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Uptake of perchlorate from aqueous solutions by amine-crosslinked cotton stalk

Xing Xu, Baoyu Gao*, Xin Tan, Xiaoxiao Zhang, DongTing Yue, Qinyan Yue

Key Laboratory of Water Pollution Control and Recycling (Shandong), School of Environmental Science and Engineering, Shandong University, Jinan 250100, PR China

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ABSTRACT

Virgin cotton stalk was produced into an effective biosorbent for perchlorate adsorption. Surface analysis including BET surface area and SEM illustrated the reduction of porous structure in amine-crosslinked cotton stalk (AC-CS). Elemental and zeta potential analysis validated the graft of some positively charged amine groups on surface of AC-CS. Spectra analysis (XPS, FTIR and Raman spectra) suggested that interaction between AC-CS and ClO_4^- should be based on electrostatic attraction. The maximum adsorption capacity (q_{max}) of AC-CS for perchlorate at different pHs (3.0, 6.0, 9.0 and 11.0) were calculated as 29.6, 42.6, 41.0 and 33.0 mg/g, respectively. The saturated perchlorate uptakes in column were in range of 25.0–38.1 mg/g at different pHs. In addition, the exhausted AC-CS column was regenerated by 0.5 mol/L of NaCl solution, which was adequate for almost complete desorption of the perchlorate.

1. Introduction

Perchlorate (ClO_4^-) was widely used in manufactures of rocket propellants, fireworks, weapons, automobile airbags, batteries and analytical chemistry products (Tan et al., 2012; Yoon, Meng, et al., 2009). The major sources of perchlorate pollution are linked to military use, because of its rich oxygen content and highly oxidized form of chlorine (Atikovic, Suidan, & Maloney, 2008; Kucharzyk, Crawford, Cosens, & Hess, 2009). As an emergent environmental contaminant, perchlorate has been detected in soil, public groundwater and surface water systems. This form of contamination has been reported at numerous locations in Unites States, China and some other countries (Kosaka, Asami, Matsuoka, Kamoshita, & Kunikane, 2007; Theodorakis et al., 2006; Tikkanen, 2006). Perchlorate has also been detected in plants; food products, cow's milk and human breast milk (Yoon, Meng, et al., 2009). Perchlorate is of concern because it can inhibit the iodide uptake by the thyroid gland and therefore, the presence of perchlorate in drinking water can cause thyroid ailments as well as other medical problems (Tan et al., 2012). USEPA included perchlorate in the Contaminants Candidate List (CCL) with a reference dose of 0.7 μg/kg/day; this corresponds to the equivalent level of 24.5 μg/L in drinking water. As a result, a new drinking water standard of 24.5 μg/L for perchlorate was adopted in 2005.

Perchlorate, although thermodynamically unstable, is kinetically non-reactive at the low concentrations typically found in contaminated ground and surface water. In addition, perchlorate salts have high solubility and low tendency to form complexes in water. So perchlorate is a bit difficult to be removed from water.

Many technologies including biological and chemical reduction, adsorption, electrochemical reduction, membrane filtration and integrated technologies have been applied for perchlorate (Baidas, Gao, & Meng, 2011; Lee et al., 2008, 2011; Song & Logan, 2004; Tan et al., 2012; Wang, Lippincott, & Meng, 2008; Ye, You, Yao, & Su, 2012; Yoon, Meng, et al., 2009; Yoon, Amy, et al., 2009). Perchlorate treatment using biological and chemical reduction is currently being practiced but they have some disadvantages such as the low reaction rate, sensitivity to pH, temperature and salinity changes as well as introduction of metals with chemical treatment (Baidas et al., 2011; Tan et al., 2012; Ye et al., 2012). Membrane filtration using reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) membranes plays an important role in removing perchlorate from drinking water. However, this technology has a big hindrance to its application in large scale system; perchlorate is just removed from one stream to another stream, the reject stream needing further treatment (Ye et al., 2012; Yoon, Meng, et al., 2009; Yoon, Amy, et al., 2009). Electrodialysis may be more effective than conventional membrane filtration for perchlorate but its operation costs are very high. Adsorption technology is widely used for water treatment due to its simplicity, high capacity, and capability of operating at a relatively high flow rate with a small treatment unit (Ye et al., 2012). However, in spite of the good affinity toward perchlorate,

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* Corresponding author. Tel.: +86 531 88364832; fax: +86 531 88364513.
E-mail addresses: bygao@sdu.edu.cn, baoyugao_sdu@yahoo.com.cn (B. Gao).

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a major problem of adsorption is its cost. Another challenge associated with using adsorption technology is regeneration of spent resins since perchlorate on most anion exchange resins is difficult to displace with chloride (Baidas et al., 2011).

In this research, perchlorate was removed from aqueous solution by cotton stalk based biosorbent. The cotton stalk based biosorbent was prepared by introducing some amine groups onto cotton stalk, forming the amine-crosslinked cotton stalk (AC-CS). Physicochemical properties of AC-CS were elucidated by the Raman spectra, FTIR, X-ray photoelectron spectroscopy (XPS), elemental analysis, SEM, BET surface area analysis and zeta potential analysis. Maximum adsorption capacity ($q_{\max}$) of AC-CS for perchlorate was evaluated after isotherm tests. In addition, a fixed-bed column with length of 20 cm and diameter of 1.2 cm was employed for column adsorption and desorption tests.

2. Materials and methods

2.1. Characteristics of AC-CS

AC-CS was prepared as our previous method in a lab-scale system with chemical composition as $-CH_2CHOHCH_2NHCH_2CH_2NHCH_2OHCHCH_2N(CH_2CH_2)_3{}^{+}Cl^{-}$ (Xu, Gao, Yue, Zhong, & Zhan, 2010; Xu, Gao, Tang, et al., 2011). The compositions of cellulose, hemicellulose and lignin in virgin cotton stalk are about 23.6%, 25.9% and 25.3%; the high content of holocellulose (including cellulose and hemicellulose) made it easy for cross-linking reaction. Ten grams of virgin cotton stalk was mixed with 20 mL of epichlorohydrin and 15 mL of N,N-dimethylformamide in a 500 mL three-neck round bottom flask at 85 °C for 60 min. An aliquot of 5 mL of ethylenediamine was added by dropwise and the solution was stirred for 45 min at 85 °C. Thereafter, 15 mL of 99% triethylamine (w/w) was added and the mixture was stirred for 120 min at 85 °C. The product was washed with some distilled water, dried at 60 °C for 12 h and then used in all the subsequent experiments.

Physicochemical properties of AC-CS, virgin cotton stalk as well as perchlorate loaded AC-CS were measured by the BET surface area analysis, elemental analysis, SEM, zeta potential analysis, Raman spectra, FTIR and XPS.

Specific surface area of AC-CS and virgin cotton stalk were measured with an automatic BET surface area analyzer (Model F-Sorb 2400, Beijing Jinaipu Technical Apparatus Co., Ltd., China). The detection limit of this instrument is 0.01 m^2/g (N_2). SEM micrographs of the three samples (virgin cotton stalk, AC-CS and perchlorate loaded AC-CS) were obtained by JEOL JSM-6480LV scanning electron microscope. The samples were coated with platinum before the SEM micrograph was obtained. The grafted amine groups in the AC-CS were evaluated by element analyzer (Elementar Vario EL III, Germany).

In the Raman analysis, AC-CS (0.1 g) was placed in 50 mL of perchlorate solution (10 g/L) and stirred for 24 h. The AC-CS, perchlorate loaded sample and perchlorate solution (10 g/L) were analyzed by Raman spectroscopy (Nicolet Almega XR Dispersive Raman, Thermo Electron Corporation, USA). The laser wavelength used in Raman measurement was 1050 nm.

The surface binding state and elemental speciation of virgin cotton stalk, AC-CS and perchlorate loaded AC-CS were analyzed by XPS. The measurements were performed by a spectrometer (ESCALAB 250) with Mg$K\alpha$ irradiation (1486.71 eV of photons) as X-ray source. The perchlorate loaded AC-CS was prepared by mixing AC-CS (0.1 g) with 50 mL of perchlorate solution (1000 mg/L) for 24 h.

The functional groups in virgin cotton stalk, AC-CS and perchlorate loaded AC-CS were investigated by using the FTIR technique (Perkin-Elmer "Spectrum BX" spectrometer). The spectrum was scanned from 400 to 4000 cm^{-1}. The saturated sample was prepared by mixing the adsorbent with solution containing 1000 mg/L of perchlorate.

A microelectrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China) was used to determine the zeta potentials of AC-CS and virgin cotton stalk. The AC-CS or virgin cotton stalk samples were prepared in 25 mL of distilled water containing 0.1 g of samples and shaken for 15 min at 20 °C. In addition, the perchlorate loaded AC-CS samples were prepared by maintaining the suspensions contained with 0.1 g of AC-CS and 100 mg/L perchlorate.

2.2. Isotherm, column adsorption and desorption tests

Isotherm tests were performed to determine the $q_{\max}$ for perchlorate at different pH conditions. The saturated uptake of perchlorate in column was determined in batch fixed-bed column tests. The results were evaluated by the Thomas model so as the maximum column adsorption data (q_0) were calculated and compared with the $q_{\max}$ obtained in isotherm tests. Thereafter, regeneration of the spent AC-CS was conducted in the column by eluting NaCl (0.5 mol/L) solution.

In the isotherm tests, AC-CS (0.1 g) was mixed with 50 mL of solutions in 125 mL Erlenmeyer flasks containing different concentrations of perchlorate. The suspensions were stirred for 6 h and the pH values were monitored at 3.0, 6.0, 9.0 and 11.0. After adsorption, the equilibrium pH was obtained at 3.4, 5.2, 5.8 and 7.1.

A fixed-bed column with 200 mm length and 12 mm diameter was used in the column adsorption/desorption tests. The bed depth of AC-CS in the column is 2.4 cm (AC-CS weight: 1.0 g) with flow rate of 10 ml/min and influent perchlorate concentration of 100 mg/L. Four sets of experiments were conducted to evaluate the effect of influent pH (3.0, 6.0, 9.0 and 11.0) on perchlorate adsorption. The effluent solutions were collected, and every 10 ml was selected as a sample to determine the residual concentrations in the effluent solutions. The saturated column adsorption capacity (q_{ed}) was calculated by the Eq. (1) expressed as:

$$q_{ed} = \frac{9C_0V_0 - \sum c_n v_n}{m} \tag{1}$$

where q_{ed} is the amount of perchlorate per gram AC-CS at saturation (mg/g), c_0 is the original concentration of perchlorate (mg/L), V_0 is the total volume of the influent solutions (L), c_n is the concentration of sample n (mg/L), and v_n is the volume of sample n (L), m is the amount of AC-CS (g).

Regeneration of the AC-CS was achieved by eluting NaCl (0.5 mol/L) solution through the exhausted column (from top to bottom) with flow rate 10 ml/min. The eluted perchlorate and regeneration capacities were calculated.

3. Results and discussion

3.1. Characteristics of AC-CS

3.1.1. BET surface area and elemental analysis

The elemental compositions and surface area of AC-CS and virgin cotton stalk are listed in Table 1. The virgin cotton stalk contained large numbers of C (41.34%), O (44.56%), H (6.70%) element and little N (0.32%) element. After the amine crosslinking reaction, an extent of amine groups was grafted on the framework of holocellulose so as N element (3.24%) in AC-CS was increased. As expected, the BET specific surface areas of AC-CS and virgin cotton stalk was quite small with a range of 4.56–8.82 m^2/g; this was consistent with our previous work (Xu, Gao, Tang, et al., 2011; Xu, Gao, Gao, et al., 2011) as well as the results reported by Chergui, Kerbachi,