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Electrochemical removal of haloacetic acids in a three-dimensional electrochemical reactor with Pd-GAC particles as fixed filler and Pd-modified carbon paper as cathode

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ABSTRACT

The reductive removal of haloacetic acids (HAAs) in a three-dimensional electrochemical continuous reactor with Pd-granular activated carbon (Pd-GAC) particles as fixed filler and Pd-modified carbon paper (Pd-C) as cathode was studied in this research. Pd-C electrode was prepared from PdCl₂ via electrodeposition onto carbon paper. Pd-GAC particles were prepared by the impregnation of Pd²⁺ ions onto GAC. Efficient electrocatalytic reduction of HAAs in this reactor was exhibited. Effects of current density, initial HAAs concentration, and hydraulic retention time on the HAAs removal were investigated. Under the current density of 0.3 mA/cm², HAAs with initial concentration of 120 µg/L were reduced to be less than 60 µg/L with hydraulic retention time of 20 min. Electron transfer and HAAs diffusion both played an important role in controlling the electro-reduction process under the conditions of current density less than 0.6 mA/cm² with an initial HAAs concentration ranging from 120 to 600 µg/L. However, the HAAs diffusion became the primary rate-limiting step when the current density was higher than 0.6 mA/cm². The Pd⁰ and Pd²⁺ species were detected by X-ray photoelectron spectroscopy. The stability of the electrochemical reactor in the reduction removal of HAAs was also exhibited.

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1. Introduction

Haloacetic acids (HAAs) are important disinfection byproducts in chlorinated water (Christman et al., 1983; Hong et al., 2013). Because of their toxicity and carcinogenicity, the concentrations of HAAs are regulated by the U.S. Environmental Protection Agency (Xu and Weisel, 2003; Gan et al., 2013). The

Disinfectants/Disinfection Byproducts Rule established a maximum contaminant level (MCL) of 60 µg/L for the sum of five HAAs (HAA5 = MCAA + MBAA + DCAA + DBAA + TCAA) under the Stage I (Pontinus, 1999). Biodegradation and reverse osmosis are used to remove HAAs from chlorinated water (Linge et al., 2013; McRae et al., 2004). The reverse osmosis treatment may generate a polluted waste that should be treated (Linge et al., 2013). Biodegradation may cause bacterial

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contamination in the treated water (McRae et al., 2004). Another possibility is the application of TiO_2 photocatalysis, but there exists the problem of TiO_2 separation from aqueous phase (Czili and Horvath, 2009; Spangeberg et al., 1996). The catalytic dehalogenation of HAAs is a suitable decontamination method whereas it usually requires an addition of reducing agent (such as hydrogen and zero-valent iron) (Zhou et al., 2013; Hozalski et al., 2001; Tang et al., 2013).

Electrochemical reduction is found to be the efficient and friendly method for the removal of HAAs. Because it ensures the selective removal of halogen atoms from HAAs without producing toxic byproducts or adding any toxic chemicals (Korshin and Jensen, 2001; Li et al., 2007; Altamar et al., 2010). The use of efficient catalysts can decrease the energy consumption and promotes the reaction rates during the electrochemical process. Specifically, palladium (Pd) catalysts were found to show good catalytic activity for degradation of halogenated organic compounds (HOCs) and they can operate efficiently within a broad range of pollutants concentration (Lingaiah et al., 1999; Mackenzie et al., 2006; Rego et al., 2010; Martinez et al., 2013). In our previous study, it was demonstrated that the Pd-C electrode prepared via electrodeposition showed higher activity in the dechlorination of chloroacetic acids than via impregnation and calcinations (Li et al., 2012). Some researchers have reported that dechlorination of HOCs at cathode surfaces may occur through both direct and indirect mechanisms (Li et al., 2012; Li and Farrell, 2000; Wang et al., 2010; De Pedro et al., 2011). It was observed that the presence of Pd(0) nanoparticles played a significant role in forming atomic H^* to realize indirect reduction process which could achieve the complete dechlorination of chloroacetic acids (Li and Farrell, 2000).

However, these studies are mainly carried out in batch reactors and with distilled water containing electrolyte and HAAs. The effect of coexisted ions on the performance of the electrochemical reactor was little investigated (Li et al., 2007; Altamar et al., 2010; Li et al., 2012). Besides, it has been recognized that the removal efficiency of the pollutants could be increased by use of three-dimensional electrode with extensive specific surface area in comparison to conventional two-dimensional electrodes (Kong et al., 2006; Mascia et al., 2012). Thus, optimization of the reactor configuration is useful for a high removal efficiency of the pollutants in the electrochemical process. The removal efficiency was defined as the percentage of haloacetic acid initially present that has been removed.

In this study, Pd-granular activated carbon (Pd-GAC) was prepared and used as fixed filler for the cathode cell; a three-dimensional electrochemical reactor was established for effective electrochemical dehalogenation of HAAs. Pd-modified carbon paper (Pd-C) cathode was used as cathode, which was prepared from PdCl_2 via electrodeposition onto carbon paper (Li et al., 2012). GAC was used as support of catalysts because of its low cost, high surface area and high hydrodehalogenation activity (Wei et al., 2010). The electrochemical removal of HHAs in a simulated drinking water using the three-dimensional electrochemical reactor was investigated. The stability of the electrochemical reactor in the reduction removal of HAAs was also exhibited.

2. Materials and methods

2.1. Preparation of the Pd-C electrode and Pd-GAC

The Pd-C electrode was prepared via our previously reported electrodeposition method (Li et al., 2012). The electrodeposition of Pd (0) was carried out by dipping the cleaned carbon paper in dichlorodiamminepalladium $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ complex (plating solution), composed of 1 mM palladium chloride (PdCl_2) and 10 mM ammonium chloride solution (Wang and Qu, 2006). The deposition current and time was selected as 1 mA/cm^2 and 30 min, respectively. The Pd-C electrode was treated at 200 °C for 120 min under flowing hydrogen (flow rate: 100 mL/min). The Pd-GAC was prepared using the impregnation and calcination method. GAC was firstly immersed in a 2.5% (w/w) nitric acid solution with the magnetic stirrer, and then was washed and calcined at 200 °C for 120 min in order to enhance the binding force between GAC and metal ions. The pretreated GAC was then immersed in PdCl_2 solution which contained 0.1 M hydrochloric acid, and was ultrasonically treated for 360 min. Then, the obtained samples were dried at 120 °C and calcined at 300 °C for 120 min, and was finally reduced in hydrogen at 200 °C for 300 min (flow rate: 100 mL/min). The Pd content is determined to be 3 wt% with respect to GAC in this study.

2.2. Three-dimensional electrochemical reactor and the experimental procedure

The three-dimensional electrochemical reactor was shown in Fig. 1. All electrochemical experiments were carried out in this reactor with two-compartment cells. The anode cell and cathode cell (effective volume = 300 mL) were separated by a cation-

Fig. 1 – The schematic diagram of the three-dimensional electro-catalytic reactor 1. Proton exchange membrane; 2. RuO_2 -Ti anode; 3. Pd-C cathode; 4. Pd-GAC catalysts; 5. Electrochemical workstation; 6. Inlet; 7. Peristaltic pump; 8. Reaction solution.

exchange membrane (Nafion 117, Dupont). The electrodeposited Pd-C electrode was used as cathode with an apparent surface area of 100 cm², and RuO₂/Ti electrode with the same area was used as anode. The Pd-GAC particles were used as fixed filler of the cathode cell with a total effective volume of 100 mL. The distance between the Pd-C electrode and RuO₂/Ti electrode was 4 cm. The reactor was controlled by a DC power supply source AMERLLPS302A (Dahua instrument corporation of Beijing).

HAA_s-spiked tap water was used to investigate the removal capability of the above reactor. The electrochemical experiment was performed in a continuous flow mode at a constant current density. The influent with a given concentration of HAA_s was pumped into the reactor from a reservoir with a given rate. At an appropriate time intervals, samples of 10 mL were taken from the reactor outlet and analyzed to determine the concentration of HAA_s. Effects of current density, hydraulic residence time (HRT), and the initial concentration of HAA_s were investigated.

2.3. Analysis method

The concentration of HAA in the effluent from the cathode cell was measured using a Dionex-4500i ion chromatograph (IC) with an IonPac AS-19 anion-exchange analytical column and an IonPac AG19 guard column. Mobile phase eluent for the IC was KOH solution, and the flow rate was 1.0 mL/min. The concentration of chloroacetic acids was obtained under gradient elution conditions (0.0–18.0 min: 10.0 mM KOH; 18.1 to 30.0: 35.0 mM KOH; 30.1 to 35.0: 10.0 mM KOH). The precision of the acetate mass balance in these measurements was ca. 95–105% of the nominal value. The concentrations of Ca²⁺ and Mg²⁺ in the influent and effluent were measured by the inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Co.).

2.4. Electrode characterization

Morphological and elemental analysis of the Pd-C electrode and Pd-GAC particles were performed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using a JSM 6301 microscope. The specific surface area was measured by nitrogen adsorption using the BET method with a Micromeritics ASAP 2000 (Micromeritics Co., USA) surface area analyzer. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos AXIS Ultra X-ray photoelectron spectrometer, and details of XPS were included in the Supporting Information. X-ray powder diffraction (XRD) measurements were performed to characterize the surface composition of the Pd-C electrode and Pd-GAC particles, by using an X'Pert PRO Powder diffractometer machine (PANalytical Co.) with Ni-filtered Cu K_α radiation from 5° to 90° (in 2θ). Specific surface area and pore analysis of the catalyst were performed with the ASAP 2000 (Micromeritics, USA).

3. Results and discussion

3.1. Electrochemical reduction performance

Fig. 2 shows the reduction of HAA_s in the three-dimensional electrochemical reactor for the continuous running. Under a

current density of 0.3 mA/cm², HAA_s in the effluent were reduced below 60 µg/L within hydraulic retention time (HRT) of 20 min for 30 d. The initial concentration of HAA_s was 120 µg/L, including 20 µg/L for DBAA, 50 µg/L for DCAA and TCAA, respectively. 32.50 mg/L Ca²⁺ and 15.83 mg/L Mg²⁺ were included in the influent. These results indicated that the three-dimensional reactor presented high activity in electrocatalytic removal of HAA_s.

Adsorption of HAA_s by the Pd-C electrode and Pd-GAC are presented in the Supporting Information (Fig. S1). With the same initial concentration of MCAA, DCAA, TCAA, MBAA and TBAA (120 µg/L), the Pd-C cathode and Pd-GAC exhibited low adsorption capability of HAA_s (<3%). Thus, it was concluded that the electrocatalytic reduction was the primary process for HAA_s removal in this study. A comparison of HAA_s removal efficiencies under various processes was also performed. As shown in Fig. 3, the removal efficiency by Pd-C cathode or Pd-GAC process was lower than that by the combined process of Pd-C cathode and Pd-GAC together. Meantime, the effluent from Pd-C cathode was furthermore treated by Pd-GAC process. It is clear that the removal efficiency of HAA_s in this process is still lower than that by the combined process of Pd-C cathode and Pd-GAC together. The above results indicated the high performance of a three-dimensional electrochemical reactor with Pd-GAC particles as a fixed filler and Pd-modified carbon paper as cathode for the HAA_s removal.

In the treatment process, white precipitate on the Pd-GAC particles was observed. Compared with that in the influent, the concentration of Ca²⁺ and Mg²⁺ was decreased by 50–60% and by 80% in the effluent, respectively. Thus, it was suggested that the white precipitates should be calcium hydroxide (Ca(OH)₂) and magnesium hydroxide (Mg(OH)₂). The concentration of HAA₅ was higher than 60 µg/L at 8 d. The adsorption of the precipitate to the Pd-C cathode and Pd-GAC will decrease the activity of the reaction system. Besides, chloride ion (Cl[−]) liberated during the dechlorination process, which covered available active sites of catalysts, leading to the decrease in the removal efficiency of HAA_s (Li et al., 2012; Wang et al., 2010). Therefore, the electrochemical reaction

Fig. 2 – HAA_s concentration in the effluent of continuous running (initial HAA_s concentration: 120 µg/L; current density: 0.3 mA/cm²; HRT: 20 min; Ca²⁺ concentration: 32.50 mg/L; Mg²⁺ concentration: 15.83 mg/L).

Fig. 3 – A comparison of haloacetic acids removal efficiency under various processes (initial HAA concentration: 120 $\mu\text{g/L}$; initial pH: 7; Na_2SO_4 concentration: 200 mg/L; current density: 0.3 mA/cm²; HRT: 20 min) (A, C paper cathode + GAC; B, Pd-C cathode + GAC; C, C paper cathode + Pd-GAC; D, effluent from Pd-C cathode treated by C paper cathode + Pd-GAC; E, Pd-C cathode + Pd-GAC).

system was stopped at 8, 15, 22, and 29 d for back washing; meanwhile, the Pd-C cathode and Pd-GAC were regenerated with dilute HCl (1.4 mol/L) to remove these precipitates. After that, the three-dimensional electrochemical reactor exhibited a high electrocatalytic activity in the reduction of HAAs again.

3.2. Effect of current density on the removal efficiency of haloacetic acids

The electrocatalytic reduction of HAAs was performed with various current densities ranging from 0.1 to 0.9 mA/cm². It is shown in Fig. 4 that the removal of HAAs was enhanced with increasing current density, with a maximum removal

Fig. 4 – Effect of current density on the removal of HAAs and the energy consumption (initial HAAs concentration: 120 $\mu\text{g/L}$; initial pH: 7; Na_2SO_4 concentration: 200 mg/L; HRT: 20 min).

efficiency observed at 0.6 mA/cm². A slight decrease is occurred when the current density is increased to 0.9 mA/cm². Corresponding to the current densities of 0.1, 0.2, 0.3, 0.6, and 0.9 mA/cm², the electrode potentials were determined to be 3.37, 3.63, 4.03, 4.76, 5.45 V at the initial reaction period, respectively. With the reaction evolution, the electrode potentials increased slightly.

With the increase of the current density, more electrons took part in the dehalogenation process (Korshin and Jensen, 2001; Li et al., 2007; Altamar et al., 2010). In our previous work, it was exhibited that a decrease of the electrode potential resulted in the increase of the reaction rate constants of chloroacetic acids (Li et al., 2012). Li et al. also reported that HAAs reduction happened at potentials more cathodic than -1.0 V where molecular hydrogen would evolve (Li et al., 2007). However, when the current density was higher than 0.6 mA/cm², the large amount of hydrogen bubbles would interference the electron transfer or HAAs diffusion at the electrode surface, which will lead to the decrease of the reduction efficiency of HAAs. Thus, this would inevitably deactivate the Pd-C electrode and Pd-GAC. At the current density of 0.3 and 0.6 mA/cm², similar removal efficiency of HAAs is exhibited. With respect to the energy cost, the calculated energy consumption of 0.34 kWh/t at 0.6 mA/cm² was much higher than 0.09 kWh/t at 0.3 mA/cm². Therefore, the current density of 0.3 mA/cm² was selected in the subsequent experiments.

3.3. Effect of hydraulic retention time on the removal efficiency of haloacetic acids

Effect of HRT on the reduction removal of HAAs is shown in Fig. 5. The removal efficiency at HRT 5 min and 10 min was quite low. By contrast, the removal efficiency of HAAs is obviously enhanced when HRT was increased to 20 min. The removal efficiency of DCAA and TCAA are determined to be 69% and 91%, respectively. With the increase of HRT to 30 and

Fig. 5 – Effect of HRT on the reduction removal of HAAs (initial HAAs concentration: 120 $\mu\text{g/L}$; initial pH: 7; Na_2SO_4 concentration: 200 mg/L; current density: 0.3 mA/cm²).

60 min, a slight increase of the removal efficiency of HAAs is observed. Therefore, the value of HRT was chosen as 20 min.

3.4. Effect of initial HAAs concentration on the removal efficiency of haloacetic acids

Initial concentration of HAAs was an important factor for the removal efficiency during electrocatalytic process (Li et al., 2007, 2012). As shown in Fig. 6, the reduction removal efficiency of HAAs increases slightly with increasing the initial HAAs concentration. This is because that the electrons are enough to be used in the reduction process with the increase of the initial HAAs concentration, then the interfacial reaction was enhanced leading to an increase in removal efficiency of HAAs (Li et al., 2012). Combined with the effect of current density and initial HAAs concentration on the removal efficiency of HAAs, it could be deduced that electron transfer and HAAs diffusion were simultaneously responsible for controlling the electrochemical reduction process when the current density was below 0.6 mA/cm^2 with the initial HAAs concentration of $120\text{--}600 \text{ }\mu\text{g/L}$. Both increase of the current density and initial HAAs concentration could improve the removal efficiency of HAAs. By contrast, when the current density was higher than 0.6 mA/cm^2 , the HAAs diffusion may play a primary role for the rate-limiting step of the electrochemical reduction of HAAs.

3.5. pH and turbidity variations of the influent and effluent

Fig. 7 shows the pH and turbidity variations of the influent and effluent during the electro-dechlorination process. As shown in Fig. 7(a), the pH value of effluent was slightly higher than that of the influent. This is attributed to the consumption of atomic H^* , which was formed during the process that Pd(0) used the electron delivered from the cathode to transform H^+ into atomic H^* . Moreover, indirect reduction by atomic H^* was

Fig. 6 – Effect of initial HAAs concentration on the reduction removal of HAAs (initial pH: 7; Na_2SO_4 concentration: 200 mg/L ; current density: 0.3 mA/cm^2 ; HRT: 20 min).

Fig. 7 – pH and turbidity variations of the influent and effluent (initial HAAs concentration: $120 \text{ }\mu\text{g/L}$; current density: 0.3 mA/cm^2 ; HRT: 20 min; Ca^{2+} concentration: 32.50 mg/L ; Mg^{2+} : 15.83 mg/L).

the primary process to realize the complete dechlorination of chloroacetic acids (Li et al., 2012; Wang et al., 2010). Additionally, it was shown in Fig. 7(b) that the turbidity of the effluent was also slightly higher than that of the influent, while the pH and turbidity of the effluent was in the range of the drinking water standard regulated by USEPA. The increased turbidity in the effluent after electrolysis may be induced by the precipitates of calcium and magnesium hydroxides.

3.6. Electrode characterization

3.6.1. SEM-EDX analysis

SEM images and EDX analysis of the Pd-C cathode and Pd-GAC before and after the electrochemical reaction are presented in Figs. 8 and 9, respectively. It can be shown that the electro-deposited Pd(0) particles as a film were tightly attached on the surface of the carbon paper (Fig. 8(a)). Furthermore, the tiny gaps among the Pd(0) particles can provide an optimal channel for the reduction of HAAs molecules (Fig. 8(b)). After 7 d,

Fig. 8 – SEM images and EDX analysis of the Pd-C cathode (a) the Pd-C cathode before the reaction with magnification to 1000; (b) the Pd-C cathode before the reaction with magnification to 10,000; (c) the Pd-C cathode after the reaction with magnification to 1000; (d) the Pd-C cathode after dehalogenation with magnification to 10,000; (e) regeneration of the Pd-C cathode with magnification to 1000; (f) regeneration of the Pd-C cathode with magnification to 10,000.

Fig. 9 – SEM images and EDX analysis of the Pd-GAC particles (a) the Pd-GAC particles before dehalogenation with magnification to 1000; (b) the Pd-GAC particles before dehalogenation with magnification to 10000; (c) the Pd-GAC particles after dehalogenation with magnification to 1000; (d) the Pd-GAC after dehalogenation with magnification to 10000; (e) regeneration of the Pd-GAC with magnification to 1000; (f) regeneration of the Pd-GAC with magnification to 10000.

the SEM-EDX results indicate that the Ca(OH)_2 and Mg(OH)_2 particles were precipitated on the carbon fiber (Fig. 8(c) and (d)). Besides, EDX analysis of the electrode exhibits the characteristic peaks of Cl, indicating that Cl^- was generated during

the reductive dechlorination. The precipitates of the Ca(OH)_2 and Mg(OH)_2 particles can take up the active sites of the Pd catalysts. Therefore, the Pd-C cathode need to be regenerated with dilute HCl solution. As shown in Fig. 8(e) and (f), the

precipitates on the electrode were nearly completely removed, and the uniform dispersion and small size of the electrodeposited Pd nanoparticles on the carbon paper were the same as that on the freshly prepared Pd-C cathode.

As shown in Fig. 9(a) and (b), the calcined Pd particles exhibited knobs deposited on the GAC surface, thus the calcined Pd particles on GAC were not uniform as the electrodeposited Pd particles on the carbon paper. Additionally, the SEM image indicates that the particle size of the calcined Pd was larger than that of the electrodeposited Pd particles. For 7 d, the precipitates of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ were also attached onto the GAC particles (Fig. 9(c) and (d)). Pd-GAC was also regenerated with dilute HCl, most of the precipitate was removed after the regeneration treatment as confirmed by the SEM-EDX analysis (Fig. 9(e) and (f)).

3.6.2 BET analysis

BET analysis of the Pd-GAC particles was performed. As shown in Table 1, the specific surface area and pore volume of the GAC decreased after loading Pd particles, resulting from the blockage of some pores in GAC. For the Pd-GAC samples, the specific surface area, pore diameter and pore volume decreased remarkably after 7 d treatment. This is because that GAC pores were blocked by metal hydroxides produced during the electrocatalytic reduction process, thereby decreasing the contact area between the Pd-GAC and HAAs. As a result, the electrocatalytic activity of the Pd-GAC decreased apparently. It is noteworthy that the specific surface area pore volume and pore diameter of the Pd-GAC increased significantly after the regeneration treatment. Combined with the SEM-EDX analysis, it can be deduced that precipitates on the Pd-GAC were efficiently removed and its activity towards reduction removal of HAAs was regenerated.

3.6.3. XRD and XPS analysis

The XRD patterns of the Pd-C electrode and Pd-GAC particles before and after the electrochemical reduction of HAAs are presented in the Supporting Information (Fig. S2). The diffractogram of the Pd-C electrode and the Pd-GAC particles before and after the electrochemical reaction both shows the metallic Pd peaks (Palomares et al., 2011). In addition, the XRD patterns of the Pd-C electrode before and after the reaction, as well as the Pd-GAC particles were almost the same, which can account for the stable electrocatalysis activity of the electrochemical system.

Furthermore, the XPS patterns of the Pd-C electrode before and after the electrochemical reactions are presented in Fig. 10(a). It was reported that the binding energy for metallic Pd varies between 335.0 and 335.5 eV, whereas the energy for

Pd^{2+} is 337.5 eV (Muftikian et al., 1996). For the Pd-C electrode, the binding energies of Pd 3d peaks appear at 335.3 eV and 340.6 eV, indicating the Pd(0) species before the electrochemical reaction. After 1 d, the binding energy transition increases slightly, indicating the presence of Pd⁰ and Pd²⁺ species for the used Pd-C cathode. Moreover, after 30 d, the valence state allocations of Pd⁰ and Pd²⁺ remain nearly constant, indicating the stability of the Pd-C electrode. The similar valence state of Pd was detected in the Pd-GAC particles (Fig. 10(b)). In the electrocatalytic reduction of HAAs, the transitional C–Pd–Cl bond was formed, which could promote the indirect electroreduction process of HAAs (Li et al., 2012). The concentration of Pd²⁺ in the effluent was below the detection limit as measured by the ICP-OES, indicating the stability of the Pd-C electrode and Pd-GAC particles.

4. Conclusions

In summary, the three-dimensional electrochemical reactor with the Pd-GAC particles as a fixed filler of the cathode cell showed high and stable activity in the electroreduction of HAAs. Considering the energy consumption and capacity for the reactor, the optimal value of the current density and HRT

Fig. 10 – XPS analysis of the Pd-C cathode and the Pd-GAC particles before and after the electrochemical reduction reaction (a) the Pd-C cathode; (b) the Pd-GAC particles.

Table 1 – BET analysis of the GAC and Pd-GAC particles.

	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
GAC	1591	1.0709	2.674
Pd-GAC	1043	0.7287	2.783
Pd-GAC after reaction	923	0.5600	2.088
Pd-GAC after regeneration	1040	0.7290	2.769

was determined. It could be deduced that electron transfer and concentration diffusion governed the electro-reduction process simultaneously when current density was less than 0.6 mA/cm^2 with initial HAAs concentration in the range of $120\text{--}600 \text{ }\mu\text{g/L}$. While current density was higher than 0.6 mA/cm^2 , the HAAs diffusion became the rate-limiting step. The pH and turbidity of the effluent was in the range of the drinking water standard regulated by USEPA. After being regenerated, the Pd-C electrode and Pd-GAC particles exhibit high electrochemical reduction activity. The XPS result revealed that the transitional C–Pd–Cl bond was formed, which could promote the indirect process. Combined with the XRD analysis, the high stability of the Pd-C electrode and Pd-GAC particles was exhibited.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.12.028>.

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