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Carboxylic acid functionalized sesame straw: A sustainable cost-effective bioadsorbent with superior dye adsorption capacity

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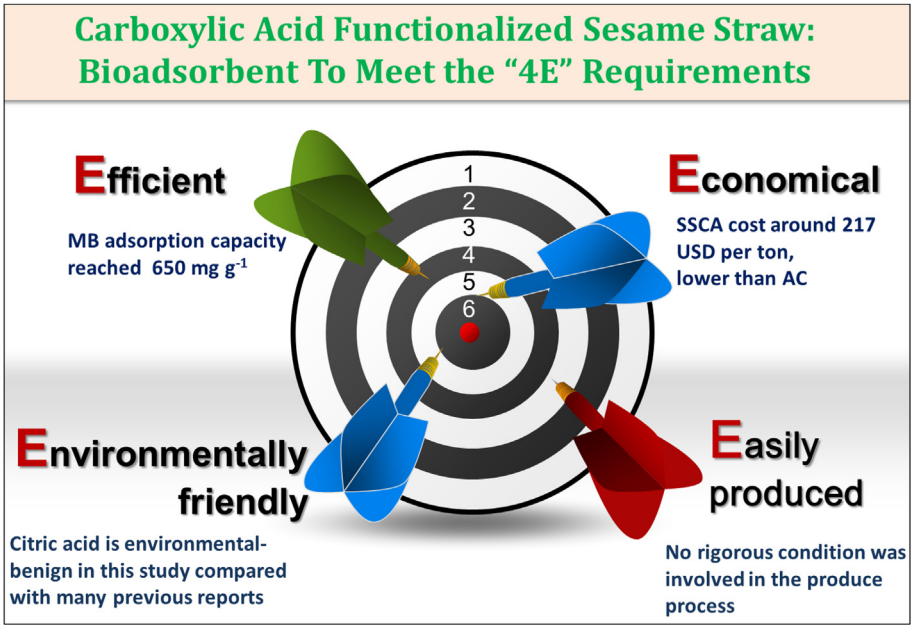
HIGHLIGHTS

- Carboxylic acids functionalized bioadsorbents was prepared for cationic dye removal.
- Citric acid and tartaric acid functionalized sesame straw (SSCA and SSTA) were prepared.
- SSCA exhibited an adsorption capacity of 650 mg g^{-1} for MB, higher than some activated carbon.
- Cost evaluation analysis showed SSCA was the most cost-effect bioadsorbent in the present study.
- SSCA met "4-E" criteria: Efficient, Economical, Environmental-friendly, and Easily-produced.

GRAPHICAL ABSTRACT



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ABSTRACT

This study prepared a carboxylic functionalized bioadsorbent that met the "4-E" criteria: Efficient, Economical, Environmentally friendly, and Easily-produced. Sesame straw (*Sesamum indicum* L.) was functionalized through treatment with citric acid (SSCA) and tartaric acid (SSTA). The products were examined for adsorption capacity and mechanisms. Langmuir model gave the best fit for the isotherm data, and the maximum monolayer adsorption capacity of SSCA was 650 mg g^{-1} for methylene blue (MB). The excellent dye adsorption capacity of SSCA can be attributed to the introduction of ester groups during citric-acid modification and the tube-like structures (i.e., sesame straw cell wall remnants). At last, the cost of carboxylic acid functionalized bioadsorbents was evaluated, which showed that SSCA would

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Sesame straw
Thermo-decomposition
Bioadsorbents

be the most cost-effective bioadsorbent. Additionally, this study presents a thermo-decomposition methodology for contaminant-loaded bioadsorbent. Results showed that SSCA is probably one of the few bioadsorbents that can be produced and applied in industrial scale.

1. Introduction

Millions of tons of synthetic dyes are released from many industrial operations every year. These synthetic toxic chemicals have carcinogenic, teratogenic, and mutagenic effects on humans and aquatic life (Shabbir et al., 2017; Zhang et al., 2013). Therefore, treatment of dye-contaminated effluents with a reliable, low-cost, and convenient technology is necessary.

The prevailing measures for removing synthetic dyes from aqueous solutions are coagulation, flocculation, microbiological or enzymatic decomposition, adsorption, membrane filtration, ion-exchange, eco-engineering method and advanced oxidation (Hussein and Scholz, 2017; Li et al., 2017; Mohammed et al., 2011; Wang and Li, 2013). Among them, adsorption is popular due to its simplicity, ease of operation, ability to respond rapidly to changing conditions, insensitivity to toxicity, and high efficiency (Dawood and Sen, 2012; Douissa et al., 2013; Song et al., 2016). The most commonly used adsorbent, activated carbon (AC), possesses a particularly high adsorption capacity (Khanday et al., 2017; Maneerung et al., 2016). However, AC is expensive to produce and regenerate (Corwin and Summers, 2010). Consequently, a lower-cost substitute for AC would be of great benefit (Velazquez-Jimenez et al., 2013; Velghe et al., 2012).

Among the low-cost adsorbents studied for dye-removal in recent years, are cellulose-based materials. However a common disadvantage of these materials in their natural state is low adsorption capacity (Daneshvar et al., 2017). Chemical modification of the biomaterials with sulfuric acid, hydrochloric acid, nitric acid, sodium hydroxide, or other chemicals (Suhas et al., 2016; Wang and Li, 2013; Yu et al., 2012; Zhao et al., 2011), is usually expensive or poses an environmental hazard. Moreover, few chemical modifications have achieved a practical dye-adsorption capacity.

To produce a promising chemical functionalized bioadsorbents, one of the most important procedures was to find highly efficient and easily available biomaterials. Based on our previous investigation, sesame byproduct processed a competitive adsorption capacity for cationic dyes. However, according to our experiment, the adsorption capacity of crude sesame byproduct was still not comparable to ACs. Thus, sesame straw was selected as a crude adsorbent to produce an efficient dye adsorbent which is competitive to commercial adsorbents such as activated carbons. In consideration of the environmental friendliness, ubiquitous, easily produced and virtually inexhaustible supply of citric acid (CA) and tartaric acid (TA) (Sun et al., 2015), sesame straw functionalized by these two carboxylic acids, i.e., sesame straw functionalized by CA (SSCA) and sesame straw functionalized by TA (SSTA), were produced and investigated in this study.

The biomass is carbohydrate and there exist many –OH groups on the surface which may be esterified by the –COOH functions of organic acids (Pezoti et al., 2016). The resulting increase of oxygen containing functional groups (such as ester) on the adsorbent surface will consequently lead to a higher electronegativity and nucleophilicity, which will likely increase the adsorption capacity of cationic pollutants. In this study, MB was selected as a model dye.

Briefly, the objectives of this study were to (1) produce & characterize carboxylic acid functionalized bioadsorbents that meet the "4-E" criteria: Efficient, Economical, Environmental-friendly, and Easily-produced; (2) describe the adsorption process of MB using mathematical model, including equilibrium study, kinetic study, thermodynamics, desorption process and (3) evaluate the cost of produced bioadsorbents and propose a sustainable economy-environment cycle for bioadsorbents.

2. Materials and methods

2.1. Preparation of MB solution and adsorbents

Methylene blue ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$, C.I. 52015) was purchased from Sinopharm Chemical Reagent Co. LTD (Shanghai, China). The dye stock concentration was 1000 mg L^{-1}. Sesame straw was collected in Shandong province, P.R. China and cut into small pieces (length 3–5 cm), washed repeatedly with deionized water (6 times) and dried at 60 °C for 24 h. The dried material was then ground, sieved (pore size, 250 μm) and activated at 110 °C for 2 h. The prepared sesame straw powder (SSP) was stored in an air-tight container.

In order to determine the most favorable concentrations of CA and TA during the chemical modification, adsorption experiments using different acid-concentration-functionalized bioadsorbents were performed. The concentrations of the two acids had been optimized. Based on Fig. 1a, the concentration of CA and TA were set as 0.4 and 0.7 mol L^{-1}, respectively. Detailed information was provided in Supporting Information (S.I.1). Hence, the two chemically functionalized bioadsorbents (SSCA and SSTA) were produced by the following procedures. Briefly, 20 g SSP was added to 200 mL of 0.4 mol L^{-1} CA or 0.7 mol L^{-1} TA, and the reactants were kept in an oven for 2 h at 70 °C. The mixture was then centrifuged (4000 rpm) and the residual solid-phase material was dried at 70 °C for 16 h and then crushed in a grinder. The crushed materials were subsequently esterified at 120 °C for 3 h. Then, the product was washed repeatedly (around 3 times) with 0.05 M $NaHCO_3$ followed with deionized water (3 times). The washed material was centrifuged, dried overnight at 70 °C, crushed, sieved (250 μm). The sieved carboxylic acid-functionalized bioadsorbents (SSCA and SSTA) were stored in brown reagent bottles until required for experiments. The modification mechanism of carboxylic acids functionalized biomaterials was presented in Fig. S1 in S.I.

2.2. Adsorption experiments

Batch adsorption experiments were conducted in a batch system which consisted of some 150-mL Erlenmeyer flasks in a thermostatic shaker (25 °C, 160 rpm). Each flask contained 50 mL MB solution. The kinetic study was carried out in several 1000-mL Erlenmeyer flasks, with 500 mL MB solution in them. If not specially notified, all experiments were conducted under these conditions: temperature was 25 °C, shaker speed was 160 rpm, solution pH was 8.0 (adjusted by $NaHCO_3$) and adsorbent dosage was 1 g L^{-1}.

MB concentration was measured using the following process. Approximately 5 mL of MB solution was filtered through 0.45 μm membrane filters (the first 2 mL solutions were discarded), diluted (the absorbency values were controlled below 0.8 through controlling the dilution to make sure that their absorbance remained within the linear calibration range) and then measured at