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Chemical Modification of Sugarcane Bagasse with Chitosan for the Removal of Phosphates in Aqueous Solution

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Abstract. Sugarcane bagasse is the major solid waste product of the sugarcane industry. As a plant-derived biomass, it is an attractive environmentally friendly alternative to petroleum-based materials. Being a non-food agriculture product, its use as a raw material is more widely accepted. Sugarcane bagasse is comprised mainly of cellulose, hemicellulose and lignin. The aim of this study was to develop a low-cost anion exchange adsorbent from sugarcane bagasse for the removal of phosphates in aqueous solution. The adsorbent was developed by crosslinking chitosan with cellulose that was extracted from sugarcane bagasse. To obtain cellulose for covalent linkage with chitosan, the bagasse was pretreated with dilute sodium hydroxide and sulphuric acid solutions followed by bleaching with hydrogen peroxide. After this process, the material was modified using chitosan functionalized with epichlorohydrin to obtain the modified bagasse (SCB-CS). SCB-CS was characterized using Fourier transform infrared spectroscopy (FTIR) analysis that indicated the successful reduction in the content of lignin and hemicellulose. The grafting of chitosan derivatives within the matrix of cellulose was confirmed by intense peaks at 1651 cm^{-1} and 1589 cm^{-1} observed on the modified SCB-CS. SCB-CS was evaluated for its ability to remove phosphates from synthetic waste water and 61.51% removal and an adsorption capacity of 52.33 mg/g, where the initial concentration was 28.36 mg/L at an adsorbent dosage of 0.1 g was achieved.

INTRODUCTION

The biomass wastes from agricultural sector have been identified as environmentally sustainable alternatives to fossil fuels-based resources [1]. The main environmental advantage of agricultural wastes is that they are biodegradable [2]. Bagasse, obtained after the extraction of juice from the sugarcane plant, is one of the most favored and abundant plant-derived solid waste [3]. It is mainly composed of cellulose, lignin and hemicellulose which are fractionated to produce various products [4]. Sugarcane bagasse wastes are often burnt to produce energy [1]. However, a large fraction remains unutilized and for which alternative applications need to be found especially to improve the economic viability of the sugar industry. Many recent studies have focused on modifying sugarcane bagasse to adsorbent products like biochar [5] and activated carbon [6] for waste water treatment.

The adsorption technology is preferred to other technologies such as biological, chemical precipitation and ion exchange due to its simplicity during operation [7]. Phosphates are a major contaminant in waste water and although they are critical to plant growth, their presence in excess reduces the quality of surface water and causes

eutrophication [5]. Extensive studies are undertaken to develop low-cost adsorbent from agricultural wastes to remove this anion [8]. In most cases, the chemicals used to modify sugarcane bagasse are either expensive or themselves not environmentally friendly.

This study focused on modifying sugarcane bagasse using chitosan, which is a natural biopolymer derived by deacetylation of chitin [9]. Chitosan has almost similar properties with cellulose, except for the presence of amine groups with cationic potentials that allows it to bind anions like phosphate. Chitosan and cellulose have been used to produce different types of materials, including films [10] and beads [11]. Mahaninia and Wilson [12] developed chitosan beads crosslinked with epichlorohydrin and glutaraldehyde for the adsorption of phosphates in aqueous solution, with the former crosslinker exhibiting a maximum uptake of 52.1 mg/g. Sargin, Arslan and Kaya [11] produced glutaraldehyde chitosan/algal (*Cladophora sp.*) composite microbead for the removal of heavy metal ions in aqueous solutions. Few studies have focused on the adsorption of phosphates using cellulose-chitosan composite. Here, we report on the preparation, characterization and phosphate adsorption of sugarcane bagasse-chitosan composite. The main aims of this study were: (i) to chemically crosslink the cellulose from sugarcane bagasse with chitosan and (ii) to test the phosphates removal activity of the bio-composite in synthetic wastewater.

MATERIALS AND METHODS

Materials

Sugarcane bagasse was obtained from private individuals as household waste whereas chitosan (CS) was purchased from Sigma-Aldrich, China. All other chemicals were purchased from Sigma-Aldrich, Germany, and of analytical grade. All the standard solutions were prepared using distilled water in the appropriate volumetric flasks.

Pretreatment of Sugarcane Bagasse

The sugarcane bagasse was pre-treated according to the method adopted by Candido et al. [1] with minor modification. The dried sugarcane bagasse was first washed using an aqueous solution of ethanol (50%, v/v) to remove dirt before it was dried at 60 °C in an air oven for 24 hours. Subsequently, a three-stage pretreatment was executed. In the first step, the dry milled sugarcane bagasse was added into a round bottom flask containing an aqueous solution of NaOH (100 mL, 10% w/v), with the solid : liquid ratio of 1 : 10 (w/v) and stirred for 1 hour at 100 °C under reflux. The mixture was then washed with distilled water (100 mL). In the second step the NaOH-treated sugarcane bagasse was added into a 250 mL round bottom flask containing an aqueous solution of H₂SO₄ (200 mL, 10% v/v) with a solid to liquid ratio of 1 : 10 (w/v) and the mixture was stirred for 1 hour at 100 °C under reflux. Next, the material was washed with distilled water (100 mL) and vacuum filtered through a sintered glass funnel. Finally, the sugarcane bagasse was added into a round bottom flask containing an aqueous solution of H₂O₂ (5% v/v)/NaOH (1.5 M) (1 : 1; v/v), with the solid : liquid ratio of 1 : 10 (w/v) and stirred for 30 minutes at 80 °C. The pre-treated material was then washed with distilled water (100 mL) and dried at 70 °C in a vacuum oven.

Preparation of Crosslinked Sugarcane Bagasse-Chitosan Bio-Composite

The pretreated sugarcane bagasse was immersed in a solution of NaOH (1.5 M) for about 2 hours at 60°C to activate the surface area, with a solid: liquid ratio of 1 : 10 (w/v), vacuum filtered and washed with distilled water (100 mL) to remove excess of NaOH. Subsequently, the washed material was suspended in distilled water (10 mL) for 3 hours with magnetic stirring at room temperature. Separately, chitosan was derivatized before blending with the previously prepared sugarcane bagasse suspensions. Briefly, chitosan (0.7 g, 4.4 mmol) was added into a three-neck round bottom flask containing aqueous acetic acid (40 mL, 1% v/v) and stirred at 60 °C for 2 hours. This was followed by the addition of a few drops of NaOH (0.5 M) to adjust the pH of the solution to ~5 before diluting with DMF (2 mL). Subsequently, epichlorohydrin (683 µL, 8.74 mmol) was added to the solution and the mixture was stirred at 60 °C for about 3 hours. The chitosan solution was slowly added into the flask containing the suspension of activated sugarcane bagasse (3.67 wt%) and DMF (8 mL) was added again and stirring of the mixture was

continued at 600 rpm for the next 12 hours at 60 °C. The total volume of DMF added into the mixture solution was 20%. Pure acetone was added to the solution to a solid : liquid ratio of 1 : 40 (w/v) to precipitate the solid material.

The solution was centrifuged, washed with an aqueous solution of acetone (50 mL, 1 : 1 (v/v)) and dried in a vacuum oven at 70 °C for 24 hours. The material is denoted SCB-CS in this report. For comparison purposes, the chitosan was functionalized with epichlorohydrin, the material is denoted CS-EPI. The modified non-crosslinked sugarcane bagasse chitosan was also prepared to investigate the effect of adding the cross-linker, the material is denoted SCB/CS.

Characterization of Modified and Unmodified Sugarcane Bagasse-Chitosan Composite

The functional groups of the unmodified and modified bio-composites were examined using the Fourier Transform Infrared (FTIR) spectroscopy. About 1 mg of the adsorbent was placed on an attenuated total reflectance (ATR) accessory attached to a Perkin Elmer 100 FTIR spectrometer. The IR spectra were ran between 400 and 4000 cm^{-1} .

Adsorption Study of Phosphates

The adsorption study was conducted to investigate the removal of phosphates using modified biocomposite. The adsorbents (0.1 g) were placed in polyethylene plastic bottles containing 30 mL of phosphates stock solutions (28.36 mg/L). The suspensions were agitated using a thermostatic shaker at a speed of 200 rpm for about 5 hours at 25 °C. The effect of pH on epichlorohydrin crosslinked sugarcane bagasse-chitosan composite was investigated between pH 3 and 8. The pH of phosphates stock solutions was adjusted using HCl (0.1 M) and NaOH (0.1 M). The supernatant was filtered using 0.45 μm syringe filter. The concentration of phosphate after adsorption was measured using the molybdenum blue colorimetric method at wavelength of 880 nm using a UV-spectrophotometer [5]. The amount of the phosphates adsorbed was calculated using equation 1:

$$qe = \left(\frac{C_o - C_e}{m} \right) v \quad (1)$$

where, q_e is the equilibrium amount of phosphate adsorbed (mg/g), C_o and C_e (mg/L) are the initial and equilibrium phosphates concentrations, respectively; v is the initial volume (mL) and m is the amount of adsorbent (g). The percentage removal of phosphates was calculated by Equation 2:

$$\%removal = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (2)$$

where, C_o and C_e are the initial and equilibrium concentrations (mg/L) of phosphates, respectively.

RESULTS AND DISCUSSION

FTIR Analysis

In Fig. 1a, (I) shows the spectrum of raw sugarcane bagasse (R-SCB) with the absorption band at 3340 cm^{-1} ascribed to the hydroxyl (O-H) groups in cellulose and lignin while the peak at 2894 cm^{-1} was attributed to C-H stretching from CH_2 groups in cellulose, respectively [13]. The peak at 1730 cm^{-1} is attributed to the uronic ester bonds of hemicellulose [3], while the peak at 1510 cm^{-1} was assigned to the phenolic ring vibrations (C=C) of lignin [4]. In contrast to R-SCB, the weakening of the intensity of peaks at 1730 cm^{-1} and 1510 cm^{-1} on pretreated

sugarcane bagasse (P-SCB) were clearly observable and this confirms the successful removal of hemicellulose and lignin during the pretreatment process (Fig. 1a, II).

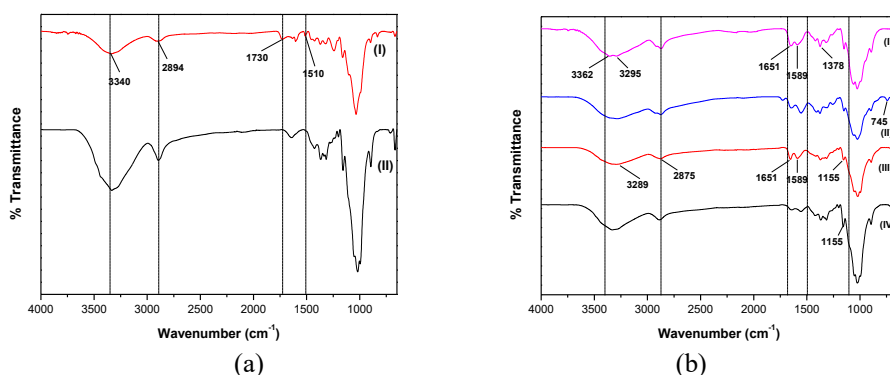


FIGURE 1. (a) FTIR spectra of (I) raw sugarcane bagasse (R-SCB) and (II) pretreated sugarcane bagasse (P-SCB); (b) (I) pure chitosan (CS), (II) functionalized chitosan (CS-EPI), (III) crosslinked modified sugarcane bagasse chitosan (SCB-CS) and (IV) non-crosslinked sugarcane bagasse chitosan (SCB/CS)

The FTIR spectrum of pure chitosan shown in Fig. 1b, (I) present absorption bands at 3362 cm⁻¹, 3295 cm⁻¹ and 2859 cm⁻¹ that are attributable to the O-H, N-H and C-H groups, respectively [11]. The vibration peak at 1651 cm⁻¹ was attributed to the C=O and N-H stretching of the amide group, whereas the band at 1589 cm⁻¹ correlates to the NH₂ functional group [7]. Figure 1b, (II) shows the spectrum of chitosan functionalized with epichlorohydrin (CS-EPI). The reduction of peak intensity at 3362 cm⁻¹ and 3295 cm⁻¹ could be due to the reaction of amine group (NH₂) and hydroxyl group (OH) with the carbon of epichlorohydrin, whereas the new absorption band observed at wavelength 745 cm⁻¹ is ascribed to the stretching of chloride (Cl). Figure 1b, (III) shows the spectrum of modified crosslinked sugarcane bagasse (SCB-CS) and Fig. 1b, (IV) exhibit the spectrum of modified non-crosslinked sugarcane bagasse (SCB/CS). The peaks at 1651 cm⁻¹ and 1589 cm⁻¹ are attributed to the C=O and N-H stretching of the amide and amine bending vibration of chitosan grafted on both composite. However, the crosslinked sugarcane bagasse composite shows the reduction of peaks intensity at 3289 cm⁻¹ could be due to the covalent crosslinking of the hydroxyl groups with carbon of epichlorohydrin. Whereas the reduction of peak intensity at 1155 cm⁻¹ is due to the reaction of β(1 – 4) glycosidic bond (C-O) with the carbon of crosslinking agent to form C-O-C bond. Moreover, the peak at 1651 cm⁻¹ is more intense which could be due to the amino groups of chitosan crosslinked on the surface of sugarcane bagasse [11].

Adsorption Experiments

The effect of pH on the adsorption of phosphates in aqueous solution was investigated on crosslinked SCB-CS in the range of pH 3.0 to 8.0 as shown in the Fig. 2.

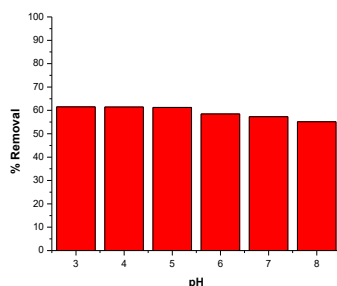


FIGURE 2. Effect of pH on the adsorption of phosphates using crosslinked modified sugarcane bagasse-chitosan composite

As shown in Fig. 2, the removal percentages of phosphates decreased inversely with pH. High removal was observed at pH 3 to 5, which could be due to the prevalent species of H_2PO_4^- and HPO_4^{2-} in this region [8]. The amines ($-\text{NH}_2$) of chitosan are protonated at acidic pH below their pKa of 6.5 [9]. Adsorption would therefore be due to the ionic attraction between the cationic amines and anionic phosphates.

CONCLUSION

The modification of sugarcane bagasse with the biopolymer chitosan was successfully achieved; the FTIR confirmed the presence of amine functional groups.

The adsorption experiment shows that the modified sugarcane bagasse-chitosan composite has the potential to be used as a low cost eco-friendly adsorbent for the removal of phosphates in aqueous solutions. However, more batch studies are required to further validate the performance of this material.

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