Journal of Water Process Engineering 25 (2018) 309–319

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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

Green synthesis of a highly efficient biosorbent for organic, pharmaceutical, and heavy metal pollutants removal: Engineering surface chemistry of polymeric biomass of spent coffee waste

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ARTICLE INFO

Keywords:
Adsorption
Chromium
Methylene Blue
Tetracycline
Spent coffee waste

ABSTRACT

The current study reports synthesis and characterization of an ecofriendly, cheap and efficient biosorbent, sulfonated spent coffee waste (SCW-SO_3H) for water remediation. SCW-SO_3H was synthesized through introducing sulfonic acid polar functionalities over the polymeric biomass (cellulose and lignin) of the spent coffee waste (SCW) by a simple, facile and versatile method. ICP-OES, SEM-EDX, FT-IR, XPS, TGA, Raman and UV–vis spectroscopy were used to analyze the developed SCW-SO_3H biosorbent and its adsorption capacity towards the removal of different environmental pollutants. In order to optimize and maximize adsorption capacity of the developed biosorbent, different variables such as initial concentration, biosorbent dosage, pH, time and temperature were evaluated. The chemically engineered biosorbent showed excellent pollutant removal capacity of 812 mg/g, 462 mg/g and 302 mg/g toward methylene blue, tetracycline and Cr (VI), respectively. Isotherms studies showed that while organic pollutants adsorption follow Langmuir isotherm, Cr(VI) adsorption follows Freundlich isotherm. It was also found that adsorption of all the adsorbates follow pseudo-second order rate kinetic and thermodynamic values, $\Delta H > 0$ and $\Delta G < 0$, showed endothermic nature as well as spontaneity of the adsorption process. The present study can provide a platform in developing new generation of eco-friendly, cost-effective and efficient biosorbent for environmental remediation.

1. Introduction

Agrofood industry annually produces enormous amounts of inedible residues, originating mainly from edible cereals and vegetables [1]. Conversion of these wastes to useful resource not just reduces ecological risk imposed by dumping them into the environment, but also eliminates the need for waste management, and the costs associated with the waste management [2,3]. Due to owning unique characteristic, for instance, renewability, eco-friendliness, abundance, low cost, and tunable chemical composition, these residues can be used as sustainable biosorbents for environmental remediation [4–9]. Unsurprisingly, biosorbents do not have many disadvantages associated with conventional adsorbents, including costly synthesis, expensive equipment requirements, high energy consumption, and environmental issues generation [10].

After tea, coffee is the second most widely used agrofood and universal production of coffee residue is around 6 million tons per year deriving from manufacturing industries, domestic, and restaurants [11]. The major components of the spent coffee waste (SCW) are cellulose and lignin, containing polar and nonpolar functionalities like hydroxyl, carboxylic, aldehydes, ketones, ether, which make SCW valuable source of fertilizer, biodiesel fuel component, animal feedstuff, and pollutants adsorbent [10–12]. Indeed, tunable functionalities over polymeric biomass of SCW can be used for adsorption of different environmental pollutants [4–9].

Nowadays, rapid industrial advancement resulted in generation and dumping various pollutants, e.g. heavy metals, organic pollutants, and pharmaceuticals to the environment causing increased global

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https://doi.org/10.1016/j.jwpe.2018.08.005
Received 24 May 2018; Received in revised form 6 August 2018; Accepted 12 August 2018

awareness, for instance, pharmaceutical antibiotics like tetracyclines (TC) have been extensively used for therapy purposes in human beings and livestock [13–18]. Ubiquitous distribution of highly soluble TC is posing serious environmental and health-related issues, at which the presence of TC in water can provoke drug resistance and challenge current antibiotic therapies [17,18]. Synthetic dyes which are also among the most hazardous organic pollutants in industrial effluents, along with heavy metals posing a serious environmental issues due to their high biotoxicity and carcinogenic effects [19–25].

Due to simplicity, low cost, and ease of operation, adsorption has been considered a versatile technique in elimination of various pollutants regardless of their physicochemical characteristic [4–9]. Recently, there has been a great interest in development of SCW-based biosorbent for environmental pollutants removal. Surface modification, e.g. chemical treatment, and composite making were shown to be a versatile technique in significantly enhancing SCW adsorption capacity [7,5–9,12,13]. However, the techniques used so far have not shown any promising results, compared to other available pollutant biosorbents, and a need for a highly efficient biosorbent can be felt.

Herein, we report fabrication of highly efficient biosorbent, sulfonated spent coffee waste (SCW-SO_3H), through modification of surface chemistry and introduction of highly polar and active sulfonic acid functionalities onto the SCW. The adsorption capacity of the developed SCW-SO_3H was tested in the removal of different range of environmental pollutants, including methylene blue (MB), tetracycline (TC), and chromium Cr(VI). The spent coffee waste derived biosorbent showed high adsorption capacity and fast adsorption rate for the removal of MB, TC and Cr(VI) due to the surface modification of the spent coffee waste.

2. Materials and methods

2.1. Materials

Spent coffee waste was collected from the Starbucks. Hydrochloric acid (36.5–38%) and concentrated sulfuric acid (95–98%) were purchased from BDH chemicals. Tetracycline (> 88% HPLC) and Sodium hydroxide (> 97%) were purchased from Sigma Aldrich. Methylene blue was purchased from Millipore Sigma and Sodium dichromate (99.5%) was purchased from Allied chemicals. Milli-Q (18.2 M) water was used in all experiments.

2.2. Fabrication of the adsorbent

Initially, the collected spent coffee waste was washed with Milli-Q water and then boiled for 1 h to remove any coloring materials (caffeine, tannin and other dyes). The solid was then filtered and washed with water repeatedly until no colored water was observed. The solid (spent coffee waste) was dried in a vacuum oven at 70 °C for 12 h. Then 3 g of dried spent coffee waste was taken in a round bottom flask and 45 ml of sulfuric acid was added slowly into it. Then the flask was placed in an oil bath to maintain a constant temperature of about 70 °C. The reaction mixture was stirred continuously and heated for 3 h at 70 °C. Then the mixture was poured out into a beaker (1000 mL) and cooled down to room temperature. 700 ml of ice cold water was then added into the beaker slowly to dilute the acid. Then the mixture was vacuum filtered and washed with copious amount of water to remove any excess acid. The sample was then placed in a vacuum oven and heated for 12 h at 80 °C. The dried sample was ground into fine powder for further use.

2.3. Characterization techniques

Morphological and elemental analysis of the synthesized adsorbents was carried out using Scanning electron microscopy equipped with an energy dispersive X-ray spectrometer with accelerating voltage of 15 kV (SEM-EDX), 3400 N TypeII SEM. UV–vis spectrophotometer (Agilent Cary 50 Conc) and ICP-OES Perkin Elmer Optima 4300 DV (Perkin-Elmer Optima 4300 DV, Shelton, CT) were used to analyze optical absorbance and elemental composition of the samples. For QC/QA purposes, a standard and a blank were read in every ten samples. Chemical composition and thermal decomposition of the synthesized adsorbents was analyzed using Thermo Scientific™ Nicolet iS5 FTIR Spectrometer, and Mettler Toledo thermogravimetric instrument at a heating rate of 10 °C /min, respectively. Elemental composition, chemical state, and electronic state of the samples were monitored by an X-ray Photoelectron Spectroscopy (XPS) using PHI 5600 spectrometer, at which a 1253.6 eV at 100 W magnesium (MgK_α) source was used.

2.4. Batch adsorption studies

At first, 800 ppm MB, 600 ppm TC and 400 ppm Cr(VI) stock solutions were prepared by dissolving them in deionized water and solutions of the each pollutants at desired concentrations were prepared by successive dilutions of their freshly prepared stock solutions. For the batch adsorption study, 10 mg of SCW-SO3H adsorbent was added to 20 ml of adsorbate solution (MB, TC and Cr(VI)) in a glass vial with constant stirring for 24 h except for the time study where 20 mg adsorbent was added to 40 ml of adsorbate solution. The adsorbate solution was bath sonicated for 30 min after adding the adsorbent into it. 1 M HCl or 1 M NaOH solution was used to adjust the pH of the adsorbate solution. An oil bath was used for the temperature study and the adsorption process was carried out at three different temperatures viz. 25 °C, 45 °C and 65 °C. After 24 h of constant stirring, the MB, TC and Cr (VI) samples were collected in centrifuge tubes by filtering through a 0.45 µm syringe filter. Then the collected MB and TC samples were analyzed by UV–vis spectroscopy to calculate the remaining concentration of MB and TC after adsorption. The collected Cr(VI) samples were analyzed by ICP-OES to calculate the remaining Cr(VI) concentration in the solution after adsorption. The adsorption maxima considered for MB and TC were 616 nm and 357 nm, respectively. The adsorption capacity (mg/g) and percentage adsorption (%) were calculated by the using the following Eq. (1) and (2), respectively [26,27]:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$$\text{Adsorption}(\%) = \frac{C_0 - C_e}{C_0} \times 100(\%) \quad (2)$$

Where, C_o is the initial concentration and C_e is the equilibrium concentration of the adsorbate (MB, TC and Cr(VI)) solutions, V is the volume of adsorbate solution (mL), m is the weight of the adsorbent (mg) and Q_e is the adsorption capacity of the adsorbent.

2.5. Water purification using continuous-flow column

SCW-SO_3H and sand were packed in a glass chromatographic column with dimensions 20 × 26 × 45.7 cm. With this respect, 1 g of SCW-SO_3H along with 110 g of sand were mixed homogeneously and filled the column as dry. To support the column sand was used at the top and cotton was used at the bottom. 500 ml DI water was used to wash the column prior to filtering MB solution. An aqueous solution of 20 ppm MB was filtered through the column at which the filtrate was analyzed using UV–vis spectroscopy to measure adsorption capacity of the filter.

2.6. Experimental data modeling

The Langmuir, Freundlich, Temkin and Dubinin Radushkevich (D-R) isotherm models were applied to examine the interaction behavior between the target pollutants and adsorbent [23,24]. Furthermore, Pseudo-first order, pseudo-second order, intra-particle diffusion and