Journal of Colloid and Interface Science 494 (2017) 223–241

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Regular Article

Optimization of cellulose and sugarcane bagasse oxidation: Application for adsorptive removal of crystal violet and auramine-O from aqueous solution

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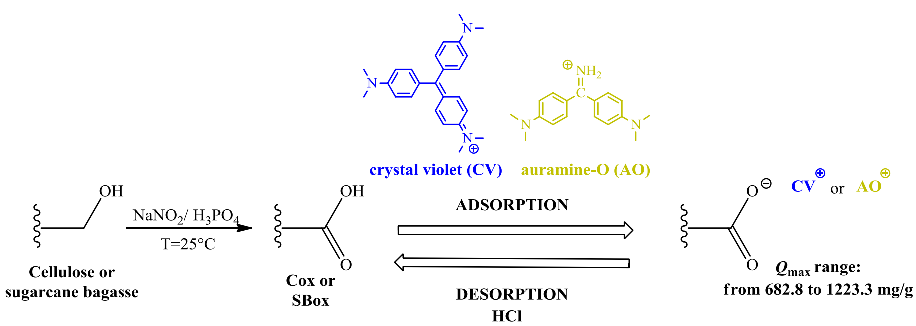
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 October 2016
Revised 19 January 2017
Accepted 22 January 2017
Available online 25 January 2017

Keywords:
Oxidized cellulose
Oxidized sugarcane bagasse
Adsorption
Desorption
Crystal violet
Auramine-O

ABSTRACT

Cellulose (Cel) and sugarcane bagasse (SB) were oxidized with an H_3PO_4-$NaNO_2$ mixture to obtain adsorbent materials with high contents of carboxylic groups. The oxidation reactions of Cel and SB were optimized using design of experiments (DOE) and response surface methodology (RSM). The optimized synthesis conditions yielded Cox and SBox with 4.8 mmol/g and 4.5 mmol/g of carboxylic acid groups, respectively. Cox and SBox were characterized by FTIR, TGA, PZC and solid-state ^{13}C NMR. The adsorption of the model cationic dyes crystal violet (CV) and auramine-O (AO) on Cox and SBox in aqueous solution was investigated as a function of the solution pH, the contact time and the initial dye concentration. The adsorption of CV and AO on Cox was described by the Elovich equation and the pseudo-first-order kinetic model respectively, while the adsorption of CV and AO on SBox was described by the pseudo-second-order kinetic model. Adsorption isotherms were well fitted by the Langmuir and Konda models, with maximum adsorption capacities (Q_{max}) of 1117.8 mg/g of CV and 1223.3 mg/g of AO on Cox and 1018.2 mg/g of CV and 682.8 mg/g of AO on SBox. Desorption efficiencies were in the range of 50–52% and re-adsorption capacities varied from 65 to 81%, showing the possibility of reuse of both adsorbent materials.

1. Introduction

Highly colored effluents, especially from textile industries, have been a matter of great environmental interest [1]. Dyes are chem-

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http://dx.doi.org/10.1016/j.jcis.2017.01.085
0021-9797/

ical compounds that can bind to surfaces or tissues to add color. Most dyes are complex organic molecules, which must be resistant in various situations, such as the presence of detergents, sunlight and heat. Every year, about 700,000 tons of dyes are produced and about 100,000 tons are commercially available.

The applications of dyes are diverse and some industries such as cosmetics, leather tanning, food, paper, plastics production, printing rubber and textile demand a large amount of synthetic dyes [2]. Realistic data on the amount of dyes dumped into the environment are not available at present time. However, it is estimated that about 1–2% is lost in dye production and 1–10% during use. Due to their large-scale production and extensive applications, synthetic dyes can thus cause environmental pollution and present serious health risks [3]. These compounds can cause unwanted changes in the color of water bodies and affect the photosynthesis of algae. In addition, some dyes and their byproducts are toxic to aquatic life and mutagenic and/or carcinogenic to humans [4].

Several methods have been developed for the removal of dyes from wastewaters. These methods can include processes such as adsorption, advanced oxidation processes (POAs), anaerobic digestion (AD), coagulation and flotation, gravity separation, enzymatic decomposition, photocatalysis and ultrafiltration. However, among these various available treatment techniques, adsorption is advantageous because of its high efficiency, ease of operation, good benefit/cost ratio, the availability of different adsorbent types and the possibility of reusing the adsorbent and/or adsorbate [5,6].

An effective adsorbent must consist of an aqueous-insoluble matrix that has good mechanical, chemical and thermal stability. Furthermore, it needs to have active groups on its surface that allow interactions with the pollutants that are to be removed [7]. Agricultural wastes such as sugarcane bagasse (SB) are very attractive renewable resources due to their low cost and easy availability and they represent excellent supports for new bioadsorbents [8,9]. Brazil is the world's leading producer of sugarcane. According to the last official survey from the National Company of Supply (CONAB), an agency of the Brazilian Ministry of Agriculture, the production of sugarcane in the 2015/2016 season was estimated to be about 658.7 million tons [10]. Since sugarcane bagasse is an important by-product of brazilian agroindustry, there is great interest in reusing it to produce new materials with valuable applications.

Sugarcane bagasse is mainly composed of 40–50% cellulose, 25–30% hemicelluloses and 20–25% lignin [11]. Cellulose, the most abundant and renewable biopolymer in nature, consists of a linear homopolymer of $\beta(1 \rightarrow 4)$ linked β-D-anhydroglucopyranose units (AGU). Its molecular structure presents many possibilities for chemical modification reactions due to the reactivity of the hydroxyl groups present in AGU [12]. At the present moment, there are several studies in the literature that have used sugarcane bagasse and cellulose as adsorbents for various types of pollutants [13,14]. In general, the solid supports are chemically modified to increase their affinity for the adsorbates that are to be removed, thereby increasing their adsorption capacity and selectivity [15–19]. The main modifications of hydroxyl groups that have been performed are esterification [20], etherification [21] and halogenation [22]. An interesting way to chemically modify cellulose or lignocellulose biomass is through the oxidation of hydroxyl groups. Depending on the oxidizing agent used, different kinds of changes in the structure and crystallinity of the lignocellulose biomass can be obtained, resulting in different types of modifications in the physical and chemical properties of the oxidized products [23]. For example, reaction of cellulose with sodium periodate selectively oxidizes the hydroxyl groups at carbons 2 and 3 of AGU to produce a C—C cleavage and a dialdehyde functionality [24]. When the TEMPO-hypochlorite/bromide [25], H_3PO_4/HNO_3-$NaNO_2$ [26], H_3PO_4-$NaNO_3/NaNO_2$ [27] or H_3PO_4-$NaNO_2$ systems [28] are used as oxidants, the oxidation of cellulose will occur preferentially at carbon 6 of AGU, allowing the introduction of carboxylic acid groups into the structure of the biopolymer. Such chemical modifications can provide materials with new and interesting properties for various applications [29].

This study aimed to evaluate the modification of cellulose and sugarcane bagasse by oxidation with an H_3PO_4-$NaNO_2$ mixture. Initially, the first part of our investigations focused on the oxidation of cellulose. Although oxidation of cellulose has already been studied before [25–28], this is the first study describing optimization by design of experiments of the oxidation of cellulose using H_3PO_4-$NaNO_2$ system. The second part of this study describes for the first time the oxidation of sugarcane bagasse using H_3PO_4-$NaNO_2$ system and its use for adsorptive removal of cationic dyes from aqueous solution. The oxidation reactions were optimized using a design of experiments (DOE) and a response surface methodology (RSM). The variables chosen for optimization were the amounts of H_3PO_4 and $NaNO_2$ and the reaction time. The main response evaluated was the number of carboxylic acid groups introduced into cellulose and sugarcane bagasse. After optimizing the oxidation process, the materials produced, named oxidized cellulose (Cox) and oxidized sugarcane bagasse (SBox), were used for the removal of the model cationic dyes crystal violet (CV) and auramine-O (AO) from aqueous solution. The adsorption studies were assessed as a function of the contact time (kinetics), the solution pH and the initial dye concentration.

2. Material and methods

2.1. Material

Grade 3MM Chr cellulose chromatography paper (Cat. No. 3030-861) was purchased from the Whatman Company, Maidstone, England. The cationic dyes auramine-O (C.I.: 41,000, $C_{17}H_{21}N_3 \cdot HCl$, λ_{max} = 432 nm and MW = 303.83 g/mol) and crystal violet (C.I.: 42,555, $C_{25}H_{30}N_3Cl$, λ_{max} = 584 nm and MW = 407.98 g/mol) (see Fig. 1) were purchased from Vetec (Brazil) and used without further purification. Phosphoric acid (85%) was purchased from Neon (Brazil). Sodium nitrite and sodium hydroxide were purchased from Synth (Brazil).

2.2. Sugarcane bagasse and cellulose preparation

Sugarcane bagasse (SB) was collected from an industrial alcohol producing plant at Ouro Preto, Minas Gerais, Brazil. SB was prepared for the oxidation reactions according to the procedure described by Ramos et al. [30]. Sheets of Whatman cellulose paper (Cel) were cut into 50 mm^2 pieces and milled in an analytical mill (IKA, model A11 basic).

2.3. Statistical design of experiments

The oxidation reaction of Cel and SB was optimized using a 2^3 central composite design (CCD). The independent variables evaluated were the volume of H_3PO_4 (mL), the weight of $NaNO_2$ (mg) and the reaction time (h). The dependent variable evaluated was the amount of carboxylic acid groups (n_{COOH}) introduced into Cox and SBox. The experiments were performed using two orthogonal blocks that satisfied the rotatability condition. Therefore, the effects of these blocks did not affect the estimated parameters in the response surface model. The first block (experiments 1–11) was a 2^3 experimental design with triplicates at the central point (screening experiments) and the second block was made by the addition of axial points in the levels of the experimental design (experiments 12–17) [31]. The full design matrix of the experi-