Chemical Physics Letters 710 (2018) 193–201

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Enhanced removal efficiency of acid red 18 from aqueous solution using wheat bran modified by multiple quaternary ammonium salts

Wei-Xing Zhang[a], Lu Lai[a,*], Ping Mei[a], Yan Li[a], Yu-Hang Li[a], Yi Liu[b,c]

[a] College of Chemistry and Environmental Engineering, Yangtze University, Jingzhou 434023, PR China
[b] State Key Laboratory of Virology & Key Laboratory of Analytical Chemistry for Biology and Medicine (MOE), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China
[c] College of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, PR China

HIGHLIGHTS

- Multiple quaternary ammonium salts-modified wheat bran for removing anionic dyes.
- The equilibrium and kinetic adsorption mechanism were investigated.
- The effects of molecular structures of surfactants on the removal efficiency.
- The dynamic adsorption studies using the packing column of wheat bran.
- Potential as biomass adsorbent for the removal of dyes from wastewater.

ARTICLE INFO

Keywords:
Multiple quaternary ammonium salts
Dye removal
Wheat bran
Adsorption mechanism
Surfactant structures

ABSTRACT

A natural biosorbent prepared from wheat bran (WB) and multiple quaternary ammonium salts (MQAS) was used to remove dye (AR-18) from aqueous solution. The adsorption kinetics and thermodynamic mechanism of the adsorption of AR-18 on MQAS-WB were also examined. Results reveal that adsorption isotherm data can be well described by Langmuir model. The calculated thermodynamic parameters indicate that the adsorption is exothermic and spontaneous. The adsorption kinetics follows the pseudo-second-order model. MQAS-WB shows potential for large-scale wastewater treatment. Dynamic adsorption studies reveal that the dye removal efficiency of the packing column of MQAS-WB is higher than that of raw WB.

1. Introduction

Different classes of synthetic dyes are widely used in various industrial fields, including textiles, food, cosmetics, and paper making [1,2]. About 10–15% of dyes are discharged during an industrial process, thereby causing inevitable environmental problems [3]. In general, dyes are so stable that they are difficult to be degraded by light, heat, oxidizing agents, and microorganisms [4]. With strict regulations on water pollution, dye removal from aqueous solution has been extensively explored [5–7].

Various methods, including membrane separation, photocatalysis, biological oxidation, adsorption, ozonation, oxidation, and electrochemical methods, have been employed to remove dye from wastewater [8]. However, these methods have some disadvantages. For example, biological methods are time-consuming and unsatisfactorily effective. Although chemical oxidation possesses a high degradation efficiency, toxic oxidation products are generated. Fenton reactive oxidation, ultrasonic oxidation, ozone-UV combined oxidation and photocatalysis are uneconomic. By comparison, adsorption is an efficient dye removal method when the adsorbent is low-priced and extensive sources [9–12]. Activated carbon is a well-known and widely used adsorbent in daily life and different industrial fields. However, relatively high treatment costs and difficult regeneration of activated carbon have prompted researchers to develop new sorbents [13].

Various nonconventional adsorbents, including clay, guar gum-based hydrogels [14], calcium alginate hydrogel beads [15], wheat bran [16,17], fly ash, walnut shell [18], microalga *Spirulina platensis* [19], *Cucumis sativus peel* [20], rice straw [21], crop residues [22], palm ash [23], corncob, barley husk [24], nanomaterials [25,26], Salxi babylonica leaves powder [27] and polymer particles [28], have been employed to remove dye from aqueous solution. Low-cost agricultural residues and byproducts show potential for wastewater treatment

* Corresponding author.
E-mail address: lailuchem@163.com (L. Lai).

https://doi.org/10.1016/j.cplett.2018.09.009
Received 7 July 2018; Accepted 5 September 2018
Available online 06 September 2018

applications because of their economic efficiency, eco-friendliness, and resource sustainability [13].

In north China, wheat is an important and abundant crop. However, the disposal of its byproduct wheat bran is considered a serious environmental problem. Wheat bran is wheat grain's outer shell, that can be obtained as an argicultural byproduct from a flour mill. Wheat bran accounts for 40% of wheat grain weight [29]. In terms of structure, wheat bran consists of an outer pericarp, an inner pericarp, a testa, and hyaline and aleurone layers [29]. The major constituent of wheat bran includes cellulose (32.1%), hemicellulose (29.2%), lignin (16.4%) and extractives (22.3%). Wheat bran can be utilized as an effective adsorbent to remove hazardous materials.

For anionic dyes, wheat bran exhibits a low adsorption efficiency because of numerous hydroxyl groups that exist in cellulose, hemicellulose, and lignin structures. The surface modification of wheat bran is practical and effective to enhance its adsorption effeciency for anionic dye. Yue et al. introduced amine groups to the structure of wheat bran through chemical modification to obtain a positive adsorbent [16]. Lee et al. modified rice hull by using ethylenediamine to remove aionic and cationic dyes from aqueous solution [17]. In another study, wheat straw is modified with polyethyleneimine to improve the adsorption capacity for anionic dyes [30]. Magnetic graphene oxide and Fe_3O_4 nanoparticles have been loaded on the surface of wheat bran [31,32] to improve the reusability and recovery of adsorbents.

Cationic surfactants are used to modify the surface of adsorbents and obtain a cationic adsorbent. Surfactant modification is a simple, low-cost, and environmentally friendly method. For example, Malek et al. used quaternary ammonium salts (hexadecyltrimethylammonium bromide, CTAB) to modify pineapple leaf powder [33]. Lafi et al. also enhanced the adsorption capacity of a commercial coffee waste by using cetylpyridinium chloride (CPC) [32].

With the special molecular structures, Gemini surfactants possess remarkably low critical micellization concentration, interesting rheological properties, and abundant microscopic aggregates [34,35]. Cationic Gemini surfactants (12-2-12) improve the adsorption capacity of wheat bran because they have two cationic head groups [29]. As a new type of cationic Gemini surfactants, multiple quaternary ammonium salts (MQAS) have three positive hydrophilic head groups and two hydrophobic alkyl chains. Owing to great performance in the printing and dyeing process, AR-18 becomes a typical kind of azo dye widely used in industrial fields, including textiles, food. In terms of its molecular structure, most importantly, it has three sulfonate groups indicating it owns good solubility and more negative charges helpful to the electrostatic interaction during adsorption process. Considering its wide application and ideal characteristic in molecular structure, AR-18 is chosen as a representative research target for our study.

In this study, a natural biosorbent prepared from wheat bran and MQAS was used to remove textile dye (AR-18) from aqueous solution. The removal efficiency of the biosorbent for AR-18 was examined by varying the initial dye concentration, pH, dosage, contact time and temperature. The adsorption kinetics and thermodynamic mechanism of the adsorption of AR-18 on the biosorbent were evaluated. Eight different surfactants were utilized to modify the surface of wheat bran and to understand the effects of molecular structures of cationic surfactants on the removal efficiency. The corresponding adsorption properties of these biosorbents were then evaluated. The dynamic adsorption properties of the packing column of MQAS-WB were analyzed.

2. Experimental

2.1. Materials

Acid Red 18 (AR-18, C.I. 16255) were purchased from Aladdin Reagent (Shanghai, China). The chemical structures of the cationic surfactants used to modify wheat bran are shown in Fig. 1. Sodium dodecyl sulfate (SDS), decyltrimethylammonium bromide (DeTAB), dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), hexadecyltrimethylammonium bromide (CTAB), and stearyltrimethylammoium bromide (STAB) were also obtained from Aladdin Reagent (Shanghai, China). Bisquaternary ammonium salts (BQAS, 12-2-12) and multiple quaternary ammonium salts (MQAS) were synthesized in our laboratory according to Ref. [36] and [37], respectively. All of the cationic surfactants were recrystallized thrice from acetone and alcohol. All of the other reagents were analytical grade.

2.2. Wheat bran adsorbent preparation

Raw wheat bran (RWB) obtained from a flour mill (Shandong, China) was ground to a particle size of 75–100 mesh. Ultrafine wheat bran powders of wheat bran were washed with distilled water thrice to remove dust and soluble impurities. The powders were dried for 12 h at 65 °C under air and were stored in a glass dryer. The cationic surfactant-modified wheat bran was prepared by mixing RWB with a cationic surfactant solution (1 mmol·L^{-1}) at a ratio (RWB weight [g]: surfactant solution volume [mL]) of 1: 50. The mixtures were stirred for 24 h at 30 °C, and filtrated to obtain the cationic surfactant-modified WB powders. The powders were washed with distilled water thrice to remove unconjugated surfactant molecules, dried again for 12 h at 65 °C and stored in a glass dryer to preserve the reserve.

2.3. Characterization of adsorbent

The morphological characteristics of the adsorbent were observed using a scanning electron microscope (SEM; S-4800, Hitachi, Japan). The samples were mounted on metal grids and coated with platinum in a vacuum evaporator before observation, and the accumulation voltage was 5.0 kV. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Nicolet, USA). The water contact angle of wheat bran surfaces were measured using a DSA 30 Drop Shape Analysis system (Krüss, Germany). The measurements of contact angle have been repeated ten times.

2.4. Adsorption and desorption studies

Appropriate wheat bran powders and 15 mL of dye solution (50 mg·L^{-1}) were mixed in a glass flask. The pH of the dye solution was measured using a pH meter (PB-10, Sartorius, German) and adjusted to 3.0 with 0.1 mol·L^{-1} HCl solution, and the experimental temperature was set at 25 °C. After the resulting solution was stirred for 12 h at 200 rpm, the wheat bran powders were separated from the dye solution through centrifugation at 5000 × g for 10 min. The concentration of the dye solution was determined using a UV–vis spectrophotometer (TU-1810, Puxi Analytic Instrument Ltd., Beijing, China) equipped with 1.0 cm quartz cells. The maximum adsorbance values of AR-18 solutions were examined at 505 nm. The removal efficiency (%) can be obtained using Eq. (1),

$$\text{Removal efficiency (\%)} = \frac{c_0 - c_e}{c_0} \times 100 \quad (1)$$

where c_0 (mg·L^{-1}) and c_e (mg·L^{-1}) are the initial concentration and the equilibrium concentration of the dye solution, respectively. The adsorption capacity (Q) of wheat bran powders can be calculated by Eq. (2),

$$Q = \frac{c_0 - c_e}{m} \times V \quad (2)$$

where V (L) and m (g) are the volume of the dye solution and the weight of wheat bran, respectively.

Different amounts of wheat bran ranging from 0 g·L^{-1} to 2.4 g·L^{-1} at an interval of 0.2 g·L^{-1} were added to the dye solution to examine the effects of wheat bran dosage on the adsorption of dye. The effects of