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Banana leaves as adsorbents for removal of metal ions from waste water

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ABSTRACT

Banana leaves and its derivatives are used as ion exchanger. Incorporation of different functional groups, e.g. phosphate, sulfate and phosphosulfonate onto banana leaves and its constituents (lignin and cellulose) increases their efficiencies toward metal ions uptake. Effect of different treatments on bleached banana leaves as acid or alkali treatment increases the amount of incorporated functional groups. Effect of ion exchange concentration on the affinity of metal ions sorption was investigated. The binding capacity of the produced phosphosulfonate and treated banana leaves toward some metal ions in mixtures was studied. The use of ion exchangers in columns was indicated. Activation of the produced ion exchanger with acid before uses was also carried out. The increase of surface of ion exchanger by mixing with sand in columns was also investigated. Molecular structure of the produced ion exchanger was followed by using infrared spectroscopy.

1. Introduction

Ion exchanger resins are broadly employed for treatment of process water and waste water. Agricultural residues have been examined for potential use as inexpensive adsorbents (Gang & Weixing, 1998; Jacob, 1997; Nada, El-Bahnsawy, & Khalifa, 2002). The native exchange capacity and general sorptive characteristics of these materials derive from their constituents polymers. Cellulose, lignin, pictins and hemicellulose (Laszlo, 1996; Nada & Hassan, 2003). Due to low exchange capacity and poor physical stability (partial solubility) of agricultural residues it must be chemically modified (Nada & El-Wakeel, 2006), co-polymerized (Abdalla, Mohamed, & Hesham, 2007), and cross-linked (Laszlo & Dintzis, 1994). Agricultural residues are mixture of complex polysaccharides and lignin. Some of isolated components of these mixtures (cellulose and starch) have increased value when new functionality is added. For example, cationic and carboxymethylated cellulose have many industrial and commercial uses. A potential waste disposal problem would be minimized because these residues would now have some commercial utility. Multiple functional groups may be placed on the same repeating unit. These reactive sites may lead to some selective reaction of cations having a large ionic radii due to polydentate bonding. Adsorption of metal ions on residues can be attributed to intrinsic adsorption and columbic interaction. The charges on both substrates as well softness or hardness of the charges on both sides are mostly responsible for the intensity of interaction or amount of adsorption (Gang & Weixing, 1998).

The aim of the study is to prepare ion exchange resin from banana leaves. Incorporation of different functional groups onto banana leaves clarified. The effect of different treatments as pulping or bleaching to prepare unbleached and bleached banana leaves pulp on the functionality of banana leaves was also studied. On the other hand, The effect of different treatments e.g. acid or alkali treatment on the quantity of functional groups e.g. phosphate and sulfate incorporated onto bleached pulp is determined. The use of the produced ion exchanger in column was carried out. The mixing of ion exchanger with sand in column was also studied. The infrared spectroscopy was used as a tool to follow the molecular structure of banana leaves resin.

2. Experimental

Raw material used in this study was banana leaves. It was grounded to particle size of 100–400 μm.

2.1. Analysis of banana leaves

a- lignin was determined according to (TL3Wd-74).
b- isolation of holocellulose (cellulose in this study) and determination of α-cellulose.
  - In this work holocellulose was prepared by the acetic acid sodium chlorite according to (Wise, Murphy, & D'Addieco, 1946) by using sodium chlorite as delignifying agent, after extracting the raw material with alcohol–benzene mixture, the experimental conditions used were as follows:5 g of the air-dried extracted material was treated with 150 ml of warm solution of (70 °C) containing 1.5 g sodium chlorite (100%) and 10 drops of glacial acetic acid at 70 °C for 1 h. Then another 10

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drops of glacial acetic acid and 1.5 g sodium chlorite were again added and this was repeated three times. The white holocellulose was cooled in ice then filtered and washed on a sintered glass funnel with cold distilled water. The holocellulose was finally washed with 50 ml acetone and dried under vacuum to constant weight.

- α-cellulose was determined according to German standard methods, Merkblatt Zellochems (Jayme et al., 1958).

c- Hemicelluloses was determined according (T19 wd-7).

d- ash was determined according (T15 wd 80).

2.2. Pulping

Banana leaves (ground) were cooked in autoclave contains 6 stainless cups (2 l capacity) rotating in ethylene glycol bath. Pulping was carried out using 20% NaOH (based on raw material) and 5:1 L.R. at 160 °C for 2 h. After pulping, the pulp separated from black liquor and washed till neutrality. Lignin was precipitated from waste black liquor using 10% H_2SO_4 After precipitation it was filtered and washed with distilled water till neutrality and then air dried.

2.3. Bleaching

Bleaching of banana leaves pulp was carried out in three stages to remove the residual lignin using H_2O_2 and hypochlorite system. The conditions of the bleaching process are given below:

- Hydrogen peroxide stage: this stage is carried out at 70 °C for 1.5 h at pH 10–11 at 10% pulp consistency, the yield is washed till neutrality.
- Hypochlorite stage: in this stage the pulp obtained from the previous step was treated with 4% hypochlorite solution at 60 °C at pH 11 for 2 h at 10% consistency, the yield is washed till neutrality.
- Finally, the pulp was treated with 4% hypochlorite solution at 60 °C at pH 11 for 2 h at 10% consistency.

2.4. Treatment of banana leaves

Bleached banana leaves were treated with 1 N HCl or 1 N NaOH under reflux for 1 h after treatment, filtered, washed with distilled water till neutrality and finally washed with methanol and air dried.

2.5. Preparation of cation exchanger

5 g of banana leaves was suspended in pyridine, cooled and then 5 ml of $POCl_3$ or $ClHSO_3$ was added and suspended in 25 ml methylene chloride for 2 h (Nada, Eid, Sabry, & Khalifa, 2003). After complete reaction, the contents poured in a beaker containing iced water and then filtered, washed with de-ionized water till neutrality and then with 0.1 N HCl and de-ionized water and then with methanol and air dried.

2.6. Metal ion sorption

0.1 g of the prepared resin was stirred in 25 ml of solution contain mixture of metal ions (Cr, Ni, Mn, Cu and Pb) each of them 20 ppm. For 30 min and then filtered, the remaining metal ions in filtrate were determined using ICP spectrometer.

2.6.1. Determination of P and S

P and S were determined by digestion of 0.2 g of resin in 10 ml Conc. HNO_3 with boiling then, cooled and diluted in 50 ml with de-ionized water in a measuring flask. P and S were determined using ICP spectrometer.

2.6.2. Activation of produced resin

1 g of phosphosulfonated acid treated bleached banana leaves was packed in column and another 1 g was packed in another column. One of the columns was not activated and the other was activated with 1 N HCl and then washed with de-ionized water. Through every column 200 ml of solution contain the mixture of ions (20 ppm) was passed with flow rate 10 ml/min. The remaining metal ions in solution after passing through the column were determined by using ICP.

2.6.3. Effect of resin weight on sorption of metal ions

In another trials, different weights of resin 0.1, 0.2, 0.4, 0.8 and 1 g, every weight was stirred in a solution containing a mixture of ions (50 ppm) for 30 min the metal ions in the filtrate were determined using ICP.

In another trial 1 g of the resin is packed in column and another column containing 1 g of resin mixed with sand (p.s. 100 μm) to increase the surface of the resin. Then poured in every column 100 ml of metal ion solution (20 ppm for every ion) was poured in every column and the remaining metal ion was determined in the passed solution from column using ICP.

2.6.3.1. Binding capacity. The binding capacity is determined as following, 0.2 g of resin was stirred in different concentrations of solution of mixture of Cr, Ni, Mn, and Cu (50, 100, 200, 400, 800 and 1000 ppm).

2.6.3.2. ICP: Inductivity Coupled Plasma atomic emission. Spectrometric measurements (model spectroflam).

Infrared spectroscopy: was used using JASCO FTIR -300k spectrophotometer using KBr disc technique.

3. Results and discussion

Raw material used in this work was banana leaves. It has he following analysis; lignin 16.5%, hemicellulose 22.4%, cellulose 39.2%, ash 5.2% and 4.1% wax, resin and soluble materials. The raw material derived from Al-Kalyobia government, Cairo, Egypt. Pulping with sodium hydroxide was found to be efficient in removing the lignin from banana leaves: the lignin content decreased from 16.5% to 2.7% leaves in unbleached pulp fiber. The cellulose content increased to 82.3% in unbleached pulp while the amount of hemicellulose decreased from 22.4% to 11.6%.

The three-stage bleaching process was used to increase the cellulose content in the pulp. Based on the chemical composition analysis, a majority of the lignin was removed from the bleached pulp, and the content of hemicellulose was remarkably reduced. The final bleached pulp presented cellulose content of 90.3%, a lignin content of 0.6% and a hemicellulose content of 4.8%.

3.1. Metal ions uptake by resin prepared from banana leaves incorporated with different functional groups

Different functional groups, e.g. phosphate, sulfate and phosphosulfonate were incorporated onto banana leaves. The functional groups improve the metal uptake percent from their solution. Fig. 1 shows that the metal uptake percent by banana phosphate is higher than the banana sulfate, although the incorporated phosphate groups onto banana leaves (80 mg/g) are lower than the incorporated sulfate groups (110 mg/g). This is explained by formation of sulfate group of monoanion while the incorporated phosphate group onto banana leaves is mono and dianion as shown in the

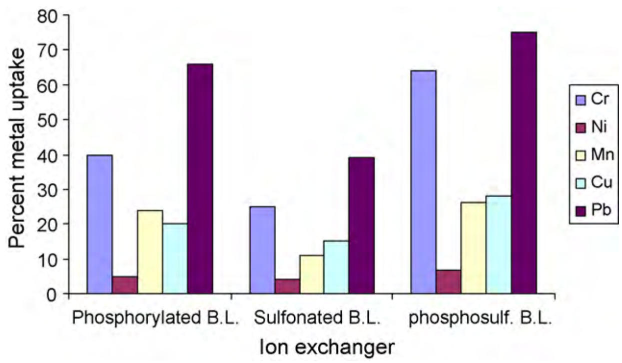
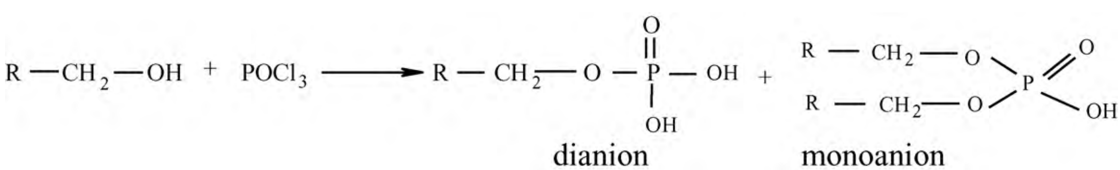


Fig. 1. Percent metal uptake by banana leaves with different incorporated functional groups.

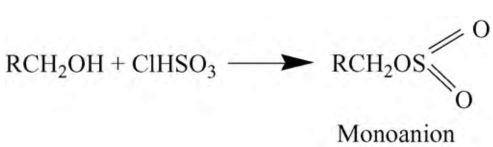
Table 1
The functional groups incorporated onto banana leaves, cellulose and lignin.

Ion exchanger	Phosphate (mg/g)	Sulfate (mg/g)
Phosphosulfonated banana leaves	65	47
Phosphosulfonated cellulose separated from banana leaves	85	60
Phosphosulfonated lignin separated from banana leaves	70	50

following equations:



(1)



(2)

The incorporation of phosphate and sulfate groups by reaction of banana leaves with $POCl_3$ and $ClHSO_3$ (4:1) produce phosphosulfonate banana leaves which results in metal uptake percent higher than phsphorylated and sulfonated banana leaves. This is due to the increase of the selectivity of the produced resin toward metal ions uptake. It was found that the sorption of metal ion is not the same, this can be attributed to intrinsic absorption and columbic interaction which results from the electro negativity of absorbents and absorbates. Also, the affinity of resin to metal ion sorption related to the charged and hydrated radius of metal ions (Weixing, Xiangjing, & Gang, 1999).

3.2. Lignosulfonation of different chemical constituents of banana leaves

Metal uptake percent by phosphosulfonated lignin and cellulose separated from banana leaves was investigated. It was found that the metal uptake percent of phosphosulfonated banana leaves is lower than that of phosphosulfonated lignin and cellulose. This is due to that, the functional groups incorporated onto banana leaves are lower than those incorporated onto cellulose and lignin (Table 1).

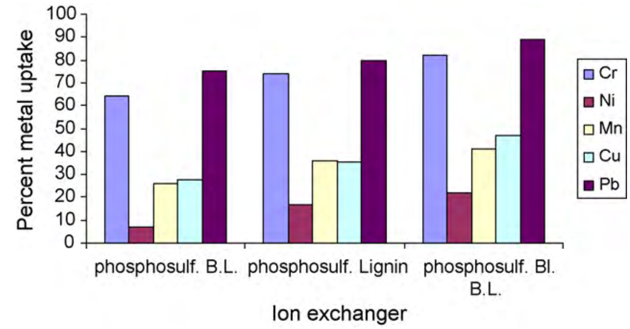


Fig. 2. Percent metal uptake by phosphosulfonated banana leaves, phosphosulfonated lignin and phosphosulfonated bleached banana leaves.

The low incorporation of functional groups onto banana leaves is attributed to its constituents (cellulose, hemicellulose, lignin and other extractives) that are associated with each other in the plant. Also lignin acts as cemented material for cellulose and hemicellulose which decreases from the porosity of banana leaves raw material. Also hemicellulose appears to be associated with both of lignin and cellulose and may be formed as intermediate barrier layer between lignin and cellulose (Boyd, Schubert, & Adamson, 1947). Metal ions uptake percent by phosphosulfonated banana leaves and its constituents was shown in Fig. 2. From Fig. 2, it is shown that, metal uptake of phosphosulfonated cellulose is higher than that in case of lignin. Hence, the efficiency of phosphosulfonated banana leaves and its constituents have the following sequence: (phosphosulfonated cellulose > phosphosulfonated lignin > phosphosulfonated banana leaves). The metal ion uptake percent of phosphosulfonated cellulose is higher than that of phosphosulfonated lignin, due to the physical structure of cellulose. In case of cellulose its chain while lignin is polymer which restricted the mobility of OH groups and consequently the reactivity of lignin lowered phosphosulfonation. Also, the OH groups in cellulose chain are higher and also more mobile than that in case of lignin.

Fig. 3 shows the metal uptake percent by phosphosulfonated banana leaves raw material, phosphosulfonated banana leaves

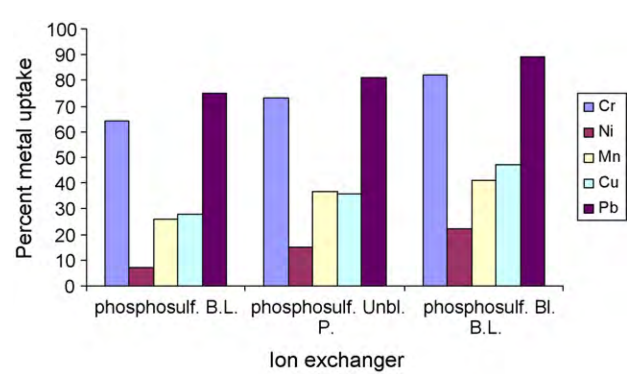


Fig. 3. Percent metal uptake by phosphosulfonated banana leaves, phosphosulfonated unbleached banana leaves pulp and phosphosulfonated bleached banana leaves pulp.

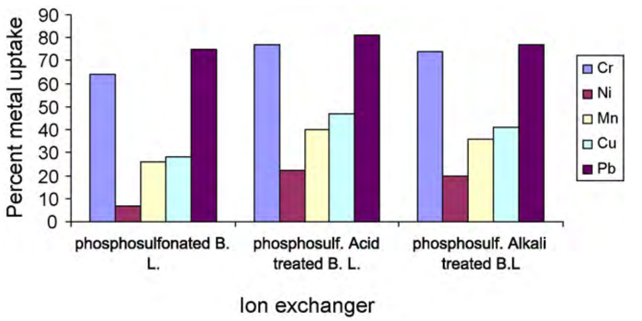


Fig. 4. Percent metal uptake by phosphosulfonated banana leaves, phosphosulfonated acid and alkali treated banana leaves.

unbleached pulp and phosphosulfonated banana leaves bleached pulp. It is seen that the phosphosulfonated banana leaves raw material has the lowest affinity toward metal ions uptake. This is due to its high content of lignin which acts as adhesive material for cellulose and hemicellulose, thus the hydrogen bonds increases between OH groups and the porosity decreases. This decreases the reactivity of the banana leaves raw material toward phosphosulfonation. In case of the unbleached banana leaves pulp the decrease of lignin content results in a decrease of the hydrogen bonds and an increase of the porosity of the pulp consequently the enhancement of the incorporation of phosphate and sulfate groups onto the pulp. Absence of lignin from bleached banana leaves pulp has high incorporated phosphate and sulfate groups than in case of unbleached pulp. So the percent of metal ions uptake by phosphosulfonated bleached banana leaves is higher than that in case of unbleached and raw material banana leaves.

3.3. Effect of treatments of bleached banana leaves pulp before phosphosulfonation

Phosphosulfonation of untreated and treated (acid and alkali) of bleached banana leaves was studied. Percent of metal uptake by these resins is shown in Fig. 4. The study of physical structure of the bleached banana leaves with these treatments is shown in Table 2.

It is seen from the table that the treated bleached banana leaves with acid has lower D.P. than the untreated and treated alkali. This can be confirmed by the increase in crystallinity index (ratio of band intensity at 1425 cm^{-1} to band intensity at 900 cm^{-1}) of the acid treated pulp is more than the others. These values are calculated from IR spectra which is shown in Figs. 5 and 6. This means that, the 1-4-β-o glucosidic link between glucose units degraded. This is calculated by the relative absorbance of C–O–C at 1120 cm^{-1} which has the lower value than the untreated and alkali treated banana leaves. This degradation increases the end groups of degraded chain and consequently increases the reactivity of the acid treated pulp toward phosphosulfonation more than the other pulp. On the other hand the reactivity of alkali treated banana leaves pulp toward

Table 2
The relative absorbance, crystallinity index and degree of polymerization (D.P.) of untreated and treated (acid and alkali) of bleached banana leaves pulp.

D.P.	Crystallinity index	Relative absorbance C–O–C	Resin
700	1.5	0.8	Phosphosulfonated bleached pulp
520	1.76	0.62	Phosphosulfonated bleached pulp treated with acid
730	1.25	0.84	Phosphosulfonated bleached pulp treated with alkali

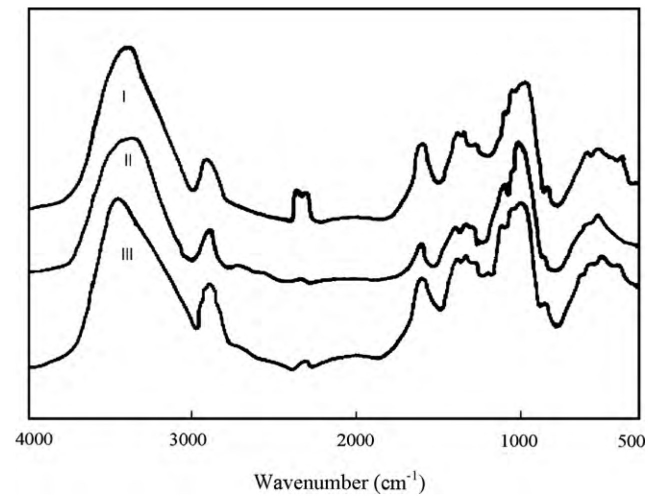


Fig. 5. Infrared spectra of I—untreated banana leaves raw material, II—acid treated banana and III—alkali treated banana.

phosphosulfonation is higher than the untreated pulp due to the increase of its swelling and increase of amorphous part which is indicated by the lower crystallinity index of the alkali treated pulp than the untreated pulp. The increase of the quantity of the phosphate and sulfate functional groups incorporated onto acid treated bleached banana leaves pulp causes an increase of its percent of metal uptake more than alkali and untreated pulp.

3.4. phosphosulfonated acid treated banana leaves in column

The prepared ion exchange resin was applied in column. The solution of mixture of metal ion (Cr, Ni, Mn, Cu and Pb) of 20 ppm for every metal ion was passed through a column contains 1 g of resin. The solution was passed in batches; every batch was 25 ml. the metal ion uptake by resin was measured after passing of every batch (Fig. 7). The rate of flow of solution through the column is 25 ml/15 min. From figure it is clear that the amount of metal ion uptake by resin decreases by increasing the number of batches passed through the column. This can be explained by the increase of occupation of incorporated phosphate and sulfate groups in resin by metal ions after every batch. On the other hand, Mn and Cr have the highest sorption by resin. Cu and Pb have the moderate metal ion uptake by resin. Ni has the lowest sorption by resin, the

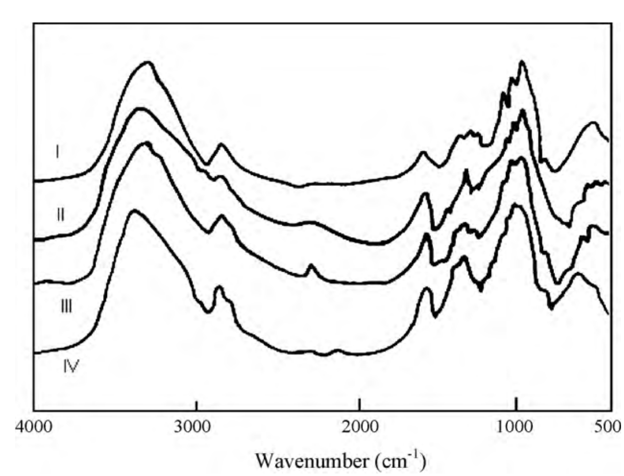


Fig. 6. Infrared spectra of I—acid treated banana leaves, II—phosphorylated acid treated banana leaves, III—phosphosulfonated acid treated banana leaves and IV—phosphosulfonated alkali treated banana leaves.

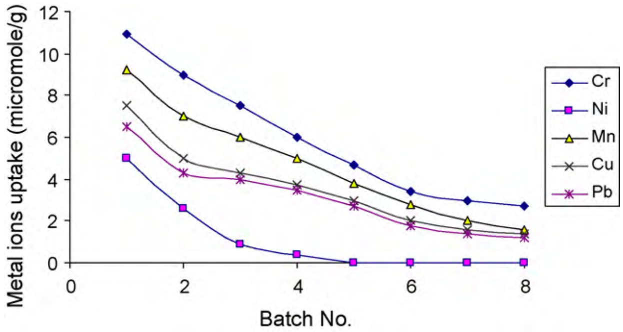


Fig. 7. Metal ion uptake (μmol/g) by phosphosulfonated banana leaves in column.

affinity of resin toward Ni sorption reaches its maximum after the third batch. The affinity of resin toward Cu, Cr, Pb and Mn sorption is continued till the end of the batches and it still has ability to sorbe metal ions. Accordingly, the tendency of phosphosulfonated bleached banana leaves pulp to absorb metal ions has the following sequence; Cr > Mn > Cu > Pb > Ni; the sorption of metal ions by resin in column is related to the charge and hydrated radius of the metal ions (Gang & Weixing, 1998).

3.5. *Effect of resin concentration on metal ion sorption*

Fig. 8 indicates the metal ion uptake by different concentrations of phosphosulfonated acid treated banana leaves. Different weights of resin ranging from 0.1 to 1.0 g were stirred, each in 25 ml of mixture of metal ions solution (Cr, Mn, Cu and Ni) 50 ppm. It is obvious from figure that the metal ions uptake increases by increasing the weight of resin. It increases sharply by increasing the weight of the resin from 0.1 to 0.2 g and then slightly increases by increasing the weight to 0.4 g. By increasing the weight of the resin more than0.4 g the metal ions uptake decreased. This proves that, the increase of the weight of the resin more than 0.4 g results in coagulation of the resin and consequently a decrease in the surface area of the resin contact with metal ions. This causes decease in sorption of metal ions by the resin. So, it is important to adjust the ratio of the weight of resin to the metal ion solution to achieve high metal ion sorption. From the figure; it is seen that Cr is slightly sorped by resin more than Mn and Ni has the lowest metal ion sorption by the resin.

3.6. *Activation of phosphosulfonated acid treated bleached banana leaves*

Three glass column, each has internal diameter10 mm and contain 1 g of the resin in two columns and the third column contains 1 g of the resin mixed with 2 g sand (250 μm). The second and the third column were activated by passing 20 ml of 1 N HCl into column and then washed with de-ionized water till neutrality. 50 ml of solution contain a mixture of ions (Cr, Mn, Cu and Ni) each one which contain the resine of 50 ppm, and the rate of flow is 20 ml/min.

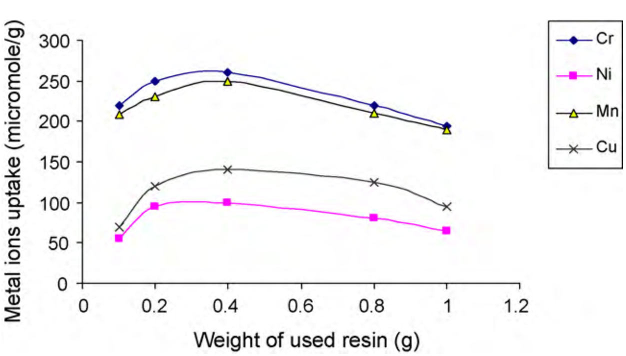


Fig. 8. Effect of weight of used resin (phosphosulfonated acid treated banana leaves) on the metal ions uptake (μmol/g).

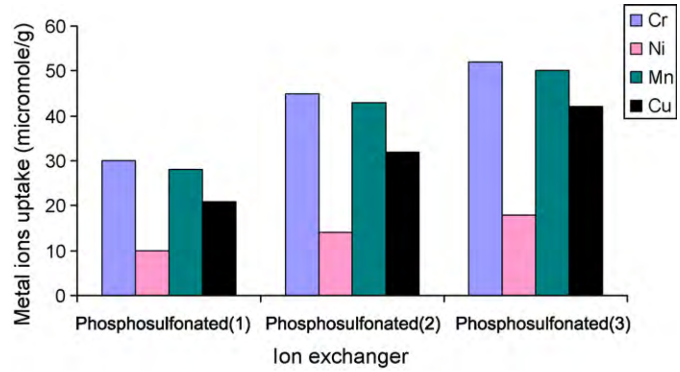


Fig. 9. Metal ions uptake (μmol/g) by using three columns, phosphosulfonated acid treated banana leaves (1), phosphosulfonated acid treated banana leaves activated with 1 N HCl (2) and phosphosulfonated acid treated with inactivated with 1 N HCl and mixing with sand.

Fig. 9 shows the metal ion uptake by the three columns which contain the resin. From the figure, it is seen that metal ion uptake by activated resin with HCl (column) is higher than that inactivated (column 1) this can be attributed to that, acid dissolves the by product formed during preparation of resin as well helps to dissolve material which causes a decrease of the efficiency of resin for metal ion sorption. Beside this, the porosity of resin in column increases by acid activation of resin. On the other hand, presence of sand with resin increases its sorption of metal ion. This is attributed to that, mixing of resin with sand increases the porosity and the surface area of the resin which consequently causes an increase of its efficiency toward metal ion sorption. On the other hand, presence of sand prevents the compatibility and adhesion between resin particles which causes an increase of penetration of metal ion solution through the resin particle which increase the contact of resin with metal ions.

3.7. *Binding capacity of phosphosulfonated acid treated bleached banana leaves pulp*

Due to the higher efficiency of phosphosulfonated acid treated bleached banana leaves pulp toward metal ions sorption than phosphorylated or sulfonated one, its binding capacity toward metal ions was determined. 0.2 g of the resin was stirred in 25 ml of solution which has different concentrations of metal ions (mix-

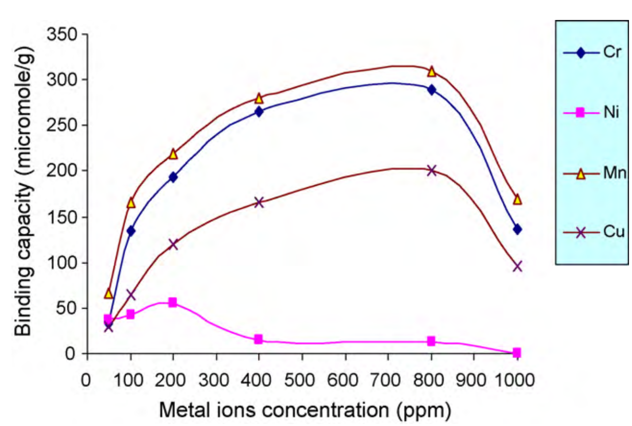


Fig. 10. Binding capacity of mixture of different metal ions (μmol/g) of phosphosulfonated acid treated banana leaves.

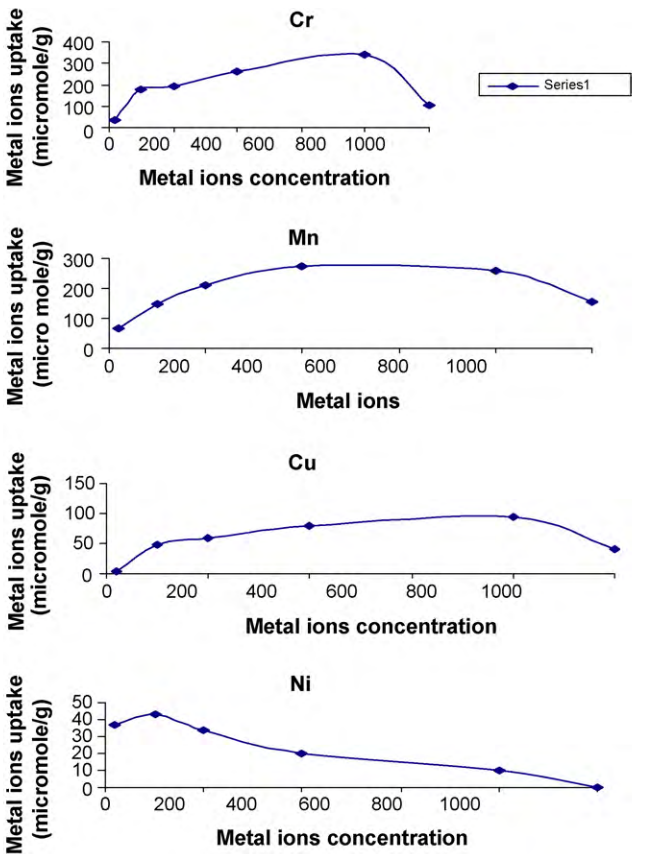


Fig. 11. Binding capacity of phosphosulfonated acid treated banana leaves for some metal ions.

ture of Cr, Ni, Mn, and Cu) 50, 100, 200, 400, 800 and 1000 ppm. Fig. 10 shows the binding capacity of the phosphosulfonated and treated bleached banana leaves pulp. It is clear from the figure that, the binding capacity of the prepared resin increased by increasing metal ions concentration. It reaches the maximum at 800 ppm for Cr, Mn and Cu and 200 ppm in case of Ni. Increasing of the metal ions concentration more than 800 ppm decreases the resin binding capacity. This is attributed to the decrease in the mobility of metal ions in solution at 1000 ppm; this lowers the contact between the resin and the metal ions which decreases the sorption of metal by resin. The metal ions sorption by the prepared ion exchanger depends on the type of metal ions. So, it is seen from the figure that Mn and Cr have the highest sorption by the resin. This is due to the probably steric and electronic effect of metal ions. The affinity of the resin to metal ion sorption is also related to the hydrated radius of metal ions (Abdalla, Nesrine, & Samar, 2008; Gang & Weixing, 1997). In addition, resin binding capacity of different metal ions is affected by the semihard acid of metal ions.

3.8. Binding capacity of phosphosulfonated acid treated bleached banana leaves pulp for some individual metal ions

The binding capacity of a mixture of metal ions in solution was discussed previously. In another study binding capacity of resin for these metal ions was discussed for every metal alone. Fig. 11 the binding capacity phosphosulfonated acid treated bleached banana leaves pulp ion exchanger of some individual metal ions (Cr, Mn, Cu and Ni). The binding capacity of resin for every metal ion alone is higher than that in mixture. So it is clear from figure that, metal ion uptake by increased by increasing metal ion concentration till 400 ppm and then slightly increased by increasing metal ion concentration to 800 ppm. The binding capacity of resin decreased by increasing the metal ion concentration to 1000 ppm. Metal ion sorption by resin depends on intrinsic adsorption and columbic interaction which results from the electrostatic energy of interaction between the absorbents and absorbates.

4. Conclusion

- Metal ion uptake percent of phosphosulfonated banana leaves is higher than phosphorylated or sulfonated banana leaves raw material.
- Phosphosulfonated bleached banana leaves pulp and lignin have higher metal uptake percent than phosphosulfonated banana leaves raw material.
- Treatment of bleached banana leaves pulp with acid or alkali increases the reactivity of bleached banana leaves pulp toward phosphosulfonation reaction.
- Acid treatment of bleached banana leaves increases incorporation of functional groups (phosphate and sulfate) more than alkali treatment.
- Mixing resin with sand in columns enhances the efficiency of resin toward metal ion uptake.
- Activation of resin with acid in column before passing the metal ions solution, increases the metal uptake sorption of the resin.
- Metal ions uptake decreases by increasing the resin weight more than 0.4 g.
- Binding capacity of phosphosulfonated acid treated bleached banana leaves pulp increases by increasing the metal ion concentration in solution till 800 ppm and then it decreases by increasing the concentration to 1000 ppm.

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