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Fourier Transform Infrared Spectroscopic Analysis of Fruit Peels before and after the Adsorption of Heavy Metal Ions from Aqueous Solution

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Supporting Information

ABSTRACT: For orange peel (OP), lemon peel (LP), and banana peel (BP) as adsorbents for removal of heavy metal ions such as Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} from aqueous solution, a simple FT-IR technique was used and discussed to study the variation in functional groups upon modification. Metal−carbon bond formation was witnessed by FT-IR during metal ion adsorption. All of these adsorbents were characterized by FT-IR, BET, and SEM. The presence of carboxylic and hydroxyl groups was confirmed by FT-IR. The FT-IR spectrum of lemon peel cellulose (LPC) showed well resolved peaks for carboxylic acid and hydroxyl groups compared to LP indicating the appreciable contents of carboxylic acid and hydroxyl groups in LPC. The widely used Langmuir adsorption isotherms were used to describe the adsorption equilibrium process. The adsorption capacity of the metal ions such as Cu^{2+} and Ni^{2+} was found to be more than those of other metal ions. Upon comparison of the adsorbents, surface modified LPC (LPCACS) was found to show enhanced adsorption activity. A comparative study of adsorption was carried out with commercially available activated carbon (AC) also from which it was inferred that the order of the adsorption capacity is as follows: LPCACS > LPC > AC > LP > OP > BP.

1. INTRODUCTION

Over the past two decades, extensive research has been carried out to identify new, effective, and economical adsorbents for removal of various heavy metal ions from aqueous solution. The effectiveness of the adsorbents depends to a large extent on their chemical composition particularly on functional groups. Carboxyl groups and hydroxyl groups can play a vital role in metal ions adsorption.[1] The adsorbents are characterized for the reactive functional groups containing O, N, S, and P donor atoms and are capable of coordinating to different metal ions.[2] To characterize the adsorbents different techniques are used carefully such as potentiometric titration, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR). Potentiometric titration can be used to evaluate the charge of adsorbents at different pH values based on the electroneutrality equation of the solution. This method has been used to characterize pK_a values of the functional groups present in the adsorbents.[3,4] FT-IR spectroscopy can be used to characterize the functional groups of adsorbents.[5] Also FT-IR is frequently capable of distinguishing adsorbed molecules on different sites and the amount of adsorption on respective sites is separately obtainable from the IR peak intensities. Many researchers have been investigating new adsorbent materials as alternatives to activated carbon, such as seaweeds,[6] marine algae,[7] activated sludge biomass,[8,9] perlite,[10] maple sawdust,[11] fruit peels and fibers,[12−14] crab shells,[15] coconut shell powder,[16] etc. for the removal of heavy metals from wastewater. Thus, so far, very little FT-IR research has been reported for the adsorbents; however the interpretation was vague and inconclusive.[17] The purpose of this study is to use FT-IR for the identification of functional groups. Because each specific chemical functional group has a specific absorption wavelength, FT-IR is a very effective technical tool. In the present work, we describe the changes in FT-IR spectra of native and surface modified adsorbents viz. lemon peel (LP), orange peel (OP), banana peel (BP), and lemon peel cellulose (LPC) before and after adsorption of different heavy metal ions such as Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} from aqueous solutions. The FT-IR spectra confirm that these adsorbents contain carboxyl and hydroxyl groups which are able to react with heavy metal ions in aqueous solutions. The FT-IR peak intensities are associated with significant variation after metal ion adsorption. An interesting observation of formation of metal−carbon (M-C) bonding after metal ion adsorption is also evidenced by the FT-IR technique.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Deionized distilled water and carbonate free water were used to prepare all solutions and suspensions. Standard metal ion solutions were commercially obtained. All of the chemicals and reagents used in this study were of analar grade (AR grade) and used without any further purification.

2.2. Fruit Peels. Orange peel (OP), lemon peel (LP), and banana peel (BP) were obtained from a local fruit market in Chungli (Taiwan). The peels were first washed with water (more than 5 times) to remove any adhering dirt or moisture. They were then dried in an oven at elevated temperature (50 °C) for 48 h before being ball-milled to form particles approximately 0.840 mm in size. Acidic and basic sites of both native and modified fruit peels were determined[18] by the acid−base

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Table 1. The Net Weight of Fruit Peels after Removing Each Constituent

adsorbents	original weight (g)	weight after removing fat and pigment (g)	weight after removing pectin (g)	weight after removing protein (g)	weight after removing hemicellulose (g)
OP	30	28.05	9.95	8.50	2.475
BP	30	26.33	17.80	10.39	1.086
LP	30	27.20	17.04	12.86	4.305

titration method proposed by Boehm.[19] Extraction of cellulose from the fruit peel and surface modification of the fruit peel was discussed in our previous work.[18]

2.2.1. Extraction of Cellulose from the Fruit Peels. The fruit peels were heated to 50 °C in a water bath for about two days to remove color and pigments. The dried and ground fruit peels (25 g) were defatted by extraction with chloroform and methanol at a ratio of 2:1 and then placed in a Soxhlet for 12 h to completely remove the color. The defatted fruit peels were mixed with 350 mL of 0.2 M Na_3PO_4 to bring the pH to 7.9 and to remove inactivated pectin enzymes. After incubation overnight at 65 °C, the samples were filtered. The deproteinated fruit peels were mixed with 100 mL of 0.5% ammonium oxalate (pH: 4.5). This mixture was shaken at 65 °C in a water bath for 180 min and then filtered. Ten % NaOH (25 mL) was added to the depectinated fruit peels. The mixture was shaken at 65 °C in a water bath for 2 days, filtered, and then washed with distilled water to remove the base. The hemicellulose-free fruit peels were mixed with 100 mL of distilled water, 5 mL of 20% acetic acid, and 2.0 g of NaCl. This mixture was shaken at 60 °C in a water bath for 120 min and then filtered. The residue was washed with distilled water and ethanol to remove the acid and then dried at 50 °C in an oven for 16 h, finally producing smaller particles of orange peel cellulose (OPC), lemon peel cellulose (LPC), and banana peel cellulose (BPC).

2.3. Surface Modification of the Fruit Peel. The surface of the lemon peel (LP) was chemically modified to form different chemically modified lemon peel. For all modification processes, the lemon peel (LP) was first washed (more than 5 times) to remove any adhering dirt or moisture. It was then dried in an oven (40 or 50 °C) for 48 h, before being ball-milled to form particles.

2.3.1. Alkali Saponification. A total of 10 g of the dried fruit peel was added to 100 mL of 0.1 M NaOH solution and mixed for 2 h at room temperature and then filtered. Next it was washed with deionized water until the pH approached neutral. The fruit peel was then called lemon peel saponification (LPS).

2.3.2. Acid Treatment (Carboxylation). A total of 10 g of the dried fruit peel was added to 100 mL of 0.1 M oxalic acid solution and mixed for 2 h at room temperature and then filtered. Next it was washed with deionized water until the pH approached neutral. The fruit peel was then called lemon peel acid carboxylation (LPAC).

2.3.3. Acid Treatment (Carboxylation) after Saponification. The LPS was dried at 50 °C in an oven. To this was added 100 mL of 0.1 M oxalic acid solution, and it was mixed for 2 h at room temperature and then filtered. Next it was washed with deionized water until the pH approached neutral. It was then dried at 50 °C in an oven. The fruit peel was then called lemon peel acid carboxylation after saponification (LPACS).

2.3.4. Cellulose Acid Treatment (Carboxylation) after Saponification. A total of 10 g of lemon peel cellulose (LPC) was added to 100 mL of 0.1 M NaOH and mixed for 2 h at room temperature. Then it was filtered and washed with deionized water until the pH approached neutral. It was then dried at 50 °C in an oven. To this was added 100 mL of 0.1 M oxalic acid solution, and it was mixed for 2 h at room temperature and then filtered. Next it was washed with deionized water until the pH approached neutral. It was then dried at 50 °C in an oven. The fruit peel cellulose was then called lemon peel cellulose acid carboxylation after saponification (LPCACS).

2.4. Batch Adsorption Studies. The adsorption of Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} was investigated in batch equilibrium experiments. Stock solutions of metal ions (1.0 g/L) were prepared using the obtained standard solution, in distilled water. The pH was adjusted with HCl or NaOH to range from 2.0 to 8.0 at the beginning of the batches and not controlled afterward. The temperature was kept at 28 °C. The experiments were carried out in a 250 mL conical flasks containing 100 mL of metal ion solutions of different concentrations (100, 200, 300, 400, 500, 600, 700, and 800) mg and 1 g of the adsorbents, shaken for 25 h at 150 rpm in a Lab-line orbit environ shaker. The adsorption of metal ions from the aqueous solutions was studied. After the desired reaction period for each batch, the aqueous phases were separated from the materials and the concentration of metal ions was measured using an atomic absorption spectrophotometer (AAS; Varian AA-400).

The amount of metal adsorbed was calculated using the following equation:

$$q_e = [(C_0 - C)V]/M$$

where q_e is the amount of metal ion adsorbed per unit amount of the adsorbent (mg/g); C_0 and C are the concentrations of metal ion in the initial solution (mg/L) and after adsorption respectively; V is the volume of the adsorption medium (L); and M is the amount of the adsorbent (g). q_{max} was calculated from q_e using the Langmuir linear isotherms and the corresponding values were obtained by a linear method.

2.5. Desorption and Reuse. The reusability of the adsorbents for metal ion adsorption was determined. Measurements were repeated after 4−5 consecutive adsorption−desorption cycles using the same adsorbent and the maximum deviation was found to be ± 4 %. The desorption of metal ions in a 10 mM HCl:HNO_3 solution was found. The adsorbents with metal ions were placed in the desorption medium and stirred at 150 rpm for 60 min at 25 °C. The final metal ion concentration in the aqueous phase was determined by using an AAS, as described above. The desorption ratio was calculated from the amount of metal ion adsorbed by the adsorbents and the final metal ion concentration in the desorption medium with the following equation:

$$\begin{aligned} &\text{desorption ratio }(\%) \\ &\quad = (\text{amount of metal ions desorbed to the elution medium}) \\ &\qquad \times 100/(\text{amount of metal ions adsorbed onto adsorbents}) \end{aligned}$$

2.6. Characterization Techniques. The average pore diameter and specific surface area (BET surface and pore volume) were measured on a Quantochrome NOVA 1000. The adsorbents were subjected to SEM (scanning electron microscope)

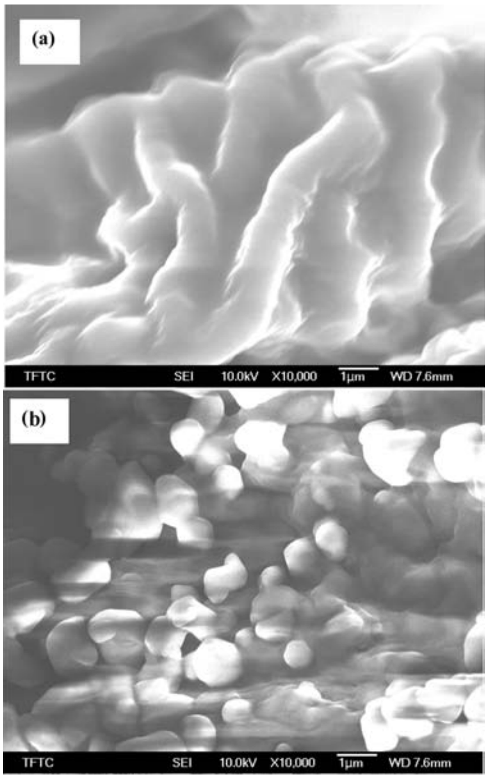

Figure 1. SEM of (a) BP and (b) BPC.

analysis. The SEM was carried out on a HITACHI-S-800, field emission scanning electron microscope. The FT-IR spectra were obtained on a Neclit 6700 model, Fourier transform infrared spectroscope (FTIR). A LM-595R rotary incubator (YIH DER Company) was used in the experiments for incubation. The pH was determined using a Micro computer models METER 6171. The adsorption of metal ions was studied using an AAS (Varian AA-400).

3. RESULTS AND DISCUSSION

In this present investigation, FT-IR spectra of the adsorbents were obtained in order to understand the nature of their functional groups. The weight of the native fruit peels after removal of each content is dispensed in Table 1. We discuss the FT-IR spectra of native and surface modified fruit peels such as orange peel (OP), lemon peel (LP), and banana peel (BP) as adsorbents for the removal of various metal ions like Cu(II), Ni(II), Zn(II), Pb(II), and Cd(II) ions in the light of FT-IR spectral data.

The measured BET surface areas were (1.999, 1.272, and 1.271) m^2/g for OP, BP, and LP, respectively. The average pore diameters were (38.47, 15.48, and 39.48) Å for OP, BP, and LP, respectively. Even though LP has a very small BET surface area (1.2714 m^2/g), it still has a significant pore size of 39.483 Å (3.9483 nm). If there is still controversy in the surface area and pore size, in spite of the small surface area, LP was still considered as a good adsorbent due to its significant pore size. The SEM analysis of these adsorbents confirmed that these adsorbents do not have any defined holes (only a few pores on the surface) on their morphology and also they have a small surface area. Figure 1 comprises the SEM of BP and banana peel cellulose (BPC). The surface modification of adsorbents led to variation in morphology, such as the structure of the surface and crystalline pattern, and hence, the difference in adsorption capacity was observed for various adsorbents. But surface modification never affected the surface area of the adsorbents.

Table 2. Langmuir Isotherm Adsorption of Heavy Metal Ions for Adsorbents

	q_{max} (mg/g)				
adsorbents	Cu^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Cd^{2+}
LPC	263.16	123.46	112.36	232.56	114.94
OPC	256.41	113.64	107.53	196.08	105.26
BPC	140.85	101.01	104.17	133.33	76.92
LP	70.92	37.87	27.85	80.0	54.64
OP	63.29	27.10	24.1	81.3	41.84
BP	52.36	25.91	21.88	54.35	34.13
AC	138.80				

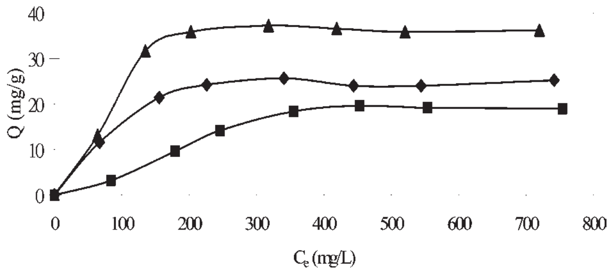

Figure 2. Adsorption of Pb^{2+} by LP (–▲–), BP (–■–), and OP (–◆–).

3.1. Adsorption of Heavy Metal Ions. In this experiment, adsorption of various heavy metal ions such as Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+} was carried out. For this purpose, various concentrations of (100 mg, [1 to 600] mg and [1 to 800] mg) heavy metal ion solutions were mixed with 1 g of adsorbent and the adsorption behavior was studied after 24 h. We also compared the activities of these adsorbents with commercially available activated carbon. To achieve the adsorption effect of adsorbents, the Langmuir linear adsorption model was used in this study. The adsorption data of metal ions and Langmuir parameters for all of the adsorbents are obtained as shown in Table 2, and the adsorption of Pb^{2+} is shown in Figure 2. From the results, it was found that the adsorption capacity of different adsorbents increased with an increase in the initial concentration of metal ions in solution. In all cases, when the initial concentration exceeded (300 to 400) mg/L, the adsorption capacity remained almost constant. This is because, when the initial concentration is between (300 to 400) mg/L, the active adsorption positions of the adsorbents were almost gradually filled by metal ions, and hence, the adsorption activity of adsorbents was limited.[20] So, if the initial concentration of metal ions was increased further, no more adsorption was observed due to the unavailability of adsorption positions in the adsorbent. So, (300 to 400) mg/L was the optimum concentration of metal ions for effective adsorption. It could be seen from the results that in all cases the calculated R^2 value was found to be 0.9 indicating that the Langmuir isotherm model fitted well in all cases. Among LP, OP, and BP, the maximum uptake of metal ions was obtained by LP, and so LP was found to be the most effective adsorbent. The

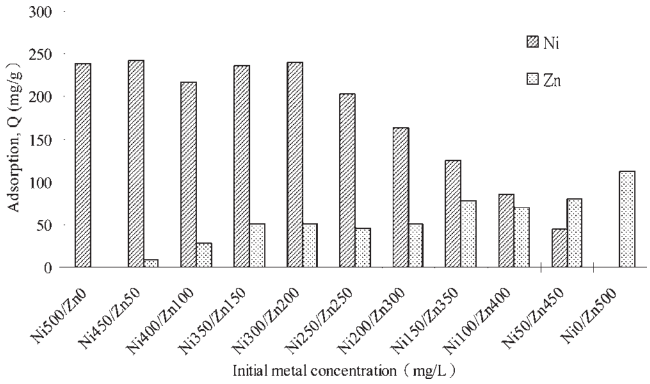

Figure 3. Competitive adsorption of heavy metal ions by LPC.

adsorption capacity of the adsorbents used in this work was compared with activated carbon as given in Table 2. According to our knowledge for uptake of Cu^{2+}, the adsorbent used by us (LPC) in this work seemed to be a better adsorbent relative to activated carbon. It was believed that the solubility of metal ions is also one of the major parameters in metal ion adsorption. The state of the metal ions can also decide the adsorption behavior of metal ions. This can be explained by taking the example of the removal of Cu^{2+} as a function of pH. In the removal of copper, the main species at different pH values are $CuOH^{+}$, $Cu(OH)_2$, $Cu(OH)_3^{-}$, and Cu^{2+} according to Wang and Qin.[21] As the pH < 6, Cu^{2+} will be the dominating species which can easily be self-adsorbed on the surface of an adsorbent. If pH > 7, hydroxide precipitation will occur which reduces the amount of free metal ions, and hence, there is an exclusion of adsorption to lower the adsorption effect. Among all the surface modified adsorbents, in LPCAOS the existence of Cu^{2+} at pH 4.0 to 6.0 was a maximum and hence a better adsorption effect (90% of Cu^{2+} adsorption) was observed for LPCAOS. The adsorption of metal ions was also carried out in the presence of 0.01 M $CaCl_2$ electrolyte to observe the effect of electrolyte as the aqueous solution can contain several electrolytes also. The experimental results showed that the presence of electrolyte accurately accelerates the adsorption of metal ions which confirms that this approach can be effectively used to treat wastewater.

3.2. Competitive Adsorption. To mimic industrial wastewater, we have taken one adsorbent LPC to carry out an adsorption experiment in the presence of Ni^{2+} and Zn^{2+} in the same solution as shown in Figure 3. The results clearly reveal that when two metal ions such as Ni^{2+} and Zn^{2+} are present at the same time in a solution, the adsorbent LPC adsorbed a large amount of Ni^{2+} regardless of the amount of Ni^{2+} in the solution. When the initial concentration of both metal ions was varied, the adsorption of Ni^{2+} was shown to be larger than that of Zn^{2+}. When the solution contains a lot of Ni^{2+}, the adsorption of Zn^{2+} has shown to be greatly reduced. Even when the amount of Zn^{2+} was larger in solution, LPC preferred to adsorb more Ni^{2+} than Zn^{2+}. When both metals were displayed in solution, the overall competitiveness of the metal ions was $Ni^{2+} > Zn^{2+}$. This approach can be used to treat aqueous solution to remove various metal ions and these adsorbents can be effectively used to remove metal ions from aqueous solution.

3.3. FT-IR Characterization. The peels were characterized by FT-IR and the constituents of these peels were determined. The major constituents of these peels are protein, pectin, cellulose, and pigments. Since cellulose contains different OH groups, FT-IR spectra can be used to explain the functional groups for metal ion coordination. The FT-IR spectra of these peels indicated that these adsorbents contain carboxyl and hydroxyl groups which are able to react with heavy metal ions in aqueous solutions. The FT-IR spectral data of native and surface modified adsorbents are given in Table 3. The FT-IR spectra of LP, OP and BP are almost similar to each other (see Figure S1), conveying that the surface of the adsorbents contained similar functional groups. A broad peak at (3200 to 3400) cm^{-1} is due to the carboxylic and hydroxyl functional groups, and the absorption was caused by stretching of free or H-bonded OH^{-} groups. Also at (2800 to 3100) cm^{-1} one main peak is arising due to sp^3 hybridized $-CH$, $-CH_2$, and $-CH_3$ bond stretching vibration on $-OH$. This CH stretching may vary, depending upon various functional groups. Hence this peak may or may not be altered during surface modification. Generally, the stretching vibration of CH_3 is complex and split due to correlation field effects. These bonds may arise from Fermi resonance between fundamental and overtone bands. However, in this case, the CH stretching bond was not complex, and it was a sharp and single spectrum. The peak at (1640 to 1760) cm^{-1} is due to the compounds containing a C=O group and at (1020 to 1300) cm^{-1} is for the compounds containing a C−O group. The C=O peaks may be due to either conjugated or nonconjugated systems, saturated or unsaturated, acidic, amide, etc., and in this study it was due to acidic and nonconjugated systems. This may generally be altered by impurities and aggregation. It can be seen that C−O peaks were stronger and broader than that of C=O groups; therefore, the existence of CO groups were considered to be significant within the surface of the adsorbents. The extracted cellulose from LP, OP, and BP were also characterized by FT-IR. Though the FT-IR spectra of LPC, OPC, and BPC are similar, LPC had a clear spectral behavior different from the remaining two. Comparison of FT-IR spectra of raw peel and extracted cellulose (see Figure S1) led to the conclusion that the peaks corresponding to carboxyl and hydroxyl groups are well resolved in the case of fruit peel cellulose. Therefore, fruit peel cellulose was considered to have markedly enhanced functional groups for metal ion coordination. In the case of LPC, the OH peak was highly resolved and had more absorption than that of LP indicating the enhanced functional groups in LPC. OPC also had more −OH absorption than that of OP but did not increase significantly as LPC. BPC also had more absorption of −OH but not as much as LPC and OPC. The remaining peaks of fruit peel cellulose also had more absorption than that of the corresponding fruit peel, but the observation in LPC was clearer than that of OPC and BPC. So, it could be stated that in LPC and OPC the cellulose content is more major than that of BPC, and BPC may also contain substances other than cellulose, and hence, the carboxyl and hydroxyl peaks were not as obvious as LPC and OPC.

Table 3. FT-IR Spectral Data of Native and Surface Modified Fruit Peels

modes	frequency (cm^{-1})
OH stretching	3200−3400
CH stretching	2800−3100
COO stretching	1745
C=O stretching	1640−1760
CH bending	1320
CO stretching	1020−1300
COC stretching	1150

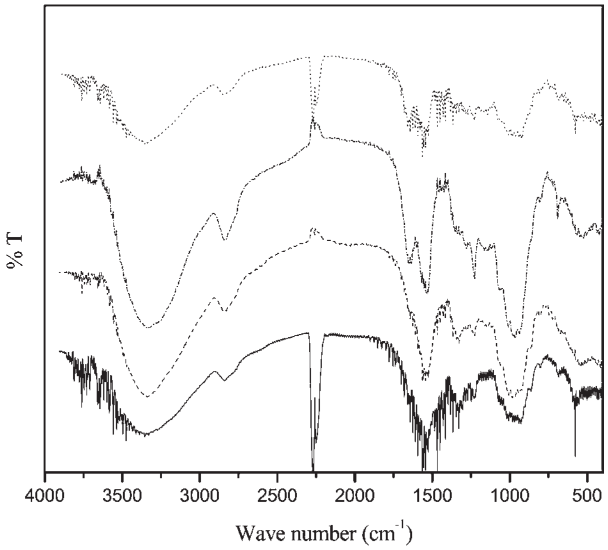

Figure 4. Comparison of FT-IR spectra of LP (—) with LPS (---), LPAC (···), and LPACS (-··-).

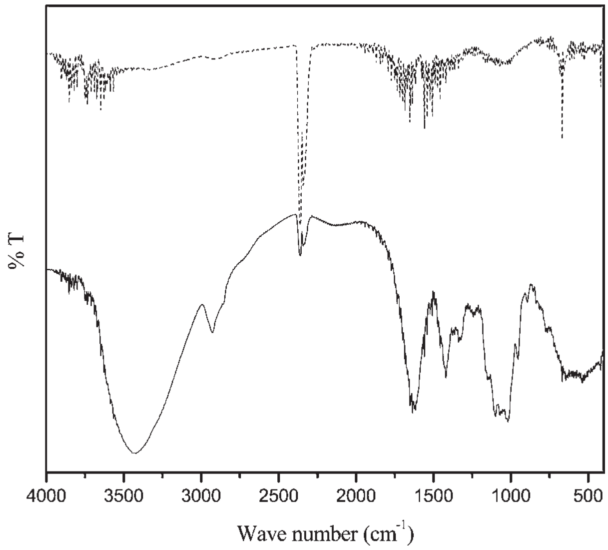

Figure 5. FT-IR spectra of LPC before (—) and after Cu^{2+} adsorption (---).

Both LP and LPC were chemically modified in various ways to obtain surface modified adsorbents such as lemon peel saponification (LPS), lemon peel acid treatment (carboxylation) (LPAC), lemon peel acid treatment (carboxylation) after saponification (LPACS), and lemon peel cellulose acid treatment (carboxylation) after saponification (LPCACS). As the surface modification led to elimination of some groups, there may be a disappearance of some peaks in the FT-IR spectra of surface modified adsorbents as shown in Figure 4. In the case of LPS, pectin, protein, and some organic substances were removed during surface modification. So the FT-IR spectrum of LPS was free from these absorptions. In the case of LPS, the absorption of −OH was higher than that of LP indicating that LPS contains more carboxyl and hydroxyl groups. In the case of LPAC no obvious FT-IR changes were observed because during this acid treatment, the carboxylic acid functional groups were just increased. The pattern of FT-IR spectra of LPACS is almost same as LPS along with some new additional peaks due to acid treatment after saponification. LPACS also had a larger −OH absorption than that of LP. Similarly the FT-IR spectrum of LPCACS also had some new peaks compared to LPC due to chemical modification. Disappearance of a few peaks due to removal of some organic substances upon modification was also observed for LPCACS. In the case of LPACS and LPCACS the appearance of new peaks around 1745 cm^{-1} due to COO stretching, 1320 cm^{-1} due to CH bending and 1150 cm^{-1} due to COC vibration are significant.

Both the native and surface modified adsorbents were used for removal of various metal ions such as Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+}. It was expected that FT-IR spectra of these adsorbents after metal ion adsorption should change since the coordination sites of functional groups were coordinated to metal ions. In this case, the FT-IR technique plays an important role in the confirmation of removal of metal ions by distinguishing the peak position and peak intensity upon comparison of the FT-IR spectra before and after metal ion adsorption as observed in Figure 5 (and see Figure S2 to S4). This could be explained by taking the example of Cu^{2+} adsorption by all adsorbents. In the case of LP, OP, and BP, the −OH peak intensity was appreciably reduced along with C═O and C−O intensities after the adsorption of Cu^{2+}. This is because almost the entire binding sites were used by metal ions for coordination.[12,13,22] It is in fact intriguing to observe that the CH stretching around (2800 to 3100) cm^{-1} after metal ion adsorption was also subjected to reduction in peak intensity. In the case of LPC, it almost disappeared as shown in Figure 5. This observation may also lead to the possibility of formation of a metal−carbon bond during metal ion adsorption, due to which the authors feel that these adsorbents may have greater importance in organic reactions. This was observed for the first time by the authors of this work, and nobody has reported this so far. In order to study the nature of M-C bonds, usually theoretical studies were applied and in general topological analysis of their electronic structure is required to describe correctly the nature of the interaction between the carbon and metal atoms. The M-C bonds rely on geometric parameters, vibrational modes, and molecular orbitals. As both the C−H and C═O stretching were affected, M-C bond could be a metal−methylidyne (MCH), metal−methylidene (MCH_2), methyl−metal (MCH_3), and metal−carbonyl (MCO) bond depending upon the ligand attached to the carbon atom. This bonding scheme is defined as an interaction between the p and d orbitals of the carbon and metal atoms respectively. Although, multiple bonding might be expected from Lewis bonding sites, and it could be a pure ionic bond in this case. The net charge was transferred from the metal to the carbon, but the electronic structure of the CH_n^- moiety would be unaltered after the interaction with the metal cations, showing little or no effect on the shape of the electron pairing. Thus, these adsorbents were not only used for removal of metal ions and may also be useful for the formation of metal−carbon bonds in organic reactions which is believed to have several applications. So, from the FT-IR technique, it was confirmed that carboxyl and hydroxyl functional groups were involved in coordination to metal ions. Among LP, OP, and BP, in LP the −OH peak became less intense after Cu^{2+} adsorption indicating the effective adsorption of Cu^{2+} by LP. This was in accordance with the fact that the cellulose content of LP is more compared to that of OP and BP. Based on the cellulose content, the ability of Cu^{2+} coordination (removal) by adsorbents is as follows: LP > OP > BP. In the case of

LPC, OPC, and BPC also the intensity of the −OH peak was markedly reduced after the adsorption of Cu^{2+}. The FT-IR spectra of LPC experienced the most reduction in corresponding peak intensities and the order of ability of metal ion removal is LPC > OPC > BPC. But the extent of reduction in peak intensities of −OH, C═O, and CO in fruit peel celluloses was larger than that of fruit peels. So, fruit peel celluloses were considered to be more effective adsorbents than the parent fruit peels. As already stated, the surface modified adsorbents were also subjected for FT-IR measurements after Cu^{2+} adsorption. In the case of surface modified adsorbents, the corresponding peak intensities were obviously reduced (almost disappeared) indicating that the surface modified adsorbents act as more effective adsorbents than the native adsorbents providing the entire functional groups for possible Cu^{2+} coordination. Based on the above FT-IR experimental data and discussion it was concluded that LPCACS acts as an effective adsorbent among all native and surface modified adsorbents which was also in good agreement with batch adsorption data.

It was obvious from the FT-IR spectra that after metal ion adsorption, the functional group peak intensities were significantly reduced and also the peak positions were shifted as the coordination of metal ion induced a shift in wavenumber. The observed variation in the sp^3 hybridized CH groups demonstrated that FT-IR spectroscopy is a sensitive probe for the reactivity of CH groups.

In the case of removal of Cu^{2+} and Ni^{2+}, the peak intensities of functional groups in FT-IR spectra were observed to reduce more significantly among all the metal ions. In the case of Zn^{2+}, the reduction was only obvious and not significant. So, based on the experimental results it was also observed that among all these heavy metal ions, the adsorption behavior of both Cu^{2+} and Ni^{2+} was appreciably higher than that of the remaining metal ions. Zn^{2+} was found to have the lowest adsorption capacity. This can be explained by the fact that both Cu^{2+} and Ni^{2+} can easily react with the functional groups containing donor sites (O, N, P, and S) which have unshared pairs of electrons to form coordination linkage and also they have the smaller size. This is because of the fact that the ionic radii of Ni^{2+} and Cu^{2+} are slightly lower than that of Zn^{2+} and also these two metal ions have a greater affinity for carboxyl groups when compared to Zn^{2+}. Hence, Cu^{2+} and Ni^{2+} can easily coordinate with carboxyl and hydroxyl groups of cellulose as they have valence shell electrons in the outer orbital. But, it is hard for Zn^{2+} to coordinate with carboxyl and hydroxyl groups[23] because the outer orbital electrons are completely filled and hence the adsorption capacity of Zn^{2+} was minimized. In this present work we have successfully handled the FT-IR technique to characterize the functional groups of various adsorbents. We were also able to notice the variation in the spectral change before and after the adsorption of metal ions. An attempt was also made to compare the FT-IR spectra of various adsorbents to derive a conclusion of the most effective adsorbent among all adsorbents used.

3.4. Desorption and Reuse. Desorption of the adsorbed metal ions from the adsorbents was also studied. The desorption efficiency of the adsorbed metal ions ranged from (95 to 97) %. The reusability of the adsorbents was measured by repeating the metal ion adsorption−desorption cycle 4 to 5 times using the same adsorbents. One possible cause of reduction in the adsorption capacity of the adsorbents could be the adverse effects of the desorbing agents on the binding sites. The regeneration of the adsorbents shows that the adsorption−desorption process is a reversible process and that the adsorbents can be used repeatedly for the removal of metal ions from aqueous solution.

4. CONCLUSIONS

The present work described the usage of the FT-IR technique to characterize various native and surface modified adsorbents. All of the fruit peels in this study were known to contain cellulose. Hence, the FT-IR spectra are highly useful to characterize the carboxyl and hydroxyl functional groups of cellulose. From the FT-IR data, it was confirmed that carboxyl and hydroxyl groups played an important role in metal ion coordination, and after the metal ion coordination, these functional groups were subjected to significant variation. FT-IR experiments in this work assisted us to derive a conclusion that LPCACS is the most efficient adsorbent among the native and surface modified adsorbents. An interesting phenomenon of metal−carbon bond formation was also observed during metal ion adsorption. Also among the metal ions, it was observed that Cu^{2+} and Ni^{2+} were effectively adsorbed by adsorbents and the adsorption of Zn^{2+} was minimized. The results of this study showed that a cost-effective and viable technology for effective elimination of heavy metal ions from wastewater could be developed using easily available fruit peels and the adsorbents used in this present study were better than commercially available activated carbon. In conclusion, the adsorption of metal ions is mainly dependent on nature of adsorbents, functional groups, and size and nature of metal ions. Extensive work will be carried out in future to explore the potential of these adsorbents in organic reactions to form metal−carbon bonding.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Supplementary Figure S1 to S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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