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Rapid removal of Cr(VI) ions using quaternary ammonium fibers functioned by 2-(dimethylamino)ethyl methacrylate and modified with 1-bromoalkanes

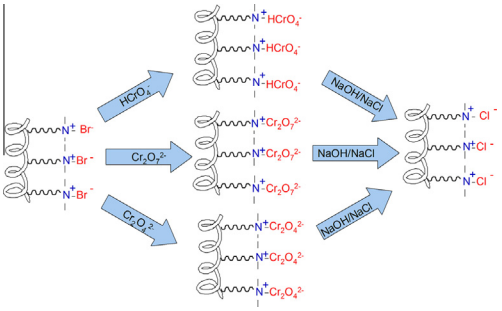
Zhi-yun Kong [a,b], Jun-fu Wei [a,c,*], Yong-hua Li [a,c], Na-na Liu [a,c], Huan Zhang [a,c], Yue Zhang [c], Li Cui [a,c]

[a] State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, No. 399, Binshuixi Road, Xiqing District, Tianjin 300387, China
[b] School of Material Science and Engineering, Tianjin Polytechnic University, No. 399, Binshuixi Road, Xiqing District, Tianjin 300387, China
[c] School of Environmental and Chemical Engineering, Tianjin Polytechnic University, No. 399, Binshuixi Road, Xiqing District, Tianjin 300387, China

HIGHLIGHTS

- The fibers for high and rapid removal of Cr(VI) were prepared by two steps.
- The removal rate of Cr(VI) could reach 97% within 4 min at pH 2–6.
- Maximum adsorption capacities of Cr(VI) ions were 105.8 mg/g.
- The mechanism for adsorption of Cr(VI) ions was ion exchange mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

The quaternary ammonium fibers which could remove Cr(VI) ions rapidly were prepared by radiation-induced grafting of 2-(dimethylamino)ethyl methacrylate (DMAEMA) onto polypropylene (PP) fibers (PP-g-DMAEMA) and modifying with 1-bromoalkanes. The FTIR, FESEM, XPS and TG-DTG spectra manifested that the quaternary ammonium group was introduced onto the surface of PP fibers. The main factors influencing the adsorption of Cr(VI) ions including contact time, pH of the aqueous solution and adsorption dosage were investigated. The removal rate could reach 97% within 4 min and the kinetics study indicated that adsorption process was surface reaction controlled. Maximum adsorption capacities of Cr(VI) ions at 25 °C were 105.8 mg/g based on the Langmuir isotherms. These results suggested that the quaternary ammonium fibers have potential application for the removal of hazardous metal pollutants from wastewater highly and rapidly.

1. Introduction

Chromium compounds are widely used in industrial activities such as electroplating, steel production, leather tanning, paint manufacturing, electric and electronic components, and pulp processing [1]. The most common forms of chromium are Cr(VI) and Cr(III). While Cr(III) is generally non-toxic and is believed to be essential in glucose metabolism in mammals [2], Cr(VI) is highly toxic, a suspected carcinogenic agent that modifies the DNA transcription process causing important chromosomal aberrations [3]. Also, it can cause kidney and gastric damage and epidermal irritation. Cr(VI) forms that dominate in the environment are diprotic chromic acid H_2CrO_4, monovalent $HCrO_4^-$, divalent CrO_4^{2-}

* Corresponding author at: School of Environmental and Chemical Engineering, Tianjin Polytechnic University, No. 399, Binshuixi Road, Xiqing District, Tianjin 300387, China. Tel.: +86 22 83955898; fax: +86 22 83955451.
E-mail addresses: minikk@sina.com (Z.-y. Kong), wjfw2013@126.com (J.-f. Wei).

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and dichromate $Cr_2O_7^{2-}$, whose prevalence depends on the concentration of Cr(VI) and the pH [1].

Various methods have been used for Cr(VI) removal including chemical reduction [4], precipitation [5], ion exchange [6], reverse osmosis [7], membrane separation [8], electrocoagulation [9,10] and adsorption [11]. In the past decades, adsorption techniques have widely been studied and seem to be a particularly attractive option due to its outstanding simplicity, low investment, high efficiency and potential recovery [12,13]. Several materials containing tertiary and quaternary amino groups have been developed for Cr(VI) adsorption, including resin [11], activated carbon [14], biomass materials [15], mineral [1], magnetite nanoparticles [16], cellulose [17], nanotubes [18], gels [19], chitosan [20], silica [21] and synthetic polymer adsorbents [22]. However, the potential shortcomings of some absorbents prevented their wide application, like impurities in the adsorbents, low adsorption capacity and slow adsorption kinetics [18].

The fibrous adsorbent is a kind of new adsorption and separation synthetic polymer which has a larger effective specific surface area, higher speeds of adsorption and elution, higher elution efficiency, and better regeneration performance [23]. The investigations based on fibers functionalized with quaternary ammonium groups have been reported due to their special properties in improving Cr(VI) adsorption [22,24–27]. However, the preparation of anion exchange fiber was complex and some toxic substances was used, for example the chloromethyl methyl ether [22,27]. A simple and non-toxic method of quaternary ammonium fibers preparation is of urgently desired.

2-(Dimethylamino)ethyl methacrylate (DMAEMA) which containing tertiary amino groups was successfully grafted onto several substrates [28–32], and manifested their capacity for adsorption and separation of heavy metal ions [19,32–34]. It has been reported that DMAEMA was grafted onto the nonwoven fabric or fibers by radiation-induced polymerization to remove phosphate, nitrate and cesium in water at high velocity [35–37]. There was no study on the removal of Cr(VI) using the quaternary ammonium fibers based on DMAEMA.

In this study, quaternary ammonium fibers based on DMAEMA were prepared though two steps. Because polypropylene fiber (PP) is inexpensive, high chemical resistibility, and enduring harsh conditions, the novel anion exchange adsorbent based on PP fibers was prepared by electron beam and then modified with 1-bromoalkanes. The adsorption behavior of Cr(VI) ions, including the adsorption kinetics, isotherms, thermodynamics as well as the effect of contact time, pH and adsorbent dosage on adsorption were studied. Quaternary ammonium fibers was proved to removing Cr(VI) ions rapidly from wastewater with high adsorption capacities.

2. Experimental

2.1. Materials

PP was provided by Shijiazhuang Tobacco Technology Center (Shijiazhuang, China). DMAEMA employed for the grafting reaction was purchased from J&K Scientific Ltd and was distilled under vacuum. 1-bromoethane(BE), 1-bromobutane(BB), 1-bromohexane(BH), 1-bromooctane(BO), 1-bromodecane(BD), 1-bromododecane(BDD) were obtained from Aladdin Chemistry Co. Ltd. Standard Stock solutions of Cr(VI) (1000 mg L^{-1}) used for analysis were purchased from the National Research Center for Standard Materials and stored in the dark at 4 °C until use. Potassium dichromate ($K_2Cr_2O_7$) and other chemicals were of analytical grade and were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. A stock solution of Cr(VI) was prepared by dissolving 2.8287 ± 0.0005 g of $K_2Cr_2O_7$ in 1000 mL of distilled water. Working solutions were prepared by diluting Cr(VI) stock solutions to appropriate concentrations.

2.2. Preparation of quaternary ammonium fibers

2.2.1. Preparation of tertiary amine fibers

PP fibers were ultrasonically cleaned in acetone to remove contaminants. After being dried, the fibers (1.0 g) were subjected to swelling with DMAEMA for 24 h in a valve bag. The solution was then bubbled with nitrogen for 20 min to remove the oxygen gas, after which the bag was sealed. Subsequently, the solution was irradiated at ambient temperature by electron beam generated from an accelerator (Wuxi EL Pont Radiation Technology Co., Ltd., Wuxi, China) at different dose. After being irradiated, the grafted fibers were washed with deionized water and ethanol to remove the residual monomers and homopolymers adhered to the fiber surface. The PP-g-DMAEMA fibers were then dried in a vacuum oven at 60 °C for 48 h.

2.2.2. Quaternization of the tertiary amine fibers

To obtain PP-g-DMAEMAE, PP-g-DMAEMAB, PP-g-DMAEMAH, PP-g-DMAEMAO, PP-g-DMAEMAD and PP-g-DMAEMADD fibers the PP-g-DMAEMA fibers were modified by quaternization with BE, BB, BH, BO, BD and BDD, respectively. 1.0 g of PP-g-DMAEMA fibers and 40 ml of 50% bromoalkane-ethanol solution were put in a round bottom flask. The reaction was carried out at 90 °C for 4 h under the protection of N_2. After reaction was terminated, the fibers were washed with ethanol and dried in a vacuum oven at 60 °C.

2.3. Characterization of fibers

The Fourier transform infrared spectroscopy (ATR-FTIR) spectroscopy of the quaternary ammonation fiber was acquired using a Bruker Vector 22 FTIR spectrometer (Bruker Corp., Germany) to analyze the functional groups on the fiber surface and recorded from 4000 cm^{-1} to 400 cm^{-1}.

The field emission scanning electron microscopy (FESEM) was used to analyze the surface morphologies of fibers. The measurements were performed using a Hitachi S-4800 FESEM (Hitachi, Japan) with 10 kV accelerating voltage.

The PP-g-DMAEMA fibers and Quaternary ammonium fibers were dried previously and analyzed the elements of the surface fibers using a K-Alpha X-ray photoelectron spectroscopy (XPS) equipment (Thermo Fisher, UK).

Thermogravimetric (TG) analysis and the differential thermal analysis were recorded using a STA409PC DTA/TGA instrument (Netzsch, Germany) at a nitrogen flow rate of 50 mL min^{-1} in the temperature range from 40 °C to 680 °C at a rate of 10 °C min^{-1}.

2.4. Sorption experiments

All the adsorption experiments were placed on a shaker at 150 rpm under 298 ± 0.5 K. 0.3 g adsorbent was added to 100 mL of Cr(VI) solutions in erlenmeyer flask. The initial pH was controlled from 1 to 12 for studying the effect of pH on adsorption. Adsorption isotherm study was carried out with different initial concentrations of 1, 5, 10, 50, 100, 200, 400 and 500 mg L^{-1}. Fig. 1 The adsorption time was selected from 1 to 60 min in kinetics experiment. Equilibrium adsorption capacity (q_e) was calculated according to the following equation:

$$q_e = V(C_0 - C_e)/m \quad (1)$$

where q_e is the mass of Cr(VI) ions adsorbed per unit mass of the adsorbent (mg g^{-1}), V is the volume of the solution (L), m is the mass of the adsorbent (g), and C_0 and C_e are the concentration of