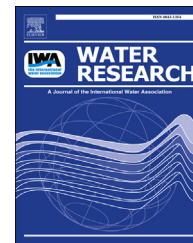




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Graphene-modified Pd/C cathode and Pd/GAC particles for enhanced electrocatalytic removal of bromate in a continuous three-dimensional electrochemical reactor

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ABSTRACT

Bromate (BrO_3^-) is a carcinogenic and genotoxic contaminant commonly generated during ozonation of bromide-containing water. In this work, the reductive removal of BrO_3^- in a continuous three-dimensional electrochemical reactor with palladium-reduced graphene oxide modified carbon paper (Pd-rGO/C) cathode and Pd-rGO modified granular activated carbon (Pd-rGO/GAC) particles was investigated. The results indicated that the rGO sheets significantly promoted the electrochemical reduction of BrO_3^- . With the enhanced electron transfer by rGO sheets, the electroreduction of H_2O to atomic H^* on the polarized Pd particles could be significantly accelerated, leading to a faster reaction rate of BrO_3^- with atomic H^* . The synergistic effect of the Pd-rGO/C cathode and Pd-rGO/GAC particles were also exhibited. The atomic H^* involved in various electroreduction processes was detected by electron spin resonance spectroscopy and its role for BrO_3^- reduction was determined. The performance of the reactor was evaluated in terms of the removal of BrO_3^- and the yield of Br^- as a function of the GO concentration, Pd loading amount, current density, hydraulic residence time (HRT), and initial BrO_3^- concentration. Under the current density of 0.9 mA/cm^2 , BrO_3^- with the initial concentration of $20 \text{ }\mu\text{g/L}$ was reduced to be less than $6.6 \text{ }\mu\text{g/L}$ at the HRT of 20 min. The BrO_3^- reduction was inhibited in the presence of dissolved organic matter. Although the precipitates generated from Ca^{2+} and Mg^{2+} in the tap water would cover the Pd catalysts, a long-lasting electrocatalytic activity could be maintained for the 30 d treatment. SEM and XPS analysis demonstrated that the precipitates were predominantly deposited onto the Pd-rGO/C cathode rather than the Pd-rGO/GAC particles.

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1. Introduction

Bromate (BrO_3^-) is an oxyhalide disinfection byproduct usually generated during ozonation in water supplies (Weinberg et al., 2003). It has been shown recently, that BrO_3^- can also be formed in distribution systems by metal-oxide catalysis of HOBr disproportionation (Liu et al., 2013). Due to its carcinogenic and genotoxic properties, many countries have promulgated a 10 $\mu\text{g/L}$ standard of BrO_3^- in drinking water (Butler et al., 2005; Huang et al., 2014). To meet this strict limitation, various kinds of methods have been developed to eliminate BrO_3^- , including filtration, chemical reduction, activated carbon techniques, and biological remediation (Kirisits et al., 2001; Li et al., 2010; Listiarini et al., 2010; Matos et al., 2008). Generally, second pollution and high consumption of reagents are inevitable in the removal process (Butler et al., 2005). It was reported by Paschoal et al. (2009) that photoelectrocatalysis using a negatively applied potential to an irradiated TiO_2 -coated photocathode could be used to selectively reduce BrO_3^- to Br^- , which was a good process with a high level of BrO_3^- conversion.

Electrochemical reductive treatment has been recognized as a promising method for eliminating BrO_3^- due to its rapid reaction rate, mild reaction conditions and the absence of recalcitrant secondary contaminants (Kishimoto and Matsuda, 2009; Ding et al., 2010; Radjenovic et al., 2012). BrO_3^- can be transformed to nontoxic Br^- by the reduction at the cathode. In the electrochemical reduction process, the cathode materials are considered as the most critical parameter because of its predominant influence on reaction pathway and treatment efficiency (Comninellis and Chen, 2010; Sun et al., 2014). Several electrode materials catalyzing BrO_3^- reduction were reported such as tungsten oxide (Casella and Contursi, 2005), activated carbon felt (Kishimoto and Matsuda, 2009), polyaniline-modified electrode (Ding et al., 2010), and phosphomolybdate-modified multi-walled carbon nanotubes (Skunik and Kulesza, 2009). However, the application of these cathodes for water treatment would be limited due to the low A/V ratio (ratio of the electrode area and solution volume). It has been recognized that the removal rate of the target compounds could be enhanced by using three-dimensional electrode with extensive specific surface area, and thereby more sufficient reactive sites and electrons as compared to other conventional two-dimensional electrodes (Kong et al., 2006; Mascia et al., 2012). In the three-dimensional electrochemical reactor, granular activated carbon (GAC) was frequently employed as the particle electrode owing to its fascinating features including low cost, chemical stability, and high surface area (Wei et al., 2010). The major drawback to GAC is the poor electrical conductivity, which would inevitably increase the energy consumption during the electrochemical process. Thus, the modification of GAC is highly desirable for the efficient removal of the pollutants in the three-dimensional electrochemical reactor. For the water treatment applications, some new and modified GAC, such as NanoFe-loaded GAC (Zelmanov and Semiat, 2014), and ammonia-treated GAC (Cheng et al., 2005) were synthesized so as to improve the surface properties.

Graphene is a monolayer of carbon atoms arranged in a two-dimensional honeycomb network. It shows many intriguing properties such as high surface area, excellent electrical conductivity, and high thermal and chemical stability (Allen et al., 2009; Kim et al., 2012). Graphene can offer substantial benefits with regard to mass transfer and charge transport, by providing shorter effective lengths for both ionic and electronic transport (Li et al., 2009). On the other hand, palladium (Pd) has been reported to possess excellent properties to facilitate electrocatalytic reduction due to its superior ability to form surface-adsorbed atomic H^* , a highly activated intermediate hydrogen radical (Li et al., 2012). The Pd–H bonds are based on multiple σ -bonding between the hydrogen atoms and the d orbitals of the Pd atoms (Conner and Falconer, 1995). Hybridization of metal catalysts with graphene has been applied in many fields such as light emitting diodes, field-effect transistors, solar cells, supercapacitors, batteries, and sensors (Yen et al., 2011; Huang et al., 2012; Sridhar et al., 2012).

To utilize the excellent electrical conductivity of graphene and the unique reactivity of Pd particles for water treatment uses, the Pd-reduced graphene oxide (rGO) modified granular activated carbon (Pd-rGO/GAC) was prepared for the first time and was used as particle electrode for the cathode cell. The Pd-rGO modified carbon paper (Pd-rGO/C) was used as the cathode. The objective of the present research was to establish a continuous three-dimensional electrochemical reactor for the removal of BrO_3^- with a typical concentration in water treatment and investigate its applicability in a realistic water matrix. The reactor was carefully designed in order to increase the A/V ratio and thus improve the mass transfer of the system. The results showed that the combination of the Pd-rGO/C cathode and Pd-rGO/GAC particles in the cathode cell exhibited a high electrocatalytic activity toward the BrO_3^- removal, highlighting the potential of three-dimensional electrochemical reactor as an effective system for eliminating BrO_3^- contamination in water.

2. Materials and methods

2.1. Fabrication of the Pd-rGO/C cathode and Pd-rGO/GAC

The Pd-rGO/C electrode was prepared through our previously reported in situ chemical reduction method followed by electrochemically depositing Pd particles (Mao et al., 2014). Briefly, the cleaned carbon paper was first heated at 400 °C for 5 h to increase the surface oxygenated functional groups, and thereby increase the impregnation in GO dispersion. Then it was sonicated in the GO suspension for 5 h. The concentration of the GO dispersion was 2.0 mg/mL unless otherwise noted. Subsequently, the GO film coated carbon paper was transferred to 10.0 mg/mL ascorbic acid. The reaction system was allowed to remain undisturbed overnight and then heated at 60 °C for 2 h. After chemical reduction of the GO film, the Pd nanoparticles were electrodeposited on the rGO/C electrode from aqueous solutions of 10 mM NH_4Cl containing 1 mM PdCl_2 (pH = 1) as precursor at a constant current of 0.02 A for 10 min. The Pd-rGO/GAC was prepared using the same

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