



# Electrocatalytic removal of humic acid using cobalt-modified particle electrodes

Wenwen Zhang, Di Xie, Xue Li, Wenjian Ye, Xiaoxue Jiang, Yuanyuan Wang, Wenyan Liang\*

Beijing Key Lab for Source Control Technology of Water Pollution, College of Environmental Science and Engineering, Beijing Forestry University, 35# Qinghua East Rd., Haidian District, Beijing 100083, P.R. China

## ARTICLE INFO

### Keywords:

Humic acid  
Particle electrode  
Cobalt oxide  
Electro-catalysis  
Three-dimensional electrode

## ABSTRACT

Humic acid (HA) is a complex polymer compound with no definite chemical formula. It seriously affects water quality and is one of the main precursors of producing disinfection by-products. In the present study, column granular electrodes ( $\Phi \times H = 4 \times 3$  mm) were prepared using cobalt loaded powder active carbon (PAC). The electrodes were applied in a continuous three-dimensional (3D) electrochemical reactor to remove HA. The crystal structure, morphology, surface chemical bonds, and pore structure of as-prepared material were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and  $N_2$  adsorption-desorption isotherms. Furthermore, parameters affecting the removal of HA and energy consumption (namely, current, electrolyte type and concentration, and initial pH) were examined. Intermediate products were analyzed using ultraviolet-visible (UV-vis) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy and three-dimensional excitation emission matrix (3DEEM) fluorescence spectroscopy. The results showed that CoO was well loaded in the PAC carriers. The CoO loaded granular electrodes (GAC-Co) had the surface area of  $782.6 \text{ m}^2/\text{g}$ , pore volume of  $0.6709 \text{ cm}^3/\text{g}$ , and average pore diameter of  $3.429 \text{ nm}$ . The 95.3% of chemical oxygen demand (COD) removal was obtained under the current of  $0.3 \text{ A}$ , hydraulic retention time (HRT) of  $8 \text{ min}$ , influent pH of  $7.0$ , electrolyte of  $0.01 \text{ mol/L Na}_2\text{SO}_4$ , and initial concentration of  $200 \text{ mg/L}$ . A large number of H radicals were involved in the electrochemical processes, which were observed using electron spin resonance (ESR) spectroscopy. The analysis of intermediate products indicated that the GAC-Co electrodes showed high electrocatalytic activity for the degradation of HA, in which HA with large molecular weight was decomposed to small molecular weight in the 3D electrochemical system.

## 1. Introduction

Humic acid (HA) is a subclass of humic substances, and accounts for a significant part of dissolved organic matters found in landfill leachate [1], sewage sludge [2], and peat water [3]. It is formed during the breakdown of animal and vegetable matters and during other biological activities of microorganisms present in the environment [4,5]. Although there is no readily identifiable structure, the HA usually contains a variety of characteristic functional groups, including phenol, quinone, aliphatics, lactone, and ether [6]. Due to the resistance to biodegradation [3], the physical/chemical technologies, such as adsorption [3], coagulation [7], ozone-biofiltration [8], photocatalysis [9], photo-Fenton oxidation [10], and electrochemical treatment [11] are applied to degrade or remove HA from water bodies.

During recent decades, electrochemical catalytic oxidation has been

recognized as a promising method for eliminating non-biodegradable contaminants because of its rapid reaction rate, mild reaction conditions, and for not producing nonrecalcitrant secondary contaminants [12,13]. Despite these advantages, some intrinsic drawbacks, such as mass transfer limitations, small space-time yield, low area-volume ratio, and temperature increase during the treatment cannot be satisfactorily solved in conventional two-dimensional (2D) electrochemical system, which means, in the reactor consisting of electrode plates [13]. Three-dimensional (3D) electrochemical system, also known as particle electrode or bed electrode system, can overcome the disadvantages of 2D electrode system [14]. When an external electrostatic field is imposed, the filled particles will be polarized to form many microelectrodes with one surface, which can be considered as the anode, while the other as the cathode [15]. Every particle acts as a bipolar electrode, and promotes the degradation of adsorbed contaminants [16].

\* Corresponding author at: Beijing Key Lab for Source Control Technology of Water Pollution, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, P.R. China.

E-mail addresses: [zhang\\_wen0902@163.com](mailto:zhang_wen0902@163.com) (W. Zhang), [xieditust@126.com](mailto:xieditust@126.com) (D. Xie), [lxfdz@126.com](mailto:lxfdz@126.com) (X. Li), [18156280959@163.com](mailto:18156280959@163.com) (W. Ye), [xiaoxuejiangs@163.com](mailto:xiaoxuejiangs@163.com) (X. Jiang), [bscswwy@163.com](mailto:bscswwy@163.com) (Y. Wang), [lwy@bjfu.edu.cn](mailto:lwy@bjfu.edu.cn) (W. Liang).

<https://doi.org/10.1016/j.apcata.2018.04.012>

Received 16 January 2018; Received in revised form 17 March 2018; Accepted 11 April 2018

Available online 14 April 2018

0926-860X/ © 2018 Elsevier B.V. All rights reserved.

The main mechanisms of contaminant transformation in 3D electrochemical system include anodic oxidation, cathodic reduction, and indirect oxidation by oxidizing substances (such as,  $\text{H}_2\text{O}_2$ , and  $\cdot\text{OH}$ ) produced at electrodes [10]. Direct oxidation or reduction of contaminants at the anode or cathode requires suitable electrode materials, which usually work at high overpotentials to obtain vigorous redox conditions for pollutant degradation [17,18]. The pollutants are adsorbed, and then, oxidized or deoxidized at the electrode surface, without involvement of any substances except electrons. The rates of direct oxidation or reduction are affected by diffusion limitations of pollutants in aqueous solution, due to which, higher adsorption capacity of electrode materials, and the better degradation effects of pollutants are severely affected [11]. Indirect anode electrolysis and cathode electro-reduction rely on the electrogeneration of various radicals produced from the reaction process. Then, the electro-Fenton like reactions occur in the presence of metal catalysts. Recently, the most commonly used metal catalysts are Pt-group metals, such as Ru, Rh, Pd, and Ir [19]. Unfortunately, these metals are among the most expensive and rarest of the materials [14]. The choices of replacement materials among non-precious metals were investigated [20,21]. Due to the low price and excellent catalytic performances, most of the research has focused on cobalt compound for catalysis, and gained good results [21,22].

The function of particle electrodes is very complex in 3D electrochemical system. Besides electrolysis, the particle electrodes can also remove pollutants through adsorption and electrosorption [19]. Because of the large specific surface area and high porosity, the particle electrodes are a very reasonable choice for the adsorption of the pollutants. When an external electrostatic field is imposed, two sides of the electrode's surface will gather opposite electrical charges. The charged ions in the solution are obligated to move towards the oppositely charged electrodes, resulting in the occurrence of electrosorption [23,24]. Complex processes, such as adsorption/desorption/electrosorption, and oxidation/catalysis will occur as stated above. Therefore, a good particle electrode requires properties, including high specific surface area, good adsorption capacity, good catalytic activity, and stability [13]. Active carbon is the most widely used material as the particle electrode and catalyst support due to its excellent adsorption, low cost, and chemical stability [24]. However, low catalytic activity and low catalyst loading have limited the commercial application of granular activated carbon (GAC) as particle electrodes and carriers [25]. Although the powder active carbon (PAC) has a tremendous surface area, its small particle size and difficulty in regeneration, hinder its direct application as the particle electrodes in a 3D electrochemical system [26].

In this work, PAC was firstly loaded with cobalt oxide, which was used as a catalyst, and then, was prepared as a column GAC. The CoO loaded GAC (GAC-Co) electrodes were filled into a continuous 3D electrochemical reactor to study the removal of HA. The characterizations of GAC-Co electrodes were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and  $\text{N}_2$  adsorption-desorption isotherms. The reactor parameters, including current, electrolyte type and concentration, and initial pH were studied. The free radicals generated in the system were investigated using electron spin resonance (ESR) spectroscopy and a chemical determination method. The intermediate products of HA degradation were analyzed using ultraviolet-visible (UV-vis) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, gas chromatography mass spectrometry (GC-MS), and three-dimensional excitation matrix (3DEEM) fluorescence spectroscopy.

## 2. Material and methods

### 2.1. Chemicals and materials

PAC was purchased from Beijing Ke Cheng Guang Hua New Technique

Co., Ltd., Beijing, China. In addition, HA,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , polyvinyl alcohol (PVA),  $\text{Na}_2\text{SO}_4$ , citric acid, ether, tertiary butanol (*t*-BuOH), and NaOH were obtained from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Furthermore, sulfuric acid ( $\text{H}_2\text{SO}_4$ ), methanol, hydrochloric acid (HCl) were purchased from Beijing Chemical Works, Beijing, China. Additionally, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, chromatographic grade) was obtained from TCI Development Co., Ltd., Tokyo, Japan. Potassium bromide (KBr, FT-IR grade) was purchased from Sigma-Aldrich Co., St. Louis, USA. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ , chromatographic grade) was purchased from Tianjin Concord Technology Co., Ltd., Tianjin, China. Except for DMPO, KBr,  $\text{CH}_2\text{Cl}_2$ , and HA, all chemicals were of analytical reagent grade, and used without further purification. HA was of chemical reagent grade with the ash content of *ca.* 10%. DMPO solution was prepared with ultra-pure water ( $\geq 18 \text{ M}\Omega/\text{cm}$  at  $25^\circ\text{C}$ ), while other solutions were prepared with distilled water.

### 2.2. HA solution

The stock solution of HA was prepared by dissolving 1.00 g HA in 1.00 L NaOH solution (1.00 g/L) under continuous stirring for 24 h. The solution was filtered through  $0.45 \mu\text{m}$  filter to remove suspended solids, and stored in dark at  $4^\circ\text{C}$ . The HA solution was diluted from HA stock solution using distilled water, whereas the chemical oxygen demand (COD) was *ca.* 200 mg/L. Solid  $\text{Na}_2\text{SO}_4$  with the concentration of 0.01 mol/L was added to provide the ionic strength. The pH of HA solution was adjusted to 7.0 by adding 0.10 mol/L NaOH and 0.10 mol/L  $\text{H}_2\text{SO}_4$ .

### 2.3. Experimental setup

The 3D electrochemical apparatus was composed of a tank, a pump, a rectangular cell, an anode electrode, a cathode electrode, particle electrodes, and a direct current power source (Fig. 1). The specification of cell was  $L \times W \times H = 25 \times 24 \times 120 \text{ mm}$ . Ti/RuO<sub>2</sub> and Ti mesh plates ( $12 \times 2.5 \text{ cm}$ ; Beijing Hengli Ti Co., Ltd., Beijing, China) were used as anode and cathode, respectively. Furthermore, 10 g GAC-Co electrodes were filled between the two mesh electrodes, and had the height of 8 cm and volume of  $72 \text{ cm}^3$ . The HA solution was continuously pumped into the cell and discharged directly without circulation.

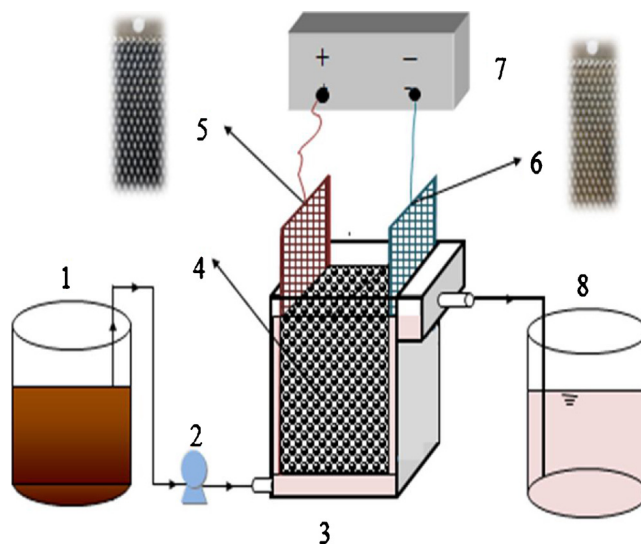


Fig. 1. Schematic view of the continuous three-dimensional electrochemical reactor. Parts of the reactor include (1) influent tank, (2) peristaltic pump, (3) electrochemical cell, (4) GAC-Co electrode bed, (5) Ti/RuO<sub>2</sub> mesh anode, (6) Ti mesh cathode, (7) power supply, and (8) effluent tank.

Download English Version:

<https://daneshyari.com/en/article/6496700>

Download Persian Version:

<https://daneshyari.com/article/6496700>

[Daneshyari.com](https://daneshyari.com)