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Cellulose-Based Native and Surface Modified Fruit Peels for the Adsorption of Heavy Metal Ions from Aqueous Solution: Langmuir Adsorption Isotherms

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A viable and cost-effective technology was explored in this present task for removal of heavy metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution using three fruit peels such as orange peel (OP), lemon peel (LP), and banana peel (BP). The surface of the LP and lemon peel cellulose (LPC) was chemically modified. All these adsorbents were characterized by FT-IR, BET, and SEM. The widely used Langmuir adsorption isotherms were used to describe the adsorption equilibrium process. The adsorption capacity of metal ions such as Cu^{2+} and Ni^{2+} was found to be more than that 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 activated carbon (AC) also from which it was inferred that the order of the adsorption capacity is as follows: LPCACS > LPC > AC > LP.

1. Introduction

Water pollution due to toxic heavy metals has been a major cause of concern. Industrial and domestic wastewater are responsible[1] for causing damage to the environment and adversely affecting the health of people. The main techniques which have been utilized to reduce the heavy metal ion content of effluents include lime precipitation, ion exchange, adsorption into activated carbon, membrane processes, and electrolytic methods. All these methods are generally expensive and have significant disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements, or generation of toxic sludge or other waste products that require disposal. Adsorption is an alternative technique for heavy metal removal.[2] Activated carbon is the most widely used adsorbent material. In fact, the relatively high operating costs and difficult procurement have limited the application on a larger scale. Many researchers have been investigating new adsorbent materials for an alternative to activated carbon, such as seaweeds,[3] marine algae,[4] activated sludge biomass,[5] fruit peels and fibers,[6−8] crab shells,[9] coconut shell powder,[10] etc., for the removal of heavy metals from wastewater. Therefore, numerous approaches have been studied for the development of low-cost adsorbents for the removal of organic and organic pollutants from water and wastewater.[11,12] Fruits and their products can serve as a vehicle for wastewater treatment, and in this present work, we have reported fruit peel as an adsorbent for the removal of metals. The use of peel not only would provide a less costly adsorbent in contrast to activated carbon or synthetic ion exchangers but is also easily available and will save the environment from the above-mentioned pollution. We believed that it was possible to convert solid fruit peel residue into an effective adsorbent for the adsorption of metal ions and compared the activity with activated carbon. Due to the easy availability, low cost, simple preparation manner of adsorbents, and effective adsorption capacity, the adsorbents of this study are considered to be better than that of activated carbon. The organic compounds of fruit peel are mainly cellulose, hemicellulose, pectin substances, chlorophyll pigments, and other low molecular weight compounds.[13] The pectin substances, which account for more than 40 % of the dry matter, are complex heteropolysaccharides containing galacturonic acid, arabinose, galactose, and rhamnose as the major sugar constituents.[14] Due to the carboxyl functions of galacturonic acid, pectin substances are known to strongly bind metal cations in aqueous solution.[15] Many documents relating to agricultural waste also explain that heavy metal absorption is due to cellulose, as cellulose has the provision of functional groups for heavy metal bonding.[6,16] In this task, we have used lemon peel (LP), orange peel (OP), and banana peel (BP) as adsorbents for the removal of various metal ions such as Cu(II), Ni(II), Zn(II), Pb(II), and Cd(II). Even though OP[8,17] and BP[18,19] have already been explored as adsorbents, to compare the adsorption activity of LP, we have chosen these adsorbents also. The authors of this study believe that the modification of surface properties of the adsorbents would definitely alter the adsorption phenomenon.

The carboxyl groups and hydroxyl groups in these adsorbents are believed to react with heavy metal ions in aqueous solution. The preparation and composition of native and modified materials are described, and the extent of metal sorption is discussed. We have tried to compare the activity of these three native and modified fruit peels with activated carbon for removal of metal ions and also the adsorption activity of different metal ions, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}. The results suggest that the adsorbents used in this study are considered to be better adsorbents than that of activated carbon.

2. Experimental

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 the chemicals and reagents used in this study were of analar grade (AR grade) and used without any further purification.

2.2. Fruit Peels. OP, LP, and BP were obtained from a local fruit market in Chungli (Taiwan) at a cheap cost. The peels

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were first washed with water (more than 5 times) to remove any adhering dirt or moisture. They were then dried in an oven at temperature (50 °C) for 48 h before being ball-milled to form particles approximately 0.840 mm in size.

2.2.1. Determination of the Point of Zero Charge. The point of zero charge (PZC) for the fruit peels was determined by the following procedure:[20−22] 100 mL of deionized water was added to an Erlenmeyer flask, which was then capped with cotton. The deionized water was heated until boiling for 20 min to eliminate the CO_2 and dissolved ions in the water. The CO_2 free water was cooled as soon as possible, and the flask was immediately capped. Now this water is free from both cations and anions, and it is considered to be a neutral one. On the other hand, 0.5 g of fruit peel was weighed and placed in a 25 mL Erlenmeyer flask to which 10 mL of CO_2 free deionized water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at 25 °C. The pH of the solution was measured, and this value is the point of zero charge.

2.2.2. Determination of Active Sites. Acidic and basic sites on both natural and oxidized fruit peels were determined by the acid−base titration method proposed by Boehm.[23] The total acidic sites matching the carboxylic, phenolic, and lactonic sites were neutralized using a 0.1 N NaOH solution, while the basic sites were neutralized with a 0.1 N HCl solution. The carboxylic and lactonic sites were titrated with a 0.1 N Na_2CO_3 solution; the carboxylic sites were determined with a 0.1 N $NaHCO_3$ solution; and the phenolic sites were estimated by the difference.

The acidic and basic sites were determined by adding 50 mL of 0.1 N titrating solution and 1 g of fruit peel to a 50 mL volumetric flask. The flask was partially immersed in a constant temperature water bath set at 25 °C, and it was left there for 5 days. The flask was agitated manually twice a day. Afterward, a sample of 10 mL was titrated with 0.1 N HCl or NaOH solution.

2.2.3. 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. NaOH (10 %, 25 mL) was added to the depectinated fruit peels. The mixture was shaken at 65 °C in a water bath for two days, then filtered and 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). The percentage composition of the fruit peel contents is tabulated in Table 1.

Table 1. Contents of Different Fruit Peels

adsorbents	pigment and fat (%)	pectin (%)	protein (%)	hemicellulose (%)	cellulose (%)
OP	6.50	60.33	4.83	20.08	8.25
BP	12.23	28.43	24.7	31.01	3.62
LP	9.33	33.87	13.93	28.52	14.35

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. Dried fruit peel (10 g) was added to 100 mL of 0.1 M NaOH solution and mixed for 2 h at room temperature and then filtered. Then 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). Dried fruit peel (10 g) was added to 100 mL of 0.1 M oxalic acid solution and mixed for 2 h at room temperature and then filtered. Then 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, 100 mL of 0.1 M oxalic acid solution was added and mixed for 2 h at room temperature and then filtered. Then 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. Lemon peel cellulose (LPC) (10 g) 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, 100 mL of 0.1 M oxalic acid solution was added and mixed for 2 h at room temperature and then filtered. Then 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 effect of the pH on the adsorption capacity was investigated using 100 mL of 300 ppm of metal ion solutions and 1 g of adsorbents. 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 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.

2.5. Analytical Procedure. The adsorption of metal ions from the aqueous solutions was studied. After the desired incubation 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

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

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 Langmuir linear isotherms, and the corresponding values were obtained by a linear method.

2.6. Desorption and Reuse. The reusability of the adsorbents for metal ion adsorption was determined. Measurements were repeated after 4 to 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 atomic absorption spectrophotometer (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

$$\text{desorption ratio (\%)} = (\text{amount of metal ions desorbed to the elution medium})\cdot 100/(\text{amount of metal ions adsorbed onto adsorbents})$$

2.7. 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) analysis. The SEM was carried out on an HITACHI-S-800, field emission scanning electron microscope. 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 model METER 6171.

3. Results and Discussion

In this present investigation, we have striven to report three different fruit peels such as orange peel, lemon peel, and banana peel as adsorbents for the removal of various metal ions like Cu(II), Ni(II), Zn(II), Pb(II), and Cd(II). Finally, the adsorption capacity of these adsorbents was compared with activated carbon.

3.1. Characterization of Fruit Peels. The major constituents of these peels were determined. From Table 1 it was inferred that the cellulose content was found to be high in LP (14.35 %) when compared to OP (8.25 %) and BP (3.62 %). It was also observed that OP has the largest pectin content, BP has the largest protein and hemicellulose contents, and LP has the largest cellulose content. As the cellulose plays an important role in the adsorption of metal ions, the content of cellulose is more significant both in native and in modified fruit peels and also in the extracted fruit peels. From the experiment of cellulose extraction, it was found that the order of cellulose content was LP > OP > BP. The FT-IR spectra of these peels revealed that these adsorbents contained carboxyl and hydroxyl groups which were able to react with heavy metal ions in aqueous solutions. The order of carboxyl group content in the peels was LP > OP > BP, and the adsorption capacity was also expected to be in the order LP > OP > BP. This clearly showed that the adsorption of heavy metals depends upon the carboxyl and hydroxyl groups present in cellulose. So, we tried to extract the cellulose from LP, and this was known as lemon peel cellulose (LPC). We were able to observe that this extracted cellulose had greater adsorption capacity than that of raw peel. It clearly revealed that the carboxyl and hydroxyl groups content will influence the adsorption capacity, and the higher the content, the better the adsorption capacity. As the cellulose content in LP was higher, the adsorption of heavy metals by LP was expected to be more. We further preceded our experiments to modify the surface of the LP by different chemical methods, and we also compared the adsorption capacities of various modified LP and native LP. The active sites present in all the adsorbents and pH_{pzc} are determined. From these data, it was observed that the presence of carboxylic groups is higher in the case of fruit peel cellulose when compared to the fruit peel. For example, in LP it is 0.400 $meq\cdot g^{-1}$, whereas in LPC it is 0.715 $meq\cdot g^{-1}$. The carboxyl content of LPS is 0.55 $meq\cdot g^{-1}$, and LPAC is 0.735 $meq\cdot g^{-1}$; LPACS is 0.825 $meq\cdot g^{-1}$; and LPCACS is 0.875 $meq\cdot g^{-1}$. Thus, LPCACS was found to show the largest content of carboxyl among the various surface modified LP and LPC adsorbents. In terms of pH_{pzc}, the pH_{pzc} of the adsorbent after surface modification was lower than that of native fruit peel. For example the pH_{pzc} of native LP is 4.65 which after surface modification was found to be 2.63 in LPACS, 2.68 in LPAC, and 8.31 in LPS. It is obvious that due to saponification the pH_{pzc} of LPS should be higher than that of LP. Also, the pH_{pzc} (2.88) of LPCACS is lower than that of LPC (8.28). It can be explained that if $pH > pH_{pzc}$ in the solution, the surface of the adsorbent will contain more functional groups such as carboxyl groups and hydroxyl groups and hence increase the adsorption capacity of the adsorbents toward metal ions. The carboxyl groups of LPACS and LPCACS were increased due to acid carboxylation after saponification. This is because of the fact that after the surface modification of acid carboxylation after saponification the adsorbents were free from unwanted organic substances. So, the functional groups were increased and free from the interference to act as robust binding sites for metal ions. In LPS the phenolic and lactone contents were reduced relative to that of LP, but the carboxyl contents were increased due to saponification of protein and other organic matter. In the case of LPAC, the carboxyl contents were still increased due to the treatment of oxalic acid which itself can provide carboxylic acid functional groups. In the case of LPACS and LPCACS, due to both saponification and oxalic acid treatment, the carboxylic group contents were increased rapidly compared to that of LP. In general, in all the adsorbents the acidic contents are higher than that of basic contents leading to the totally acidic nature of all the adsorbents except in the case of LPS. Theoretically speaking, the chemical adsorption of heavy metal ions was favored if the adsorbents are acidic in nature, and hence all the adsorbents could effectively remove the heavy metal ions.

3.2. FT-IR, BET, and SEM. The presence of carboxyl and hydroxyl groups[23] was confirmed by FT-IR spectra. The peak at (3380 to 3480) cm^{-1} is due to ν(O−H); the peak at (2920 to 2940) cm^{-1} is due to $\nu(CH_3, CH_2, CH, \text{and } OH)$; the peak at (1630 to 1650) cm^{-1} is due to ν(C=O); and the peak at (1020 to 1060) cm^{-1} is due to ν(C−O). Comparison of FT-IR spectra of raw peel and extracted cellulose led to the conclusion that the peaks corresponding to carboxyl and hydroxyl groups were well resolved in the case of fruit peel cellulose. The surface area and pore size of the adsorbent generally determine the adsorption phenomenon. We can see that OP (1.9996 $m^2\cdot g^{-1}$), BP (1.2728 $m^2\cdot g^{-1}$), and LP (1.2714 $m^2\cdot g^{-1}$) have very small surface areas (<2 $m^2\cdot g^{-1}$) but large pore sizes 38.4702 Å, 15.4810 Å, and 39.4830 Å for OP, BP, and LP respectively. Even though LP has a very small BET surface area (1.2714 $m^2\cdot g^{-1}$), it still has a significant pore size of 39.483 Å (3.9483 nm). If there is still a controversy in the surface area and pore size,[20] 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 they do not have

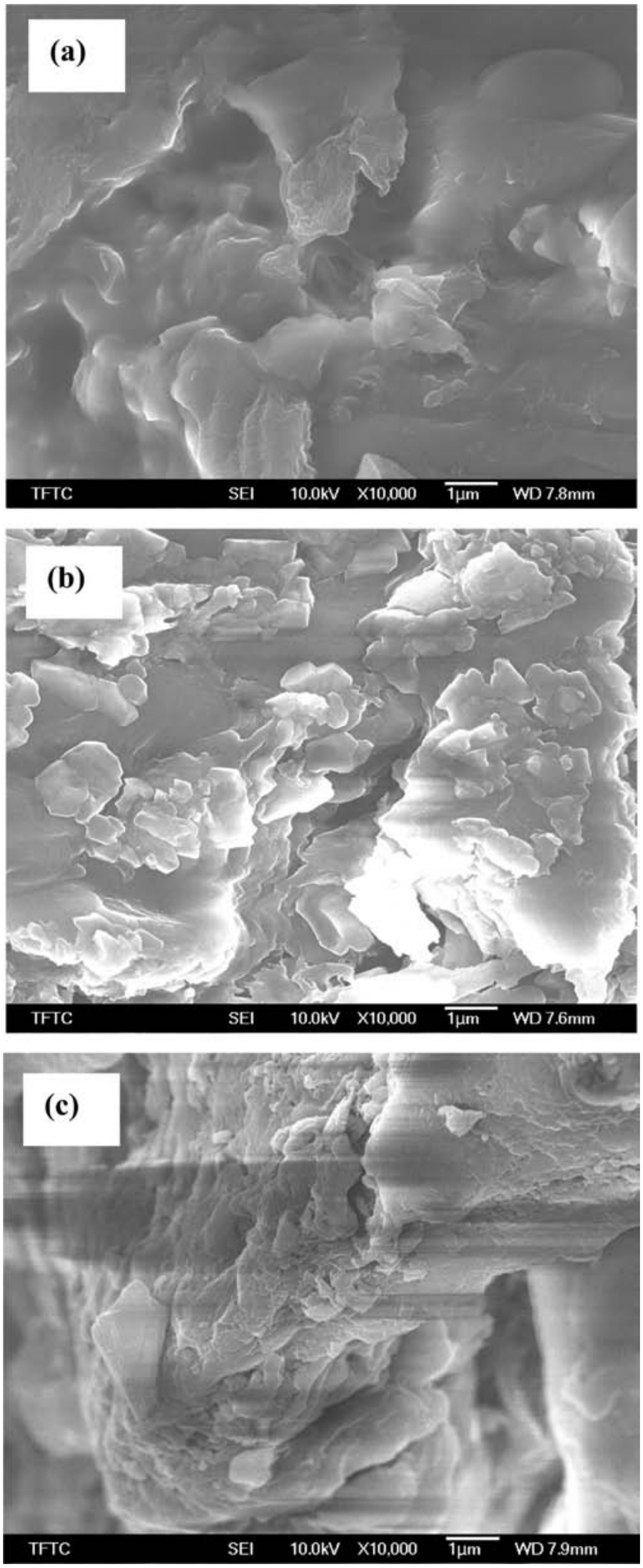

Figure 1. SEM of (a) LP, (b) LPC, and (c) LPCACS.

any defined holes (only a few pores on the surface) in their morphology. Figure 1 comprises the SEM of LP, LPC, and LPCACS and also confirmed the chemical modification of the surface of the adsorbent. The surface modification of adsorbents led to variation in morphology, like the structure of the surface and crystalline pattern, and hence the difference in adsorption capacity was observed for various adsorbents. But surface modification did not affect the surface area of the adsorbents.

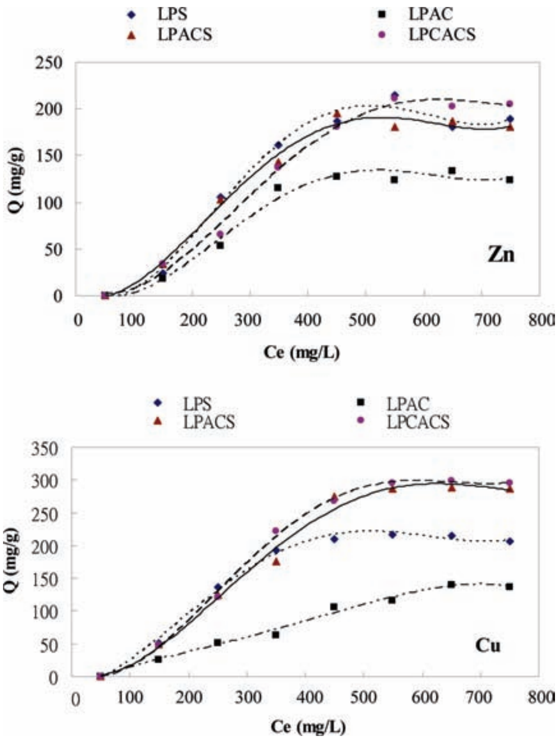

Figure 2. Adsorption of heavy metal ions (Cu^{2+}, Zn^{2+}) by surface modified LP and LPC.

3.3. 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 masses of 100 mg, (1 to 600) mg, and (1 to 800) mg heavy metals were used in solutions and were mixed with 1 g of adsorbent cellulose (LP, OP, BP, LPC, OPC, BPC, LPS, LPAC, LPACS, LPCACS), and the adsorption behavior was studied after 24 h. Generally, Langmuir and Freundlich adsorption models were used to study the adsorption phenomenon.[24−26] To access the adsorption effect of adsorbents, the Langmuir linear adsorption model was used in this study. The adsorption of various metal ions (Cu^{2+}, Zn^{2+}) by surface modified LP and LPC is shown in Figure 2. The adsorption data of metal ions and Langmuir parameters for all the adsorbents fruit peel and fruit peel cellulose were obtained. 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) $mg \cdot L^{-1}$, the adsorption capacity remained almost constant. This is because during that initial concentration of (300 to 400) $mg \cdot L^{-1}$ the active adsorption positions of the adsorbents were almost gradually filled by metal ions, and hence the adsorption activity of adsorbents was limited.[27] So, if the initial concentration of metal ions was increased further, no more adsorption was observed due to the unavailability of adsorption sites. So, (300 to 400) $mg \cdot L^{-1}$ 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 results of LPC, OPC, and BPC reveal that the maximum uptake of metal ions was by LPC. Among the surface modified LP, LPACS had the largest adsorption capacity of all heavy metal ions. Surface modified LPCACS showed an increased adsorption capacity compared to that of

Table 2. Comparison of the Adsorption Activity of LP, LPC, Surface Modified LP, Surface Modified LPC, and AC

	adsorption of metal ions ($mg \cdot g^{-1}$)				
adsorbents	Cu^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Cd^{2+}
LP	70.92	37.87	27.86	80.00	54.64
LPS	227.27	204.08	196.08	238.10	172.41
LPAC	208.33	99.01	142.86	200.00	117.65
LPACS	314.83	256.41	192.31	277.78	185.19
LPC	263.16	123.46	112.36	232.56	114.94
LPCACS	344.83	277.78	222.22	285.71	192.31
AC	138.80	109.30	112.30	–	–

LPC. The comparison of adsorption capacity of LP, surface modified LP, LPC, and AC was also carried out, and the results are given in Table 2. For the same amount of adsorbent used in all cases, fruit peel cellulose showed the highest adsorption capacity compared to that of the corresponding native fruit peels. Also, the surface modified fruit peel cellulose showed enhanced adsorption activity compared to that of surface modified fruit peel. LPCACS had shown the maximum heavy metal ion adsorption capacity among all the adsorbents used in this study. This is due to the fact that the carboxyl content of LPCACS is greater than that of other adsorbents. Thus, the dependence of adsorption capacity on carboxyl contents of cellulose was confirmed. Many previous researchers[16,28] have speculated that cellulose, hemicellulose, and lignin contain carboxyl and hydroxyl groups which can easily bind with metal ions to remove the metal ions from solution. Hence, the overall conclusion was made that LPCACS is an effective and efficient adsorbent among all the adsorbents used in the present work for removal of heavy metal ions. The adsorbents were also characterized by FT-IR after metal ion adsorption and compared with the original result as shown in Figure 3. This clearly revealed that the prominent peak intensity of carboxylic groups and hydroxyl groups[23,29] at (3380 to 3480) cm^{-1}, (1630 to 1650) cm^{-1}, and (1020 to 1060) cm^{-1} was appreciably reduced, confirming the coordination linkage of carboxylic acid and hydroxyl groups with heavy metal ions. The availability of free functional groups was reduced, and hence the corresponding peak intensities were also reduced. These experiments vividly explain that the carboxyl groups and hydroxyl groups which have unshared pairs of electrons can form coordination linkages with metal ions.

3.4. Comparison of Adsorption Capacity of Heavy Metal Ions. On the basis of the experimental results, it was observed that among all these heavy metal ions the adsorption behavior of both Cu and Ni was appreciably higher than that of the remaining metal ions. Zn was found to have the lowest adsorption capacity. This could be explained by the fact that both Cu^{2+} and Ni^{2+} can easily react with the functional groups containing donor sites (F, O, N, P, S) which have unshared pairs of electrons to form a coordination linkage, and also they have a 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 relatively have greater affinity to carboxyl groups when compared to Zn^{2+}. The stronger the effect of the ligand, the more there will be crystal field splitting which generally promotes extra stability for complexes. The extent to which the e_g and the t_{2g} orbitals are separated is denoted by the quantity 10Dq or Δ (Δ = crystal field splitting parameter). Generally, for d^9 (Cu^{2+}) systems, crystal field stabilization energy is $(-3/5)\,\Delta_{(\text{octahedral})}$ [−6Dq] or $(-2/5)\,\Delta_{(\text{tetrahedral})}$ [−4Dq], whereas for the d^{10} (Zn^{2+}) system it is almost zero, i.e., $0\ \Delta_{(\text{oct/tetrahedral})}$ [0Dq] (may be no crystal field splitting at all). Because of this crystal field splitting, 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. As we have used cellulose as the adsorbent in this study, it is hard for Zn^{2+} to coordinate with carboxyl and hydroxyl groups[30] as it is inactive because the outer orbital electron is completely filled and hence the adsorption capacity of Zn^{2+} is minimized. This result is in good agreement with the Irving and Williams series.[27,31] They have formed the following series based on the activity of metal ions: $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+}$. From the experimental results and observations, the order of heavy metal ions (based on their adsorption capacity) could be drawn as follows: in the case of LP, OP, and BP, Ni > Cu > Cd > Pb > Zn; in the case of LPC, OPC, and BPC, Cu > Ni > Pb > Cd > Zn; in the case of surface modified LP and LPC, Cu > Ni > Pb > Zn > Cd. Concerning the experimental observation, it could be understood that the type of metal ions, the size of the metal ions, valence shell electrons, concentration of metal ions, pH of the solutions, functional groups of the adsorbent, and nature of the adsorbent are important key factors that would greatly affect the adsorption phenomenon. Even though there are several factors that can affect the adsorption effect,[32] only the concentration of the metal ions and pH of the solution can be varied to study their effect on adsorption. An attempt was made to compare the activity of these adsorbents with activated carbon also, from which the following conclusion was made that the order of adsorption of capacity of adsorbents was LPCACS > LPC > AC > LP.

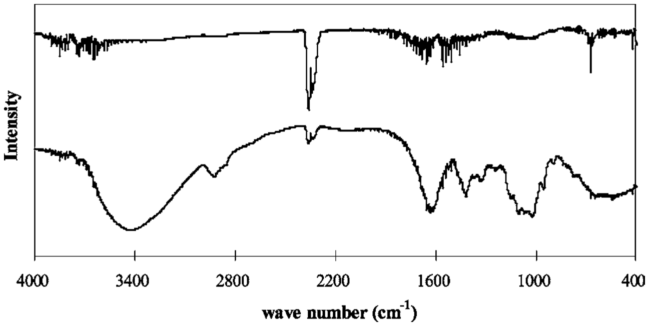

Figure 3. FT-IR spectra of LPC before (lower) and after (upper) adsorption of Cu^{2+}.

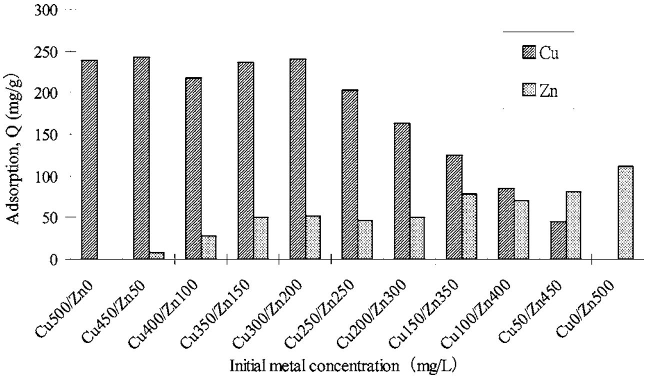

Figure 4. Competitive adsorption of Cu^{2+} and Zn^{2+} heavy metal ions by LPC (confirmation of the high affinity of Cu^{2+} in the presence of Zn^{2+}).

3.5. Confirmation of High Affinity of Cu^{2+} in Coexistence with Zn^{2+} (Competitive Adsorption of Cu^{2+} and Zn^{2+} by LPC). To confirm the high affinity of Cu^{2+} in the presence of Zn^{2+}, we have taken one adsorbent LPC to carry out an adsorption experiment in the presence of Cu^{2+} and Zn^{2+} in the same solution. The adsorption capacity is shown in Figure 4. The

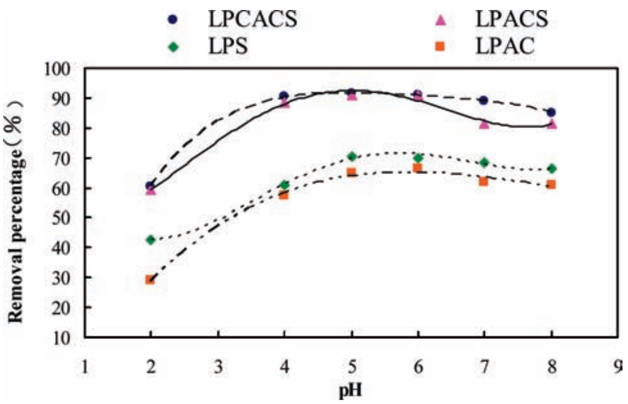

Figure 5. pH effect on adsorption of Cu^{2+} by surface modified LP and LPC.

results clearly reveal that when two metal ions such as Cu^{2+} and Zn^{2+} are present at the same time in a solution the adsorbent LPC adsorbed a large amount of Cu^{2+} regardless of the amount of Cu^{2+} in the solution. When the initial concentration of both metal ions varied also, the adsorption of Cu^{2+} has shown to be larger than that of Zn^{2+}. When the solution contains a lot of Cu^{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 Cu^{2+} than Zn^{2+}. When both metals were displayed in solution, the overall competitiveness of the metal ions was $Cu^{2+} > Zn^{2+}$. Thus, high affinity[25] of Cu^{2+} ions for carboxylic and hydroxyl group contents of cellulose by LPC was confirmed when two metal ions coexist.

3.6. Effect of pH and Solubility (Speciation) on Heavy Metal Adsorption. The heavy metal ions adsorption was strictly pH dependent,[33,34] and so the pH of the aqueous solution is an important controlling parameter in the heavy metal ion adsorption process.[35] To investigate the effect of pH, the experiment of adsorption of various metal ions was carried out at different pH values, viz., 2, 4, 5, 6, 7, 8, etc. The adsorption of Cu^{2+} ions as a function of pH (2 to 8) for surface modified LP and LPC is shown in Figure 5. In the assay, if the pH of the solution was lowered, the positively charged protons in solution will compete with the heavy metal ions, and hence there would be a decline in the adsorption of heavy metal ions. But when pH was increased, there would be a dissociation of weak acid[14,29,36] (pK_a of oxygen containing carboxylic and phenolic OH groups) which could make the adsorbent surface negatively charged to attract the positively charged metal ions, and hence the opportunity of heavy metal binding on adsorbents also increased.[17] Since the pH_{pzc} of LPAC, LPACS, and LPCACS was less than 3, the pH of the assay was maintained greater than that of 3. It could be seen that as the pH increased the adsorption of heavy metal ions also increases. Also, the maximum uptake was observed between the pH range 4.0 and 6.0, and the adsorption capacity of LP was more than that of BP and OP. In all cases at pH 2.0, poor uptake of metal ions (10 %) was observed as the $pH < pH_{pzc}$. On comparison, it was observed that the fruit peel cellulose had more adsorption capacity than that of the corresponding fruit peels. In the case of fruit peel cellulose, also the maximum uptake was between pH 4.0 and 6.0, and LPC showed enhanced adsorption capacity. In this case also, the uptake at pH 2.0 was less but still higher than that of fruit peels. Hence, LP and LPC were considered to be the efficient adsorbents among all fruit peels. Among the surface modifications of LP, LPACS was found to be the most effective adsorbent. Beyond pH 6.0, a decline in metal adsorption was observed.[27,35] The small decrease in removal of metal ions at higher pH values was due to the formation of hydroxides. 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 could also decide the adsorption behavior of metal ions. This could 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 were $CuOH^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, and Cu^{2+} according to Wang and Qin.[37] As the $pH < 6$, Cu^{2+} would be the dominating species which could easily be self-adsorbed on the surface as the solubility of Cu^{2+} is more at this pH. If $pH > 7$, insoluble hydroxide precipitation would occur which reduced 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 LPCACS the existence of Cu^{2+} at pH 4.0 to 6.0 was maximum and hence had a better adsorption effect (91 % of Cu^{2+} adsorption). For the same experimental condition (300 $mg \cdot L^{-1}$) the adsorption of metal ions by LPCACS was decreased from 91 % to 89 % when pH increased to 7 from 6. At pH 8, still there is a small decrease (85 %) in the adsorption. Thus, a small decrease in adsorption from pH 6 to 8 was observed for all adsorbents. The increase in metal removal as pH increased could be explained on the basis of a decrease in competition between proton and metal species for the surface sites.[9,27,28,35] At lower pH, the concentration of protons in solution is higher and stronger than that of the metal ions to occupy the surface of the adsorbent, and they compete with the metal ions for the chelating sites. So, the opportunity of heavy metal binding was minimized. As the pH increased gradually, the H^+ ions in solution declined, and hence the adsorption of heavy metal ions was favored at higher pH values.[9,27,28,35]

Table 3. Comparison of the Adsorption Activity of LP, LPC, and LPCACS for Cu^{2+} Adsorption with the Reported Work in the Literature

adsorbents	amount of adsorption ($mg \cdot g^{-1}$)	reference
rice husk	10.90	Krishnani et al., 2008[35]
sugar beet pulp	28.50	Aksu and Isoglu, 2005[33]
crab shell	243.90	Vijayaraghavan et al., 2006[9]
soybean hulls	83.30	Marshall, 1996[38]
cottonseed hulls	58.80	Marshall, 1996[38]
dry activated sludge	294.00	Gulnaz et al., 2005[5]
carrot residue	32.74	Nasernejad et al., 2005[28]
papaya wood	12.81	Saeed et al., 2005[6]
banana pith	13.50	Low et al., 1995[39]
apple waste	10.80	Lee and Yang, 1995[40]
sawdust	1.74	Vaishya and Prasad, 1991[41]
Tree fern	11.70	Ho, 2003[30]
LP	70.92	this study
LPS	222.27	this study
LPAC	208.33	this study
LPACS	314.83	this study
LPC	263.16	this study
LPCACS	344.83	this study
AC	138.80	this study

The adsorption capacity of the adsorbents used in this work was compared with some earlier reported work as given in Table 3. According to our knowledge for uptake of Cu^{2+}, the adsorbents used by us in this work seemed to be the better adsorbents among all those reported in earlier works.

4. Conclusions

Among the three fruit peels, LP was found to be a good adsorbent. So, we have extracted cellulose from the LP and also chemically modified the surface of LP and LPC. It was concluded that carboxylic acid and hydroxyl groups of cellulose play a vital role in binding the metal ions. The FT-IR spectra of the adsorbents after metal ion adsorption showed a decrease in the intensity of carboxylic and hydroxyl group peaks due to coordination with metal ions. LPCACS had enhanced adsorption capacity among all the adsorbents due to an increase in the functional groups. Among the five metals, Cu^{2+} and Ni^{2+} could effectively be adsorbed by the adsorbents. The adsorption phenomenon depended upon several factors like size and nature of metal ions, concentration of metal ions in solution, and pH of the solution. The results of this study showed that the adsorbents used in this present study were better than those of activated carbon and some other adsorbents reported so far. This study indeed suggested that a cost-effective and viable technology for effective elimination of heavy metal ions from industrial wastewater could be developed using easily available, familiar, and eco-friendly fruit peels.

Supporting Information Available:

Supplementary tables (Table S1 to S4) and figures (Figure S1 to S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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