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FTIR, Raman, and XPS analysis during phosphate, nitrate and Cr(VI) removal by amine cross-linking biosorbent

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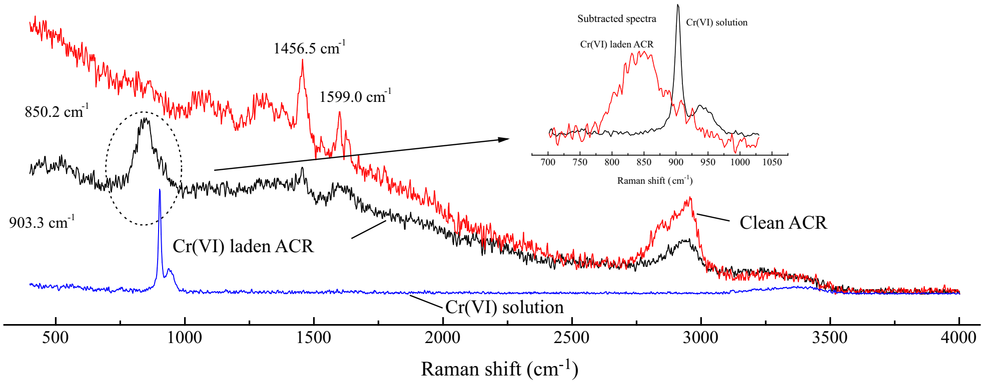
GRAPHICAL ABSTRACT



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ABSTRACT

This study explores the potential use of amine cross-linked reed (ACR) for removing nitrate, phosphate and Cr(VI) from aqueous in a fixed-bed column. Characteristics (surface area, pore structure, FTIR, Raman spectra, XPS, zeta potential and solid NMR) of ACR as well as anions laden samples were intensively investigated. Results indicated that FTIR, Raman and XPS of nitrate and phosphate laden ACR were quite different from those of Cr(VI) laden samples, which corresponded well to their adsorption properties. Tertiary amine group played the main role in uptake of nitrate and phosphate by electrostatic attraction. Characteristics of Cr(VI) laden samples indicated that a reduction of Cr(VI) to Cr(III) occurred on surface of ACR (this was also proved by the zeta potential analysis). However, the main adsorption mechanism for Cr(VI) onto ACR was still based on electrostatic attraction. The maximum dynamic adsorption capacity of ACR for nitrate, phosphate and Cr(VI) was estimated to be 118.9 mg/g, 103.1 mg/g and 135.3 mg/g. The nitrate/phosphate adsorption capacities of spent ACR after 3 cycles of adsorption–desorption were recovered with 97.3–98.4%. In contrast, only 49.2% of Cr(VI) recovery was achieved, partially due to the destruction of the functional groups on surface of ACR during the Cr(VI) adsorption.

1. Introduction

Cr(VI), nitrate and phosphate are usual anionic pollutants exist in surface- and groundwater [1,2]. In the processes of electroplating, leather tanning, paint, steel fabrication, and textile dyeing, generating chromate wastewater in large quantities [3]. Cr(III) and Cr(VI) are the two states of chromium oxidation existed in environments. Compared with Cr(III), Cr(VI) is considered to be much more toxic, carcinogenic and mutagenic to living organisms [1,4,5]. And Cr(VI) ingestion results in maladies such as epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhage [6]. The

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overuse of fertilizers in agricultural and the over-exploitation of phosphate rock generate mass of nitrate and phosphate [7,8]. High concentration of nitrate and phosphate in water can lead to eutrophication, which frequently cause phytoplankton blooms, esthetic problems, and the deterioration of water bodies [2,7,9]. Therefore, it is necessary to control the concentrations of Cr(VI), nitrate, and phosphate in wastewater before discharging into aquatic environments.

Several technologies have been used to remove Cr(VI), nitrate and phosphate from wastewater, such as chemical reduction [10,11], adsorption [12–14], membrane techniques (nanofiltration, reverse osmosis, and ultrafiltration) [15–17], and microbial remediation [18–20]. Among them, adsorption techniques are considered as the most preferable methods partially due to their high efficiency, low cost and simple operation condition [7,21]. Besides, so many adsorbents are easy to be re-generated that cause fewer disposal problems [21]. Although so many commercial adsorbents have been well tested with excellent uptake of anions removal, the major obstacle was their substantial costs for commercial materials, which would limit their applications in industries.

Recently, more attentions have been paid to the low-cost renewable plant/agriculture by-products, such as rice bran, fruit shell, coconut coir pith, sugarcane bagasse, waste tea leaves, wheat bran, peanut shell, orange peels, wheat straw, sawdust of various plants, groundnut shells, Chinese reed, coconut shells, giant reed, and corn stalk [3,6,14,21–34]. Investigations indicated that those plant/agriculture wastes containing high polysaccharides are promising biomaterials for preparing some innovative biosorbents. For example, cellulose and hemicellulose in agricultural by-products have reactive hydroxyl groups in each anhydroglucose unit. Wartelle has inducted the N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride onto these by-products for removal of various anions (e.g. phosphate, chromium, selenium, and arsenic) from aqueous solutions [35]. The merits of these biomaterials were based on their low costs, availability in abundance, and renewability [21,8].

Giant reed was a plant waste with contents of cellulose and hemicellulose more than 60%. As a result, it was a suitable material that could be used as biosorbent. In this study, we used surface modification reagents to modify giant reed and investigated its performance for adsorption of nitrate, phosphate and Cr(VI) from aqueous solutions in different concentrations. The parameters we measured include: bed depth, influent concentrations, flow rates. All these parameters were prepared for subsequent analysis with Thomas models. Combined FTIR, Raman, XPS analysis as well as zeta potentials was highlighted in this work by determining the changes of binding conditions between the adsorbed anions and functional groups in the bio-sorbent, which would be helpful to understand the adsorption mechanisms for various anions. In addition, relationships between characteristics of anions laden samples and anions adsorption properties were also evaluated.

2. Material and methods

2.1. Preparation of amine cross-linked reed

We obtained the virgin giant reed (GR) samples from the suburb of Jinan, China. They were dried in sunlight until all the moisture was evaporated. Then the giant reed was smashed to pieces with 0.02–0.5 cm by the vertical type mill and sieved to desired mesh size (300–600 μm) for use. We should emphasize that the preparing method for the giant reed based biosorbent was in accordance with our previous work but with some modifications to optimize its adsorption properties for different anions [34,36]. A 250-mL three-neck round bottom flask was employed for the synthetic process and the reaction was conducted in at 90 °C. Four grams of virgin reed was added into the flask and mixed with epichlorohydrin (15 mL) and N,N-dimethylformamide (DMF) (15 mL), stirring for 1 h. Ethylenediamine (4.5 mL) was then added and the mixture was stirred for 30 min; this was followed by the addition of 10 mL of triethylamine (99%, w/w) (3 h). The crude product was washed with deionized water, dried at 80–100 °C for 12 h. The primary product was then smashed and sieved to obtain appropriate mesh size (300–600 μm) samples as absorbent. The scheme of ACR was shown in Fig. 1.

2.2. Column adsorption experiments

We prepared an organic-glass column for our fixed-bed column adsorption tests. The column that was 200 mm in length and 12 mm in diameter was filled with 1.2 g of amine cross-linked reed (ACR). The concentrations of phosphate solutions and nitrate solutions were 50, 80 and 120 mg P (or N)/L, and the concentrations of Cr(VI) were 150, 200 and 250 mg (Cr)/l. The reagents we used were disodium hydrogen phosphate, potassium nitrate and potassium dichromate. The feed solution were pumped by the peristaltic pump upward through the fixed-bed column. The influent were controlled at rates of 5–10 ml/min and the effluents were collected by a 100 mL measuring cylinder with each 100 mL effluent solutions as a data point to measure the concentrations of anion in it. The flow process was finished until the concentration of effluent (C_t) reached 95% of the influent concentration (C_0).

2.3. Desorption experiments

The regeneration of spent ACR was studied through sequential cycles of adsorption–desorption experiments. When ACR was exhausted after adsorption under high concentration of nitrate (50 mg/L), phosphate (50 mg/L) or Cr(VI) (150 mg/L), a dilute HCl solution (0.5 mol/l) was then eluted through the column for the desorption of nitrate, phosphate and Cr(VI) from the spent ACR. Then the ACR was washed with 100–500 mL of distilled water, and the regenerated ACR absorbent was used again in the re-adsorption experiment by feeding with fresh adsorbate solution. The adsorption and desorption cycles were repeated for three times and the concentrations of various anion in the effluent solution during the adsorption process were continuously monitored with the UV–visible spectrometer (UV754GD, Shanghai).

2.4. Column data analysis

The breakthrough curve is usually used to evaluate the performance of fix-bed column. The C_t reaches about 5% of the C_0 is called “breakthrough point”. The point where the C_t reaches 95% is called “point of column exhaustion” [37]. The breakthrough curve can be

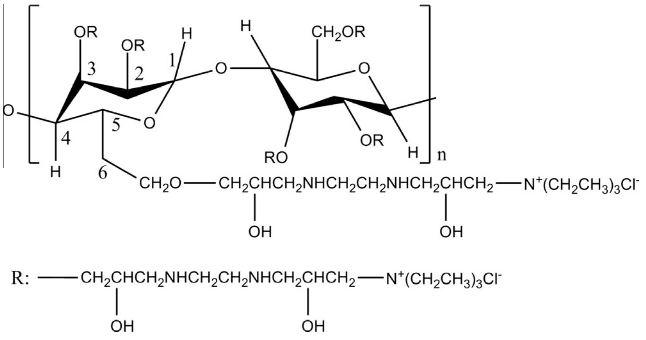

Fig. 1. Scheme of ACR.