

Use of a new bi-functionalized sugarcane bagasse derivative for removal of As(V) and Cd(II) from aqueous solutions

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Abstract

A new bi-functionalized bioadsorbent (SBAE) was produced from sugarcane bagasse (SB) in a three step one-pot reaction comprised by *i*) a two-step chemical modification of SB with epichlorohydrin and triethylamine, without catalyst and using *N,N*-dimethylformamide as a solvent; *ii*) esterification of the remaining SB hydroxyl groups with butane-1,2,3,4-tetracarboxylic dianhydride. A Doehlert experimental design was utilized to determine the optimum conditions for esterification reaction. The different SBAE materials were employed for removal of As(V) and Cd(II) from spiked aqueous solutions.

Keywords: bioadsorption; inorganic contaminants; lignocellulosic material; agricultural waste.

1. Introduction

The contamination of water resources is a significant challenge to the long-term sustainability of the environment and the well-being of human populations. Inorganic contaminants, including arsenic and cadmium, present a significant risk due to their toxicity. Arsenic and cadmium are listed by WHO among the 10 chemicals of public health concern [1]. Therefore, adequate treatment is required for the removal of these substances from water and wastewater.

The most commonly methods used for water treatment are coagulation and flocculation, precipitation, ion exchange, complexation and electrochemical techniques. Nevertheless, these methods are constrained by limitations pertaining to their efficiency, cost, complexity, and/or generation of waste requiring disposal [2]. In addition to these methods, adsorption is a potential method for water treatment due to its high efficiency, flexibility of implementation and simplicity of operation. Furthermore, it can be used as a tertiary treatment method [3]. Biosorption is a particularly promising technique for water treatment given the potential to produce biosorbents from several agroindustrial waste materials.

This way, sugarcane bagasse (SB) is suitable to produce new bioadsorbents, since it is a low cost agro-industrial residue generated in a large amount

in Brazil, and if chemically modified, it can become a highly efficient bioadsorbent [4].

Maia et al. [5] prepared a quaternary ammonium anion exchanger (SBTEA-LS) from sugarcane bagasse (SB) using an improved two-step method involving chemical modification with epichlorohydrin (EPI) and triethylamine (TEA), with *N,N*-dimethylformamide (DMF) acting as the solvent and without the use of a catalyst. Maia et al. [5] used a Doehlert experimental design to determine optimal conditions for the SBTEA-LS synthesis. On the other hand, Elias et al. [4] prepared a bioadsorbent from SB (PSB) by the esterification of SB hydroxyl groups with butane-1,2,3,4-tetracarboxylic dianhydride (BAD). Elias et al. [4] optimized the syntheses and applied PSB to remove Cd(II) and Pb(II) from mono-, bi-, and multi-component aqueous systems, in batch and continuous modes.

In this work, based on the works of Elias et al. [4] and Maia et al. [5], a new bi-functionalized bioadsorbent (SBAE) was produced for the removal of As(V) and Cd(II) from spiked aqueous solutions. A bi-functionalization was made to incorporate two different organic functionalities with disparate physicochemical properties that can enhance the overall performance of the bioadsorbent for water and wastewater treatment [6]. Furthermore, the selectivity of the bioadsorbent can be regulated by introducing varying proportions of the two organic

compounds in its structure [6]. SBAE contains pH-independent positively charged quaternary ammonium groups, introduced by amination, and pH-dependent carboxylic groups (negatively charged from pH 4 onwards), introduced by the esterification. Therefore, SBAE can be used for simultaneous removal of anions and cations, which is advantageous due to the increasing complexity of water pollution.

2. Methods

2.1. Synthesis and characterization of SBAE (SB modified with TEA and BAD)

The chemical modification of SB with EPI and TEA was performed under the optimal conditions reported by Maia et al. [5].

The optimal esterification condition was provided by a Doehlert 2² experimental design, comprising five replicates at the center point. The experimental conditions, factors (*t* and *T*) and their levels (Table 1) were defined according to the methodology developed by Elias et al. [4]. The responses selected for evaluation of the different entries were weigh gain (*wg*) and adsorption capacity of As(V) ($q_{e,As(V)}$) and Cd(II) ($q_{e,Cd(II)}$) onto SBAE.

All the syntheses (Table 1) were conducted as described here. SB was firstly washed with distilled water in a beaker under magnetic stirring (60 min, 70 °C), followed by extraction in a Soxhlet apparatus with a 1:1 (v v⁻¹) mixture of ethanol and cyclohexane for 4 h.

The initial step, i.e., the etherification followed by amination of SB, involved the reaction of 0.5 g of SB in 10 mL of DMF (Synth, treated with 3 Å molecular sieve) and addition of 6.4 mL of EPI (Sigma-Aldrich), under heating (100 °C) in an oil bath and with magnetic stirring (300 rpm) for 30 min. Subsequently, 11 mL of TEA (Sigma-Aldrich) were added slowly and left to react under magnetic stirring for 2 h. Then, the second step, i.e., esterification of SB, was performed in the same system (one-pot reaction). 2 g of BAD were added in each entry, with the variables *t* and *T* varying according to the experimental design (Table 1).

SBAE was characterized by FTIR and weight gain (*wg*), as described by Maia et al. [5].

2.2. Adsorption experiments

All the adsorption tests were conducted in triplicate in 250 mL Erlenmeyer flasks, which were agitated (25 °C, 200 rpm) for 16 h in an orbital shaker incubator (Marconi, Model MA-830). It was used 0.020 ± 0.001 g of SBAE and 100.0 mL of solute solution (30.40 mg L⁻¹ of As(V), pH_{initial} = 7.00, or 27.40 mg L⁻¹ of Cd(II), pH_{initial} = 5.75). After adsorption, the suspensions were filtered on JP-41 quantitative filter papers. As and Cd were quantified in the filtrates by ICP-OES (Agilent®, Model 725), after adequate dilutions.

Table 1. Levels and responses of the 2² Doehlert experimental design for optimization of the esterification of aminated sugarcane bagasse with butane-1,2,3,4-tetracarboxylic dianhydride and comparison to the literature

Entry	<i>T</i> / min	<i>T</i> / °C	<i>wg</i> / %	$q_{e,As(V)}$ / mg g ⁻¹	$q_{e,Cd(II)}$ / mg g ⁻¹
SBAE [this work]					
1	180.0	85.0	23.4	24.9	2.01
2	142.5	100.0	18.1	27.3	< LQ
3	30.0	85.0	17.3	27.3	< LQ
4	67.5	70.0	24.7	25.1	1.94
5	142.5	70.0	20.0	24.8	4.68
6	67.5	100.0	24.7	24.2	< LQ
7	105.0	85.0	22.8	23.8	< LQ
8	105.0	85.0	23.9	26.8	2.26
9	105.0	85.0	20.1	24.3	4.21
10	105.0	85.0	20.1	22.4	4.80
11	105.0	85.0	21.0	28.7	< LQ
μ ± SD	-	-	21 ± 3	25 ± 2	3 ± 1
SBTEA-LS [5]					
	60.0	100.0	22.0	27.4 ± 0.8	2.6 ± 0.5*
PSB [4]					
	60.0	70.0	16.1	-	62 ± 2

*This work

3. Results and discussion

3.1. Characterization of SBAE by FTIR

The main changes in the SBAE FTIR spectrum compared to the raw SB FTIR spectrum (Fig. 1), due to introduction into the SB structure of *i*) BA (from BAD) units were: the broadening and increased intensity of the band at 3332 cm⁻¹

corresponding to the $\nu_{\text{O-H}}$ (alcohol) and $\nu_{\text{O-H}}$ (carboxylic acid), the appearance of a band at 2994 cm^{-1} corresponding to the $\nu_{\text{C-H}}$ (aliphatic, methine), the broadening of the band at 1731 cm^{-1} corresponding to the $\nu_{\text{C=O}}$ (ester) and $\nu_{\text{C=O}}$ (carboxylic acid) and the splitting of the band at 1372 cm^{-1} corresponding to the ν_{COO} (carboxylate) [7]; *ii*) TEA group were: the broadening of the band at 2889 cm^{-1} corresponding to the $\nu_{\text{N-CH}_3}$ (amine) [7]. Furthermore, the appearance of a band at 729 cm^{-1} in the SBAE FTIR spectrum related to the vibration of C-Cl bonds suggested that some EPI units did not react with TEA [5] and, therefore, chlorine atom was not displaced by TEA ($\text{S}_{\text{N}2}$). It should be highlighted that the complexity of the composition of SB can lead to overlapping of peaks of the organic groups introduced by chemical modification with EPI, TEA and BA (from BAD) with peaks characteristic of raw SB [4, 5].

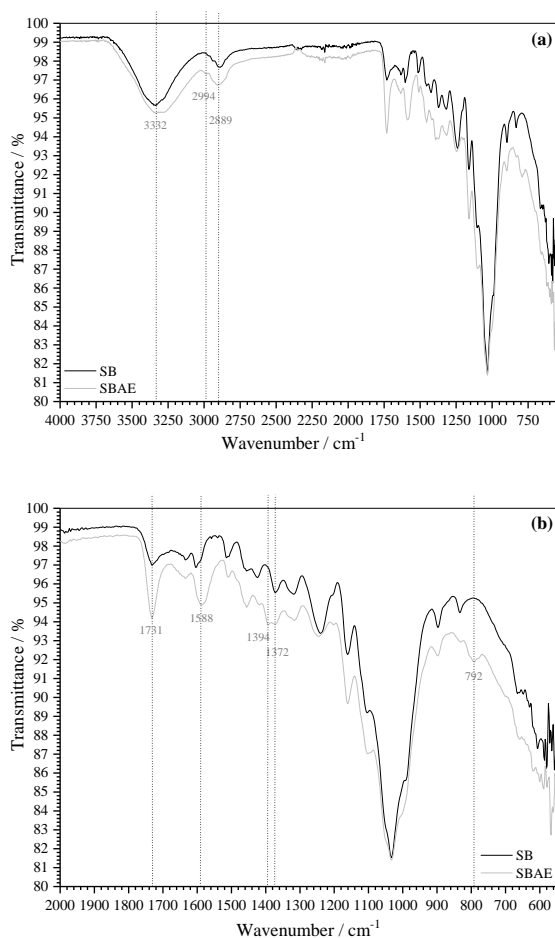


Fig. 1. FTIR spectra for the raw SB and SBAE from (a) 4000 to 500 cm^{-1} and (b) 2000 to 500 cm^{-1} .

3.2. Weight gain (w_g) and adsorption studies

The w_g and q_e values of As(V) and Cd(II) of SBAE were 21 ± 3 and 25 ± 2 and 3 ± 1 , respectively (Table 1). The low values of the standard deviations suggested that the experimental conditions did not influence expressively $q_{e, \text{values}}$ for As(V), although some experimental conditions did not lead the removal of Cd(II). Therefore, to synthesize SBAE, it can be chosen the experimental conditions that involved less energy expenditure making the synthesis more economic and environmentally sustainable.

It can be noticed that, considering the standard deviations, the w_g and q_e values of As(V) and Cd(II) for SBAE were close to those reported by SBTEA-LS. However, the q_e value of Cd(II) for SBAE was much lower than that for PSB (Table 1). It may suggest that the esterification with BAD to produce SBAE was not so effective to produce PSB as was expected. This result should imply that the presence of TEA in the structure promoted, in addition to a steric hindrance for BAD molecules to access the non-modified SB hydroxyl groups, a lower reactivity towards the esterification of SB with BAD. Other hypothesis are: 1) the diesterification reaction involving carbonyl anhydride groups from BAD and the remaining hydroxyl groups from SB may also occur, resulting in a decrease in the adsorption capacity due to the lower number of degrees of freedom of the carboxylate groups to form interactions with Cd(II) and 2) the formation of a repulsive potential on the surface of SBAE due to the presence of positively charged quaternary ammonium groups, hampering the adsorption of Cd(II) [5].

4. Conclusions

The zwitterionic bioadsorbent SBAE, produced from etherification of SB with EPI followed by amination with TEA and esterification with BAD, presented similar performance to SBTEA-LS reported by Maia et al. [5]. Even with a similar performance compared to SBTEA-LS, SBAE can remove Cd(II) simultaneously to As(V), showing potential as a bi-functionalized adsorbent for treating water contaminated with toxic species such as oxyanions and metal cations. To increase the performance of SBAE, other synthesis strategies

and reaction conditions will be tested in a future work.

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