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Full Length Article

Electrosorption of As(III) in aqueous solutions with activated carbon as the electrode

Min Dai [a,b], Ling Xia [a], Shaoxian Song [a,*], Changsheng Peng [c,d], Jose Rene Rangel-Mendez [e], Roel Cruz-Gaona [b]

[a] School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China
[b] Doctorado Institucional de Ingeniería y Ciencia de Materiales, Universidad Autonoma de San Luis Potosi, Av. Sierra Leona 530, San Luis Potosii, 78210, Mexico
[c] The Key Lab of Marine Environmental Science and Ecology of Ministry of Education, Ocean University of China, Qingdao 266100, China
[d] School of Environment and Chemical Engineering, Zhaoqing University, Zhaoqing, 526061, China
[e] Division de Ingenieria Amiental, Instituto Potosino de Ciencia y Tecnologia, San Luis Potosi, Mexico

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ABSTRACT

The electrosorption of As(III) in aqueous solutions by using activated carbon (AC) as the electrode was studied in this work. This study was performed through the measurements of adsorption and desorption, Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and X-ray photoelectron spectra (XPS). Three parameters, applied voltage, solution pH and initial As(III) concentration, on the electrosoprtion of As(III) were investigated. The experimental results have demonstrated that the electrosorption followed three steps: migration of As(III) to the anode, oxidation of As(III) to As(V) and accumulation of As(V) in the electric double layers of the anode. The electrodorption capacity increased with increasing applied voltage and initial As(III) concentration, whereas the effect of pH was complicated for the variation of arsenite species and the competition of OH^-. The oxidation of As(III) increased with the increasing voltage and pH due to the increasing redox potential acted on As(III). The electrosorption served to reduce the toxicity of arsenic and was a promising technology for As(III) removal from water.

1. Introduction

Arsenic is ubiquitous in nature water, existing mainly as arsenite in reduced redox condition and arsenate in aerobic water. The negative effects of arsenic on biota, especially the cancer threat to human health, have raised great attention on arsenic removal from drinking water. To minimalize the harmful effects, the World Health Organization (WHO) recommends that the maximum contaminant level of arsenic in drinking water is 10 μg/L [1]. To remove the elevated arsenic in water, several methods have been developed, such as coagulation, adsorption, ion-exchange, reverse osmosis, bioremediation and so on [2–4].

Among them, electrosorption is a relative new technology. Electrosorption, or capacitive deionization (CDI), is an advanced technology first developed for deionization. Based on the voltage drop between two electrodes, the charged ions are electrostatically entrapped in the electrode-electrolyte interface, forming electrical double layer (EDL). When a reverse potential is applied, the adsorbed ions release from EDL. Then the concentrated water wash out and the electrode regenerate [5–7]. The low energy consumption, easy regeneration and environmental friendly make it a promising method in removal of ionic contaminants.

Recently, the technology is used in removal of Cu^{2+}, Fe^{3+}, $AsO_4{}^{3-}$, $Cr_2O_7{}^{2-}$ and so on [8–11]. A few studies focused on the electrosorption of arsenic. Beralus et al. certified that arsenic can be electrosorbed on carbon materials and the removal efficiency increased with increasing potential [12]. The electrosorption of arsenate was studied in the solution containing Cr^{3+}, Ni^{2+} and Fe^{3+} ions. The As-Fe system had the highest arsenic removal and the regeneration efficiency was in excess of 90% [13]. Morallón et al. observed arsenic redox reactions that arsenate was reduced to As(0) and AsO1.5 on cathode [14]. The removal of arsenite and arsenate by CDI were compared by Fan et al. [15]. And the conversion of As(III) to As(V) was proposed in the study. Since As(III) is more soluble, mobile and far more toxic than As(V), the oxidation of As(III) during the electrosorption would reduce the toxicity of

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* Corresponding author.
E-mail addresses: shaoxian@uaslp.mx, ssx851215@whut.edu.cn (S. Song), pcs005@ouc.edu.cn (C. Peng).

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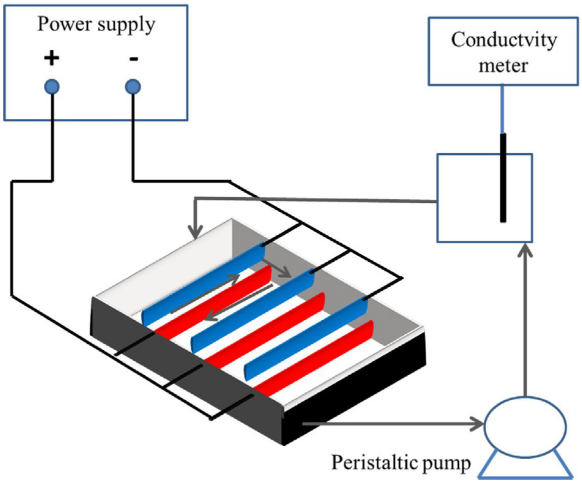

Fig. 1. Schematic representation of the electrosorption of As(III) in CDI process.

the solution. However, little attention was paid on the conversion and removal of As(III) by electrosorption.

In this work, As(III) oxidation and removal by CDI using activated carbon (AC) electrodes were experimentally studied through the measurements of adsorption capacity and X-ray photoelectron spectra (XPS). The effects of concentration, applied voltage and pH on the electrosorption and conversion were investigated. The objective was to approach into the mechanism of the conversion of As(III) to As(V) in the electrosoprtion of As(III), in order to improve As(III) removal from water.

2. Experimental

2.1. Materials

The wood AC powder used for the fabrication of electrodes was the commercial product from the Sinopharm Chemical Reagent Company, China. It was determined by the Brunauer–Emmett–Teller (BET) method to have the surface area of 1331 m^2/g. Titanium plate was purchased from Yongsheng Company, China.

Sodium arsenite ($NaAsO_2$) and polyvinylidene fluoride (PVDF) used in this work was produced by the Sigma Aldrich, while all the other reagents were from the Sinopharm Chemical Reagent Company, China. The stock solution of 200 mg/L As(III) was prepared with deionized water produced by a Millipore Milli-Q Direct 8/16 water purification system.

2.2. Fabrication of AC electrodes

The AC powder first was mixed with conductive carbon black and PVDF at the mass ratio of 8:1:1. The *N*, *N*-dimethylacetamide (DMAc) was used as organic solvent. Then, the mixture was stirred for 2 h at room temperature, followed by spreading it on a titanium plate. After that, the electrodes were heated at 50 °C in a vacuum oven for 12 h, and dried at 60 °C in an oven for 4 h.

2.3. Electrosorption of As(III)

The tests of the electrosorption of As(III) from water was performed in a self-made CDI system, which was schematically represented in Fig. 1. Six electrodes were put in the polymethyl methacrylate cell with a gap distance of 1 mm 200 ml As(III) solution was continuously circulated into the container at the flow rate of 50 rpm/min by a peristaltic pump (BT600-2J). The changes of conductivity and pH in the solutions were monitored frequently in the electrosorption.

When the equilibrium was reached, a reversed potential was applied to the electrodes to perform the desorption tests without any other change. Water sample was taken after 5 min to further analyze the variation of arsenic species in the desorption. Then the electrode was washed with deionized water and reused in the next experiments.

The concentration of arsenic was measured by using Molybdenum blue colorimetric method [16,17] with Ultraviolet-visible (UV–vis) absorption spectra, which was recorded with a Thermo Scientific Orion AquaMate 8000 UV–vis spectrophotometer. The electrosorption capacity (q), defined as the quantity of arsenic ions adsorbed per unit mass of mixture on the electrode, was calculated as follows:

$$q = \frac{(C_0 - C) \times V}{m} \qquad (1)$$

where C_0 and C were the arsenic (As(III) and As(V)) concentrations at the beginning and at any time in the electrosorption, respectively; V was the volume of the solution.

2.4. Measurement

The specific surface area of the AC was determined by using N_2 adsorption–desorption isotherm (BET method) at 77 K with a Micromeritics ASAP 2020 physical sorption.

Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were conducted to investigate the electrochemistry performance of AC electrode in a three-electrode cell system using an electrochemical work station (VersaStat 4, AMETEK). The AC electrode with 1 cm^2 surface area was used as the working electrode, while the platinum electrode and Ag/AgCl electrode were used as the counter and reference electrode, respectively. 1.0 mol/L Na_2SO_4 was used as electrolyte solution. After the electrosorption, the chemical status of arsenic species on the anode was determined by X-ray photoelectron spectra (XPS, VG Multilab 2000) with Al Kα source. The anode was specifically rinsed with deionized water in the presence of potential to remove the free ions on the AC surface and dried in a vacuum oven at 50 °C for 12 h.

3. Results and discussions

The electrochemical performance of the AC electrode was studied with CV and EIS. The CV curve of electrode in electrolyte solution was shown in Fig. 2(a). The curve deviated slightly from the ideal rectangular shape duo to some functional groups on the surface of the AC electrode, and showed no evident oxidation/reduction peak, suggesting an ideal EDL capacitance appeared on the electrode surface. Therefore, the electrode was feasible for the electrosorption of As(III) in water. The specific capacitance of the electrode was 53.92 F/g, which was calculated on the basis of following expression [18]:

$$C_s = \int_{V_a}^{V_c} IdV/2(V_c - V_a)mv \qquad (2)$$

where C_s is the specific capacitance of individual sample, V_a and V_c are the cutoff potentials in cyclic voltammetry; I is the instantaneous current; m is the mass of the sample, and v is the potential scan rate.

Fig. 2(b) illustrated the Nyquist plots of the electrode, which showed two regions with the semicircle and nearly vertical lines in the high and low frequency zones. The x-intercept of the plot indicated the electrolyte resistance, depending on the concentration of the electrolyte. The following semicircle was attributed to the