Development and Optimization of a Succinylated Sugarcane Bagasse for Cadmium Removal from Water

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ABSTRACT

ABSTRACT - Bioadsorbents obtained from functionalization of lignocellulosic biomass contribute to the circular economy and address environmental issues such as cadmium contamination in water. This work aimed to develop and optimize the succinylation of sugarcane bagasse catalyzed by triethylamine (SSBT) for cadmium (II) removal. An experimental design optimized the synthesis conditions (succinic anhydride (AS) mass, temperature, and time), identifying a milder and more sustainable condition (1.60 g AS, 89 °C, 2.5 h) with high adsorption capacity (q_{Cd} = 105.9 mg g^{-1}). Further evaluation revealed that 26 mol% TEA maximized carboxylic acid group insertion (3.93 mmol g^{-1}). The performance of the optimized material was comparable to literature despite significantly reduced reagent use and reaction severity, confirming its potential for application in water treatment.

Keywords: water treatment, succinic anhydride, triethylamine, cadmium, adsorption

Introduction

The increasing demand for safe drinking water is challenged by pollution from anthropogenic activities, with cadmium being a primary contaminant of concern due to its high toxicity (1). The circular economy promotes the valorization of agro-industrial residues, such as sugarcane bagasse (SCB), into value-added products (2). Chemical modification of SCB by introducing carboxylic acid groups via esterification with SA can produce highly effective adsorbents for cationic metals (3,4). This work revisits the succinylation of SCB, using triethylamine (TEA) as a more sustainable catalyst than the traditionally used pyridine, due to its lower toxicity, higher biodegradability, and greener synthesis (5,6), aiming to develop an efficient adsorbent for water cadmium removal.

Experimental

Materials

SCB (100-mesh), SA, *N*,*N*-dimethylformamide (DMF), and TEA were used.

Synthesis of Succinylated Sugarcane Bagasse Catalyzed by Triethylamine (SSBT)

SSBT was synthesized by reacting 1.0 g of pretreated SCB with SA in DMF, using TEA as a catalyst.

Design of experiments

The synthesis optimization of SSBT, shown in Figure 1, was evaluated by a 2^3 experimental design. Three independent variables were evaluated: time (t, min), temperature (T, ºC), and mass of SA (m_{SA}, g).

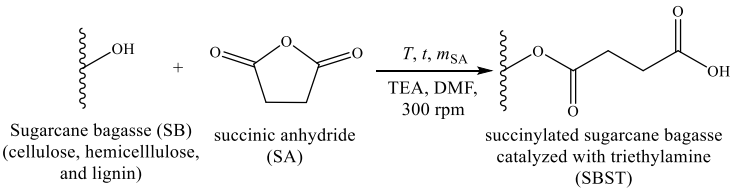

Figure 1. Synthesis scheme of SBST.

Catalyst variation

The effect of the catalyst was also studied by varying the TEA concentration (13, 26, 65, and 130 mol% of SA).

Characterization

Weight gain (wg) was determined gravimetrically. The number of carboxylic acid groups ($n_{T,COOH}$) was quantified by acid-base back-titration. FTIR spectroscopy was used to confirm the functionalization.

Adsorption Experiments

The cadmium adsorption capacity (q_{Cd}) was determined from batch experiments carried out at pH 7.00 ± 0.01, using an initial cadmium concentration of ~22.5 mg L^{-1}.

Results and Discussion

The synthesis of SSBT was optimized using a Doehlert design to maximize the q_{Cd}. The desirability function, which models each response variable individually and combines them into a single performance metric, referred to as global desirability (GD), identified two optimal conditions: a more severe condition (GD = 0.92) and a milder one (GD = 0.90) (Figure 2).

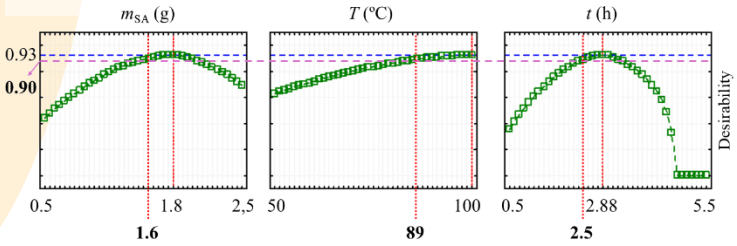

Figure 2. Desirability profile for the optimization of the q_{Cd} for SSBT synthesis.

Upon experimental validation, both materials showed nearly identical adsorption capacities: the material obtained from the severe condition had a q_{Cd} of 108.8 ± 3.20 mg g^{-1}, while the material obtained from the milder condition had a q_{Cd} of 105.9 ± 0.93 mg g^{-1} (Table 1). Given the comparable performance, the milder synthesis condition (1.60 g SA, 89 ºC, 2.5 h) was selected as the optimum condition for further studies.

Table 1. Results of the material synthesis performed under the GD conditions established in the experimental design.

Material	*wg* (%)	$n_{T,COOH}$ (mmol g^{-1})	q_{Cd} (mg g^{-1})
0.92 GD	48 ± 3	3.75 ± 0.01	108.8 ± 3.2
0.90 GD	38 ± 1	3.93 ± 0.01	105.87 ± 0.93

The influence of the catalyst (TEA) concentration was then investigated. As the TEA concentration increased from 13 to 130 mol%, the *wg* increased steadily from 31.1 to 43.2% (Figure 3). However, the $n_{T,COOH}$, which dictates the active sites for adsorption, peaked at 3.93 mmol g^{-1} with 26 mol% TEA and then slightly decreased at higher concentrations. This indicates that 26 mol% is the optimum catalyst loading to maximize functionalization (and avoid diesterification).

This suggests that excessive TEA concentrations may promote intermolecular diesterification between carboxylic groups inserted and unreacted hydroxyls, as previously reported (7), reducing the number of active sites and limiting adsorption capacity.

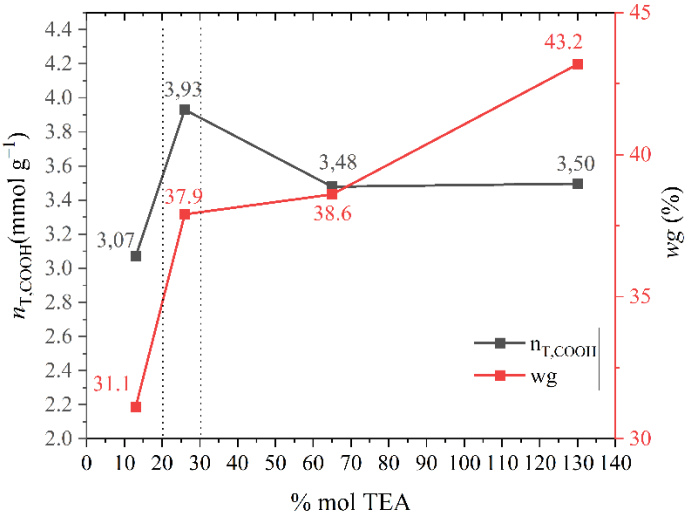

Figure 3. Influence of TEA concentration on the number of carboxylic acid groups ($n_{T,COOH}$) and weight gain (*wg*) of the SSBT.

The *wg* values ranged from 12.5 to 45.6%, with higher values observed in reactions conducted under increased m_{AS}, *T*, and *t*. The $n_{T,COOH}$ varied from 2.32 to 4.00 mmol g^{-1}, and notably, harsher reaction conditions did not always result in higher $n_{T,COOH}$ values, corroborating literature reports on intermolecular diesterification.

FTIR analysis confirmed esterification by intensified bands at ~1720 cm^{-1} (C=O stretching of carboxylic acids and esters) and ~1155 cm^{-1} (C–O–C stretching of esters) (8), along with broadening and decreased intensity of the O–H band at ~3340 cm^{-1}, indicating partial conversion of hydroxyls into esters.

The material obtained with GD of 0.90 was compared to a similar succinylation performed by (9) using 2.5 g of SA, 24 mL of pyridine, 115 ºC and 18 h. This represents a 36% SA reduction, 23% lower temperature, and 7.2-fold shorter reaction time. Catalyst volume was 97.5% lower, however pyridine acted both as catalyst and solvent, whereas in our study TEA was used solely as catalyst. Even under milder conditions, our material showed slightly higher $n_{T,COOH}$ (3.93 *vs*. 3.83 mmol g^{-1}), though lower q_{Cd} (105.87 *vs*. 196 mg g^{-1}). The higher performance in (9) likely stems from $NaHCO_3$ pretreatment, which enhances surface deprotonation. However, such a step may limit its suitability for domestic use, as it could result in Na^+ release into the treated water, besides, requiring more complex preparation.

Conclusions

The optimization of succinylation conditions was justified by economic and environmental concerns. TEA proved to be an effective and more sustainable catalyst for the functionalization of SCB. The material obtained under mild conditions showed a high $n_{T,COOH}$ and significant q_{Cd}. These characteristics highlight its potential for application in the treatment of cadmium contaminated water, and, in future studies, its applicability may be extended to other cationic contaminants.

Acknowledgments

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