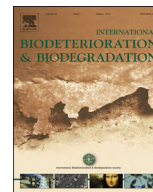




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## Utilization of corn fibers and luffa peels for extraction of pollutants from water



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### ABSTRACT

Corn fibers and luffa peels were evaluated for removing toxic heavy metal ions and dissolved organic dyes from water. Fresh peels were pretreated to remove all soluble components before using them for extraction studies. Presence of –OH and –CO<sub>2</sub>H functional groups on the surface of the peels and rough morphologies were characterized using Fourier transform infrared spectroscopy and scanning electron microscopy investigations, respectively. Corn fibers and luffa peels showed maximum extraction efficiencies within the pH range of 4–10 and adsorption reached a steady state within 2–3 h. Prewashed corn fibers and luffa peels extracted 159 mg g<sup>-1</sup> and 90 mg g<sup>-1</sup> of alcian blue, 70 mg g<sup>-1</sup> and 124 mg g<sup>-1</sup> of methylene blue, 50 mg g<sup>-1</sup> and 108 mg g<sup>-1</sup> of neutral red as well as 35 mg g<sup>-1</sup> and 40 mg g<sup>-1</sup> of coomassie brilliant blue from water, respectively. Both materials did not show significant extraction affinity towards heavy metal ions such as Pb<sup>2+</sup> (1 mg g<sup>-1</sup>), Ni<sup>2+</sup> (4 mg g<sup>-1</sup> for corn fiber and 12 mg g<sup>-1</sup> for luffa peels), and chromate (3 mg g<sup>-1</sup> for corn fibers and 6 mg g<sup>-1</sup> for luffa peels) ions from water. The Langmuir and Freundlich isotherms were used to understand the adsorption process on the surface of the adsorbents. Langmuir isotherm model yielded the best fit for the data obtained in the study, indicating a monolayer adsorption of pollutants on the adsorbent surface. Both adsorbents can be regenerated at acidic pH and could be reused for up to five cycles without significant loss of efficiency. Our experimental results suggest that both natural materials are effective towards removing dissolved dyes from water.

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### Introduction

Pollutants such as heavy metal ions and dissolved organic compounds are highly toxic to living systems (Veglio and Beolchini, 1997; Ghimire et al., 2003). Such pollutants often get into local water supply chain from industrial effluents and agricultural usage and cause health hazards to living organisms (Vandevivere et al., 1998; O'Neill et al., 1999). Water purification methods such as chemical coagulation, precipitation, flocculation, activated sludge bioreactors, membrane separation and ion exchange methods have been developed to remove pollutants from water (Nawar and Doma, 1989; Veglio and Beolchini, 1997; Ghimire et al., 2003; Kumar and Bandyopadhyay, 2006b). But no single technique or ideal material exists for the removal of all pollutants from water.

Biosorbents are considered as renewable adsorbents and show potential application towards removal of a range of pollutants from water. Banana peel (Hossain et al., 2012), orange peel (Nawar and Doma, 1989; Ghimire et al., 2003; Biswas et al., 2008), grape waste, rice husk (Kumar and Bandyopadhyay, 2006a,b), tea waste (Malkoc and Nuhoglu, 2005, 2007), maize corn cob, sugarcane bagasse (Garg et al., 2007) and pine bark (Al-Asheh et al., 2000) were proposed as potential adsorbents for water purification. However, many of these studies are limited to specific pollutants and not applied for a range of toxic pollutants, which includes metal ions, dissolved organics or other pollutants. The main disadvantages for bioadsorbents are low stability and release of soluble organic compounds into water during treatment which limits their use in large scale applications. This warrants the development of efficient adsorbents that will not contaminate water by releasing soluble components during the purification. Adsorption of pollutants on the surface of biosorbents involves one or more factors such as ion exchange, complexation and electrostatic interactions (Biswas et al., 2008; Gadd, 2009). Plant based materials consisting

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of lignin, hemicellulose, phenolic compounds and flavonoids have multiple polar –COOH and –OH groups. Such functional groups act as binding sites or ion exchange sites for pollutants. The cations present in water exchange with H<sup>+</sup> of functional groups on the absorbent surface (Ghimire et al., 2003). During the extraction, electrostatic attraction between charged pollutants and functional groups of the adsorbent in the solution plays a significant role in the extraction of pollutants (Malkoc and Nuhoglu, 2005).

Here, corn fibers and luffa peels (*L. acutangula*) were evaluated for removal of heavy metal ions and dissolved dyes from water. Luffa peels contain carotenoids, oleanolic acid and phenolic compounds (Kao et al., 2012) and functional groups such as –OH and –COOH on the surface could act as potential adsorption sites for pollutants. In order to understand the adsorption mechanism and evaluate the effectiveness of the adsorbents, different adsorption and kinetic models were used to analyze the data in detail.

## Materials and methods

Alcian blue (AB), coomassie brilliant blue G-250 (BB), neutral red (NR) and methylene blue (MB), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), lead nitrate (Pb (NO<sub>3</sub>)<sub>2</sub>) and nickel nitrate (Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Sigma–Aldrich and used without further purification. Purity grades of all chemicals used were in the range of 95–99.9%. Ultrapure water was used for all experiments. Stock solutions were prepared by dissolving appropriate amounts of corresponding chemicals in water.

### Preparation of biopeel adsorbent

Fresh corn and luffa (*L. acutangula*) vegetables were bought from a local supermarket. The corn fibers were removed from the corn husks while the outer layer of green luffa fruit was carefully peeled off and cut into small pieces (0.04 cm<sup>2</sup>). The corn fibers and luffa peels were washed with water, followed by sodium hydroxide solution (0.01 M) until the washing solutions were clear. Sodium hydroxide washing aids saponification of esters, removal of chlorophyll pigments and low molecular weight species which may leach into water or interfere with extraction studies (Dhakal et al., 2005). Treated peels were washed with copious amounts of deionized water to remove trace amounts of base left on the surfaces. The fibers and peels were then sonicated with 50% isopropyl alcohol solution to remove all leachable organic species such as polyphenols. Thoroughly washed peels were dried and stored at room temperature for further characterization and extraction experiments. Alcian blue (AB), coomassie brilliant blue G-250 (BB), neutral red (NR) and methylene blue (MB) were dissolved separately in 50% methanol to prepare stock solutions. Similarly solutions of heavy metal ions (Ni<sup>2+</sup>, Pb<sup>2+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) were prepared by dissolving stoichiometric amounts of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, respectively, in Millipore water. Aqueous HCl and NaOH solutions (0.1 M) were used to adjust the pH of solution.

### Characterization of the peels

The surface structure and morphologies of the fibers and peels were established using Field Emission Scanning Electron Microscopy (SEM, JEOL JSM-6701F). Energy dispersive X-ray spectroscopy (EDS) was used in conjunction with SEM to investigate the chemical composition of the fibers and peels. The IR spectra were recorded in the range from 4000 to 400 cm<sup>-1</sup> using a Bruker ALPHA FT-IR spectrophotometer in KBr matrix. The quantitative analysis of heavy metal ions was done using a dual view optima 5300DV ICP-OES system and elemental analyses of the adsorbents were done

using an Elementar Vario Micro Cube elemental analyzer. The quantitative determination of the dyes before and after extraction was done using a Shimadzu UV-1601 UV–Vis spectrophotometer.

### Effect of solution pH

The effect of solution pH on extraction of dyes and heavy metal ions was studied by adjusting the pH from 2 to 12 by adding appropriate amounts of 0.01 M HCl or 0.01 M NaOH solution. The initial concentrations used for the dyes and heavy metal ions were 100 mg L<sup>-1</sup> and 50 mg L<sup>-1</sup>, respectively. For extraction studies, corn fibers or luffa peels (50 mg) were added to aqueous solutions (10 mL) of metal ions of different concentrations (2–400 mg L<sup>-1</sup>). All extraction experiments were conducted at room temperature (30 °C) at a neutral pH range of 6–7, using an orbital shaker at 250 rpm for 24 h until the system has reached a steady state. The solutions were filtered through 0.4 micron filter paper to get a clear filtrate, which was analyzed for determining the concentration of pollutant. The percentage removal was calculated using equation (1)

$$\text{Removal \%} = \left( \frac{C_i - C_f}{C_i} \right) 100 \quad (1)$$

where  $C_i$  and  $C_f$  are the initial and final concentration (in mg L<sup>-1</sup>) of the dye or heavy metal ions, respectively.

### Effect of initial adsorbate concentration and time

Dye solutions (1 mL) of different concentrations (2–400 mg L<sup>-1</sup>) were mixed with corn fibers or luffa peels (10 mg) in separate vials. Experimental factors such as the mass of adsorbent used, agitation speed and temperature were kept the same. The amount of pollutants adsorbed at equilibrium ( $q_e$  in mg g<sup>-1</sup>) was calculated using the equation (2):

$$q_e = (C_0 - C_e) V/M \quad (2)$$

where  $C_0$  is the initial concentration of the adsorbate,  $C_e$  is the concentration of the adsorbate under equilibrium conditions,  $V$  is the volume of the adsorbate solution in litres and  $M$  is the mass of the adsorbent used in grams. An optimum concentration of each of the adsorbate was chosen to study the effect of time on efficiency of extraction. Experiments were conducted at different time intervals (5 min, 10 min, 30 min, 1 h, 2 h, 4 h, 6 h, 12 h and 24 h) at room temperature. All data presented in the manuscript are the average data collected from triplicate experiments.

### Adsorption isotherm and kinetics studies

The equilibrium adsorption isotherms for the extraction of dyes and heavy metal ions were studied using the Langmuir and Freundlich models. The adsorption mechanisms of the various species were proposed by studying the kinetics of adsorption (Gadd, 2009; Guodong et al., 2012, 2013; Langmuir, 1916, 1918).

$$\text{Langmuir isotherm equation : } \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{Kq_m C_e} \quad (3)$$

$$\text{Freundlich isotherm equation : } \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

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