

## **SPECTROSCOPY AND CHEMICAL STUDIES OF CATION EXCHANGERS PREPARED FROM CORN COBS**

Abd Allah Mohamed Abd Allah Nada,<sup>\*</sup> Ahmed Ahmed Mahdy,<sup>\*\*</sup> and Ahmed Ali El-Gendy<sup>\*</sup>

A series of ion exchangers was prepared from corn cobs. Phosphate, sulfate, phosphosulfonate, and carboxylic groups were incorporated onto the corn cobs. The magnitude of functional groups incorporated onto corn cobs, as well as of the cross-linking, was taken as a measure of reactivity of the produced ion exchanger. The effect of treatment of corn cobs with different concentrations of sodium hydroxide, volume of used pyridine, and efficiency of the produced resin toward metal ions adsorption was investigated. The effect of cross-linking of corn cobs on the incorporation of phosphate group was studied. Sodium binding capacity as well as the adsorbed efficiency of metal ions efficiency as Zn, Pb, Ni, Fe, and Cr by produced resin from corn cobs was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). It was found that the quantity and the type of incorporated functional groups, as well as the type of metal ions, play an important role in the efficiency of resin toward adsorption of metal ions.

*Key Words: Corn cobs; Phosphorylate; Phosphosulfonate; Carboxylic; Sodium binding capacity; Metal ions uptake*

*Contact information: \*\*Phys. Department, Faculty of Science, Al Azhar University, Cairo, Egypt, corresponding author, \*Cellulose & Paper Department, National Research Center, Dokki, Cairo, Egypt.*  
[drelgendy2000@yahoo.com](mailto:drelgendy2000@yahoo.com)

### **INTRODUCTION**

Large amounts of agricultural residues are produced during the harvesting and processing of food and industrial crops. The harvest residues produced from corn (corn cobs), bagasse, rice straw, and cotton stalks were investigated (Nada and Elsaied 1995). The use of these wastes causes a minimization of potential waste disposal problems. However, agricultural waste represents a cheap and environmentally safe source for preparation of ion exchangers that are useful for metal and color removal from water (Laszlo and Dintzis 1994). It is known that ion exchangers have different uses and are broadly employed for treatment of waste water (Laszlo 1996). They are also used in chromatography and for removing ammonia from air. Agricultural residues are a mixture

of complex polysaccharides and lignin. Some of the isolated components of these mixtures (cellulose, starch) have increased value when new functionality is added. So, chemical modification, copolymerization (Nada et al. 2007) or cross-linking (Simkovic et al. 1996) of these agricultural wastes allow for the development of efficient ion exchangers (Nada et al. 2006). Also, incorporation of phosphate (Nada et al. 2008), sulfate (Nada et al. 2007), phosphosulfonate (Nada, et al. 2002), and carboxylic groups (Nada et al. 2006) to the agricultural residues increases their efficiency toward cation exchange. It is found that the chelating polymers based on cellulose and agricultural residues are more efficient for ion exchange than the usual synthetic polymers due to their fibrous structure, which increases their sorption capacity. On the other hand, the efficiency of agricultural wastes toward anion exchangers can be increased by changing these materials to quaternary ammonium groups (Simkovic 1999).

In the present investigation, incorporation of phosphate, sulfate, phosphor-sulfonate, and carboxylic groups onto corn cobs was carried out. The potential usefulness of these derivatized residues as a cation exchange agent was evaluated. The effect of the treatment of corn cobs with different concentration of NaOH and ratio of pyridine on the incorporation of functional groups onto corn cobs was investigated. Inductively coupled plasma atomic emission spectrometry (ICP) was used throughout the work for the determination of metal concentrations. Fourier transform infrared spectrometry (FTIR) was carried out in order to study the molecular structure of the investigated samples. The efficiency of the produced resin toward metal ion adsorption (Zn, Pb, Fe, Ni, and Cr) from their solution as well as sodium binding capacity were determined.

## EXPERIMENTAL

### Materials

The raw material used in this study was corn cobs, which were delivered from Zagazig, Egypt. This resource has the following analysis: cellulose 44%, hemicelluloses 31%, lignin 8.5%, and pectin 4%. Corn cobs were ground to 2mm before use. The remainder was extractives and ash.

### Treatment With NaOH

Corn cobs were treated with different concentrations of NaOH (5%, 7.5%, and 10%) under reflux for 1hr using 1:15 liquor ratio (L:R), then it was filtered and air dried. Part of these treated corn cobs was washed with distilled water and acidified with 10% acetic acid, to remove any alkali and change the sodium salt of corn cobs to acid form and washed with distilled water until neutrality, and then air dried. Chemicals used were of analytical grade: POCl<sub>3</sub>, ClHSO<sub>3</sub>, epichlorohydrin, pyridine, methylene chloride, sodium metperiodate, and sodium chlorite.

### Phosphorylation and Sulfonation

The derivatization was carried according to Leirfold (1996). Thus, 5g of untreated ground corn cobs was heated at 105°C for 4h and then cooled in a desiccator. 50 ml pyridine was added and content was cooled in ice, then 5ml of either POCl<sub>3</sub> or

$\text{ClHSO}_4$  was added, which was mixed with 20ml  $\text{CH}_2\text{Cl}_2$  drop-by-drop. For phosphorylation, another 5g of treated corn cobs with 7.5% NaOH, which was acidified with acetic acid was used. The content was refluxed for 2h at 115°C with stirring.

In another experiment for phosphorylation, 5 gm of corn cobs were treated with different concentrations of NaOH (5%, 7.5%, and 10%) without washing in 50ml pyridine and 30ml pyridine and then cooled. Then 5ml  $\text{POCl}_3$  in 20ml  $\text{CH}_2\text{Cl}_2$  was added and refluxed at 115°C for 2h. For phosphosulfonation, 5g of untreated ground corn cobs in 50ml pyridine was cooled in ice and then combined with a mixture of (4ml  $\text{POCl}_3$  and 1ml  $\text{ClHSO}_3$ ) in 20ml  $\text{CH}_2\text{Cl}_2$  (Nada et al. 2003) then refluxed for 2h at 115°C. After complete reaction, the contents were poured into a beaker containing ice water and then filtered, washed, acidified with 1N HCl, and then washed with deionized water and methanol until neutrality and air dried.

*Cross-linking:* 5g ground corn cobs (2mm) was cross-linked using epichlorohydrin (100ml) under reflux for 3h. The cross-linked to corn cobs were filtered and washed with ethanol and water and finally dried under vacuum at 65°C for 12h (Nada et al. 2006).

*Carboxylation:* 5g of bagasse was mixed with 100ml of 10%  $\text{NaIO}_4$  solution. The mixture was stirred gently at room temperature for 24h. The product was further treated with 50ml 0.4M sodium chloride solution in 2M acetic acid at room temperature for 48h. The product was thoroughly washed with water and left to air dry.

## **Inductively Coupled Plasma for Determination of Trace Elements ICP as an Excitation Source**

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) was used in the present study. The ICP plasma was generated in argon by a Greenfield type torch using a free running RF generator (Linn FS-4, Germany) with a frequency of 27.12 MHz and a maximum power of 4 kW. A plasma gas flow rate of 18.0 L/min and auxiliary gas flow rate of 1.0 L/min were employed. A GMK Babington nebulizer (Labtest, Germany) at a carrier gas pressure of 4.0 bar was used for aerosol generation of different analytical samples.

## **Spectrometric Setup**

Light from ICP-OES was directed to a 1.0 m focal length computer controlled monochromator (Jobin Yvon 24), Czerny-Turner type. The spectrometer was equipped with a holographic grating 2400g/mm. Both the wavelength selection and the spectral line intensities were performed by computer controller, which enables alternate measurements of line and background intensities on both sides of the line. The analytical lines chosen were those which showed no spectral interference in either samples or standards. However, the highest intensity ratios of line-to-background were used. The maximum optimal conditions which allow the maximum line-to-background and base on linear calibration curves allow for determination of different elements with a high accuracy. The limits of detections were normally calculated on the base of three times the standard deviation of the background ( $3\sigma$ ) of the background and were found to be as low as 0.4, 0.57, 0.06, 0.01, and 0.02  $\mu\text{g/ml}$  for Zn, Pb, Ni, Fe and Cr, respectively. This

lower limit of detections in this analytical technique is considered as a one of the important features to use it for elemental analysis in the present study.

### Sample Preparation

#### *1- Phosphorus and sulphur determination:*

0.2g of the prepared ion exchanger was treated with 10ml of conc. HNO<sub>3</sub> in a PTFE beaker, and the mixture was evaporated on a hot plate until near dryness. After digestion, the residue was diluted to 100ml with doubly-distilled water in a measuring flask.

#### *2-Determination of metal ions uptake:*

0.2 g of the prepared ion exchanger was stirred at room temperature for 30min in 25ml of a solution containing 30 µg/ml of different metal ions (Zn, Pb, Fe<sup>++</sup>, Ni, Cr<sup>+++</sup>), and the pH of the solution was 1.5-3.0. The suspension was then filtered, and the remaining metal ions in the filtrate were determined using ICP-OES. Also P and S were determined using ICP.

#### *3- Carboxyl content:*

The carboxyl content was calculated from infra red spectra as a relative absorbance.

### Infrared Analyses

A Fourier transform infrared system (FTIR), JASCO FTIR800 spectrometer was used. Samples were prepared using the KBr disc technique. The molecular structure of untreated and treated corn cobs was investigated. The infra red absorption spectra were recorded in the region of 4000–400 cm<sup>-1</sup>.

### Sodium Binding Capacity

The sodium binding capacity was determined as a measure of the extent of phosphorylation, sulfonation, phosphosulfonation, and carboxylation (Nada and Hassan 2003). With 0.2g of resin, 10 ml of 0.01N NaOH was added and the matrix was stirred for 2h. and left overnight. 20ml of 0.01N HCl was added, and the mixture left overnight. Excess HCl was determined using 0.01N NaOH. Sodium binding capacity was calculated from the equation,

$$[(B - V) \times N \times 1000] \times W \quad (1)$$

where B is the volume of 0.01N NaOH consumed in titration of resin samples,

V is the volume of 0.01N NaOH consumed in titration of blank sample,

N is normality of NaOH and,

W is the weight of oven dry sample.

## RESULTS AND DISCUSSION

### Infrared of Untreated and Treated Corn Cobs with NaOH

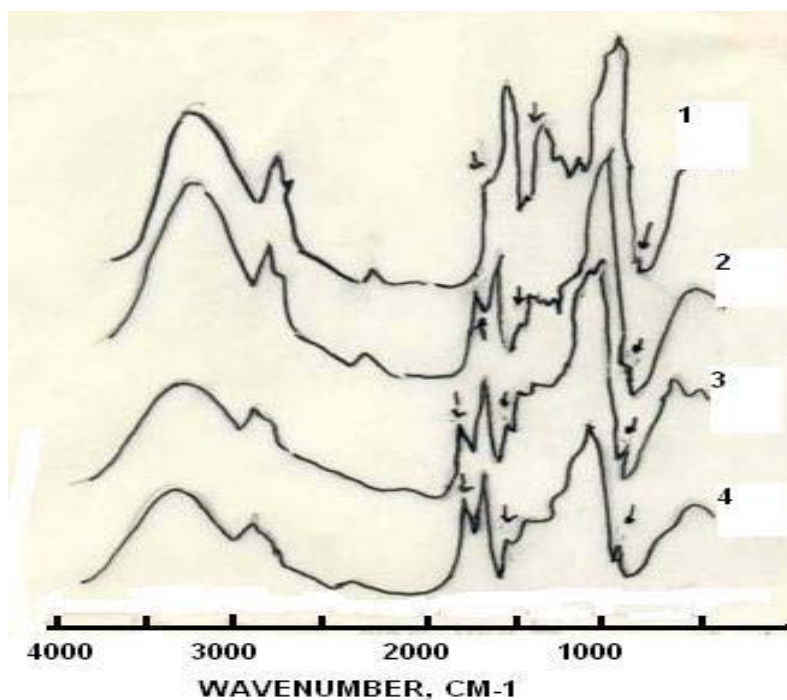
Corn cobs were treated with different concentrations of NaOH (5%, 7.5%, and 10%). The aim of this treatment was to reduce the volume of pyridine used in resin preparation as well as activation of corn cobs. Treatment of corn cobs with sodium hydroxide decreases the strength of the hydrogen bond and decreases the quantity of lignin in corn cobs and consequently leads to a cellulose increase.

From the infra-red spectral results shown in Fig. 1 and Table 1, it can be seen that the relative absorbance (ratio of intensity of any band to the intensity of the band at  $1325\text{ cm}^{-1}$ ) (Yu Levdek et al. 1967) of the OH group at  $3487\text{ cm}^{-1}$  was increased by treating corn cobs with sodium hydroxide. This was attributed to the decrease in lignin of low OH group content with respect to cellulose. Also the OH groups of treated corn cobs with NaOH increased due to the degradation of hydrogen bonds between OH groups. The relative absorbance of the band at  $1375\text{ cm}^{-1}$ , which corresponds to the phenolic OH vibrations, increased. On the other hand, the relative absorbance of the band at  $2830\text{ cm}^{-1}$  of CH vibrations of  $\text{CH}_2$  or  $\text{CH}_3$  groups, decreased upon NaOH treatment due to the dissolution of lignin and hydrolysis of  $-\text{OCH}_3$  groups to phenolic groups. From the table it is clear that the band at  $1120\text{ cm}^{-1}$ , which is characteristic of the glycosidic linkage, slightly decreased as a consequence of treating the corn cobs with NaOH. The relative absorbance increased with increasing sodium hydroxide concentration.

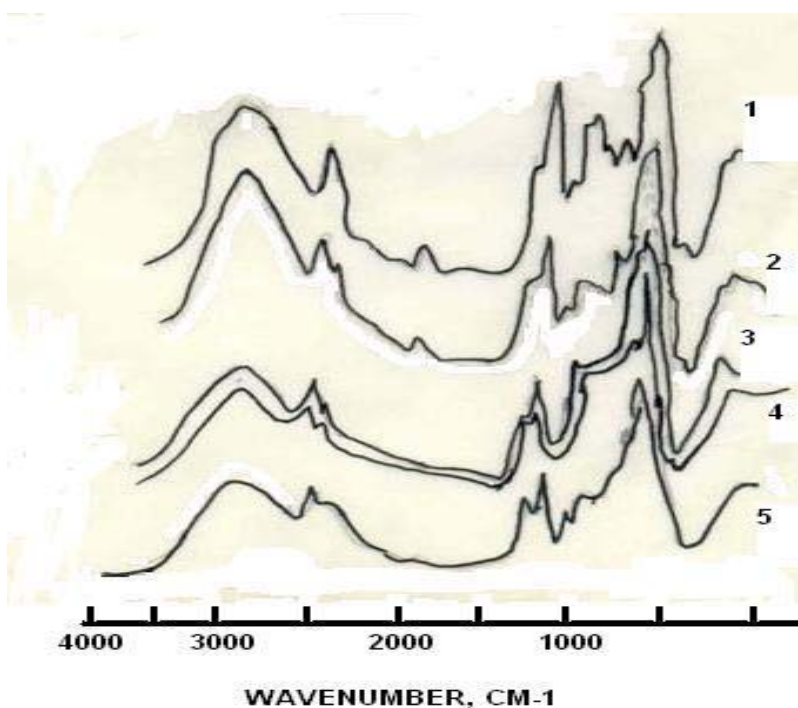
Finally, it is seen that the crystallinity indices (ratio of band intensity at  $1425\text{ cm}^{-1}$  to that at  $900\text{ cm}^{-1}$ ) (Nelson and O' Connor 1964) of cellulose chains was decreased by treating corn cobs with sodium hydroxide. This is most likely due to the degradation of the crystalline part of cellulose chains and dissolution of lignin. This can be confirmed by the shift of OH group of  $3410\text{ cm}^{-1}$  to higher wave numbers ( $3420, 3425, 3427\text{ cm}^{-1}$ ).

**Table 1.** Relative Absorbance of Untreated Corn Cobs and Treated Corn Cobs

Material	Relative absorbance					Crystalline
	3400	2830	1710	1500	1120	
Untreated corn cobs	1.4	1.7	0.30	1.2	1.1	1.80
5% NaOH	1.5	1.68	0.36	1.13	1.08	1.75
7.5% NaOH	1.55	1.65	0.40	1.11	1.06	1.70
10% NaOH	1.62	1.60	0.43	1.09	1.04	1.71
Cross-linked corn cobs	1.43	1.86	0.44	1.25	1.18	1.86
Phosphorylated corn cobs	1.46	1.69	0.36	1.18	1.06	1.7
Sulfonated corn cobs	1.41	1.62	0.34	1.13	1.05	1.72
Phosphosulfonated corn cobs	1.42	1.66	0.38	1.15	1.08	1.69
Carboxylated corn cobs	1.6	1.68	0.75	1.2	1.04	1.66



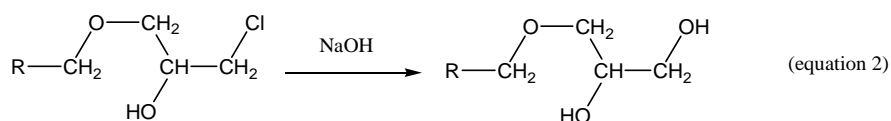
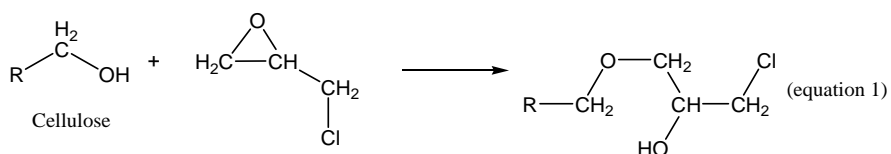
**Figure 1.** Infrared spectra of treated corn cobs with sodium hydroxide: (1) untreated, (2) treated at 5% level, (3) treated at 7.55% level, (4) treated at 10% level,.



**Figure 2.** Infrared spectra: (1) untreated corn cobs, (2) phosphorylated corn cobs, (3) phosphorylated, cross-linked corn cobs, (4) sulfonated corn cobs, and (5) phosphsulfonated corn cobs

### Cross-linked Corn Cobs

From Fig. 2 and Table 1, it can be seen that the relative absorbance of CH vibration at  $2930\text{cm}^{-1}$ , which is characteristic of  $\text{CH}_2$ , and OH groups ( $3410\text{ cm}^{-1}$ ) in cross-linked corn cobs had a higher value than in the case of untreated corn cobs. This is due to the reaction of epichlorohydrin with corn cobs, as shown in equation 1. The crystallinity index of cross-linked corn cobs slightly increased, due to the increase of OH groups in cross-linked corn cobs (equation 1).



### Infrared Spectra of Corn Cobs Incorporated with Different Functional Groups

Figure 2 shows the infrared spectra of corn cobs incorporated with different functional groups, e.g., phosphate, sulfate, and carboxylic. The spectra show new characteristic bands at  $400$  and  $1200\text{ cm}^{-1}$ . Two bands at  $1200$  and  $960\text{ cm}^{-1}$  are characteristic to the C-O-P bond. In the case of the sulfonated corn cobs, a characteristic band appeared at  $1410\text{cm}^{-1}$ , which was assigned to C-O-S. In the case of phosphosulfonated corn cobs, the spectra showed characteristic bands that correspond to both sulfonate and phosphate groups. The relative absorbance of these bands is related to the quantity of the incorporated functional groups. It is seen from Table 2 that the relative absorbance of C-O-P in phosphorylated corn cobs was higher than that in case of phosphosulfonated corn cobs. However, the phosphosulfonated corn cobs contained phosphate and sulfonate groups. Also, it can be seen from Table 2 that the relative absorbance of bands at  $960$  and  $1200\text{cm}^{-1}$  had a higher value in the case of phosphorylated cross-linked corn cobs than the uncross-linked corn cobs. This is due to the increase of phosphate groups incorporated onto cross-linked corn cobs due to the increase of OH groups that incorporated onto cross-linked corn cobs.

**Table 2.** Relative Absorbance of Diffused Bands of Phosphorylated, Sulfonated, Phosphosulfonated, and Carboxylated Corn Cobs

Material	Relative absorbance				Phosphate group	Sulphate group
	960	1200	1400	1715		
Untreated corn cobs	–	–	–	0.3	–	–
Phosphorylated	0.38	1.08	–	0.31	62	–
Sulfonated	–	–	1.4	0.33	–	84
Phosphosulfonated	0.78	0.39	0.62	0.30	38	48
Carboxylated	–	–	–	0.77	–	–
Phospho-cross-linked	0.49	1.21	–	0.26	79	

## ION EXCHANGE PROPERTIES OF TREATED CORN COBS

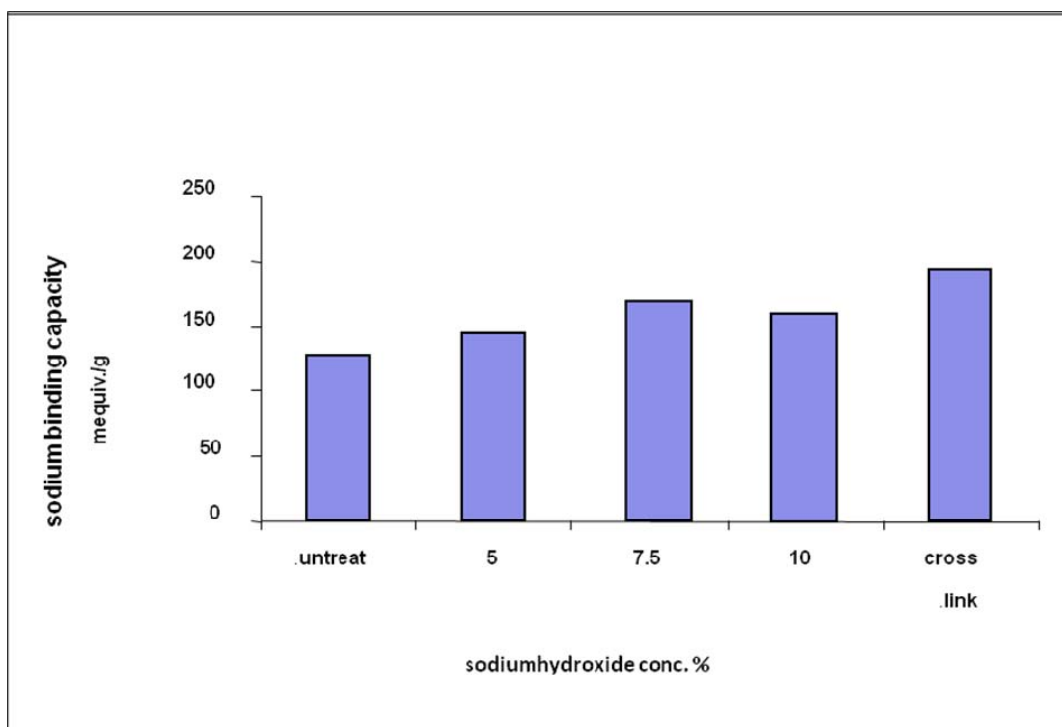
### Sodium Binding Capacity

#### *Treated corn cobs with sodium hydroxide*

Figure 3 and Table 3 show the sodium binding capacity of untreated and treated corn cobs with sodium hydroxide, and also cross-linked corn cobs.

**Table 3.** Sodium Binding Capacity of Untreated and Treated Corn Cobs with NaOH

Material	m. equiv./g
Untreated corn cobs	128
Corn cobs treated with 5% NaOH	145
Corn cobs treated with 7.5%	168
Corn cobs treated with 10%	160
Cross-linked corn cobs	194



**Figure 3.** Sodium binding capacity of treated corn cobs with sodium hydroxide

From Fig. 3 it can be seen that the sodium binding capacity of treated corn cobs with sodium hydroxide increased with increasing concentration of sodium hydroxide from 5% to 10%. The increase in sodium binding capacity of treated corn cobs at the 10% level was lower than the increase due to treatments at 5% to 7.5%. This means that the treatment of corn cobs with 7.5% of NaOH was more effective than the 10%. The increase in sodium binding capacity of treated with NaOH corn cobs is attributed to the increase of incorporated COOH groups as well as a decrease of hydrogen bonds, which causes a decrease in the crystallinity index. The use of 50ml pyridine as reaction medium



with alkaline corn cobs decreases the incorporated groups onto corn cobs, this attributed to the increase of alkalinity of the medium which lowers the reaction.

From the same figure it can be seen that the cross-linked corn cobs with epichlorohydrin increased the sodium binding capacity due to the increase in OH groups and the chain length of the branched chain attached with corn cobs.

### Phosphorylated, sulfonated, and carboxylated corn cobs

#### *Phosphorylation*

Before phosphorylation, corn cobs were treated with different concentrations of NaOH to see the effect of alkali treatment on the added volume of pyridine. From Table 4, it was found that alkaline corn cobs with 50ml of pyridine/origin volume used in experiments decreased the incorporated phosphate groups onto corn cobs. This is attributed to the increase of alkalinity of the reaction medium which causes a consumption of chemicals. The incorporated phosphate group in the corn cobs not treated with alkali had higher incorporated functional groups than those treated with alkali. A decrease of added pyridine volume to 30ml instead of 50ml in the reaction medium increased the incorporated functional groups onto corn cobs treated with alkali. This is because the alkalinity of the reaction medium is favorable for reaction and is produced as a by-product from reaction of phosphorylation groups.

**Table 4.** The Effect of Alkali Treatment of Corn Cobs before Phosphorylation

Material	Phosphate group(mg/ml) ( at 50ml pyridine )	Phosphate group(mg/ml) ( at 30ml pyridine )
Untreated corn cobs	62	54
Corn cobs treated with 5%NaOH	56	66
Corn cobs treated with 7.5%NaOH	50	70
Corn cobs treated with 10%NaOH	48	63

From Table 4 it is seen that the treated corn cobs with 7.5% NaOH using 30ml pyridine in reaction medium had a higher level of phosphates groups than untreated and treated corn cobs with 5 and 10%NaOH solution.

### Sodium Binding Capacity of Corn Cobs Incorporated with Different Functional Groups

From Table 5 the phosphorylation of treated corn cobs at the 7.5% level yielded a higher sodium binding capacity than untreated corn cobs. This is attributed to the fact that the treated corn cobs had a higher level of phosphate groups than the untreated ones. On the other hand, the phosphorylated cross-linked corn cobs had a higher sodium binding capacity than the uncross-linked corn cobs. This is attributed to the high level of OH groups incorporated onto cross-linked corn cobs, besides the increase in side chain length. This enhances the quantity of phosphorylate groups. From the table it is also clear that the sodium binding capacity of sulfonated corn cobs was higher than the phosphorylated ones. This is attributed to the selectivity of sulphonated corn cobs toward sodium ions being higher than that of phosphorylated corn cobs. Also the phosphosulfonated corn

cobs had a higher sodium binding capacity than the phosphorylated ones. On the other hand it had a lower sodium binding capacity than the sulfonated corn cobs. From the table it is also found that the carboxylated corn cobs had a higher binding capacity than the phosphorylated corn cobs and slightly more than the sulfonated corn cobs. This is due to the selectivity, in which the adsorption of sodium ion by the carboxylated corn cobs is faster than phosphorylated and sulfonated corn cobs.

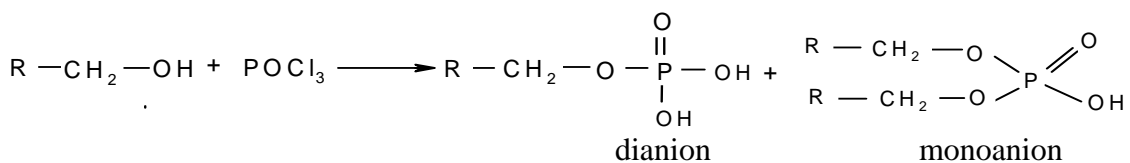
**Table 5.** The Sodium Binding Capacity of Phosphorylated, Sulfonated, Phosphosulfonated, and Phosphorylated Cross-linked Corn Cobs

Material	Sodium binding capacity m. equiv./g	Phosphate	Sulphate
Phosphorylated corn cobs	600	62	--
Phosphorylated alkali corn cobs (7.5%)	650	66	--
Phosphorylated cross-linked corn cobs	690	71	--
Sulfonated corn cobs	810	--	84
Phosphosulphonated corn cobs	720	38	48
Carboxylated corn cobs	900	--	--

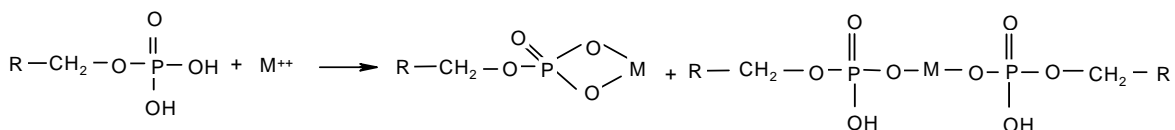
### Metal Ions Adsorption of Phosphorylated Corn Cobs Treated with Different Concentrations of NaOH

Industrial effluents may contain a mixture of heavy metal ions, and therefore, testing of an ion exchange is recommended for each case. The ion exchange adsorption affinities are affected by the magnitude of the charge and the hydrated radius of the ions in solution (Smit and Van Grieken 1980). The sorption of the metal ions Zn, Pb, Fe, Ni, and Cr by the prepared ion exchanger was studied. The results of the analysis by inductively coupled plasma atomic spectroscopy are shown in Fig. 4.

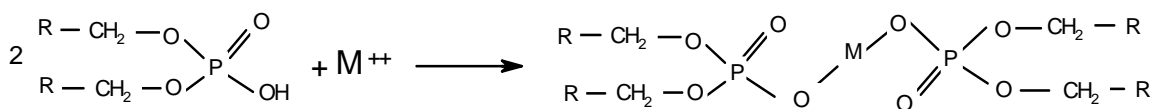
Ground corn cobs treated and untreated with sodium hydroxide (at the 5%, 7.5%, and 10% levels) were esterified with POCl<sub>3</sub>. POCl<sub>3</sub> can react at a single site to form dianion corn cobs phosphate or with two OH groups of corn cobs to form the corresponding monoanion (equation 3). The mechanism of the adsorption of the metal ions is given below in equations 3, 4, 5, and 6.



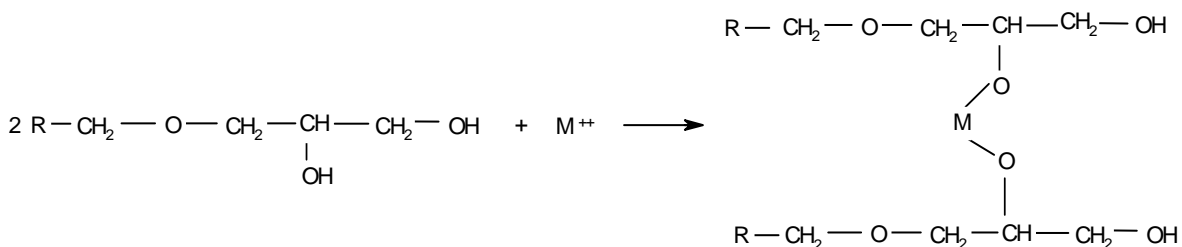
"Equation 3 "



"Equation 4 "



"Equation 5"



"Equation 6"

Figure 4 shows the metal ion uptake with phosphorylated untreated, treated corn cobs with different concentrations of NaOH (5%, 7.5%, and 10%), cross-linked, and phosphorylated cross-linked corn cobs towards metal ion uptake.

The ion exchange affinity is related to intrinsic adsorption and columbic interactions, which results from the electrostatic energy of interactions between the adsorbates and adsorbents. This involves the charge on the substances and the softness or hardness of charge on both sides.

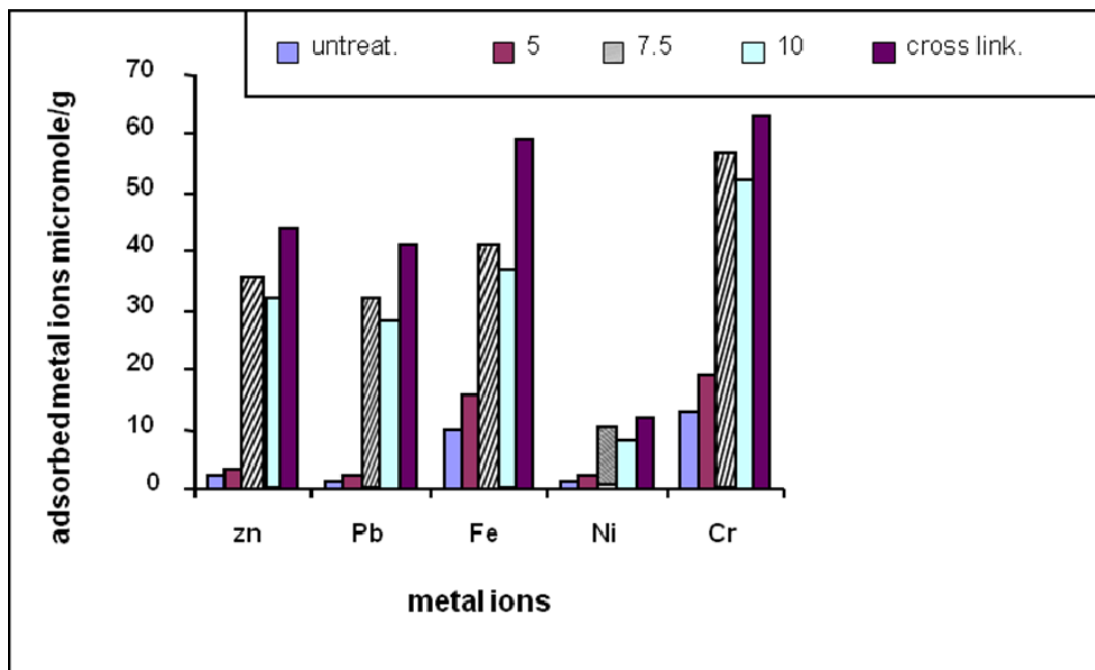
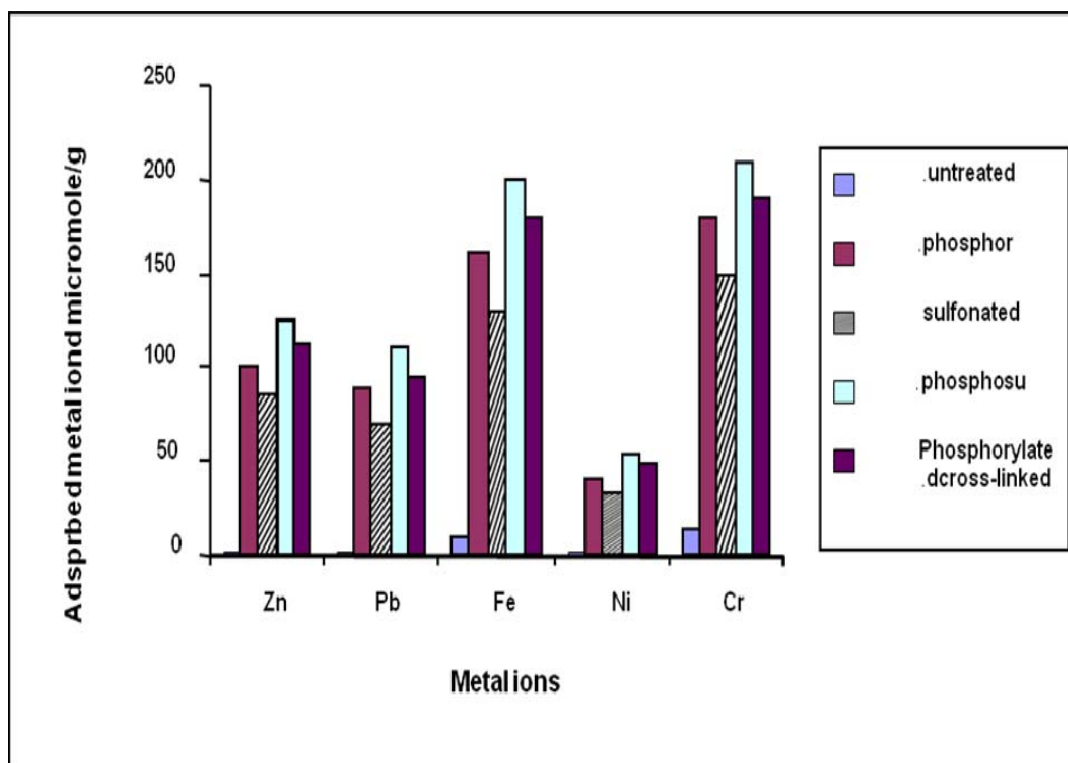


Figure 4. Metal ions adsorption of untreated and treated corn cobs with sodium hydroxide

From Fig. 4, it is clear that the phosphorylated corn cobs treated with 7.5% NaOH solution had a higher metal ion uptake than the phosphorylated corn cobs that were either untreated or treated with 5 or 10% NaOH. This can be attributed to the higher level of phosphate groups incorporated onto treated corn cobs with 7.5% NaOH than the phosphorylated untreated and treated corn cobs with 5 and 10% NaOH. On the other hand, the phosphorylated cross-linked corn cobs with epichlorohydrin had a higher absorption of metal ions than phosphorylated corn cobs treated with 7.5% NaOH. This is due to the higher phosphate groups incorporated with cross-linked corn cobs than treated corn cobs with 7.5% NaOH. Also, the long chains attached with corn cobs due to cross-linking increased the contact between the ion exchanger and metal ion. Also from Fig. 4 it is seen that the Cr ion was adsorbed by the ion exchanger to a greater degree than the other ions.

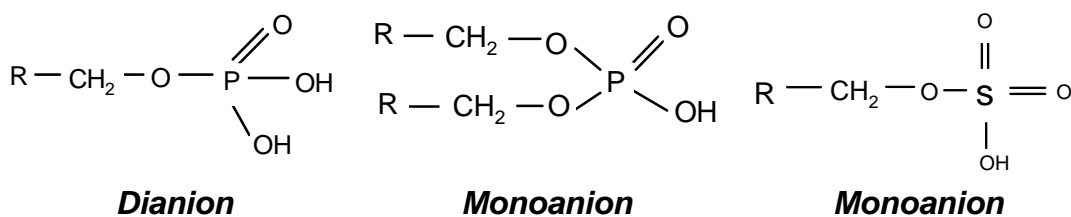


**Figure 5.** Metal ions adsorption of untreated phosphorylated, sulfonated phosphosulfonated, and phosphorylated cross-linked corn cobs

From Figure 5 it can be seen that the phosphorylated cross-linked corn cobs had a higher metal ions uptake than phosphorylated but not cross-linked cobs. This can be attributed to the higher phosphate groups incorporated in the phosphorylated cross-linked corn cobs versus the uncross-linked cobs.

## Adsorption of Metal Ions by Ion Exchanger with Different Functional Groups

Figure 5 shows a histogram of sorbed metal ions by corn cobs having different incorporated functional groups. It is seen that the phosphorylated corn cobs had higher affinity for sorption of metal ions from the solution which contained 30ppm from every metal ion (Zn, Pb, Fe, Ni, and Cr) than the sulfonated corn cobs. However, the incorporation of sulfate functional groups onto corn cobs was more extensive than that in case of phosphate groups. The fact that the phosphate derivatization still yielded higher adsorption may be due to the fact that the phosphate group in corn cobs had dianion and monoanion groups, while the sulfate group was just a mono anion (equation 2) .



Incorporation of phosphate, sulfate, phosphosulfonate groups, and phosphorylated cross-linking in corn cobs increased the ability of these materials to act as cation exchangers. The number of groups suspended on the corn cobs is directly related to their capacity to act as cation exchangers. The phosphosulfonated corn cobs had a higher affinity for metal ions uptake more than phosphate and sulfated corn cobs. This is likely due to phosphosulfonated corn cobs ion exchange system containing phosphate and sulfate functional groups, which increases the selectivity toward metal ions uptake. This can be due to the fact that the OH functional group on corn cobs is amenable to substitution with a wide variety of electrostatic reagents. Multiple functional groups may be placed on the same repeating unit or on adjacent units in close proximity. These reactive sites may lead to some degree of selectivity of cationic ions (based on ionic radii) as a result of steric hindrances to adsorption.

## CONCLUSIONS

Incorporation of certain functional groups onto corn cobs, e.g. phosphate , sulfate, phosphosulfonate, and carboxylic groups increases the efficiency of corn cobs toward metal ions sorption. Treatment of corn cobs with sodium hydroxide solution before phosphorylation increases the reactivity of corn cobs for phosphorylation and decreases the volume of pyridine which consumed in the reaction medium. Cross-linking of corn cobs with epichlorohydrin increases the phosphorylation process and consequently its affinity toward metal ion uptake increases. The phosphosulfonated corn cobs have a higher affinity toward metal ion uptake versus phosphorylated, sulfonated, or carboxylated substrates. Finally, the sorption of metal ions by the prepared corn cobs ion exchanger depends on the electronegativity and radii of the adsorbed metal ions.

## REFERENCES CITED

- Laszlo, J. A. (1996). "Preparing an ion exchange resin from sugar, cane bagasse to remove reactive dyes from waste water," *Text. Chemist and Colorist* 28(5) 13-17.
- Laszlo, J. A., and Dintzis, F. R. (1994). "Crop residues as ion exchange materials. Treatment of soy bean hull and sugar beet fiber (pulp.) with epichloraydrin to improve cation exchange capacity and physical stability," *J. Appl. Polym. Sci.* (52), 531-538.
- Leirfold, J. (1996). "Conversion of agricultural residues into cation exchange materials," *J. Appl. Polym. Sci.* 61, 2089-2105.
- Nada, A. M. A., Alkady, M. Y., and Fekry, H. (2007). "Synthesis and characterization of grafted cellulose for use in water and metal ions sorption," *Bioresources* 3(1) 46-59.
- Nada, A. M. A., Eid, M. A., Sabry, A., and Khalifa, M. N. (2003). "Preparation and some applications of phosphsulfonated bagasse and wood cation exchangers," *J. Appl. Polym. Sci.* 90, 1250-1258.
- Nada, A. M. A., El-Bahnsawy, R. M., and Khalifa, M. N. (2002). "Preparation and characterization of cation exchangers from agricultural residue," *J. Appl. Poly, Sci.* 50, 971-978.
- Nada, A. M. A., and El-Saied, H. (1995). "Some aspects on lignocellulosic pulping by using phenolysis," *Res. & Industries* 40, 141-150.
- Nada, A. M. A., El-Sherif, S., Nasr, A., and Kamel, M. (2007). "Infrared spectroscopic and thermal analysis of prepared cation exchangers from cellulose materials," *J. Mol. Structure* 841, 1-6.
- Nada, A. M. A., El-Wakeal, N., Hassan, M. L., and Adel, A. (2006). "Differential adsorption of heavy metal ions by cotton stalks cation-exchangers containing multiple functional groups," *J. Appl. Polym. Sci.* 101, 4124-4132.
- Nada, A. M. A., and Hassan, M. L. (2003). "Phosphorylated cation exchangers from cotton stalks and its constituents," *J. Appl. Polym. Sci.* 89(11) 2950-2956.
- Nada, A. M. A., and Hassan, M. (2006). "Ion exchange properties of carboxylated bagasse," *J. Appl. Polym. Sci.* 102, 1394-1404.
- Nada, A. M. A., Hassan, M. L., and Adel, A. (2008). "Application of phosphorylated chitin and wood pulp for removal of heavy metal ions," *O`PAPEI* August 84-97.
- Nelson, M. L., and O`Connor, R. T. (1964). "Relation of certain infra red bands to cellulose crystallinity and crystal lattice type P. II A new infrared ratio for estimations of crystallinity in cellulose I and II X," *J. Appl. Polym. Sci.* 8, 1325-1341.
- Simkovic, I. (1999). "Preparation of anion exchangers from beach sawdust and wheat straw," *Industrial Crops and Products* 10, 167-173.
- Simkovic, I., Laszlo, J. A., and Thompson, A. R. (1996). "Preparation of a weakly basic ion exchanger by cross-linking starch with epichloraydrin in presence of  $\text{NH}_4\text{OH}$ ," *Carbohydrate Polymer* 30, 25-30.

Smit, A. J., and Van Grieken, E. (1980). "Characterization of 2,2-diaminoethyl-amino-cellulose filter toward metal cation extraction," *Anal. Chem.* 52(13) 1479-1484.

Yu Levdek, K. I., Inshakovo, M. D., Myurova, E. P., and Kitin, N. N. (1967). *Travres Naveth Issled Inst. Tselly, Burm Prom.* 52, 109.

Article submitted: Dec. 21, 2008; Peer review completed: May 15, 2009; Revised version received and accepted: June 2, 2009; Published: June 10, 2009.