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Characterization of Adsorptive Capacity and Investigation of Mechanism of Cu^{2+}, Ni^{2+} and Zn^{2+} Adsorption on Mango Peel Waste from Constituted Metal Solution and Genuine Electroplating Effluent

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Abstract: The present study reports the potential of mango peel waste (MPW) as an adsorbent material to remove Cu^{2+}, Ni^{2+}, and Zn^{2+} from constituted metal solutions and genuine electroplating industry wastewater. Heavy metal ions were noted to be efficiently removed from the constituted solution with the selectivity order of $Cu^{2+} > Ni^{2+} > Zn^{2+}$. The adsorption process was pH-dependent, while the maximum adsorption was observed to occur at pH 5 to 6. Adsorption was fast as the equilibrium was established within 60 min. Maximum adsorption of the heavy metal ions at equilibrium was 46.09, 39.75, and 28.21 mg g for Cu^{2+}, Ni^{2+}, and Zn^{2+}, respectively. Adsorption data of all the three metals fit well the Langmuir adsorption isotherm model with 0.99 regression coefficient. Release of alkali and alkaline earth metal cations (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) and protons H^{+} from MPW, during the uptake of Cu^{2+}, Ni^{2+}, and Zn^{2+}, and EDX analysis of MPW, before and after the metal sorption process, revealed that ion exchange was the main mechanism of sorption. FTIR analysis showed that carboxyl and hydroxyl functional groups were involved in the sorption of Cu^{2+}, Ni^{2+}, and Zn^{2+}. MPW was also shown to be highly effective in removing metal ions from the genuine electroplating industry effluent samples as it removed all the three metal ions to the permissible levels of discharge legislated by environment

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protection agencies. This study indicates that MPW has the potential to effectively remove metal ions from industrial effluents.

Keywords: Adsorption, desorption, electroplating effluent, heavy metals, mango peel waste

INTRODUCTION

Unabated release of heavy metals through industrial wastewaters into natural water bodies is a serious threat to global ecosystems. The industries mainly responsible for this problem include mining, milling, electroplating, tanneries, surface-fishing, agrochemicals, and polymers and plastics, which are discharging a variety of toxic metals, such as cadmium, copper, nickel, cobalt, zinc, and lead into the environment (1). These metals, some even at low concentrations, are toxic to living organisms including human beings (2). Various conventional treatment procedures, such as chemical precipitation and coagulation, ion exchange, reduction, osmosis and reverse osmosis, membrane-intervention processes, and electrolytic technologies, are available to remove heavy metals from aqueous solutions (3). However, technologies like chemical precipitation and coagulation become less cost-effective when high effluent volumes and wastewater with low metal concentrations are to be treated (4). The precipitation process, likewise, has other disadvantages, such as the generation of toxic sludge (5). The application of membrane-intervention technology and activated carbon are also prohibitive due to high operational cost (3). There is a growing interest, therefore, in finding alternative low-cost procedures having least technological limitations for the removal of heavy metals from industrial effluents. Towards the development of efficient and environment-friendly alternative technologies, various low-cost agrowaste materials, such as rice husk (6), wheat straw (7), black gram husk (8), mungbean husk (9), apple residues (10), carrot residues (11), orange and banana peel (12), peanut hull (13), and coffee wastes (14), to name only a few, have been investigated for their biosorptive properties. Different types of biomass have shown different levels of metal adsorption capacity (1). The knowledge generated thus far, nevertheless, is still insufficient to solve the problem. Further work is, therefore, still needed to investigate the metal adsorption potential of several other abundantly available low-cost agrowaste materials for the removal of heavy metals from aqueous solutions.

In the continuing search to achieve the desired objective, mango peel waste, an abundantly available waste from the fruit processing industry, was evaluated as a new biosorbent for the removal of heavy metals from aqueous solutions. Mango (*Mangifera indica* L., family Anacardiaceae) is a delicious fruit grown in almost all the tropical and subtropical regions of the world. With about 27 million tons of annual production, mango ranks 5th among major fruit crops (15). The edible part (the pulp), which makes upto 33–85% of the fresh fruit (16), is processed for such products as juice, nectar, concentrate, jam, and jelly powder (17). During the processing of mango, peel and kernels are generated as waste which contributes 7–24% and 9–40%, respectively, to the total fruit weight (16). Whereas the utilization of mango kernels as source of fat (18), natural antioxidants (19), starch (20), flour (21), and feed ingredients (22) has been extensively investigated, studies on the use of peel are limited. Mango peel, having no commercial application is therefore discarded as a garbage waste, which not only becomes a source of pollution but causes a further cost-input on its disposal to the industry. MPW also requires special treatment for its disposal due to high level of residual phenolics content, which may have adverse environmental impact, mainly because of the inhibitory effects of polyphenols on seed germination (23). The mango processing industry, therefore, has to incur additional cost on its waste treatment-disposal unit operation. In addition to the polyphenols, mango peel also contains other constituents including pectin, cellulose, hemicellulose, lipids, proteins, and carotenoids (24). Pectin and cellulose are the predominant types of polysaccharides present in MPW. Functional carboxylic groups of pectin (galacturonic acids) and alcoholic-hydroxyl groups of cellulose are known to strongly bind metal cations in aqueous solutions in the adsorption process (25,26). MPW is likely, therefore, to find application in the development of a low-cost adsorbent for removal of toxic metals, dyes and other organic wastes from industrial effluents.

The present paper reports on the application potential of this pectin- and cellulose-rich biowaste material (MPW) as a new, inexpensive, and environment-friendly adsorbent for the treatment of wastewater containing toxic metals. Metal ions, such as Cu^{2+}, Ni^{2+}, and Zn^{2+}, commonly present in electroplating wastewater, were selected as adsorbates for this investigation. The mechanism of sorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} by MPW was investigated using FTIR, EDX analysis and concomitant release of alkali and alkaline earth metal cations (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) from MPW with the uptake of selected metal ions. The effect of various operating parameters on adsorption, such as the amount of adsorbent, contact time, solution pH, and metal ion concentration were monitored to optimize the adsorption process for possible use of MPW as a low-cost adsorbent for wastewater treatment. Potential of the new adsorbent was further investigated for the removal of some selected metal ions from genuine electroplating effluent.

MATERIALS AND METHODS

Adsorbent Material

MPW was obtained from the mango juice production unit of Food and Biotechnology Research Centre, Pakistan Council of Scientific and Industrial Research Laboratories Complex, Lahore, Pakistan. After thorough washing with tap water, the MPW was washed with double-distilled water, then oven dried at 70°C. The dried MPW was ground and sieved. Powdered material containing particle sizes from 0.85–1.0 mm was used for metal adsorption studies.

Metal Solutions

Standard stock solutions of Cu^{2+}, Ni^{2+}, and Zn^{2+} (1000 ± 2 mg/L as nitrate salts, Merck Ltd., Poole, UK) were used to prepare appropriate concentrations of each metal for the adsorption studies. pH of the working solution was adjusted at 5.0, unless otherwise stated, using 0.1 M NaOH. Fresh dilutions were used for each adsorption study.

Determination of Point of Zero Charge

The point of zero charge (pH_{pzc}) of the solid biomass is a function of pH. The pH at which the charge of the solid surface is zero is referred to as the point of zero charge (pH_{pzc}). For the determination of pH_{pzc}, 45 ml of KNO_3 solution of known strength was transferred to a series of 100 ml Erlenmeyer flasks. A range of initial pH (pH_i) values of the metal solutions were roughly adjusted from 2 to 12 by adding either 0.1 M HNO_3 or NaOH. The total volume of the solution in each flask was made-up to exactly 50 ml by further addition of KNO_3 solution of the same ionic strength. The pH_i values of the solutions were then accurately noted and 0.1 g of MPW was added to each flask, which were securely capped immediately. The suspensions were intermittently shaken manually and allowed to equilibrate for 48 h. The suspension was then centrifuged at 5000 rpm for 5 min and the final pH values of the supernatant liquid (pH_f) were recorded. pH_{pzc} is the point where the curve pH final (pH_f) verses pH initial (pH_i) crosses the line equal to pH_f (27).

Adsorption Studies

The adsorption capacity of MPW (500 mg) was determined by contacting it with 100 ml of metal solutions of known concentration (10–500 mg/L) in 250-ml Erlenmeyer flasks. The flasks were shaken on an orbital shaker at 100 rpm for 120 min at room temperature (25 ± 2°C) followed by centrifugation at 5,000 rpm for 5 min to separate MPW from the metal solution. Residual metal concentration in the metal supernatant was determined using an atomic absorption spectrophotometer (UNICAM-969, Unicam, Cambridge, UK). To determine the rate of metal adsorption by MPW, the supernatant was analyzed for residual metal ions after contact periods of 15, 30, 45, 60, 90, and 120 min. The effect of pH was determined by adjusting the initial pH of each metal solution to values ranging between 2 and 7 using 0.1 M HCl or 0.1 M NaOH. The final pH of the adsorbent-adsorbate mixture was measured at equilibrium. All experiments were performed in triplicate. Metal- and MPW- free blanks were used as controls.

FTIR Spectroscopy

FTIR spectroscopy was done to identify the chemical functional groups present on MPW using a Thermo Nicolet IR-100 spectrometer (Thermo Nicole Corporation, Madison, USA). IR absorbance data were obtained for wavenumbers 400–4000 cm^{-1} and analyzed using the software Encompass® provided by the FTIR spectrometer manufacturer.

Treatment of Genuine Effluent from Electroplating Industry

Genuine electroplating effluent samples were collected from three different electroplating units located in Lahore, Pakistan and stored at 5°C until use. The sorption studies were conducted by contacting 0.5 g MPW biomass with 50 ml wastewater, pH 5.0, in the same manner as described above.

Reproducibility and Data Analysis

Unless indicated otherwise, the data reported are the mean values from three independent experiments. The amount of metal ions adsorbed per unit MPW biomass (mg metal/g dry adsorbent) was determined using the following expression:

$$q = V(C_i - C_f)/M \tag{1}$$

Where q = metal uptake (mg metal/g dry weight of MPW biomass);

V = volume of metal solution (L);
C_i = initial concentration of metal ions in the solution (mg/L);
C_f = final concentration of metal ions in the solution at any time;
M = dry weight of MPW (g).

RESULTS AND DISCUSSION

Characterization of MPW

Chemical composition of MPW is complex, principal constituents being polysaccharides and pectin, while proteins, fats, carotenoids, polypenols, and minerals are present as minor components (24). Dried MPW contains about 28% soluble fibers (pectin) and 43% insoluble fibers (cellulose and hemicellulose) (28). Both the fiber fractions contain hydroxyl and carboxylic functions, which are readily available to interact with metal cations, first by exchanging with protons and subsequently by chelating with metallic ions. These attributes make MPW a good candidate for use as an efficient low-cost adsorbent for removing heavy metals from aqueous solution. In order to confirm the presence of these functional groups on MPW, and also to study their involvement in metal uptake, FTIR spectra of MPW before and after metal adsorption were obtained. The main stretching frequencies of functional groups normally present in pectin as reported in literature (29) are given in Table 1. The FTIR spectrum of MPW, before the adsorption of metal ions (Fig. 1a), shows all the major functional groups reported in literature to be present in pectin (Table 1), thus confirming the presence of pectin in MPW as the major component. The broad intense adsorption peak at 3424 cm^{-1} may be attributed to the O–H stretching of carboxylic acids. The stretchings observed at 2924 and 2854 cm^{-1} may be assigned to C–H bonds. Peaks observed at 1732 cm^{-1} and 1619 cm^{-1} are due to esterified C=O group and COO– asymmetric stretching of a carboxylic acids. The

Table 1. Functional groups commonly present in pectin (20)

Wavenumber (cm^{-1})	Functional groups
3660–2500	O–H stretching
3000–2800	C–H stretching, symmetric, asymmetric
1760–1745	C=O, esterified stretching
1640–1620	COO– asymmetric stretching
1400	COO– symmetric stretching
1380	C–H bending
1300–1000	C=O stretching

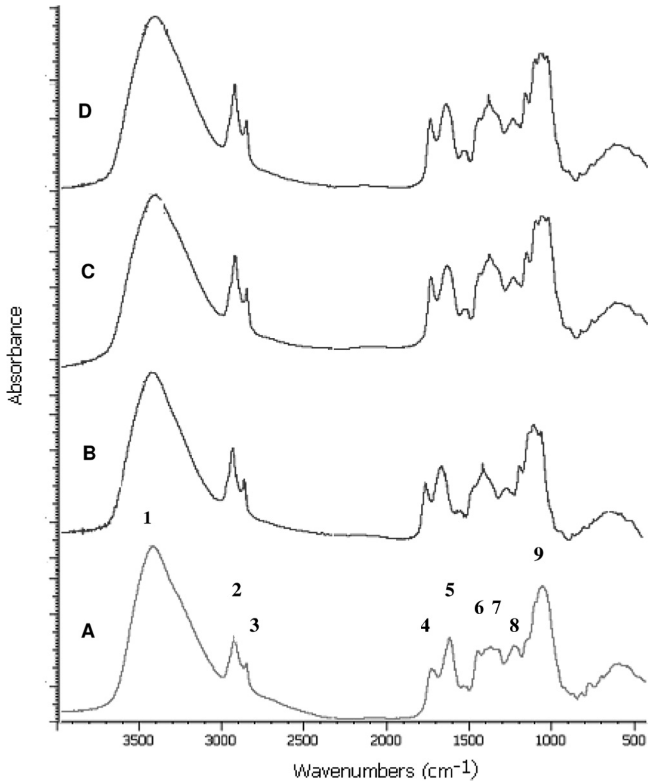


Figure 1. FTIR spectra of MPW: (a) before, and after the adsorption of (b) Cu^{2+}, (c) Ni^{2+} and (d) Zn^{2+}; loading; 1: O–H stretching; 2,3: C–H stretching; 4: C=O esterified stretching; 5: COO– asymmetric stretching; 6: COO– symmetric stretching; 7: C–H binding; 8: C–O stretching 9: C=O stretching.

COO– symmetric stretching is shown by the peak at 1440 cm^{-1}. The peak at 1373 cm^{-1} is due to C–H stretching. The peak at 1054 cm^{-1} may be assigned to C=O stretching of carboxylic acids. The FTIR spectra of MPW loaded with Cu^{2+}, Ni^{2+}, and Zn^{2+} were also obtained (Figs. 1b, c, d, respectively). The peaks expected at 3424, 1732, 1619, 1373, and 1054 cm^{-1} were respectively, shifted to 3441, 1736, 1638, 1383, and 1070 cm^{-1}. These shifts may be attributed to a change in the counterions associated with carboxylate and hydroxylate anions. It is evident from these spectra that carboxyl and hydroxyl groups were principally involved in the metal binding to MPW. Similar results of FTIR band changes of pectin rich biosorbents were also observed for the adsorption of Cr^{3+} and Pb^{2+} (30).

Metal Adsorption Kinetics

The rate of metal adsorption is an important factor and a prerequisite for determining the reactor design and process optimization for the development of a practicable unit operation procedure. The effect of adsorbent-adsorbate contact time on metal adsorption by MPW was accordingly determined (Fig. 2) The metal uptake was found to be rapid for all the three metals during the first 30 min of contact, accounting for 89.8, 87.56, and 82.5% of the total adsorption at equilibrium for Cu^{2+}, Ni^{2+}, and Zn^{2+}, respectively. Time required for attaining equilibrium for all the metal ions was about 60 min. The maximum metal uptake capacity of MPW at 25 mg/L metal solution for the three metals was noted to be 89.02, 76.40, and 67.27% for Cu^{2+}, Ni^{2+}, and Zn^{2+}, respectively. These results suggest that affinity of MPW for each metal was different, with the highest uptake capacity for Cu^{2+} and the lowest for Zn^{2+}. This difference in the maximum uptake level for various metal ions has been explained in terms of difference in the ionic size of the metals, the nature and distribution of active groups on the adsorbent and the mode of interaction between the metal ions and the adsorbent (31).

Various kinetic models have been applied to describe the transient sorption behavior in a batch adsorption process. However, pseudo-second order equation is usually used to describe the kinetic process, which can be represented as follows:

$$t/q_t = [1/k_{2ad}q_{eq}^2] + t/q_{eq} \tag{2}$$

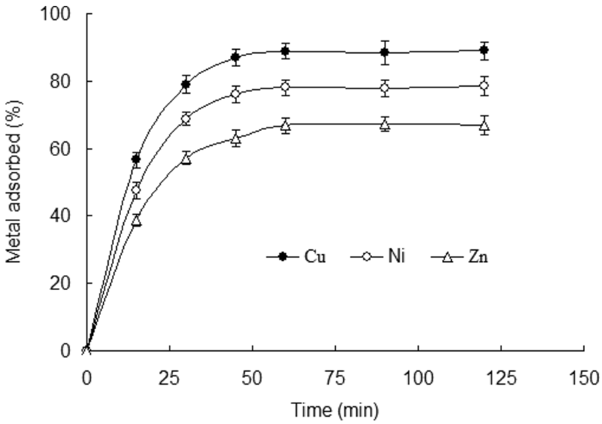


Figure 2. Adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} from 25 mg/L metal solution, pH 5.0, by 5 g/L mango peel waste (MPW) as related to contact time during orbital shaking at 100 rpm at 25 ± 2°C.

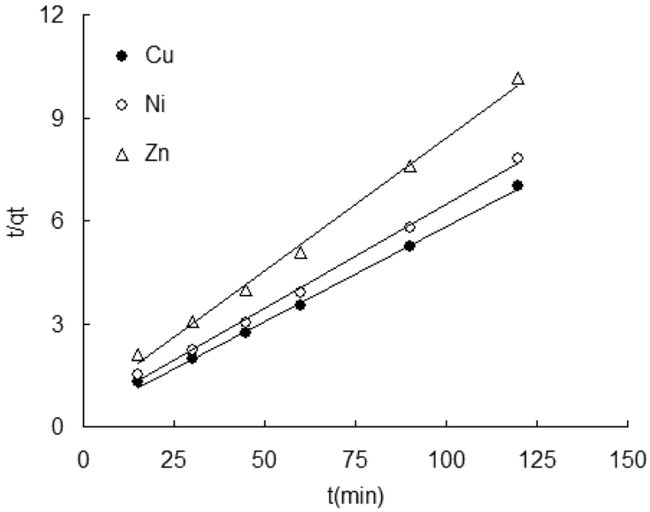


Figure 3. Plots of t/q_t versus time t (pseudo-second order kinetic model) for the adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} on mango peel waste. Experimental conditions are the same as given in Fig. 2.

Where k_{2ad}(g mg/min) = pseudo-second order reaction rate equilibrium constant.

A plot of t/q_t against t should yield a linear relationship for the applicability of the pseudo-second order kinetic model. The experimental data obtained in the present study were observed to fit well to the pseudo-second order equation (Fig. 3). A comparison of MPW experimental adsorption capacity for all the three metals, as well as the theoretical values calculated from the pseudo-second order kinetic equation are presented in Table 2. The correlation coefficients for the linear plots of t/q_t against t for the pseudo-second order equation were observed to be close to 1 for all the three metals. The theoretical q_{eq} values for all these metal ions were also very close to the experimental q_{eq} values. These

Table 2. The pseudo-second order kinetic equation constants for adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} on mango peel waste

Metal ions	Experimental q_{eq}(mg/g)	Theoretical q_{eq}(mg/g)	k_{2ad} (g/mg/min)	r^2
Cu^{2+}	16.98 ± 0.34	16.55	0.00923	0.998
Ni^{2+}	15.41 ± 0.55	14.83	0.00868	0.997
Zn^{2+}	11.83 ± 0.46	11.25	0.00853	0.996

observations suggest that metal adsorption by MPW followed pseudo-second order kinetic model.

Effect of pH on Metal Ion Adsorption

Solution pH has been reported to be the most important variable governing the removal of metal ions by adsorbents (32). The reaction of metal ions in solution with an adsorbent may be described as:

$$M^{+n} + BH_n \rightleftharpoons BM + nH^+ \tag{3}$$

Where M = metal; n = its charge and B = active centers of the adsorbent.

As per Eq. (3), pH influences metal ion adsorption due to the competition between metal and H^+ ions for the active sorption sites (33). pH affects both the solubility of metal ions and ionization states of functional groups, such as carboxyl and hydroxyl groups on pectin- and cellulose-rich adsorbents. In order to establish how pH affects metal ion adsorption onto MPW, batch equilibrium studies were conducted at different initial pH values in the range of 2–7 (Fig. 4). Very little adsorption took place at the initial pH 2 (14.75% Cu^{2+}, 9.81% Ni^{2+}, 10.75% Zn^{2+}). The low metal biosorption at pH 2 may be explained on

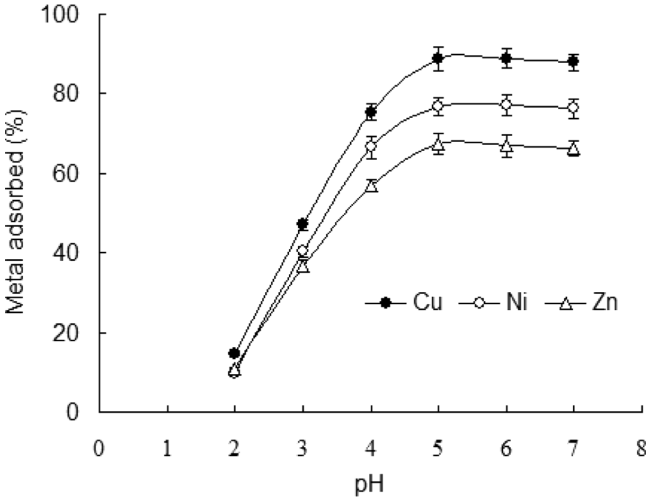


Figure 4. Effect of pH on the adsorption of Cu^{2+}, Ni^{2+} and Zn^{2+} from 25 mg/L metal solution by 5 g/L mango peel waste during orbital shaking at 100 rpm at 25 ± 2°C for 60 min.

the basis of protonation of active sites, resulting in H^+ and M^{2+} competing to occupy the binding sites (34). A continuous increase in biosorption capacity of MPW occurred in the pH range of 2–5 (88.71% Cu^{2+}, 76.92% Ni^{2+}, 67.30% Zn^{2+} at pH 5.0). This increase in metal ion removal, as the pH increased, may be explained on the basis of decrease in competition between H^+ protons and metal cations for the same functional groups and by decrease in the positive surface charge resulting in a lower electrostatic repulsion between the surface and metal ions (35). Further increase in adsorption with the increase of pH was insignificant as the optimum adsorption for all the three metals was reached at pH 5.0. For this reason, further metal adsorption studies were carried out at pH 5.0.

The increase in metal removal, as pH was increased, may be explained in terms of point of zero charge (pH_{pzc}) of the adsorbent in the solution. The point of zero charge (pH_{pzc}) of MPW was experimentally found to be at pH 4.4 (Fig. 5). At $pH > pH_{pzc}$, the adsorbent is negatively charged and the adsorbate species are positively charged. Such a situation enhanced the electrostatic attraction between the positive sorbate species (Cu^{2+}, Ni^{2+}, and Zn^{2+}) and the negatively charged adsorbent (MPW) surface, which ultimately resulted in the increased adsorption of metal ions. At $pH < pH_{pzc}$, on the other hand, the surface of the adsorbent is positively charged, thus a decrease in the removal of metal ions at $pH < pH_{pzc}$ was apparently due to the higher concentration

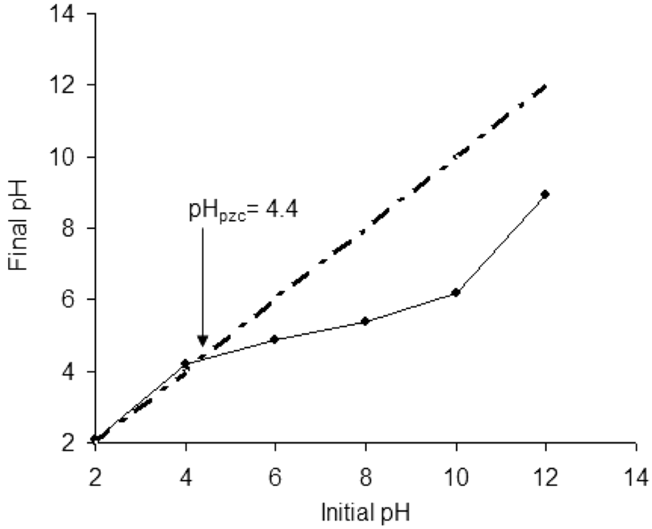


Figure 5. Point of zero charge (pH_{pzc}) curve of mango peel waste.

of H^+ ions in the reaction mixture that were competing with the positively charged metal ions for adsorption sites of MPW.

Adsorption Capacity of MPW

In order to evaluate the maximum metal adsorption capacity of MPW, the adsorbent was contacted with varying concentrations of Cu^{2+}, Ni^{2+}, and Zn^{2+} in single metal solution until equilibrium. The metal removing capacity of MPW, for all the three metals, was noted to increase with the increase in metal ion concentration in solution until it reached the maximum capacity of 46.09, 39.75, and 28.21 mg/g for Cu^{2+}, Ni^{2+}, and Zn^{2+}, respectively (Fig. 6). To examine the relationship between the metal adsorption capacity (q_{eq}) and the concentration of metal ions at equilibrium (C_{eq}), the adsorption equilibrium data for all the three metals were fitted to Langmuir and Freundlich isotherm equations. The Langmuir isotherm model has a theoretical basis, which relies on the chemical or physical interaction (or both) between the solute and the vacant sites on the adsorbent surface that may be described as follows:

$$q_{eq} = \frac{q_{\max} b C_{eq}}{(1 + bC_{eq})} \tag{4}$$

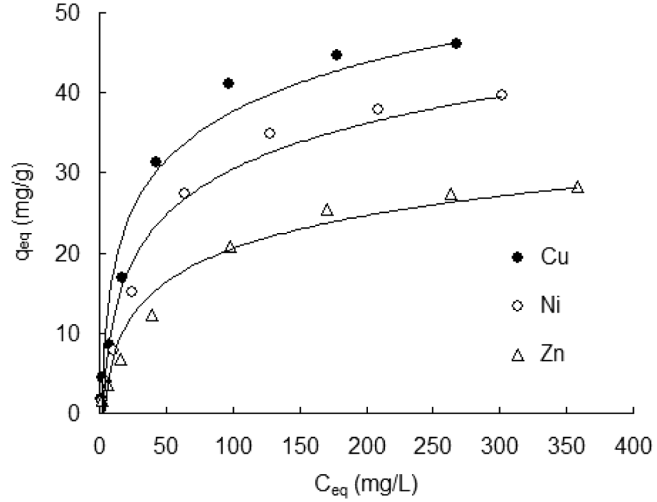


Figure 6. Effect of initial metal ions concentration (10–500 mg/L) on dsorption of Cu^{2+}, Ni^{2+} and Zn^{2+} by 5.0 g/L mango peel, pH 5.0, for the contact period of 60 min at 100 rpm shaking at 25 ± 2°C, where C_{eq} is the equilibrium metal ion concentration and q_{eq} is the metal uptake capacity per unit adsorbent at equilibrium.

Where q_{eq} = equilibrium uptake capacity (mg/g biosorbent); $q_{\max}$ = maximum uptake capacity (mg/g biosorbent); C_{eq} = equilibrium concentration (mg/L metal solution) and b = coefficient related to the affinity between metal ion and adsorbent (L/mg).

On the other hand, the Freundlich isotherm equation proposes an empirical model, which is based on sorption on a heterogeneous surface and is expressed as:

$$q_{eq} = K_{\mathrm{F}} C_{eq}^{1/n} \tag{5}$$

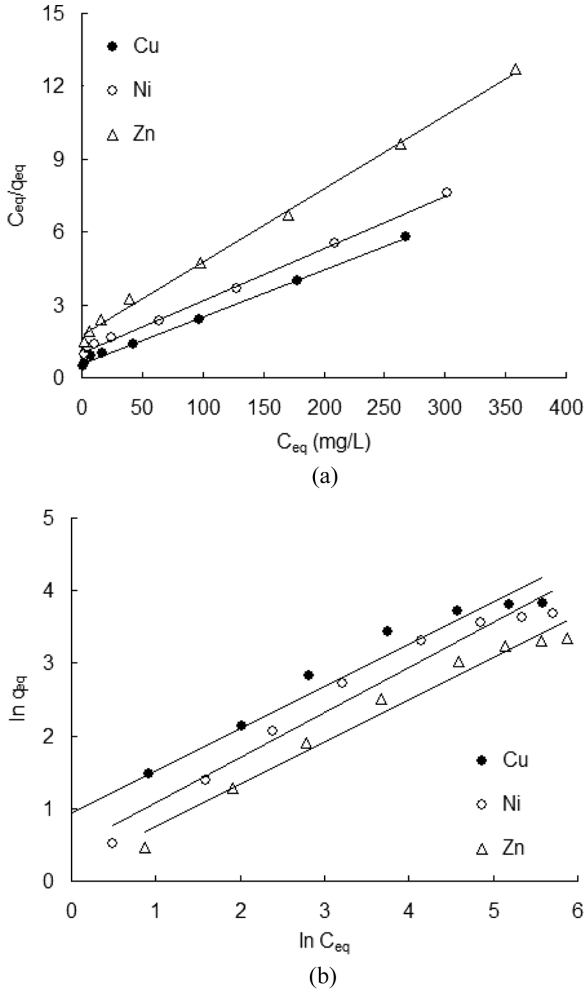
Where K and n = Freundlich constants, characteristic of the system.

The Langmuir and Freundlich adsorption isotherms of all the three metals are, respectively, presented in Figs. 7a and 7b. The Langmuir and Freundlich constants and their correlation coefficients (r^2) as evaluated from the isotherms for Cu^{2+}, Ni^{2+} and Zn^{2+} are presented in Table 3. The correlation regression coefficients for metal ions show that the adsorption process is better defined by the Langmuir than by the Freundlich equation. The Langmuir fit is consistent with strong monolayer sorption onto specific sites.

The order of metal sorption capacity (q_{max}) by MPW, on a molar ratio basis was noted in order of $Cu^{2+} > Ni^{2+} > Zn^{2+}$. This order of sorption capacity of MPW for these metals is in agreement with the findings of Southichak et al. (36) who reported that for metal binding on reed biomass on a molar basis, the order of metal removal was $Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$ and of Leusch et al. (37) who reported the metal removing order as $Pb^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$ by marine alga *Ascophyllum nodosum*. Similarly, Zhang and Banks (38), while working with sphagnum moss for the biosorption of metal ions, reported the uptake for these metals in the order of $Cu^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+}$. These observations along with the results of the present study, however, do not reflect the involvement of degree of hardness of metals, which depends on the charge and radius of the cations as has been reported in some previous studies (39). This type of discrepancy in the order of metal sorption capacity has been also reported by Boonamnuayvitay et al. (40) and Budinova et al. (41) and needs to be further investigated to explain the metal ions-biomass affinities for higher or lower uptake capacities.

Mechanism of Sorption

The mechanism of Cu^{2+}, Ni^{2+}, and Zn^{2+} sorption by MPW was elucidated on the basis of displacement of alkali and alkaline earth metal cations after metal sorption and EDX analysis before and after the sorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} on MPW.



(a)

(b)

Figure 7. Linearized (a) Langmuir and (b) Freundlich adsorption isotherms for the sorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} on mango peel waste, where C_{eq} is the equilibrium concentration and q_{eq} is the metal uptake capacity per unit adsorbent at equilibrium.

Displacement of Metal Cations During Metal Sorption

In order to investigate the involvement of ion exchange mechanism in the uptake of Cu^{2+}, Ni^{2+} and Zn^{2+} by MPW, the release of alkali and

Table 3. Langmuir and Freundlich isotherm model constants and their correlation coefficients for adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} from aqueous solution by mango peel waste, where q_{max} is maximum metal adsorption capacity and b is the equilibrium constant for Langmuir isotherm model, K_F and n are the Freundlich constants, and r^2 is the correlation coefficient

	Langmuir isotherms model			Freundlich isotherms model		
Metal ions	q_{max} (mg/g)	b (L/mg)	r^2	K_F	n	r^2
Cu^{2+}	42.71	0.0473	0.994	2.54	1.72	0.962
Ni^{2+}	35.36	0.0267	0.995	1.58	1.61	0.964
Zn^{2+}	25.33	0.0246	0.995	1.17	1.70	0.973

alkaline earth metal cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and protons H^+ during the sorption of metal ions by MPW was monitored. The net release of Ca^{2+}, Mg^{2+}, K^+, and Na^+ due to the sorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} was calculated by subtracting the amount of their release in deionized water (used as the control) from the amount of metal cations released in the supernatant at metal sorption equilibrium, whereas the amount of proton H^+ released during the sorption of Cu^{2+}, Ni^{2+} and Zn^{2+} was calculated from the amount of NaOH added to maintain the pH at 5.0 at equilibrium. The results presented in Table 4 show the release of a significant amount of Ca^{2+} followed by K^+, Mg^{2+}, and Na^+ from MPW due to the uptake of Cu^{2+}, Ni^{2+},

Table 4. Release of metal cations Ca^{2+}, Mg^{2+}, K^+ and Na^+ and protons H^+ after sorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} by 5 g/L mango peel waste from 500 mg/L initial metal concentration, initial pH 5.0 during shake flask at 100 rpm for 60 min at 25 ± 2°C

		Net amount of cations and protons released (meq/g)[a]					
Metal ions	Total metal sorbed (meq/g)	Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+	$R_{a/r}$[b]
Cu^{2+}	1.45	0.496	0.121	0.262	0.011	0.35	1.169
Ni^{2+}	1.35	0.453	0.114	0.254	0.008	0.3	1.196
Zn^{2+}	0.86	0.465	0.109	0.241	0.005	0.05	0.992

[a] Difference between metals released after metal sorption and that by the control (deionized water);

[b] $R_{a/r}$: ratio of metals adsorbed to cations released.

and Zn^{2+}. These results indicate the displacement of alkali and alkaline earth metals cations by heavy metal ions. If the equivalent ratio of the adsorbed heavy metal ions to the alkali and alkaline earth metal cations released is equal, then it indicates that the process of heavy metal binding to the sorbent (MPW) is predominantly ion exchange of cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and protons H^{+} present in the sorbent. For the purpose, the coefficient $R_{a/r}$, calculated as the ratio of meq/g, of each metal sorbed on the MPW to the sum of metal cations and protons H^{+} released in meq/g were determined. As shown in Table 4, the value of $R_{a/r}$ was close to 1 for Zn^{2+}. However, for Cu^{2+} and Ni^{2+}, this ratio was greater than 1. Thus, it may be concluded from these results that ion exchange was the main mechanism involved in the uptake of Zn^{2+} by MPW. However, for the uptake of Cu^{2+} and Ni^{2+}, other mechanisms, such as adsorption-complexation in addition to ion exchange might be involved (42). A similar type of ion exchange mechanism has been suggested for other agrowaste materials (43,44). For further confirmation of the involvement of ion exchange during the sorption of heavy metals by MPW, desorption of adsorbed Cu^{2+}, Ni^{2+}, and Zn^{2+} from metal-loaded MPW was investigated with 0.1 M HCl. It was noted that 87%, 84%, and 99% of the adsorbed Cu^{2+}, Ni^{2+}, and Zn^{2+} were recovered by contacting metal-loaded biomass with 0.1 M HCl, which confirmed the suggested hypothesis that the main mechanism of Zn^{2+} biosorption was ion exchange, whereas for Cu^{2+} and Ni^{2+}, in addition to ion exchange, other mechanism(s) such as complexation-adsorption might be involved.

Analysis of MPW by Energy Dispersive X-ray Spectrometry (EDX)

Further confirmation of the involvement of ion exchange in the uptake of heavy metals by MPW was done by energy dispersive X-ray (EDX) analysis. A typical EDX pattern for MPW, before and after the adsorption of Zn^{2+}, is shown in Fig. 8. The EDX spectrum of raw MPW (before metal sorption) did not show the characteristic signal of Zn^{2+} (Fig. 8a), whereas clear signal of the presence of Zn^{2+} was observed in the Zn^{2+}-loaded MPW (Fig. 8b). Furthermore, the presence of Ca^{2+} and K^{+}, which have been shown to be involved in the ion exchange with Zn^{2+} (Table 4), was indicated in the spectra of unloaded (raw) MPW. After the adsorption of the Zn^{2+} onto MPW, however, these cations were not detected in the EDX spectrum of Zn^{2+}-loaded MPW. These findings on EDX analysis further indicate the involvement of ion exchange mechanism for the removal of metal ions by MPW.

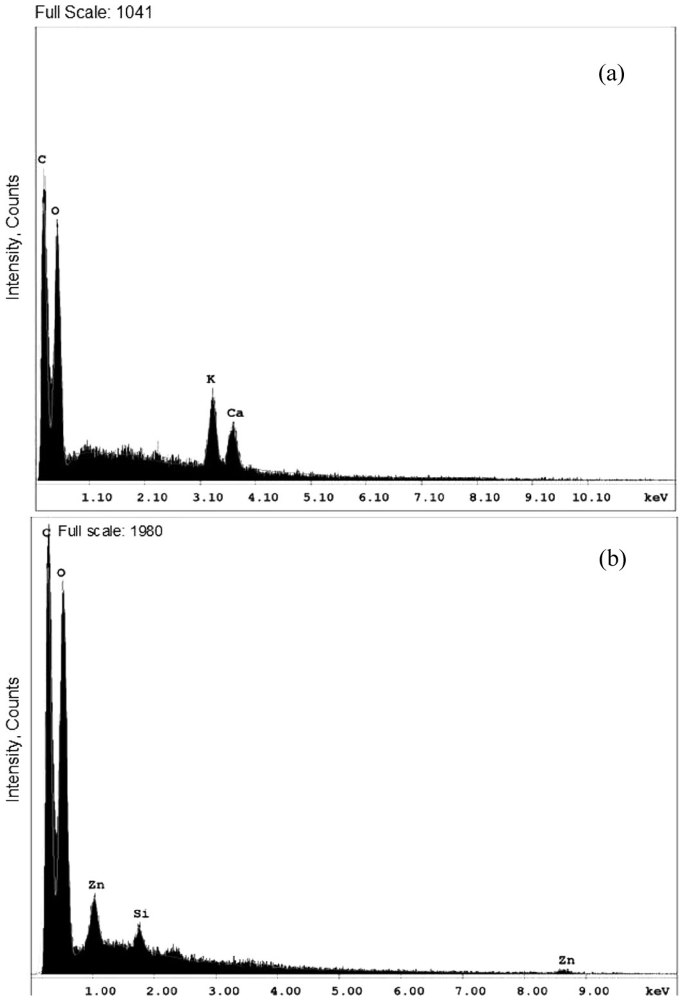


Figure 8. Energy dispersive X-ray (EDX) analysis of mango peel waste (a) before and (b) after the sorption of Zn^{2+}.

Application of MPW Biomass for the Treatment of Genuine Effluent from Electroplating Industry Effluents

Observations obtained on the adsorption capacity of MPW indicate it to be a better adsorbent for the removal of Cu^{2+}, Ni^{2+}, and Zn^{2+}, when compared with the metal adsorption capacity of other fruit and vegetable wastes reported in literature, since MPW stands out as having

Table 5. Metal adsorption capacity of MPW and other fruit and vegetable wastes reported in the literature

Metal ions	Adsorbent	Adsorbent (g/L)	Initial metal concentration (mg/L)	pH	Adsorption capacity (mg/g)	Ref.
Cu^{2+}	Apple peel	n.a	n.a	n.a	10.80	10
	Banana peel	1	25	6–8	4.75	12
	Orange peel	1	25	6–8	3.65	12
	Orange residue	10	300	4.5	21.70	46
	Carrot residue	10	500	4.5	32.74	11
	Mango Peel	5	500	5.0	46.09	This study
Ni^{2+}	Banana peel	1	25	6–8	6.88	12
	Orange peel	1	25	6–8	6.01	12
	Mango Peel	5	500	5.0	39.75	This study
Zn^{2+}	Banana peel	1	25	6–8	5.80	12
	Orange peel	1	25	6–8	5.25	12
	Carrot residue	10	500	4.5	29.61	11
	Mango Peel	5	500	5.0	28.21	This study

n.a: not available.

Table 6. Sorption capacity and efficiency of mango peel waste (MPW) to treat genuine electroplating effluent[a]

Metal ions	Concentration of metal ions in the effluents (mg/L)	Concentration of metal ions remaining in effluents after sorption with MPW (mg/L)	UNEP maximum limits for effluent discharge[b] (mg/L)
Effluent-1			
Cu^{2+}	8.27	0.79	3.3
Ni^{2+}	11.45	1.92	4.0
Zn^{2+}	6.83	1.45	2.6
Effluent-2			
Cu^{2+}	10.91	1.53	3.3
Ni^{2+}	16.96	3.49	4.0
Zn^{2+}	5.82	1.03	2.6
Effluent-3			
Cu^{2+}	9.65	0.86	3.3
Ni^{2+}	5.91	0.7	4.0
Zn^{2+}	11.34	2.46	2.6

[a] Experimental conditions: 50 ml wastewater, pH 5.0, 0.5 g MPW biomass (10 g/L), orbital shaking at 100 rpm at 25 ± 2°C for 60 min.

[b] UNEP(35).

appreciably greater potential (Table 5). To test this potential further, the ability of MPW to adsorb Cu^{2+}, Ni^{2+}, and Zn^{2+} from industrial effluents was done using genuine wastewater from electroplating industry. As the data reported heretofore was on the adsorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} from single metal solutions, the metal adsorption capacity of MPW from genuine industrial effluent will not only reflect its adsorption potential from multimetal solutions, but will also generate useful information on its evaluation for practical application considerations. The results of this evaluation on the metal adsorption potential of MPW, carried out on three genuine effluents obtained from different industrial units, are shown in Table 6. It may be noted from the table that the concentrations of Cu^{2+}, Ni^{2+}, and Zn^{2+} in the post-treated genuine industry effluents were reduced much below the maximum limits prescribed by UNEP (45) for their discharge into water bodies. These observations clearly indicate that MPW biomass may be used for effective and environment-friendly treatment of genuine wastewaters from electroplating industries in practical field applications.

CONCLUSIONS

1. Mango peel waste (MPW) has been shown to be highly effective in removing heavy metals (Cu^{2+}, Ni^{2+}, Zn^{2+}) from both single metal constituted solutions and genuine electroplating industry wastewater.
2. The sorption kinetics followed the second-order kinetic equation, while the experimental equilibrium data fit well to the Langmuir adsorption isotherm model.
3. FTIR spectra showed that the carboxyl and hydroxyl functional groups were involved in the sorption of metals.
4. Release of metal cations such as Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} and, H^{+} protons during the uptake of Cu^{2+}, Ni^{2+}, and Zn^{2+} indicated that the main process of sorption was ion exchange.
5. The capacity and efficiency of MPW to remove Cu^{2+}, Ni^{2+}, and Zn^{2+} in multimetal concentrations in the genuine electroplating industry wastewater indicates the potential of MPW as a suitable adsorbent for the development of a low-cost wastewater treatment procedure for practical field applications.

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