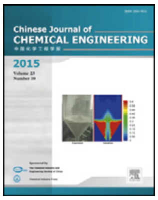
Chinese Journal of Chemical Engineering 23 (2015) 1705–1711

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE



Energy, Resources and Environmental Technology

Adsorption of cadmium ions from aqueous solutions by activated carbon with oxygen-containing functional groups☆

Yu Bian [1], Zhaoyong Bian [1,*], Junxiao Zhang [1], Aizhong Ding [1], Shaolei Liu [2], Lei Zheng [1], Hui Wang [2,*]

[1] *College of Water Sciences, Beijing Normal University, Beijing 100875, China*
[2] *College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China*

ARTICLE INFO

Article history:
Received 22 October 2014
Received in revised form 17 February 2015
Accepted 11 May 2015
Available online 30 August 2015

Keywords:
Activated carbon
Oxygen-containing functional groups
Cd(II)
Adsorption mechanism

ABSTRACT

The adsorption of aqueous cadmium ions (Cd(II)) have been investigated for modified activated carbon (AC-T) with oxygen-containing functional groups. The oxygen-containing groups of AC-T play an important role in Cd(II) ion adsorption onto AC-T. The modified activated carbon is characterized by scanning electron microscopy, Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The results of batch experiments indicate that the maximal adsorption could be achieved over the broad pH range of 4.5 to 6.5. Adsorption isotherms and kinetic study suggest that the sorption of Cd(II) onto AC-T produces monolayer coverage and that adsorption is controlled by chemical adsorption. And the adsorbent has a good reusability. According to the FT-IR and XPS analyses, electrostatic attraction and cation exchange between Cd(II) and oxygen-containing functional groups on AC-T are dominant mechanisms for Cd(II) adsorption.

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1. Introduction

Heavy-metal contamination in aqueous environments is of great concern because of the toxic effects to the ecosystem, especially to humans in the form of Minamata disease and itai-itai disease. Cadmium, one of the most commonly used heavy metals, has been released into the environment by combustion of fossil fuels, mineralization, cement production, electroplating and manufacturing of batteries and pigments [1,2]. Because cadmium ions are toxic even at very low concentrations, cadmium has been classified as a human carcinogen by the US National Toxicology Program.

To treat aqueous heavy-metal contamination, absorbents such as activated carbon (AC) are widely used due to their excellent absorbing ability [3]. AC exhibits porous structure with large surface area. However, common AC does not have sufficient functional groups to adsorb heavy metals economically [4]. In the absence of functional groups, little or no adsorption occurs on ACs [5]. Heavy-metal-adsorption onto carbonaceous materials is considered to mainly take place at oxygen-containing functional groups, such as carboxylic and lactonic groups [6–9]. Additionally, the amount of heavy metal ions adsorbed onto AC is not the stoichiometric one of the oxygen-containing functional groups. Huang *et al.* reported that oxidized ACs with 1.4 $\text{mmol}\cdot\text{g}^{-1}$ oxygen-containing functional groups had the maximal cadmium sorption capacity of 51.02 $\mu\text{mol}\cdot\text{g}^{-1}$ [10]. Motoi *et al.* showed that the oxidized AC with 1.39 $\text{mmol}\cdot\text{g}^{-1}$ oxygen-containing functional groups adsorbed 0.11 $\text{mmol}\cdot\text{g}^{-1}$ cadmium [5]. The poor relation between the amount of functional groups and the adsorption capacity indicates that AC adsorption process is complex. The interaction between oxygen-containing functional groups and heavy metal ions is not yet understood well.

The present work aims to analyze the effect of the oxygen-containing functional groups of AC in the adsorption of Cd(II). Strong oxidation acids such as nitric acid are used to increase the oxygen-containing functional groups on AC. Batch experiments are performed to evaluate the effect of contact time and initial pH value on the Cd(II) adsorption. The chemical nature of adsorption is characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) to propose the Cd(II) adsorption mechanisms onto AC.

2. Experimental

2.1. Materials

Commercial AC pellets were used as the adsorbent. All of the chemical reagents used in this study were of analytical grade. A Cd(II) stock solution of 1000 $\text{mg}\cdot\text{L}^{-1}$ was prepared by dissolving 1000 mg cadmium powder in a nitric acid solution. Experimental solutions with desired concentrations were obtained by appropriate dilution of the stock solution.

☆ Supported by the Fundamental Research Funds for the Central Universities (TD2013-2, 2012LYB33), the National Natural Science Foundation of China (51278053, 21373032), and grant-in-aid from Kochi University of Technology and China Scholarship Council.

* Corresponding authors.
E-mail addresses: bian@bnu.edu.cn (Z. Bian), wanghui@bjfu.edu.cn (H. Wang).

http://dx.doi.org/10.1016/j.cjche.2015.08.031
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2.2. Preparation of modified activated carbon

Approximately 15 g activated carbons were impregnated into an HCl solution (2 mol·L^{-1}) at an impregnation ratio of 2 ml HCl solution/g activated carbon, stirred for 12 h. The resulting mixture was filtered and washed several times with distilled water until the pH reached a constant value. The product was dried and stored in dry, clean and well-closed bottles; named as AC. The AC sample was mixed with a 200 ml solution of concentrated HNO_3 (10 mol·L^{-1}) and then heated at 363 K for 3 h under stirring and refluxing conditions. The resulting mixture was filtered and washed several times with distilled water until the pH reached a constant value. Then, the product was dried at 383 K to obtain the modified activated carbon (AC-T).

2.3. Characterization

Surface morphology and microcompositional analysis were conducted on a HITACHI-S4800 scanning electron microscope (SEM) equipped with an Oxford X-ray energy dispersive spectroscopy (EDS) system. The infrared transmittance spectra in the range between 400 and 4000 cm^{-1} were collected using a Nexus 670 spectrometer in KBr pellet state. The spectrum of pure KBr pellets prepared under the identical conditions as those for sample pellets was subtracted to avoid the influence of water absorbed by KBr powder. The XPS spectra were obtained using an ESCALAB 250Xi physical electronics spectrometer. The photoelectron spectra were analyzed with a hemispherical mirror, assuring an energy resolution of approximately 0.5 eV. After 5 h *in situ* at 10^{-7} Pa vacuum, the sample surfaces were sufficiently clean for measurements. The binding energy in the range of −10 to 1350 eV and the core-level characteristic peaks for C 1s and O 1s were measured. The background was subtracted using Shirley's approximation. The concentrations of Cd(II) ions in batch experiments were determined using an AFS-230E atomic fluorescence spectrometer (AFS).

2.4. Batch experiments

2.4.1. Determination of the point of zero charge (pH_{pzc})

For determination of pH_{pzc}, certain amount (30 mg) of adsorbent was suspended in 10 ml of 0.1 mol·L^{-1} $NaNO_3$ solution, used as an inert/background electrolyte in a 50 ml stopper conical flask. The initial pH of the solution was adjusted to 3.0 using 0.01 mol·L^{-1} HNO_3 or 0.01 mol·L^{-1} NaOH. The suspension was allowed to equilibrate for 4 h at 200 r·min^{-1} in a shaker bath at room temperature of (20 ± 1) °C. After the equilibration time, the mixture was filtered and the final pH value of the filtrate was measured. This set of experiments was performed at a pH interval of 1.0.

2.4.2. Adsorption experiments

The batch adsorption experiments were performed with 30 mg AC-T and 10 ml aqueous Cd(II) solutions at desired concentrations and appropriate pH. The initial pH was adjusted by the addition of 0.01 mol·L^{-1} HCl or 0.01 mol·L^{-1} NaOH. Then, the suspensions were shaken in an oscillator at 200 r·min^{-1} for 4 h to achieve adsorption equilibration. Then the residual aqueous Cd(II) concentrations in solutions were determined by AFS. The uptake amount of Cd(II) at equilibrium (q_e, mg·g^{-1}) is calculated by

$$q_e = (C_0 - C_e)V/W \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of Cd(II) (mg·L^{-1}), respectively, V is the solution volume (L), and W is the mass of adsorbent used (g).

2.4.3. Desorption experiments

The dry and saturated AC-T was placed in 50 ml of 0.1 mol·L^{-1} HNO_3 for 6 h with stirring at 120 r·min^{-1}. The liquid phase was filtered and analyzed by AFS (AFS-230E). The desorbed percentage is determined as follows.

$$\text{Desorbed} = (\text{Amount of desorbed ions}/\text{Amount of adsorbed ions}) \times 100\% \tag{2}$$

The reuse assays were performed in cycles, starting with the adsorption and ending with the desorption of cadmium ions.

3. Results and Discussion

3.1. Characterization of AC and AC-T

Fig. 1 shows the SEM pattern of original AC and AC-T. The surface of AC-T has less impurity and exhibits more pores. In addition, elemental analysis by SEM/EDS reveals the presence of 90.6% of C and 9.1% of O as the basic elements in AC, while with 65.6% of C and 33.9% of O in AC-T. It indicates that the nitric acid treatment favors the formation of oxygen-containing functional groups.

FT-IR is an important analytical technique to identify characteristic functional groups on carbon surfaces. In Fig. 2, peaks from the hydroxyl group –OH and C–O–C of AC are at 1065 and 1184 cm^{-1}, respectively [11]. However, in the FT-IR spectrum of AC-T, strong peaks are at 1713 and 1613 cm^{-1}, attributed to the stretching vibrations of –COOH and COO^-, respectively [12,13]. It indicates an increase in the oxygen-containing functional groups after the oxidation that generates carboxyl and carboxylate groups. For the AC-T treated with aqueous cadmium ions, the intensity of the peaks at 1604 and 1401 cm^{-1} increases. This could be attributed to an increase in the amount of carboxylate group

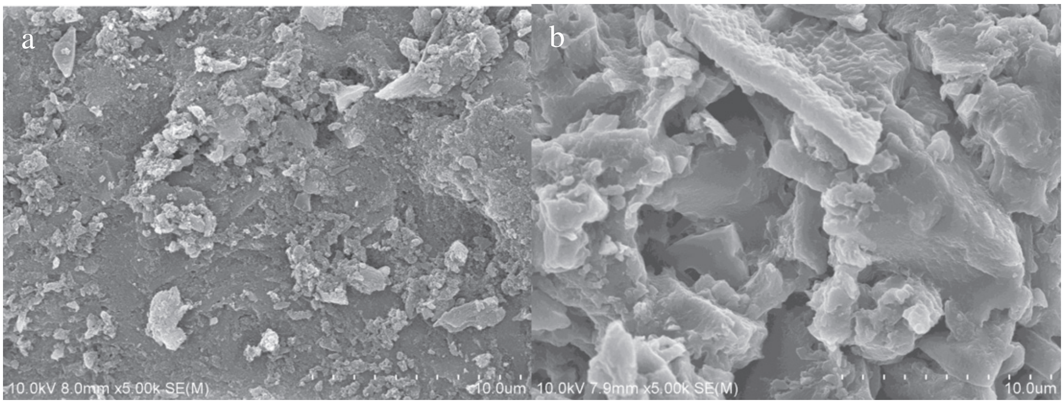

Fig. 1. SEM micrographs of original AC (a) and AC-T (b).

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