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Removal of Cr(VI) by modified and immobilized *Auricularia auricula* spent substrate in a fixed-bed column

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ABSTRACT

To remove the heavy metals from industrial wastewater and reclaim valuable materials from edible fungus production, *Auricularia auricula* spent substrate (AASS) modified by cetyltrimethyl ammonium bromide (CTAB) and immobilized by sodium alginate was used as a novel adsorbent (MIAASS) for Cr(VI) removal. The modification and immobilization did not change the surface morphology, but changed the property of the adsorbents revealed by SEM, BET and FT-IR analysis. Batch adsorption experiments showed the modification and immobilization had the uptake capacity improved 21.44 to 27.34% at influent Cr(VI) concentration ranging from 25 to 125 mg/L. In fixed-bed column adsorption experiments, the breakthrough and exhaustion time were prolonged about 2 to 4.5 times with bed height increasing from 50 to 70 cm, influent concentration and flow rate decreasing from 200 to 50 mg/L and 40 to 20 mL/min respectively. The concentration-time profile and the adsorption process was better predicted and described by Thomas model than Adams-Bohart model indicating that the external and internal diffusions were not the bottle neck of the process. The stability of MIAASS was validated through three cycles of adsorption-desorption processes, and the final regeneration efficiency amounted to 52.48%.

1. Introduction

Hexavalent chromium (VI) is a highly toxic, carcinogenic and mutagenic pollutant in wastewater generated from tannery, electroplating factory, dyestuff manufactures, etc (Silvana et al., 2015). Cr(VI) can compromise the immune system and trigger the problems in respiratory and reproductive system of aquatic organism. As for human being, long term exposure to Cr (VI) may cause liver, kidney and lung damage as well as skin ulceration (Cieslak-Golonka, 1995). The World Health Organization (WHO, 2004) recommends that the typical Cr(VI) concentration be less than 220 mg/L in wastewater and 0.05 mg/L in drinking water, while that in industrial effluent often ranges from 50 to 1000 mg/L. Therefore, it is imperative to remove Cr(VI) from industrial effluents before they are discharged into the aquatic environment.

Conventional technologies applied in chromium species removal include chemical precipitation, evaporation, ion exchange and membrane separation. These methods are not preferentially utilized for low concentration Cr(VI) polluted water because of their high operating costs, low selectivity, incomplete removal and secondary pollution (Devaraj et al., 2016; Mittal et al., 2010b; Gupta and Nayak, 2012). Compared to conventional techniques, biosorption process has emerged as an economical, efficient and environment friendly approach for metallic ions removal from wastewater (Saravanan et al., 2016; Saleh and Gupta, 2012; Gupta and Rastogi. 2009). Currently, a number of biomaterials including food and agricultural wastes have been exploited as biosorbents (Zafar et al., 2007; Mittal et al., 2010a). Spent substrate of mushroom has high biosorption capacity due to its composite component of mycelia and sawdust (Qu et al., 2015). In previous research, *Pleurotuso streatus* spent substrate has been used to remove Zn(II) from simulated wastewater and immobilized fragrant mushroom spent substrate has been employed to eliminate Cu(II) from aqueous solution in batch experiments (Hu et al., 2014a, 2014b). *Auricularia auricular*, also called black fungus, is most popular in China because of its largest production and consumption in the world. However, growing concerns over the huge amount of spent substrate wastes in resources squander and environmental contamination come with the boom of black fungus industry. *Auricularia auricula* spent substrate (AASS) is a kind of fibrous and porous material consisting of celluloses, hemicellulose, lignin, and chitin in intertwined mycelium. Abundant function groups such as hygroxyl, carbonyl, carboxyl, amino, and phosphate groups on AASS surface can offer binding sites for metallic ions in aqueous solution.

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As most Cr(VI) exists in its anion forms of $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$, the modification of adsorbents by cationic surfactants such as amine salt and quaternary ammonium salt has emerged for efficient removal of Cr(VI). Cetyltrimethyl ammonium bromide (CTAB) is a cationic detergent commonly used in the preparation of genomic DNA from plants and bacteria. The positive charges on the micelles of CTAB can concentrate anionic reactants and bind anion chromate to the surface of the adsorbents, which makes the transfer of electrons between Cr(VI) and binding site more easily. Mungasaalli et al. demonstrated that adsorption capacity of *Aspergillus niger* for Cr(VI) was increased 33% through the enrichment of amino and imino groups on adsorbents by CTAB treatment (Mungasavalli et al., 2007). Bingol et al. found that CTAB could endow the adsorbents with positive charges by altering surface zeta-potential which substantially improved the biosorption efficiency (Bingol et al., 2009). Based on these studies, it is conceivable that cationic surfactant modified spent mushroom substrate can efficiently remove Cr(VI) from aqueous solution. However, there is few reports on physicochemical characteristics and adsorption properties of CTAB modified and sodium alginate immobilized *Auricularia auricula* spent substrate (MIAASS) for Cr(VI) biosorption.

In this study, a novel biosorbent MIAASS was developed for Cr(VI) removal. The physicochemical characteristics of MIAASS were revealed by SEM, BET and FT-IR techniques. The uptake capacities of MIAASS and AASS were compared in batch adsorption experiments. The effects of bed height, influent concentration and flow rate on the breakthrough and exhaustion time were investigated in fixed-bed column adsorption experiments. The regeneration parameters were also determined.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals used in this study were analytical grade. The stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving appropriate amount of potassium dichromate (K_2CrO_7) in deionized water and working solution at desired concentration was prepared by the dilution of stock solution (Ahmad et al., 2013). The initial pH was adjusted with 0.1 M NaOH or 0.1 M HCl solution.

2.2. Modification and immobilization of biosorbent

AASS flotsam kindly provided by Wood Edible Fungi Plants (Harbin, China) was rinsed and dried overnight in an oven at 60 °C. 30 g of dried AASS was ground to fine powder with mesh size below 300 mm and placed in 1 L of CTAB solution with critical micell concentration (CMC) of 9.2×10^{-4} mol/L in an orbital rotator at a speed of 150 rpm and 293 K for 24 h. The modified adsorbents were washed by distilled water to remove residual CTAB and dried at 333 K overnight. Then the adsorbents were mixed with 2% sodium alginate solution in a mass ratio of 1:15. Subsequently, this slurry was dispersed dropwise into 2.5% calcium chloride solution using a peristaltic pump (BT100-2J, Longer Pump, China) and the formed 3–5 mm beads of immobilized adsorbents were collected and dried to constant weight at 333 K (Chatterjee and Schiewer, 2014).

2.3. Morphological and physicochemical characteristics of biosorbent

For surface morphology comparison, AASS and MIAASS were fixed with glutaraldehyde and analyzed by a scanning electron microscope (QuANTA200 model, American FEI, American). For surface area, pore volume and pore diameter analysis, samples were degassed with nitrogen at 423 K for 4–6 h and then detected with a surface area analyzer (ASAP 2020, micromeritics, American) according to Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938). The biosorbent was pressed into pellet in a mass ratio of 1:150 for sample to KBr. The pellet was then scanned with a Fourier Transform Infrared (FT-IR) spectrometer (Alpha, Bruker, German) in a frequency range of 4000–400 cm^{-1} and the possible functional groups of AASS and MIAASS were determined by FT-IR spectral analysis.

2.4. Biosorption batch experiments

Batch experiments were performed in 100 mL simulated wastewater with pH value of 6, biosorbent dose of 0.2 g and rotational speed of 150 rpm in 250 mL flask. The filtrate for equilibrium (residual) concentration was analyzed by atomic absorption spectrometer (AA- 6800 model, Shimadzu-GL, Japan).

2.5. Fixed-bed column biosorption experiments

Cr(VI) adsorption was conducted in a down-flow plexiglass column with an internal diameter of 0.1 m and length of 1.2 m. To obtain a bed depth of 50, 60 and 70 cm, column was packed with 417, 500 and 583 g of MIAASS respectively. Small wood chips in diameter of 3–5 cm were embedded therein to prevent the adhesions of adsorbents. The chromium solution at a various concentration of 50, 100 and 200 mg/L was pumped through the column of sorbent using a peristaltic pump with a flow rate of 20, 30 and 40 mL/min at room temperature. The pH value was set to 5.0 to keep the stability of MIAASS. The effluent was analyzed by atomic absorption spectrometer to determine the residual chromium concentrations.

In order to determine the operation and dynamic response of adsorption column, the breakthrough time and exhaustion time were used to evaluate the breakthrough curves. The breakthrough time was the point where effluent concentration (C_t) from the column was about 5% of the influent concentration (C_0) (Song et al., 2015). The point of column exhaustion was where the effluent concentration reached 95% of the influent concentration (Kumar and Bandyopadhyay, 2006a).

q_{total} (mg), the total mass of adsorbed metal represented by the area under the breakthrough curve at a given feeding concentration and flow rate, can be calculated according to the following equation:

$$q_{total} = \frac{Q}{1000}\int_0^{total} C_{cad}dt = \frac{Q}{1000}\int_0^{total}(C_0 - C_t)dt$$

Where C_0 and C_t are the influent and effluent concentration (mg/L), Q is the flow rate through the column (mL/min).

The amount of metallic ions adsorbed at equilibrium or biosorption capacity, q_e (mg/g), can be determined using the following equation:

$$q_e = \frac{q_{total}}{m}$$

where m is the mass of adsorbent (g).

2.6. Breakthrough curves modeling

In order to design and optimize the fixed-bed column adsorption process, mathematical models were developed to predict the breakthrough curve for the metallic solution. In this study, Adams-Bohart and Thomas models were used to match experimental data and predict the dynamic behavior of Cr(VI) adsorption onto the MIAASS in the fixed-bed column (Chen et al., 2012)