

Postconsumer HDPE/Agave fibre Composites Coated with Chitosan used for Removal of Heavy Metals

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1. Abstract

Composites of post-consumer high density polyethylene (HDPE) with agave fibre were prepared by extrusion and coated with chitosan. The absorption capacity of the composite coated with chitosan (CCC) was evaluated for Cd(II) and Cu(II). CCC was characterized by SEM, ATR-IR and XPS. Atomic Absorption Spectroscopy was used to measure metal uptake after contact with solution in batch studies. The equilibrium isotherms were described by the Langmuir model. Experimental results show the composite's ability to immobilize chitosan on its surface and capacity to adsorb metal ion. CCC represents an attractive low cost recycled material to adsorb metal ions from polluted waters.

2. Introduction

Composites of natural fibres with thermoplastic materials provide engineers new options for novel product developments. One of the principal purposes of composite production is to improve the mechanical properties of matrix, e.g., reinforcing its toughness and strength.

The removal of heavy metals from wastewater is an important industrial challenge as well as of concern to human health. Several solid extractants have been proposed for the removal of heavy metals from aqueous streams. However, the use of these materials presents disadvantages of both high synthesis and operational costs.

Currently, natural fibers or biopolymers are been used to adsorb metals from wastewater. Among them, Chitin and chitosan are used for metal ions recovery due to their excellent metal chelating properties [1,2]. Chitin is obtained in large quantities from wasted crustacean shells of seafood processing industries whereas chitosan is obtained from deacetylation of chitin.

Pure chitosan is soft and has the tendency to agglomerate or to form gels in aqueous solutions; exhibits low mechanical strength and is difficult to manipulate [3]. On the other hand, chitosan has been coated on different rigid supports used as an affinity matrix. In this study it is proposed the use of composites as support material for chitosan and their application in the removal of heavy metals from polluted waters.

3. Experimental

3.1 Materials. Agave fibres used for this study were residues from tequila production industries (Jalisco, Mexico). The High-density polyethylene (HDPE) is from scrapped milk bottles. Both agave fibers and HDPE were washed, dried and milled before processing. Azodicarbonamide (ACA) at 0.5% wt was used as the chemical blowing agent to produce foams in the composite. Powder chitosan with an average particle size of 173 μm was used. Stock solutions containing Cd(II) and Cu(II) ions were prepared by dissolving CdO and CuO respectively. Alkali and acid solutions for chemical treatment were prepared with NaOH, HNO₃ and CH₃COOH.

3.2 Composite Preparation. The agave fibre treatment process is described elsewhere [4]. After this treatment, the fibres were compounded with recycled HDPE in a Haake Rheomex 254; composition was set at 30% wt of fibre and 70% wt HDPE. The extruding temperature profile was 150, 160, 175 and 170°C, at 20 rpm screw speed. The pellets of the composites were subject to a chemical treatment (details are elsewhere [5]) which consisted of immersion in an alkali bath (a 10% wt NaOH solution) for 24 h followed by immersion for 3 h in a 2% V/V CH₃COOH solution. 100g of dried pellets were immersed into 500 mL of a 2% wt chitosan solution, thus allowing the solvent to evaporate and promoting the incorporation of chitosan as a film on the surface of pellets. The composite coated with chitosan (CCC) was repeatedly washed with distilled water to remove excess chitosan (until the pH of washings remained unchanged) and dried at 60°C prior to use. Surface morphology of CCC was studied employing Scanning Electron Microscopy (SEM). Additionally the treated composite was characterized using Attenuated Total Reflectance infrared spectroscopy (ATR-IR).

3.3 Adsorption Experiments. Experiments were conducted independently for copper and cadmium in a batch mode at a pH range of 4.0-7.0. This is the pH range at which many wastewaters from industries are disposed. Initial solutions were prepared (10-1000 mg L⁻¹ for cadmium and 50-400 mg L⁻¹ for copper) and fixed pH (4.0, 5.0 and 6.0 for copper; 4.0, 6.0 and 7.0 for cadmium) by dilution from the stock solution. The pH was adjusted with NaOH or HNO₃. Adsorption experiments were carried out in 15 mL glass vials by contacting (2h for Cu(II) and 24h for Cd(II)) about 1g of composite sample (CCC) with 10 mL of each metal initial solution in a reciprocal Barnstead Shke5000-7 shaking water bath at 298K. The pH of

initial and final solutions is measured and the solutions analyzed for total metal concentration with an Atomic Absorption Spectrophotometer. The amount of metal adsorbed on the surface of both composites is calculated by a mass balance given as:

$$q = \frac{V}{w} ([Me(II)]_0 - [Me(II)]_{eq}) \quad (1)$$

where *Me* refers to the metal (Cu or Cd), *q* is the amount of metal adsorbed in mg g⁻¹, $[Me(II)]_0$ and $[Me(II)]_{eq}$ are the concentrations of metal in the initial and final solutions (mg L⁻¹), respectively, *V* is the volume (L) of solution containing the metal ions and *w* is the weight (g) of composite. Composite samples after contacted with copper and cadmium ion solutions were identified as CCC-Cu and CCC-Cd, respectively.

3.4 XPS Analysis. XPS (*X-ray Photoelectron Spectroscopy*) was used to determine the chemical states of the surface functional groups. The XPS data were obtained using a ThermoElectron instrument with a XPS110 electron analyzer employing non-monochromatic Mg X-rays ($h\nu=1253.6$ eV). The calibration of the binding energy (E_{BE}) of the spectra was performed with the C 1s peak of the carbons due to atmospheric contamination, which is at 284.6 eV. The XPS peaks were decomposed into subcomponents using the software AAnalyzer v 1.07.

4. Results and discussion

Chemical treatment to the pellets was given to improve its affinity towards chitosan. The Figure 1 shows micrographs of the composite with and without chitosan. White regions can be observed in Fig. 1b after the washing step, which can be attributed to chitosan on the pellet surface and into the pores. Chitosan incorporation is mainly due to surface modifications during chemical treatment. The exposure of fibres in addition to the cavities obtained during processing resulted on an irregular surface, improving surface area (over a smooth pellet) and chitosan anchoring capacity.

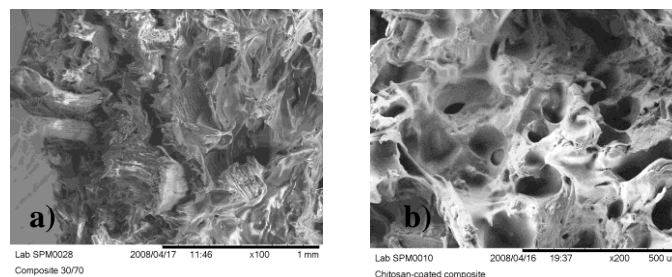


Figure 1. Micrographs showing white regions (b) caused by the treatment effect on the composite surface. a) without chitosan b) with chitosan.

ATR-IR analysis indicated that the alkali and acetylation treatments applied to the composite increased the presence of reactive hydroxyl, carbonyl and carboxylic groups, on the surface (data not shown) [6]. The effect of pH on Cd(II) and Cu(II) ions adsorption by CCC is shown in Figure 2a and b respectively. In the case of cadmium uptake, it is observed that effective cadmium extraction starts at pH 4.0 for equilibrium cadmium concentrations of ~20 mg/L whereas in the case of Cu uptake, effective copper extraction starts at pH 4.0 for equilibrium Cu concentration of 8 mg/L.

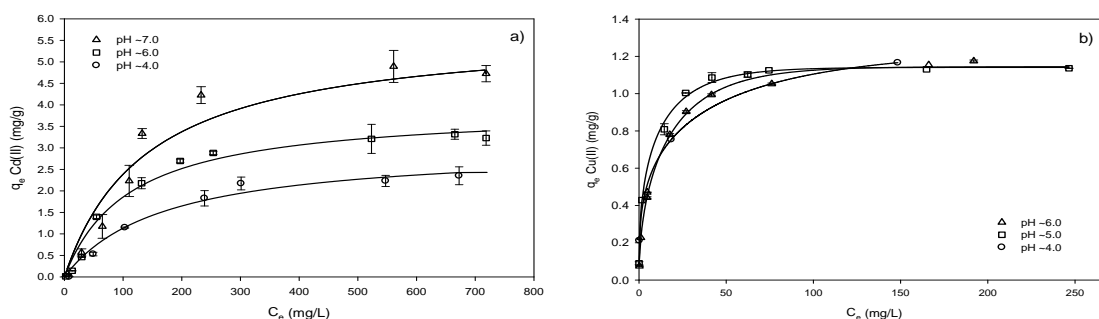


Figure 2. Results of fitting experimental adsorption data to the Langmuir isotherm including the effect of solution pH on adsorption extent of (a) Cadmium and (b) Copper on CCC. Continuous line: Langmuir model predictions; symbols: experimental data.

The Langmuir adsorption isotherm represented by the linearized equation was employed here to fit the experimental adsorption data [7]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (2)$$

where q_e is the solid phase metal concentration (mg/g), C_e is the aqueous phase metal concentration at equilibrium (mg/L), q_{\max} is the maximum uptake of metal (mg/g) and b is a coefficient related to the strength of adsorption. Maximum uptakes of 4.78 mg/g for Cd and 1.20 mg/g for Cu are observed at pH values of 7.0 and 6.0, respectively. The change of solution pH is attributed to exchange of released H^+ ions between the surface of CCC and the solution. In the case of chitosan, the main functional group responsible for metal ion adsorption is the amine group ($-NH_2$) as will be demonstrated from the XPS results. As the pH increases, the protonation of amine groups may occur, resulting in a decrease of competition between proton and metal species for surfaces sites of the CCC. Depending on

the solution pH, these amine groups can undergo protonation to NH_3^{3+} or $(NH_2-H_3O)^+$ [8], the $-NH_2$ group of the chitosan has one pair of electrons from nitrogen, which primarily act as an active site for the formation of chitosan-metal-ion complex.

Table 1. Results of regressed parameters of the Langmuir adsorption isotherm at 298 K.

Metal ion	Material	pH	b (L/mg)	q_{max} (mg/g CCC)	q_{max} (mg/g Chitosan)	R^2
Cd(II)	CCC ^{a)}	4.0	0.0056	3.030	98.1	0.9761
	CCC	6.0	0.0125	3.667	118.7	0.9981
	CCC	7.0	0.0485	4.785	154.8	0.9966
	C ^{b)}	7.0	0.0565	0.253	---	0.9807
	CF ^{c)}	7.0	0.0275	416	416	0.9451
Cu(II)	CCC	4.0	0.1715	1.207	39.1	0.9961
	CCC	5.0	0.3480	1.150	37.2	0.9996
	CCC	6.0	0.1315	1.208	39.1	0.9988
	C	6.0	0.0083	0.207	---	0.9724
	CF	6.0	0.0014	312	312	0.9473

Table 1 shows the results of the regressed parameters are presented of equation (2). For comparison with the composite (C), chitosan films (CF) were also contacted to assess the metal uptake capacity with the two metals studied and the results are shown same Table 1. The isotherms were linear over all concentrations studied, as indicated by the linear correlation coefficient (R^2). The results of this table indicate uptake values Cd(II) and Cu(II) for the materials prepared in this study. In the case of Cd(II) 4.78 mg/g of CCC or 154 mg/g of chitosan was obtained. For Cu(II) q_{max} was 1.21 mg/g of CCC or 39.1 mg/g of chitosan.

Synthesized composites are studied by XPS before and after metal deposition (cadmium or copper) to determine the chemical states of the surface functional groups as well as of adsorbed metal.

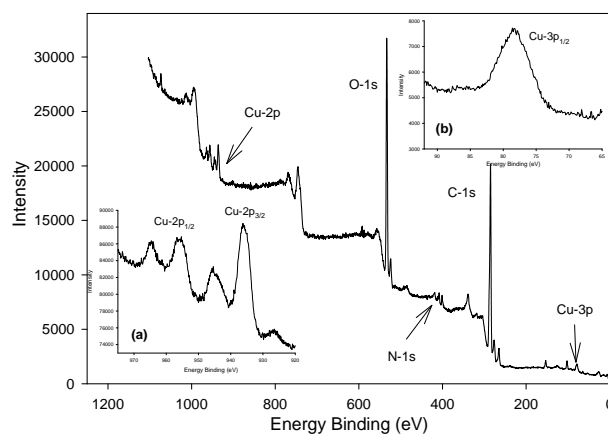
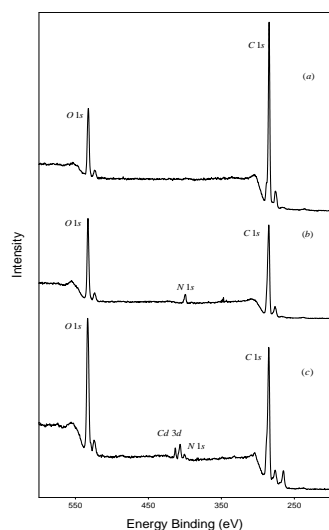


Figure 3. XPS survey scan spectra of a) composite, b) CCC and c) CCC after cadmium sorption

Figure 4. XPS survey scan spectra of composite-coated chitosan exposed to copper solution, a) Cu 2p b) Cu 3p

The Figure 3 shows the XPS spectra for composite (C) (Fig. 3a) and composite coated with chitosan (CCC) before (Fig. 3b) and after (Fig. 3c) cadmium adsorption. The predominant peaks are O 1s (532.1 eV) and C 1s (284.6 eV). The presence of N 1s in the Figure 3b corresponds to the amino group of chitosan in CCC. The Figure 3c shows Cd $3d^{3/2}$ and $3d^{5/2}$ peaks, observed for metal loaded CCC. Before cadmium adsorption, the N 1s peak was initially located at 399.1 eV, attributed to the amino nitrogen ($-NH_2$) in chitosan. On the other hand, the Figure 4 depicts the XPS survey data for CCC exposed to the copper solution. This figure shows the peak positions of carbon, oxygen, nitrogen and metal loaded present in CCC, similar to the Figure 3. The Cu-2p spectrum (Fig. 4a) of the sample showed two main peaks, which are fingerprints of divalent copper (Cu(II)). Survey scan shows peaks at 936 eV which correspond to Cu $2p_{3/2}$ and another peak at 956 eV for Cu $2p_{1/2}$.

5. Conclusions

A new application of natural fiber-HDPE composite is presented in this study. Immobilization of chitosan on the composite surface is crucial for metal ion adsorption. By coating the composite with chitosan, we created a low-cost, adsorbent which requires little processing, features good adsorption capacities for toxic metal ions removal such as Cu(II) and Cd(II) attributed to the good chelating ability of chitosan. The agave fibre and chitosan are industrial by-products and HDPE is recycled. The results of this study will certainly help to optimize and improve the processing conditions related to chitosan coating in composites, especially to increase the chitosan content.

6. References

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