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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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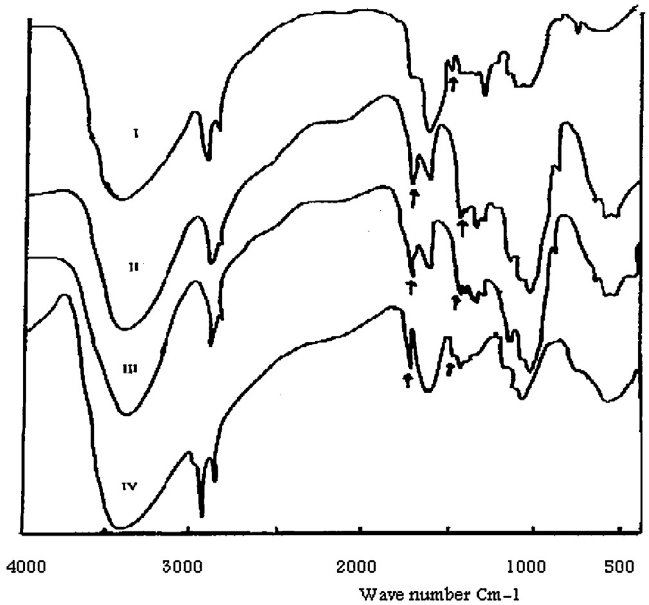


Fig. 1. Infrared spectra of I – banana leaves raw material, II – banana leaves treated with 0.2 M $KMnO_4$, III – banana leaves treated with 0.4 M $KMnO_4$ and IV – banana leaves treated with 0.8 M $KMnO_4$.

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.

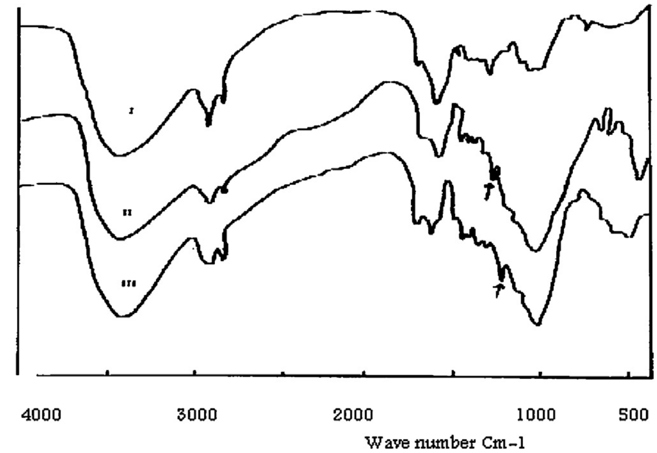


Fig. 2. Infrared spectra of I – banana leaves raw material, II – phosphorylated banana leaves and III – phosphorylated banana leaves treated with 0.8 M $KMnO_4$.

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

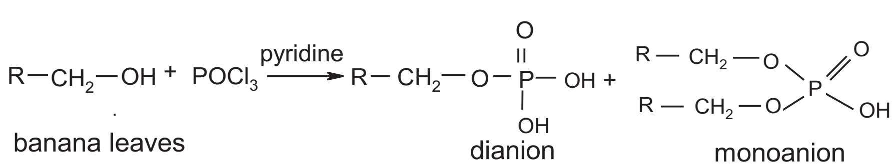
Table 1
Relative absorbance of different infrared bands of untreated and treated banana leaves with $KMnO_4$.

Band	Relative absorbance of material used			
	Banana leaves	Banana leaves treated with 0.2 M $KMnO_4$	Banana leaves treated with 0.4 M $KMnO_4$	Banana leaves treated with 0.8 M $KMnO_4$
OH (3420 cm^{-1})	1.94	1.80	1.17	1.43
CH_2 (2851 cm^{-1})	1.31	1.16	1.17	1.02
C=O of COOH (1725 cm^{-1})	0.4	0.75	0.80	0.84
Keto group (1635 cm^{-1})	1.35	0.68	0.74	0.77
CH_2 (1425 cm^{-1})	0.82	0.96	0.97	0.98
1–4-β-O-linkage (1120 cm^{-1})	1.64	1.55	1.46	1.38
Cr I (1425 cm^{-1}/900 cm^{-1})	2.5	1.59	1.55	1.26
Mercerization depth (1375 cm^{-1}/1325 cm^{-1})	0.84	1.04	1.06	1.06
CH of aromatic (1500 cm^{-1})	0.86	0.71	0.62	0.51

Table 2
Relative absorbance of different bands of banana leaves and its derivatives.

Band (cm^{-1})	Relative absorbance		
	Banana leaves raw material	Phosphorylated banana leaves	Phosphorylated banana leaves treated with 0.8 $KMnO_4$
OH (3420 cm^{-1})	1.94	1.90	2.04
CH_2 (2851 cm^{-1})	1.31	1.31	1.26
C=O of COOH (1725 cm^{-1})	0.4	0.69	1.76
Keto group (1635 cm^{-1})	1.35	0.90	0.83
CH_2 (1425 cm^{-1})	0.82	0.72	0.65
1-4-β-O-linkage (1120 cm^{-1})	1.64	1.73	1.63
Cr I (1425 cm^{-1}/900 cm^{-1})	2.50	1.51	1.43
Mercerized depth (1375 cm^{-1}/1325 cm^{-1})	0.84	1.20	1.32
CH of aromatic (1500 cm^{-1})	0.86	0.69	0.60
1200 cm^{-1} C-O-P	–	1.41	1.63

that the mercerization depth of phosphorylated banana leaves and phosphorylated banana leaves treated with 0.8 $KMnO_4$ is higher than the untreated banana leaves. From Table 2 it is clear that appearance of new band at 1200 cm^{-1} which characterized to incorporated phosphate group onto banana leaves as the following equation:



Pd, Ni and Cd) is not the same. The adsorption of metal ions in case of treated banana leaves with $KMnO_4$ is higher than the untreated and its adsorption increased by increasing the molarity of $KMnO_4$. This can be attributed to the increase of carboxyl groups incorporation to banana leaves, as well as, the increase of swelling banana leaves due to the decrease of lignin in the banana leaves during treatment with $KMnO_4$. This can be confirmed by the increase of the relative absorbance of C=O of COOH at wave number 1720 cm^{-1} and the decrease of relative absorbance of CH vibration of aromatic ring at 1505 cm^{-1} of lignin molecules, which are calculated from infrared spectra. The decrease in lignin increases the swelling of treated banana leaves with $KMnO_4$. Also from Fig. 3 it is seen that Ni ions uptake percent and partition coefficient are lower than that in case of other metal in the solution. This can be attributed to the selectivity of the treated banana leaves ion exchanger to metal ions which depends on the intrinsic adsorption and the electrostatic energy of adsorbents and adsorbates as well as the softness of the charge on both sides. The affinity of the prepared ion exchangers toward metal ions has the following sequence Pb > Cu > Cd > Ni. From Fig. 3a, it is seen that the metal ion uptake of Pb by the banana leaves ion exchangers is higher than that in case of Cu. This is due to the fact that the Pb metal ion has a higher atomic number, 207, than for Cu, 63. Also, the adsorption percent and partition coefficient of different metal ions (Cu, Pd, Ni and Cd) in the solution are increased by increasing the concentration of $KMnO_4$ molarity which treated banana leaves. In case of Cu and Cd, it was found that the Cd metal ion exhibited lower adsorption rate by the produced ion exchanger

3.1. Adsorption of metal ions

In general functionality of the agricultural residues has an affinity to substitution with wide variety of electrophilic reagents. Multiple functional groups may be placed on the same repeating unit or on one in close proximity (Lehrfeld, 1997); these reactive sites may lead to some degree selective rejection of large ionic radii of cations due to the steric hindrance factors or selective adsorption due to polydentate bonding. On the other hand, adsorption of metal ions can be attributed to intrinsic adsorption and coulombic interaction (which results from electrostatic energy of interaction between adsorbents and adsorbates) (Gang & Weixing, 1998). Charge of both substrates as well as softness or hardness of the charges on both sides is mostly responsible for interaction. The coulombic interaction can be reflected from adsorption of cationic versus anionic species on adsorbents. Intrinsic adsorption of material is determined by their surface area which can be related to the different sizes of adsorbents on adsorption.

Fig. 3 shows the metal ion uptake %, and partition coefficient of untreated and treated banana leaves with different molarities of $KMnO_4$ (0.2, 0.4 and 0.8 mole). The efficiency of banana leaves (untreated and treated with $KMnO_4$) toward metal ions uptake (Cu,

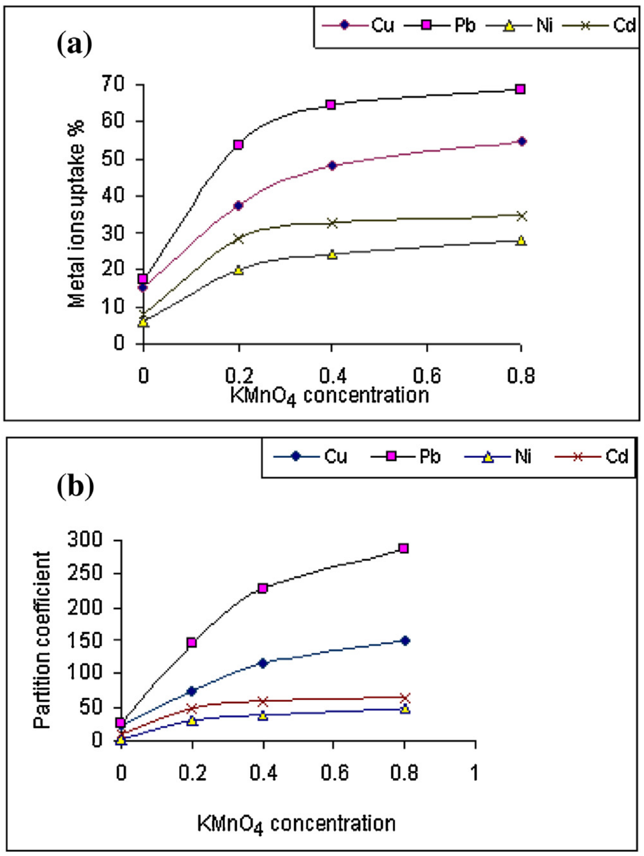


Fig. 3. Metal ions uptake % (a) and partition coefficient (b) of untreated and treated banana leaves with $KMnO_4$.

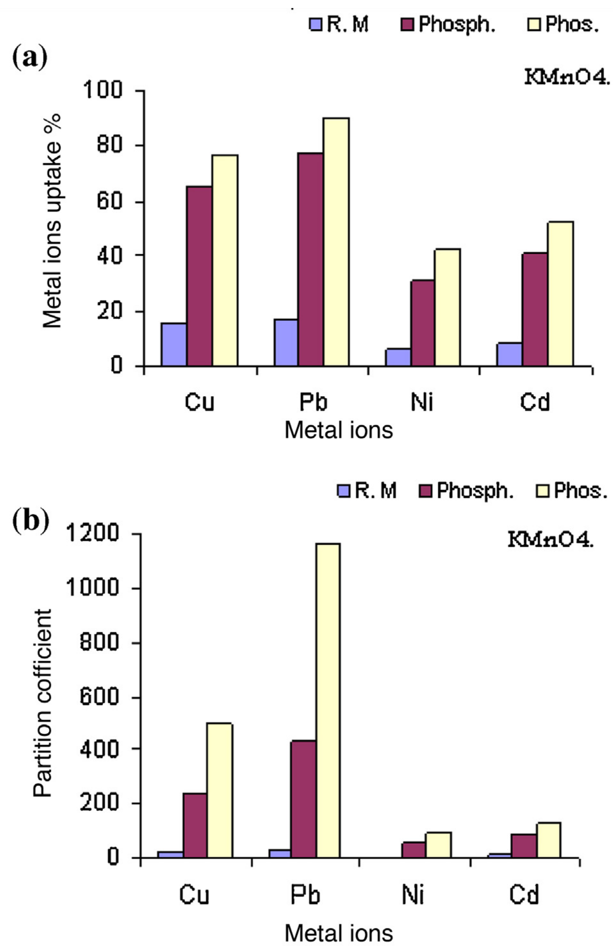
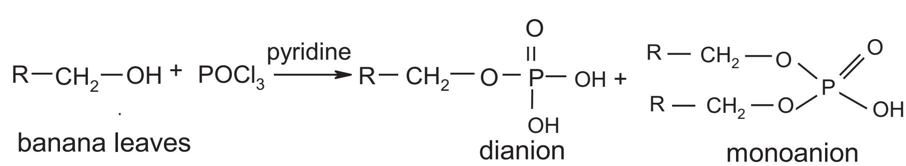


Fig. 4. Metal ions uptake % (a) and partition coefficient (b) of untreated, phosphorylated banana leaves and phosphorylated banana leaves treated with 0.8 $KMnO_4$.

from banana leaves than Cu. This can be attributed to that Cd ion is bulker than Cu, which may inhibit the rate of its adsorption on the sites of banana leaves. So the space of the ions may be an important factor that determines the competition of the ions (Gang & Weixing, 1998).

Fig. 4a, b shows metal ion uptake percent and partition coefficient of untreated, phosphorylated untreated and phosphorylated treated banana leaves with 0.8 M $KMnO_4$ ion exchangers. From the figure it is clear that incorporation of phosphate groups onto banana leaves increases its efficiency toward metal ion uptake. Adsorption of metal ions (Cu, Pd, Ni and Cd) by phosphorylated treated banana leaves treated with $KMnO_4$ is higher than phosphorylated untreated banana leaves. This is attributed to the presence of two different functional groups in the banana leaves (carboxyl and phosphate) which increase the selectivity and adsorption of metal ions. On the other hand, the incorporated phosphate group onto treated banana leaves (80 μg) is higher than the phosphorylated untreated one (60 μg). The figures also show that lead ions uptake percent and partition coefficient are higher than those of other metal ions. The sequence of metal ions uptake by the prepared ion exchanger is Pb > Cu > Cd > Ni. On the other hand, structural aspects of ion exchanger backbone are important factor affecting metal ions adsorption. It is clear from Figs. 3 and 4 that phosphorylated banana leaves have higher affinity toward metal ion adsorption than banana leaves treated with $KMnO_4$ (produces a COOH group incorporated onto banana leaves). So the phosphorylation produced phosphate group with mono and dianion (Nada et al., 2008) while carboxylic group has one anion as follows:



Incorporation of active functional groups onto banana leaves gains metal ion by exchange or by simple chelation or adsorption due to the spinning of polymer matrix (Chauhan, Singh, Chauhan, Verma, & Mahajan, 2005).

Partitioning of ions between banana leaves matrix and liquid phase reflected in rather high value of partition coefficient. On the other hand, structure and nature of incorporated functional groups have a high significant effect on metal ion uptake.

3.2. Thermal gravimetric analysis (TGA) of banana leaves treated with $KMnO_4$

From TGA curves, it is seen that untreated banana leaves have 3 stages in loss of its weight. First one is due to the evaporation of moisture content and it is about 11.2% at temperature from 40 to

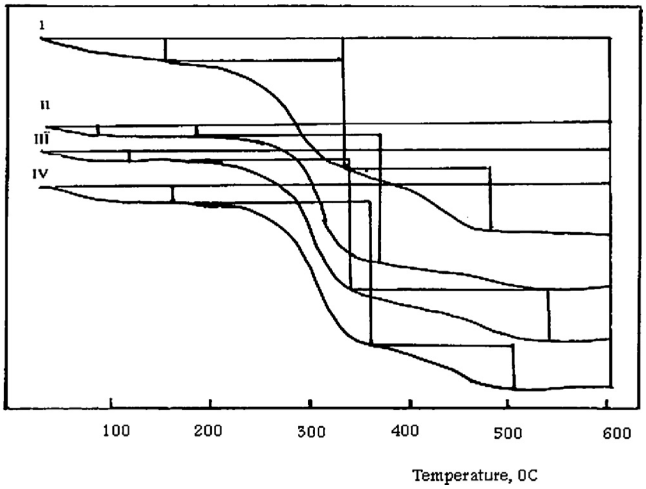


Fig. 5. TGA of I – banana leaves raw material, II – banana leaves treated with 0.2 M $KMnO_4$, III – banana leaves treated with 0.4 M $KMnO_4$ and IV – banana leaves treated with 0.8 M $KMnO_4$.

160 °C. Second stage accompanied by loss of weight about 51.48% and it begins from 160 to 335 °C which is due to the combination and depolymerization of banana leaves. The loss in weight in the third stage was 28.87% at 335–480 °C due to the combination and burning of the produced gases and the degraded cellulose.

From Fig. 5, it is clear that degradation behavior is not the same owing to the thermal decomposition of banana leaves and its derivatives. From TGA curves, the initial decomposition of treated banana leaves with $KMnO_4$ is lower than untreated one; it was 160, 80, 136 and 160 °C for untreated and treated banana leaves with 0.2, 0.4 and 0.8 $KMnO_4$ respectively. The maximum decomposition temperature of the treated banana leaves is higher than that in case of untreated banana leaves, as it was 315, 368, 360 and 360 °C with loss in weight 28.9, 13.1, 25.7 and 21.2% for untreated and treated banana leaves with 0.2, 0.4 and 0.8 M $KMnO_4$ respectively. This means that at higher temperature the presence of COOH group in the treated banana leaves increases the stability of the banana leaves. Generally, the maximum temperature of thermally treated banana leaves is higher than that of untreated; it was 478, 556, 542 and 505 °C.

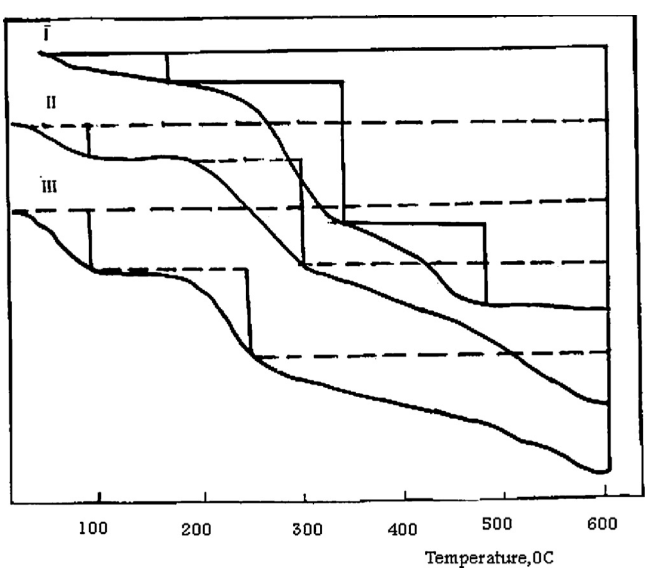


Fig. 6. TGA of I – banana leaves raw material, II – phosphorylated banana leaves and III – phosphorylated banana leaves treated with 0.8 M $KMnO_4$.

3.3. *Thermal gravimetric analysis (TGA) of phosphorylated banana leaves*

TGA of the phosphorylated untreated and treated banana leaves is shown in Fig. 6 and banana leaves were degraded in two stages mainly by degradation and depolymerization as well as glucosan formation (Chauhan, Gulerla, & Lal, 2003). Thermal degradation of banana leaves and its derivatives reveals the degradations in two stages at temperatures 160–335 °C and 335–480 °C while phosphorylated banana leaves degraded at temperatures 180–292 °C and 292–600 °C and phosphorylated treated banana leaves with 0.8 M $KMnO_4$ at 92–248 °C and 248–600 °C. This means that the maximum degradation temperature of phosphorylated banana leaves is higher than that of the unphosphorylated one; i.e. the phosphorylation increased the thermal stability of banana leaves especially at higher thermal temperatures. From Fig. 6 it is seen that the loss in weight in the first initial decomposition temperature 51.48, 36.106 and 31.38% and in final decomposition temperature 28.865, 49.543 and 42.24 for unphosphorylated and phosphorylated untreated and treated banana leaves with 0.8 M $KMnO_4$ respectively.

4. Conclusion

- Treatment of banana leaves with $KMnO_4$ increased its efficiency toward ion uptake. Phosphorylation of banana leaves increased its efficiency toward ion uptake more than banana leaves treated with $KMnO_4$.
- Presence of two functional groups, Phosphate and carboxyl groups, in the banana leaves increase the metal ion adsorption more than one functional group.
- The adsorption of metal ions by the produced ion exchangers is affected by the charge and size as well as softness and hardness of metal ions.
- The metal ions adsorption and partition coefficient of treated banana leaves are higher than that for untreated banana leaves.
- Thermal stability of the carboxylated and phosphorylated banana leaves at high temperature is higher than that for untreated banana leaves.

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