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Ion exchanger from chemically modified banana leaves

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ABSTRACT

Cation exchangers from chemically modified banana leaves have been prepared. Banana leaves were treated with different molarities of $KMnO_4$ and cross linked with epichlorohydrin and their effect on metal ion adsorption was investigated. Phosphorylation of chemically modified banana leaves was also studied. The metal ion uptake by these modified banana leaves was clarified. Effect of different varieties, e.g. activation of produced cation exchanger, concentration of metal ions was also investigated. Characterization of the prepared ion exchangers by using infrared and thermal analysis was also taken in consideration.

1. Introduction

Large quantities of low value residual are produced during the harvesting and processing of food and industrial crops. Plant residues, lignocellulosic materials, can adsorb waste chemicals such as dyes and cations in water. Agricultural residues are abundant, inexpensive and available as material sources for chemical and paper productions. It is intended to use the agricultural residues as cheap and environment friendly material for preparation of ion exchangers for removal of dyes and heavy metal ions from water (Fadhel, Sami, & Jalel, 2006; Lehrfeld, 1997; Mahnaz, Mansor, Mohamad, Mohamad, & Susan, 2012; Nada and Hassan, 2006; Nada, El-Wakil, Hassan, & Adel, 2006; Nada, El-Kady, & Fekry, 2007; Nada, Kassem, & Mohamed, 2008). Agricultural residues are a mixture of complex of polysaccharides and lignin. Some of the isolated components of these mixtures have increased value when new functionality is added (Mesfin, Maitra, & Usama, 2011; Nada, Abd El-Mongy, & Abd El-Sayed, 2009; Reza et al., 2012). Epichlorohydrin can be used as cross linking agent which effectively stabilizes agricultural residues for preparation of ion exchangers (Laszlo & Dintzis, 1994; Nada and Hassan, 2006; Nada et al., 2006). Different chemical modifications have been carried out to introduce different functional groups onto agricultural wastes to increase its ion exchange capacities, e.g. phosphorylation (Nada, Eid, Sabry, & Khalif, 2003; Nada, El-Gendy, & Mohamed, 2010), sulfonation and amidoximation (Laszlo & Dintzis, 1994; Yu Levdek, Inshakova, Miyurov, & Nikitin, 1967).

The aim of this study is to prepare phosphorylated banana leaves as ion exchanger for adsorption of metal ions. The effect of treatment of banana leaves with different molarities of $KMnO_4$ (0.2–0.8) and cross linking agent (epichlorohydrin) in phosphorylation process on the efficiency of banana leaves for metal ions uptake were investigated. The infrared spectroscopy and thermal analysis of the prepared ion exchanger are also studied.

2. Experimental

The raw material used in this work was banana leaves and delivered from El-Sharkia, Egypt.

2.1. Treatment of banana leaves

Banana leaves were ground to 125 μm particle size. The grounded banana leaves were treated with $KMnO_4$ solution of different molarities (0.2–0.8 M).

2.2. Phosphorylation of banana leaves

Untreated cross-linked banana leaves and treated grounded banana leaves with 0.8 M $KMnO_4$ were phosphorylated using phosphorous oxichloride in the presence of pyridine. 5 g of oven dry material was suspended in 50 ml pyridine and cooled to low temperature. Add 20 ml methylene chloride mixing with 5 ml $POCl_3$ to the cooled system drop by drop, then refluxed at 115 °C for

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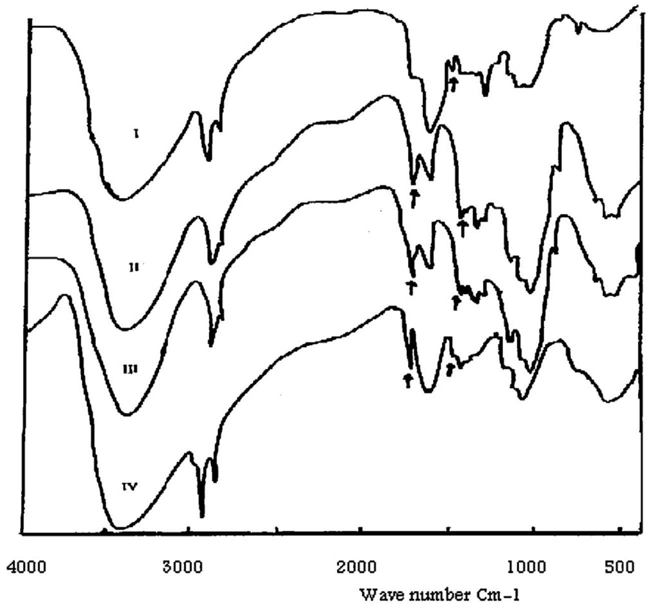

Fig. 1. Infrared spectra of I – banana leaves raw material, II – banana leaves treated with 0.2 M $KMnO_4$, III – banana leaves treated with 0.4 M $KMnO_4$ and IV – banana leaves treated with 0.8 M $KMnO_4$.

2 h with stirring. The mixture was filtered after the reaction and washed with deionized water and then with 0.1 N HCl and finally with deionized water till neutrality (Lehrfeld, 1997).

2.3. Determination of phosphorous

0.2 g of the phosphorylated material was digested in 10 ml of HNO_3; after digestion, the solution was completed to 100 ml with deionized water in a measuring flask. Phosphorous was determined using an induced coupled plasma spectrophotometer ICPES Jobin Yvon J4/84 spectrometer.

2.4. Adsorption of metal ions

0.1 g of the prepared banana leaves treated with 0.8 M $KMnO_4$, cross-linked and phosphorylated of banana leaves were stirred in 25 ml of aqueous solution containing different metal ions (Cu, Pd, Ni and Cd) each has 50 ppm (microgram) for 30 min. After stirring the mixture was filtered and the remained metal ions in the filtrate were determined using ICP spectrometer.

The metal ions adsorption (μmole/g), metal ions uptake % and partition coefficient were measured:

$$\text{Partition coefficient} = \frac{\text{Amount of ion in polymer} \times \text{Volume of solution (ml)}}{\text{Amount of ions left in the solution} \times \text{Weight of dry polymer (g)}}$$

$$\text{Percent uptake} = \frac{\text{Amount of the metal ion in the polymer}}{\text{Amount of the metal ion in the solution}} \times 100$$

2.5. Infrared measurements

Infrared for the prepared ion exchanger was obtained by using JASCO Jourier transformer infrared (FTIR) 800E spectrometer. The samples were measured using KBr disk technique.

2.6. Thermal analysis

A Perkin-Elmer thermo gravimetric analyzer was used to study the thermal properties of the ion exchange in banana leaves. Heating rate 10 °C/min over a temperature range 50–600 °C. Measurements were carried out in a nitrogen atmosphere with a rate of flow 50 cm^3/min.

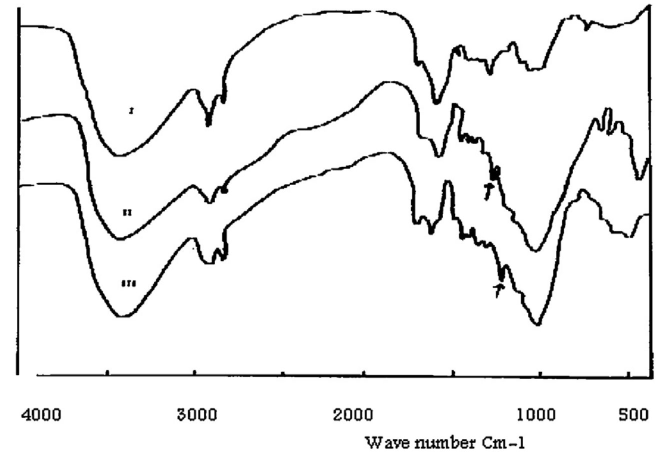

Fig. 2. Infrared spectra of I – banana leaves raw material, II – phosphorylated banana leaves and III – phosphorylated banana leaves treated with 0.8 M $KMnO_4$.

3. Results and discussion

Infrared spectroscopy of the prepared ion exchangers from banana leaves was estimated and it is shown in Figs. 1 and 2. Infrared spectroscopy is a very useful tool for obtaining information about the chemical changes taking place with the various treatments. The bands relative absorbances were determined via baseline correction. It is calculated as the band intensity at subsequent wave number to the band intensity of the wave number at 1325 cm^{-1} which is due to $-CH_2$ rocking of the ring (Yu Levdek et al., 1967).

Table 1 shows the relative absorbance of banana leaves (untreated and treated with different molarities of $KMnO_4$). From Table 1 it is seen that the relative absorbance of OH band at about 3400 cm^{-1} decreased by increasing the concentration of $KMnO_4$; this can be attributed to oxidation of OH groups with $KMnO_4$.

On the other hand, the treatment with $KMnO_4$ increases the relative absorbance of band at 1715–1710 cm^{-1} which relates to $-C{=}O$ of carbonyl group and also causes a degradation of lignin in banana leaves. This can be confirmed by the decrease in relative absorbance of band at 1500 cm^{-1} which is related to the CH vibration of aromatic ring of lignin. On the other hand the relative absorbance of β-O-linkage between glucose units of cellulose increased by treating banana leaves with $KMnO_4$.

As shown from the table, it is clear that the crystallinity index (ratio of band intensity at 1425 cm^{-1} to band intensity at 900 cm^{-1}) decreases by treatment with $KMnO_4$, this is attributed to oxidation of lignin which acts as adhesive between cellulose chains (Nelson & O'connor, 1964). This can be confirmed by calculated value of mercerization depth (ratio of band intensity at 1375 cm^{-1} to band intensity at 1325 cm^{-1}) (Laszkiewicz & Wcislo, 1990) which increased by treating banana leaves with $KMnO_4$ solution. This is attributed to the oxidation of lignin which acts as adhesive between cellulose chains and hemicellulose and also to the formation of carbonyl groups.

Table 2 shows the relative absorbance of banana leaves raw material, phosphorylated banana leaves and phosphorylated banana leaves treated with 0.8 M $KMnO_4$. From the table it is clear