is classified as one of the 17 chemicals posing greatest threat to humans. The Cr(VI) itself and the in-situ generated reactive oxygen species (ROS) can cause skin and stomach allergies at short-term exposure, or severe liver and nerve damages at long-term exposure [7]. Therefore, the United States Environmental Protection Agency set the standard for Cr(VI) in drinking water (maximum contaminant level) at 50 µg/L [6,8].

In order to reduce the Cr(VI) concentration below the regulatory standard, considerable remediation techniques have been attempted. Conventionally, the Cr(VI)-containing effluent is treated by the chemical reduction into nontoxic Cr(III) [9,10]. It is simple and effective to execute, while the drawbacks are the considerable reductants consumption and resulting sludge discharge. Besides, biological degradation is another favorable Cr(VI) treatment approach, which requires

fewer reagents and produced less sludge [11]. However, its removal kinetic is sluggish, and the potential oxidative hazards of employed bacteria may need further elimination. Recently, efficient Cr(VI) adsorption by activated carbons and agriculture waste has been developed [12, 13]. Nevertheless, the adsorption column needs to be regenerated after treatment, and further degradation/detoxification of the adsorbed Cr(VI) may also be required.

Alternatively, the electrochemical Cr(VI) treatment attracts increasing attention [14] via the employment of “clean” electron. Cr(VI) can be completely removed via different electrochemical methods such as electrocoagulation, electrochemical reduction and electrodialysis [15]. Among these techniques, considerable efforts have been made in electrochemical reduction since it can be highly selective, efficient, operation flexible and environmental compatible. It has been demonstrated that electrochemical reduction of Cr(VI) can be successfully carried out at various electrode materials, such as carbon felt electrodes, conducting polymer and gold electrodes [15,16]. And the electrochemical Cr(VI) reduction even can be employed as the cathode reaction to generate power in the microbial fuel cell (MFC) system [17].

Generally, the electrochemical Cr(VI) reduction occurs through direct reduction and indirect pathways, respectively [18]. Direct reduction takes place through the exchange of electrons directly with electrode surface. On the other hand, indirect reduction proceeds through the generation and consumption some strong reductive mediator. However, the mediators need further regeneration after treatment and the long-term stability is relatively limited. Obviously, it is highly desirable

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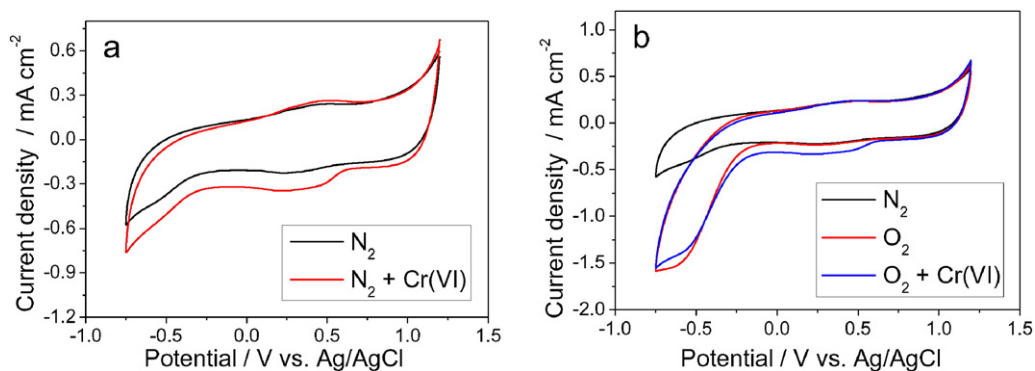
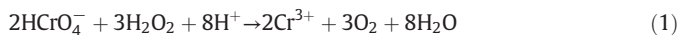


Fig. 1. (a) Cyclic voltammograms of graphite in the presence and absence of 10 mg/L Cr(VI) in de-aerated solutions, respectively; (b) cyclic voltammograms in the N_2 -saturated and O_2 -saturated solutions without 10 mg/L Cr(VI), O_2 -saturated solution with Cr(VI), pH = 2, scan rate = 100 mV/s.

to developed an integrated direct and indirect Cr(VI) reduction at the same cathode materials, which can overcome the recent limitation of indirect reduction and further enhance the remediation efficiency.

Hydrogen peroxide possesses a promising potential as the desired mediator [19]. It has been demonstrated that H_2O_2 can efficiently reduce Cr(VI) as illustrated in Eq. 1 [20], and H_2O_2 could be in-situ generated to react with Cr(VI) [21] depending on the cathode materials. Furthermore, both electrochemical Cr(VI) reduction [22] and H_2O_2 formation via two-electron oxygen reduction reaction (ORR) [23] can occur at the carbon-based electrodes, respectively. In this regard, the aim of this study is to develop an integrated direct and indirect electrochemical reduction approach of Cr(VI) by electro-generated H_2O_2 , the graphite electrode is selected to better illustrate the contribution of indirect reduction. It is expected to provide further information that in-situ generated H_2O_2 not only interact with Fenton's reagents in advanced oxidation processes (AOPs) [24], but also can efficiently mediate and enhance the Cr(VI) reduction.



2. Experimental section

$Na_2CrO_4 \cdot 4H_2O$ (99% mass fraction), 0.25 M H_2SO_4 solution (99.99% mass fraction) were purchased from Sigma-Aldrich and used without further purification. All solutions were prepared with purified Milli-Q water (18 M Ω cm) in a nitrogen-filled glove box.

Cyclic voltammetry (CV) experiments were conducted in a 150 mL three-electrode electrochemical cell at 25 ± 0.5 °C using a CHI760e (Chenhua, Shanghai) workstation. Graphite rod electrodes (99.995% purity) were employed as the working electrodes, the effective areas were

0.2 cm² and 4 cm² for the cyclic voltammetry and chronoamperometry measurements, respectively. A large-area platinum mesh was used as the counter electrode, while all potentials were measured and presented versus an Ag/AgCl electrode. Prior to each measurement, the working electrode was washed and sonicated in purified water, and then electrochemically activated by cycling between the onset potential of H_2 and O_2 evolution reactions in the corresponding N_2 -saturated solution until reproducible and well-defined CV curves were obtained. The cyclic voltammetric studies were then performed in either N_2 -saturated or O_2 -saturated solutions by potential cycling in the scan rate of 100 mV/s. Besides, chronoamperometric studies were performed with electrolyte stirring to approximate the hydrodynamic conditions of the cell. The potential for chronoamperometry was set at -1.3 V to offer enough driving force for the required electrochemical reactions.

The concentration of Cr(VI) obtained after corresponding treatment was determined using a Labtech model 9100B double beam UV-vis spectrophotometer at a 1 nm/s scanning rate from 200 to 500 nm. It was quantified by measuring the characteristic Cr(VI) absorbance (the solution pathlength is 1.0 cm) with respect to the corresponding pH environment, while the molar extinction coefficients of Cr(VI) is 1500 M⁻¹·cm⁻¹ at pH of 2. The pH values were determined by Mettler FE20K. All the data values of electrochemical, UV-vis and pH were repeated at least three times to obtain the mean value, the corresponding error bars were illustrated in the figures.

3. Results and discussion

3.1. Electrochemical behavior of Cr(VI) under different atmospheres

In order to understand the electrochemical reduction of Cr(VI), the cyclic voltammetry (CV) measurements were performed in the absence and presence of 10 mg/L Cr(VI). As compared to the CV curve in blank solution of pH 2.0 in Fig. 1a, a broad reduction wave commencing at

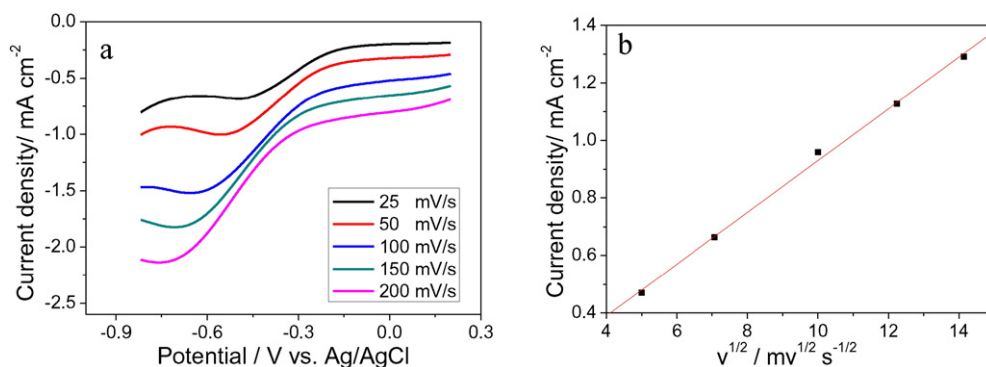


Fig. 2. (a) Cyclic voltammograms of graphite in O_2 -saturated solutions at different scan rates; (b) the variation of peak current as a function of the square root of scan rates (25–200 mV/s).

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