Journal of Hazardous Materials 164 (2009) 161–171

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste

Muhammad Iqbal[a,*], Asma Saeed[a], Saeed Iqbal Zafar[b]

[a] Biotechnology Group, Centre for Environment Protection Studies, PCSIR Laboratories Complex, Ferozepur Road, Lahore 54600, Pakistan
[b] School of Biological Sciences, University of Punjab, Lahore 54590, Pakistan

ARTICLE INFO

Article history:
Received 26 April 2008
Received in revised form 26 July 2008
Accepted 31 July 2008
Available online 6 August 2008

Keywords:
Mango peel waste
Cadmium
Lead
Sorption mechanism
Ion exchange

ABSTRACT

Mango peel waste (MPW) was evaluated as a new sorbent for the removal of Cd^{2+} and Pb^{2+} from aqueous solution. The maximum sorption capacity of Cd^{2+} and Pb^{2+} was found to be 68.92 and 99.05 mg g^{-1}, respectively. The kinetics of sorption of both metals was fast, reaching at equilibrium in 60 min. Sorption kinetics and equilibria followed pseudo-second order and Langmuir adsorption isotherm models. FTIR analysis revealed that carboxyl and hydroxyl functional groups were mainly responsible for the sorption of Cd^{2+} and Pb^{2+}. Chemical modification of MPW for blocking of carboxyl and hydroxyl groups showed that 72.46% and 76.26% removal of Cd^{2+} and Pb^{2+}, respectively, was due to the involvement of carboxylic group, whereas 26.64% and 23.74% was due to the hydroxyl group. EDX analysis of MPW before and after metal sorption and release of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and proton H^{+} from MPW with the corresponding uptake of Cd^{2+} and Pb^{2+} revealed that the main mechanism of sorption was ion exchange. The regeneration experiments showed that the MPW could be reused for five cycles without significant loss in its initial sorption capacity. The study points to the potential of new use of MPW as an effective sorbent for the removal of Cd^{2+} and Pb^{2+} from aqueous solution.

1. Introduction

Cadmium and lead are among the heavy metals considered as most toxic to human and aquatic life [1,2]. There has been a sharp rise in the global use of cadmium and lead for batteries and other applications, such as in pigments, polyvinyl chloride stabilizers and electroplating [3]. Wastewaters generated by these and related industries contain high levels of these toxic metal ions, which are mandatory to be treated to safe limits before disposal into natural water bodies and open terrain spaces. Various treatment procedures, such as chemical precipitation and coagulation, ion exchange, reduction, osmosis and reverse osmosis, membrane processes, and electrolytic technologies are available for the removal of heavy metal contaminants in effluents and industrial wastewaters. Technoeconomic considerations, however, limit their wide scale application [4]. As a result of these shortcomings, considerable attention has been paid to the development of safe technologies that can reduce heavy metal concentrations to environmentally acceptable levels at affordable cost [5,6].

Many natural polymers, such as alginate, pectin, cellulose, chitosan and chitin are known to strongly bind heavy metal ions [5,7,8]. These polymers not only have excellent heavy metals sorption capability, but they are also environment-friendly due to their renewable, biocompatible, biodegradable and nontoxic nature. However, it is difficult to use such polymers for commercial applications because of their water solubility under some practical conditions, and technoeconomical considerations related with their isolation and stabilization [5]. This difficulty can be overcome by using raw biomass wastes generated in agriculture, forestry and fisheries, which are rich in biopolymeric materials [3,8,9]. The stability of these materials as metal biosorbents is also higher than isolated-stabilized natural polymers. From such a viewpoint, several studies have been devoted during recent decades to investigate metal-binding efficiency of several biowastes [6]. In continuation of these efforts, mango peel waste was evaluated to determine its potential as a metal biosorbent.

Mango (*Mangifera indica* L., family Anacardiaceae) is a delicious fruit grown in almost all tropical and subtropical regions of the world. Currently, with about 27 million ton production annually,

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[*] Corresponding author. Tel.: +92 42 9230688; fax: +92 42 9230705.
E-mail addresses: iqbalm@fulbrightweb.org, iqbalmdr@brain.net.pk (M. Iqbal).

0304-3894/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2008.07.141

mango ranks 5th in production among the major fruit crops [10]. The edible part (the pulp), which makes up to 33%–85% of the fresh fruit, is processed for products such as juices, nectars, concentrates, jam, jelly powders, fruit bars, and dried mango products [11]. During the processing of mango, peel, which is 7%–24% of the total fruit weight, is generated as a by-product/waste. The peel serves no commercial purpose, which is discarded as a waste thus becoming a source of pollution. Mango peel contains pectin, cellulose, hemicellulose, lipids, protein, polyphenols and carotenoids [12]. Among these, pectin and cellulose are the predominant types of polysaccharides present in mango peel. These polymers are rich in functional groups such as carboxylic (galacturonic acids in pectin) and hydroxyl (in cellulose), and are known to strongly bind metal cations in aqueous solution [3,8,9]. Therefore, mango peel, due to its high pectin and cellulose content, offers the potential of use as adsorbent for the removal of toxic metals, dyes, and other organic materials from industrial effluents. The present work was thus undertaken to evaluate the application potential of pectin- and cellulose-rich mango peel waste as a new, inexpensive and environment-friendly adsorbent material for treating wastewaters containing toxic metals. We understand that to date no study on the use of MPW as a metal sorbent to treat wastewaters has been reported. Metal ions, such as Cd^{2+} and Pb^{2+}, being most toxic to human and aquatic life, and commonly released in the environment via wastewaters of many industrial processes, were selected as sorbates for this investigation. The effect of principal operational parameters on metal sorption, such as sorbent quantity, contact time, pH, and metal ion concentration, were monitored to optimize the sorption process for its possible use as a low-cost adsorbent for wastewater treatment. Mechanistic aspects of metal biosorption by MPW were investigated using different experimental approaches, such as FTIR, chemical blocking of functional groups and concomitant release of cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) from MPW with metal (Cd^{2+}, Pb^{2+}) uptake, to determine the role of carboxyl, hydroxyl and alkaline and alkaline earth metals present in MPW in an ion exchange process.

2. Material and methods

2.1. Sorbent material

Mango peel waste (MPW) was obtained from the juice production pilot plant of Food and Biotechnology Research Centre, Pakistan Council of Scientific and Industrial Research Laboratories Complex, Lahore, Pakistan. After thorough washing with tap water, MPW was washed with double-distilled water, oven dried at 70 °C, ground and sieved. Powdered material of particle size 0.85–1.0 mm was used for metal sorption studies.

2.2. Metal solutions

Standard stock solutions of Cd^{2+} and Pb^{2+} (1000 ± 2 mg l^{-1}, as their respective nitrate salts, Merck Ltd., Poole, UK) were used to prepare appropriate concentrations of each metal for the sorption studies. pH of the working solutions was adjusted at 5.0, unless otherwise stated, using 0.1 M NaOH. Fresh dilutions were used for each sorption study.

2.3. Point of zero charge

The point of zero charge (pH_{PZC}) of the MPW was determined by the solid addition methods [13]. To a series of 100 ml Erlenmeyer flasks, 45 ml of KNO_3 solution of known strength was transferred. The initial pH (pH_i) values of the solutions were roughly adjusted from 2 to 12 by adding either 0.1 N HNO_3 or NaOH. The total volume of he solution in each flask was made exactly to 50 ml by adding the KNO_3 solution of the same 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 then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid (pH_f) were noted. The difference between the initial and final pH values (ΔpH) was plotted against the pH_i.

2.4. Sorption studies

Sorption capacity of MPW was determined by contacting 250 mg (2.5 g l^{-1}) with 100 ml metal solutions of known concentration (10–600 mg l^{-1}) in 250 ml Erlenmeyer flasks, shaken on an orbital shaker at 100 rpm for 120 min at room temperature (25 ± 2 °C), followed by centrifugation at 5000 rpm for 5 min to separate MPW from the metal solution. Residual metal concentration in the supernatant metal solutions was determined by atomic absorption spectrophotometric analysis. Rate of metal sorption by MPW was determined by analyzing residual metal ions in the supernatant after contact periods of 15, 30, 45, 60, 90 and 120 min. The solid phase mass was varied between 0.5 and 10 g MPW l^{-1} metal solution for determining the effect of sorbate to sorbent ratio for the percentage and unit metal sorbate sorption capacity of the MPW sorbent. For determining the effect of pH on metal sorption by MPW, initial pH of each metal solution was adjusted to the desired value (2–7) using 0.1 M HCl or 0.1 M NaOH. Final pH of the sorbate–sorbent sorption mixture was measured at sorption equilibrium. Metal-free and MPW-free blanks were used as the controls. All the experiments were performed in triplicate.

2.5. FTIR, SEM and EDX analysis

FTIR spectroscopy (Thermo Nicolet IR-100 Spectrometer, Thermo Nicole Corporation, Madison, USA) was done to identify the chemical functional groups present on native MPW and the metal (Cd^{2+}, Pb^{2+})-loaded MPW. IR absorbance data were obtained for wavenumbers in the range of 400–4000 cm^{-1} and analyzed using software Encompass®. The surface structure of the MPW before and after Cd^{2+} and Pb^{2+} sorption was analyzed by scanning electron microscopy (SEM LEO DSM-982 Gemini, Cambridge, UK) and for electron dispersive X-ray analysis (EDX-System, INCA-Oxford, High Wycombe, UK). The EDX-system was coupled with SEM using mixed BSE (back scatter electron) + LSE (lateral secondary electron) signal detectors.

2.6. Major cations content of MPW biomass

Release of alkali and alkaline earth metals (Mg^{2+}, Ca^{2+}, K^+, Na^+) from acid-washed (0.1 M HCl) MPW was used to determine its approximate ion exchange capacity. Protonation of MPW was done to show that the exchangeable cations present on the native MPW could be released into solution after the uptake of protons. For this purpose, 1.0 g of MPW was treated with 100 ml of 0.1 M HCl. The suspension was stirred on magnetic stirrer for 60 min at room temperature, then separated by centrifugation at 5000 rpm for 5 min. The residue MPW was resuspended in fresh 0.1 M HCl solution and the treatment was repeated twice. MPW residue so obtained was analyzed for the release of Mg^{2+}, Ca^{2+}, K^+, and Na^+ using atomic absorption spectrophotometer (UNICAM 969, Unicam, Cambridge, UK). Replacement of HCl with deionized water in a similar procedure served as the control. Elemental composition of MPW was determined by the standard AOAC dry ashing method [14], followed by atomic absorption spectrophotometer metal analysis.

2.7. Blocking of carboxyl and hydroxyl functional groups

Blocking of carboxylic groups of MPW was done according to the method of Gardea-Torresdey et al. [15], which involved the following reaction:

$$\mathrm{RCOOH} + \mathrm{CH_3OH} \xrightarrow{\mathrm{H^+}} \mathrm{RCOOCH_3} + \mathrm{H_2O} \qquad (1)$$

For this purpose, MPW biomass (9.0 g) was suspended in anhydrous CH_3OH (633 ml) and conc. HCl (5.4 ml), with continuous agitation on magnetic stirrer at 100 rpm for 6 h. The MPW biomass residue was then separated by centrifugation at 5000 rpm for 10 min and washed repeatedly with deionized water to remove excess HCl and CH_3OH. The final product was freeze-dried and stored for subsequent use. Blocking of hydroxyl groups of MPW was done in accordance with Chen and Yang [16], which involved the following reaction:

$$2\mathrm{R{-}OH} + \mathrm{HCHO} \rightarrow (\mathrm{R{-}O})_2\mathrm{CH_2} + \mathrm{H_2O} \qquad (2)$$

For this purpose, MPW biomass (5.0 g) was suspended in HCHO (100 ml) and continuously agitated with magnetic stirrer at 100 rpm for 6 h. The residue biomass was then separated and further processed as mentioned for the carboxyl groups blocking procedure.

2.8. Desorption studies

Metal-loaded MPW sorbent (1.0 g) was shaken with 50 ml of 0.1 M HCl as the desorbing agent in 250 ml Erlenmeyer flasks at 100 rpm on an orbital shaker for 60 min at room temperature. The metal-loaded MPW–HCl suspension was centrifuged and the supernatant was analyzed for metal ions desorbed. The metal-desorbed MPW was used as the regenerated sorbent in five repeated sorption–desorption cycles to determine reusability potential of the adsorbent.

2.9. Data analysis

Data analysis for adsorption kinetics was done on the pseudo-first order Lagergren and pseudo-second order equations for determining the nature of rate reaction and finding the correlation coefficient of fit to these equations. Testing of the data was further done on Langmuir and Freundlich adsorption isotherms models, which are usually used as a measure of the validity of the data and for evaluating maximum sorption capacity of the sorbent. The correspondence of the uptake of Cd^{2+} and Pb^{2+} from their respective solutions with the release of alkali and alkaline earth metals (Ca^{2+}, Mg^{2+}, Na^+, K^+) by MPW adsorbent was considered as the likely involvement of ion exchange mechanism in the metal sorption process.

3. Results and discussion

3.1. Fourier transform infrared (FTIR) spectroscopy of MPW

The pattern of sorption of metals onto plant materials is attributable to the active groups and bonds present on them [17]. FTIR spectroscopy was, therefore, done for preliminary quantitative analysis of major functional groups present in native MPW used as sorbent of Cd^{2+} and Pb^{2+} in the present studies (Fig. 1a). FTIR spectra of metal (Cd^{2+} and Pb^{2+})-loaded MPW were also obtained to determine correspondence of respective metal biosorption at the stretching and bending of active groups present in native MPW (Fig. 1b, c). Peaks appearing in the FTIR spectrum of native MPW were assigned to various groups and bonds in accordance with their respective wavenumbers (cm^{-1}) as reported in literature. The broad and intense peak at 3418 cm^{-1} was assigned to the stretching of O—H group due to inter- and intramolecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin. The O—H stretching vibrations occur within a broad range of frequencies indicating the presence of "free" hydroxyl groups and bonded O—H bands of carboxylic acids [18]. The band at 2924 cm^{-1} indicates symmetric or asymmetric C—H stretching vibration of aliphatic acids [7]. The peak at 2854 cm^{-1} was the symmetric stretching vibration of CH_2 due to C—H bonds of aliphatic acids [19]. Peak observed at 1733 cm^{-1} is the stretching vibration of C═O bond due to non-ionic carboxyl groups (–COOH, $-COOCH_3$), and may be assigned to carboxylic acids or their esters [7]. Asymmetric and symmetric stretching vibrations of ionic carboxylic groups ($-COO^-$), respectively, appeared at 1619, and 1446 cm^{-1}. The peaks at 1373 cm^{-1} may be assigned to symmetric stretching of $-COO^-$ of pectin [20], and aliphatic acid group vibration at 1228 cm^{-1} to deformation vibration of C═O and stretching formation of –OH of carboxylic acids and phenols [19], and at 1055 cm^{-1} can be assigned to stretching vibration of C—OH of alcoholic groups and carboxylic acids [19]. It is well indicated from FTIR spectrum of native MPW that carboxyl and hydroxyl groups were present in abundance. These groups in biopolymers may function as proton donors, hence deprotonated hydroxyl and carboxyl groups may be involved in coordination with metal ions [21].

FTIR spectra of metal (Cd^{2+} and Pb^{2+})-sorbed MPW showed that the peaks expected at 3418, 1733, 1619, 1446, 1373, 1228 and 1055 cm^{-1} (Fig. 1a) had shifted, respectively, to 3424, 1736, 1637, 1441/1439, 1383/1384, 1236/1237 and 1069/1067 cm^{-1} due to Cd^{2+} and Pb^{2+} sorption (Fig. 1b, c). These shifts may be attributed to the changes in counter ions associated with carboxylate and hydyroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, are predominant contributors in metal ion uptake [21].

3.2. Chemical modification of MPW for blocking of carboxyl and hydroxyl groups to quantify their role in metal sorption

In an attempt to confirm and quantify the involvement of carboxyl and hydroxyl groups in the uptake of Cd^{2+} and Pb^{2+}, the two groups were individually blocked in separate experiments [15,16]. Metal-binding capacity of MPW with chemically blocked carboxyl and hydroxyl groups is presented in Table 1. Sorption of metal ions was noted to be severely inhibited when carboxyl groups were blocked. A decrease of 72.46% and 76.26% in the sorption for Cd^{2+} and Pb^{2+}, respectively, was observed after blocking carboxyl groups of MPW, suggesting the dominant role of carboxyl groups in the process of sorption. Similar decrease in the metal uptake by algal biomass has been reported when their carboxyl groups were blocked by acidified methanol [15,16]. Nevertheless, 27.54% Cd^{2+} and 23.74% Pb^{2+} ions were taken-up by MPW, even after the blockage of carboxyl groups, indicating the presence of other metal-binding sites. For confirming the involvement of other active sites, sorption of Cd^{2+} and Pb^{2+} by MPW with blocked hydroxyl groups was also carried out. As shown in Table 1 a decrease of 26.64% and 23.57% in the adsorption of Cd^{2+} and Pb^{2+}, respectively, was noted when hydroxyl groups of MPW were blocked. This decrease may be attributed to the blockage of hydroxyl groups of MPW and confirms its role in sorption of heavy metals by native MPW. Interactions of metals with vicinal hydroxyl groups of pectin and cellulose have been suggested [7,19]. The amount of metal ions taken-up by MPW with blocked hydroxyl groups (49.76 mg g^{-1} Cd^{2+} and 75.55 mg g^{-1} Pb^{2+}) and by MPW with blocked carboxyl groups (18.68 mg g^{-1} Cd^{2+} and 23.47 mg g^{-1} Pb^{2+}) was almost equal (Cd^{2+}: 49.76 + 18.68 = 68.44 mg g^{-1}; Pb^{2+}:

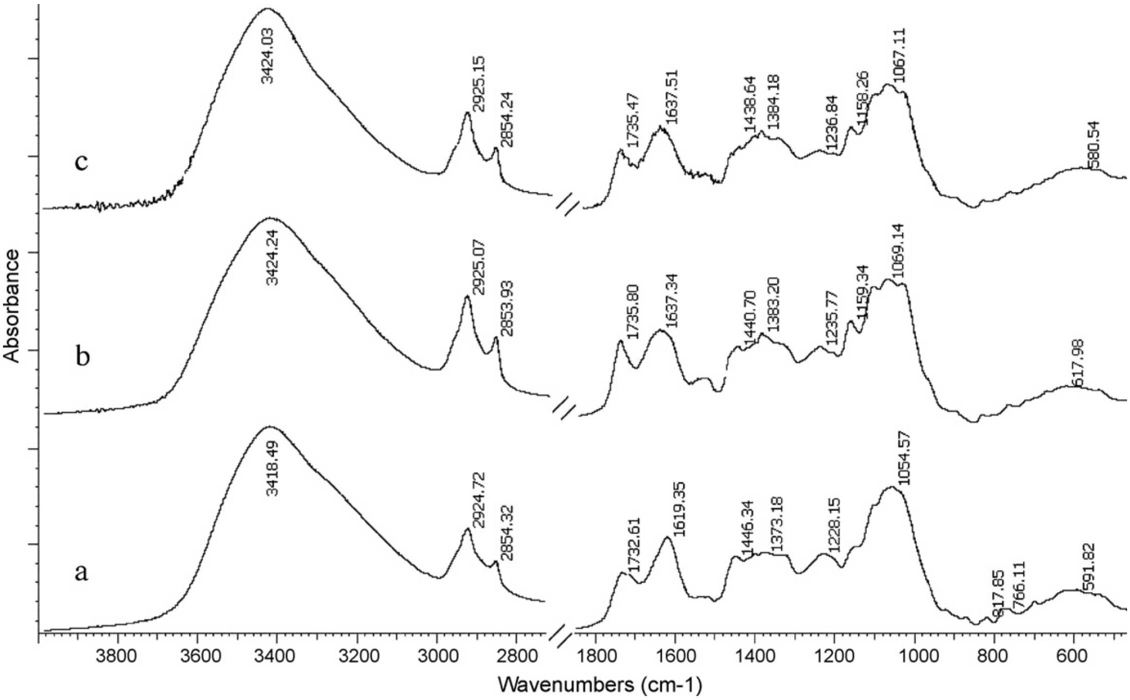

Fig. 1. FTIR spectra of (a) native mango peel waste (MPW), (b) and (c) respectively, Cd^{2+}- and Pb^{2+}-MPW.

Table 1
Sorption of Cd^{2+} and Pb^{2+} by native mango peel waste (MPW), and by MPW with chemically blocked carboxyl and hydroxyl functional groups

Metal ions	Metal ions adsorbed				
	Native MPW ($mg\,g^{-1}$)	MPW with carboxyl groups blocked ($mg\,g^{-1}$)	Decrease in metal sorption (%)	MPW with hydroxyl groups blocked ($mg\,g^{-1}$)	Decrease in metal sorption (%)
Cd^{2+}	67.83 ± 2.37	18.68 ± 0.84 (27.54%)	72.46	49.76 ± 1.39 (73.36%)	26.64
Pb^{2+}	98.85 ± 1.78	23.47 ± 1.11 (23.57%)	76.26	75.55 ± 2.34 (76.43%)	23.74

$75.55 + 23.47 = 99.02\,mg\,g^{-1}$) to the removal of these two metals ($67.83\,mg\,g^{-1}$ Cd^{2+} and $98.85\,mg\,g^{-1}$ Pb^{2+}) by the native MPW with no active sites blocked. These observations, along with the possible functional groups assigned to peaks appearing in the FTIR spectra (Fig. 1), confirm that these two groups were mainly responsible for the uptake of Cd^{2+} and Pb^{2+} by MPW.

3.3. *Effect of solid to liquid ratio on metal sorption*

One of the parameters that strongly affects the sorption capacity is the concentration of the sorbent in the liquid phase [9]. The influence of the solid to liquid ratio on the sorption capacity of MPW was investigated for the constant initial concentration of Cd^{2+} and Pb^{2+} ions of $50\,mg\,l^{-1}$ (liquid phase) and the MPW mass (solid phase) varied between 0.5 and $10\,g\,l^{-1}$. The results are presented in Fig. 2. Increase in the solid phase mass from 0.5 to $2.5\,g\,l^{-1}$ resulted in a rapid increase in the uptake of both Cd^{2+} and Pb^{2+} ions. Further increase in the solid phase mass, however, did not result in sufficient increase in the sorption capacity of MPW for the two met-

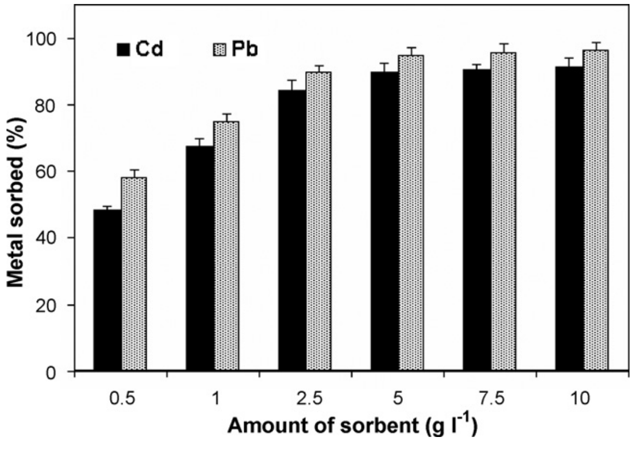

Fig. 2. Effect of quantity of mango peel waste on the sorption of $50\,mg\,l^{-1}$ Cd^{2+} and Pb^{2+}, solution pH 5.0, during 60 min orbital shaking at 100 rpm at 25 ± 2 °C.

Table 2
Theoretically determined constants of pseudo-first order and pseudo-second order reaction kinetics based on the sorption of metals from $50\,mg\,l^{-1}$ solutions, pH 5.0, by $2.5\,g\,l^{-1}$ mango peel waste (MPW) during shake flask sorbent–sorbate contact at 100 rpm for 60 min at 25 ± 2 °C

Metal ions	Experimental q_{eq} ($mg\,g^{-1}$)	Pseudo-first order constants			Pseudo-second order constants		
		q_{eq} ($mg\,g^{-1}$)	K_1 (min^{-1})	r^2	q_{eq} ($mg\,g^{-1}$)	K_2 ($g\,mg^{-1}\,min^{-1}$)	r^2
Cd^{2+}	16.55	8.78	−0.052	0.93	16.71	0.0103	0.997
Pb^{2+}	17.47	10.73	−0.057	0.96	17.60	0.111	0.998

als. As the difference in metal sorption capacity of MPW between 2.5 and 10 g l^{-1} solid phase mass was noted to be insignificant, the solid phase mass of 2.5 g l^{-1} was selected for further studies. It may be concluded from these results that at lower MPW dosage (i.e., below 2.5 g l^{-1}), the metal ions were competing for sorption at limiting sorption sites. However, as the quantity of MPW was increased, the availability of sorption sites eased resulting in greater percentage removal of both the metals. The insignificant increase in uptake of Cd^{+2} and Pb^{+2} at MPW dosage higher than 2.5 g l^{-1} may be attributed to the presence of excess/surplus metal-binding sites on MPW than the available Cd^{+2} and Pb^{+2} ions present in solution at the fixed concentration of 50 mg l^{-1}. These observations are in agreement with others reported in literature for the sorption of metal ions by different biological materials [4,9].

3.4. Metal sorption kinetics

The rate of metal sorption is an important factor and a prerequisite for determining the reactor design and process optimization for a successful practical application. For establishing an appropriate contact time between the biomass (2.5 g l^{-1}) and metal ion solutions (50 mg l^{-1}), sorption capacity of MPW for the two metal ions was measured as a function of time. As shown in Fig. 3, Cd^{2+} and Pb^{2+} uptake, as a function of contact time, was noted to occur in two phases. The first phase involved rapid metal uptake during the first 30 min of sorbent–sorbate contact, which was followed by a slow phase of metal removal spread over a significantly longer period of time until the equilibrium was reached. The rapid uptake of metal ions during the first 30 min of contact accounted for 90.56% and 92.50% of the total sorption (16.55 and 17.47 mg g^{-1}) at equilibrium for Cd^{2+} and Pb^{2+}, respectively. Time required for attaining equilibrium for both the metal ions was 60 min. The two-phase metal uptake process, the first being rapid and the second slower, has been extensively reported in literature [22]. The rapid phase is probably due to the abundant availability of active sites on the biosorbent, whereas with the gradual occupancy of these sites, sorption becomes less efficient during the slower phase. Taking into account these observations, the metal-MPW contact time of 60 min was used for further studies.

The controlling mechanism of Cd^{2+} and Pb^{2+} uptake was investigated by fitting the experimental sorption data to pseudo-first order and pseudo-second order kinetics models. The pseudo-first order rate equation of Lagergren [23] is represented as:

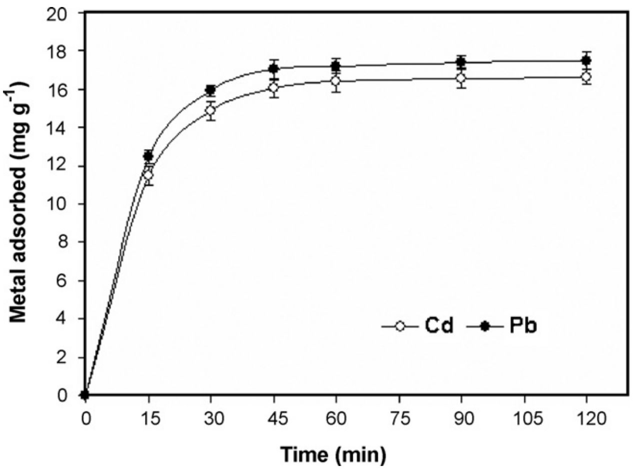

Fig. 3. Sorption of Cd^{2+} and Pb^{2+} from 50 mg l^{-1} metal solution, pH 5, by 2.5 g l^{-1} mango peel waste (MPW) as a function of sorbent–sorbate contact time during orbital shaking at 100 rpm at 25 ± 2 °C.

$$\ln(q_e - q_t) = \ln q_e - K_{1.adt} \tag{3}$$

where q_e (mg g^{-1}) is the mass of dye adsorbed at equilibrium, q_t (mg g^{-1}) is the mass of metal adsorbed at time t, and $K_{1.adt}$ (min^{-1}) is the pseudo-first order reaction rate equilibrium constant. The pseudo-first order considers the rate of occupation of sorption sites to be proportional to the number of unoccupied sites. A straight line of $\ln(q_e - q_t)$ versus t indicates application of the pseudo-first order kinetics model. In a true pseudo-first order process, $\ln q_e$ should be equal to the intercept of plot of $\ln(q_e - q_t)$ against t.

The pseudo-second order equation [24], based on the sorption equilibrium capacity, may be expressed as below:

$$\frac{t}{q_t} = \left[\frac{1}{K_{2ad} q_e^2}\right] + \frac{t}{q_e} \tag{4}$$

where K_{2ad} (g mg^{-1} min^{-1}) is the pseudo-second order reaction rate equilibrium constant. A plot of t/q_t against t should give a linear relationship for the applicability of the pseudo-second order kinetics model.

The results of the kinetics parameters for both the metals, calculated from the linear plots of pseudo-first order and pseudo-second order kinetics models are presented in Table 2. The low correlation coefficient values obtained for the pseudo-first order model indicate that sorption of metal ions did not follow the pseudo-first order reaction. The insufficiency of the pseudo-first order model to fit the kinetics data could possibly be due to the limitations of boundary layer controlling the sorption process. The experimental data were observed to fit well to the pseudo-second order equation. The correlation coefficients (r^2) for the linear plots of t/q_t against t for the pseudo-second order equation were observed to be close to 1 for both metals. The theoretical q_e values for both the metal ions were also very close to the experimental q_e values. These observations suggest that metal sorption by MPW followed the second-order reaction, which suggests that the process controlling the rate may be a chemical sorption involving valence forces through sharing or exchanging of electrons between sorbent and sorbate [24].

3.5. Effect of pH on metal ion sorption

Solution pH has been reported to be the most important variable governing the adsorption of metal ions by the sorbent [25]. The reaction of metal ions in solution with the sorbent may be described as:

$$M^{+n} + BH_n \leftrightarrow BM + nH^+ \tag{5}$$

where M represents the metal, n its charge and B the active sorption sites of the adsorbent. As per Eq. (5), pH influences metal ion sorption due to the competition between the metal and H^+ ions for active sorption sites [7]. pH affects both the solubility of metal ions and the ionization states of functional groups, such as carboxyl and hydroxyl on pectin- and cellulose-rich sorbents. In order to establish how pH affects metal ion sorption onto MPW, batch equilibrium studies were conducted at different initial pH values in the range of 2–7 (Fig. 4). Very little sorption took place at the initial pH 2 (15.5% Cd^{2+}, 11.99% Pb^{2+}). The low metal sorption at pH 2 may be explained on the basis of active sites protonation, resulting in H^+ and M^{2+} competition to occupy the binding sites [4]. A continuous increase in the sorption capacity of MPW occurred in the pH range of 2–5 (81.6% Cd^{2+}, 87.05% Pb^{2+} at pH 5.0). This increase in metal removal, as pH increased, can be explained in terms of pH_{PZC} (point

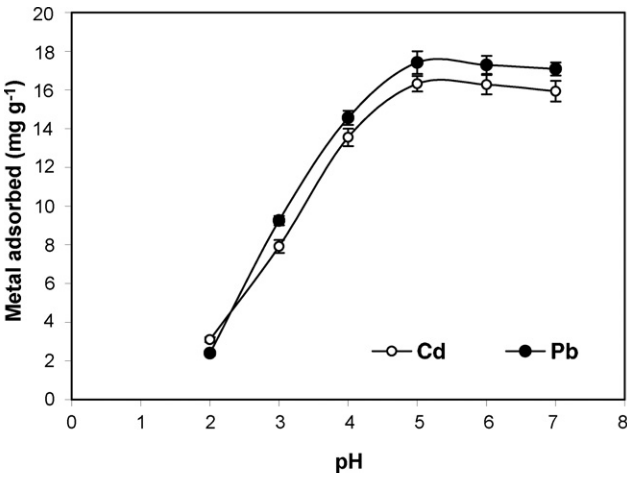

Fig. 4. Effect of pH on the sorption of Cd^{2+} and Pb^{2+} from 50 mg l^{-1} solutions by 2.5 g l^{-1} mango peel waste during orbital shaking at 100 rpm at 25 ± 2 °C for 60 min.

of zero charge) of the adsorbent and metal speciation occurring in the solution. The pH value, at which the charge of the solid surface is zero is referred to as the point of zero charge (pH_{PZC}). 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 (Cd^{+2}, Pb^{+2}) and the negatively charged adsorbent (MPW) surface, which ultimately resulted in the increased adsorption of metal ions. At $pH < pH_{PZC}$, the surface of the adsorbent is positively charged. Thus, a decrease in the removal of metal ions at $pH < pH_{PZC}$ is apparently due to the higher concentration of H^+ ions in the reaction mixture that are competing with the positively charged metal ions for adsorption sites of MPW.

Another aspect that must be considered is the metal speciation in solution which is also pH dependent. The speciation of Cd^{+2} and Pb^{+2} ions was determined by using MINEQL+ [26], which showed that free Cd^{+2} and Pb^{+2} ions were the predominant species at the pH values below 8 and 6, respectively, for the two metals. At pH values higher than 8 for Cd^{+2} and higher than 6 for Pb^{+2}, several hydroxyl low-soluble species may be formed, such as $Cd(OH)_2$, $Cd(OH)_3{}^-$ and $Pb(OH)_2$ [27]. Maximum adsorption for both Cd^{+2} and Pb^{+2} by MPW was achieved at pH 5 as no increase in metal uptake was observed above pH 5. For this reason, further metal sorption studies were carried out at pH 5 which is well below the pH levels where Cd^{+2} and Pb^{+2} ions are precipitated.

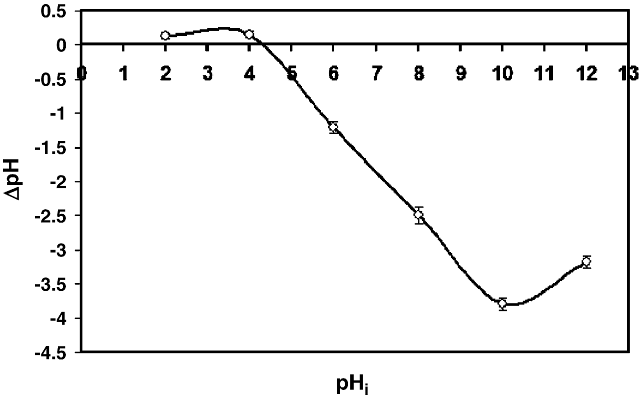

Fig. 5. Point of zero charge (pH_{pzc}) curve of mango peel waste.

3.6. Metal sorption capacity of MPW and isotherms modeling

In order to evaluate the maximum metal sorption capacity of MPW, the sorbent was contacted with varying concentrations (10–600 mg l^{-1}) of Cd^{2+} and Pb^{2+} in single metal solutions at pH 5.0, until equilibrium was reached. Metal removing capacity of MPW, for both the metals, was noted to increase with the increase in metal ion concentration in solution until it reached the maximum capacity of 68.92 and 99.05 mg g^{-1} for Cd^{2+} and Pb^{2+}, respectively (Fig. 6). To examine the relationship between the metal sorption capacity (q_{eq}) and the concentration of metal ions at equilibrium (C_{eq}), the sorption equilibrium data for both the metals were fit to Langmuir and Freundlich isotherms models. These two models are widely used for adsorption data analysis, since they have the ability to describe experimental results for a wide range of initial metal concentrations. Langmuir and Freundlich adsorption isotherms are also classical models for describing equilibrium between metal ions adsorbed onto the sorbent and metal ions remaining in solution at equilibrium at a constant temperature. Both the isotherm models can be easily transformed into linear forms to obtain adjustable parameters by linear regression analysis [28].

The theoretical Langmuir isotherm relies on the chemical or physical interaction (or both) postulated to occur between the solute and the available vacant sites on the sorbent surface, which may be described as below:

$$q_{eq} = \frac{q_{max} b C_{eq}}{(1 + b C_{eq})} \qquad (6)$$

where q_{eq} is the amount of sorbate sorbed at equilibrium (mg g^{-1}), q_{max} is the maximum metal uptake capacity (mg g^{-1} sorbent), C_{eq} is the equilibrium concentration (mg l^{-1} metal solution), and b (l mg^{-1}) is a coefficient related to the affinity between the metal ion and the sorbent.

The Freundlich isotherm is an empirical equation that is based on the sorption of a sorbate on a heterogeneous surface of a sorbent as given by the equation:

$$q_{eq} = K_F C_{eq}^{1/n} \qquad (7)$$

where K and n are the Freundlich empirical constants indicative of sorption capacity and sorption intensity, respectively.

The Langmuir and Freundlich constants and their correlation coefficients (r^2) evaluated from these isotherms for Cd^{2+} and Pb^{2+} are given in Table 3. The sorption characteristics of both Cd^{2+} and Pb^{2+} on the MPW followed more closely the Langmuir isotherm

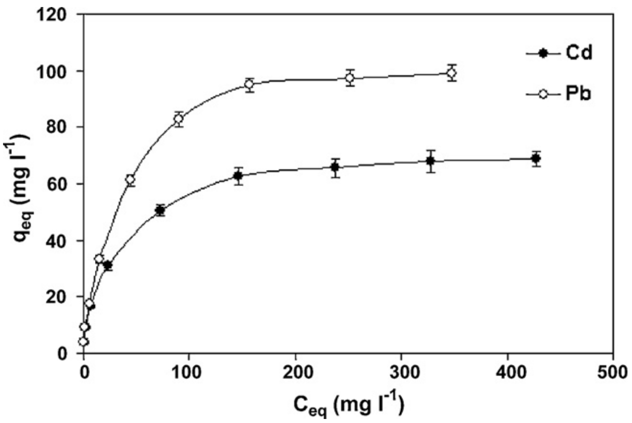

Fig. 6. Equilibrium adsorption isotherms for sorption of Cd^{2+} and Pb^{2+} from 10 to 600 mg l^{-1} solution by 2.5 g l^{-1} of mango peel waste at pH 5.0 at 100 rpm orbital shaking at 25 ± 2 °C for 60 min, where q_{eq} is the metal sorbed at equilibrium and C_{eq} is the equilibrium metal concentration remaining in solution.

Table 3

Langmuir and Freundlich isotherms constants and the linearized plot correlation coefficients for sorption of Cd^{2+} and Pb^{2+} from aqueous solution by mango peel waste; q_{max} is maximum metal uptake (mg g^{-1} sorbent) and b is the equilibrium constant for the Langmuir isotherm model, K_F and n are the Freundlich constants, and r^2 is the correlation coefficient

Metal ions	Langmuir isotherm model			Freundlich isotherm model		
	q_{max} (mg g^{-1})	b (l mg^{-1})	r^2	K_F	n	r^2
Cd^{2+}	67.08	0.085	0.998	6.3	2.22	0.952
Pb^{2+}	96.32	0.101	0.996	7.26	1.94	0.975

model than the Freundlich isotherm model. This observation is further supported by the evaluation of the respective correlation coefficients, which is a measure of how well the predicted values from a forecast model match with the experimental data. The r^2 in respect to sorption of Cd^{2+} was noted to be 0.998 and 0.952, respectively, for Langmuir and Freundlich models, while the corresponding values for Pb^{2+} were 0.996 and 0.975. The theoretical monolayer capacity (q_{max}) of Cd^{2+} and Pb^{2+} on the MPW was calculated as 67.08 and 96.32 mg g^{-1}, respectively, against 68.92 and 99.05 mg g^{-1} found experimentally. As may be noted from Table 4, the maximum metal uptake capacity of MPW for Cd^{2+} and Pb^{2+} was significantly higher than the metal sorption capacity of other agrowaste materials that have been already evaluated and reported in literature.

3.7. *Total cations content of MPW*

The amount of cations released when MPW was treated with acidic solution (0.1 M HCl), and with deionized water as the control is presented in Table 5. The total amount of cations released by MPW was 0.964 meq g^{-1}, which comprised of 0.523, 0.129, 0.294 and 0.018 meq g^{-1} of Ca^{2+}, Mg^{2+}, K^+ and Na^+, respectively. It has been suggested that the total cationic content can be considered as a measure of the approximate cation exchange capacity (CEC) of an adsorbent material [29].

3.8. *Sorption mechanism and role of alkaline and alkaline earth metals*

The real challenge in the field of metal sorption studies is to identify the mechanism of metal uptake by the sorbent. One of the mechanisms suggested to be involved in sorption is the ion exchange process between protons and/or light metals as counterions present in the biomass and heavy metal ions taken-up from the metal containing aqueous solution [6]. In order to investigate the mechanism of heavy metal ions (Cd^{2+} and Pb^{2+}) sorption by MPW, the release of alkali (K^+ and Na^+) and alkaline earth metals (Ca^{2+} and Mg^{2+}), initially present in the MPW (Table 5), and proton H^+ during sorption was determined. The net release of Ca^{2+}, Mg^{2+}, K^+ and Na^+ due to the sorption process was calculated by subtracting the amount of their release when MPW was washed with deionized water (used as the control) from the amount of these cations released in the supernatant at metal sorption equilibrium, whereas the amount of proton H^+ released during the sorption of Cd^{2+} and Pb^{2+} was calculated from the amount of NaOH added to maintain the pH at 5 at equilibrium. The results showed a significant release of Ca^{2+}, followed by K^+, Mg^{2+} and Na^+, from MPW due to the uptake of Cd^{2+} and Pb^{2+} (Table 6). It was observed that on contacting 500 mg l^{-1} of Cd^{2+} with MPW, 1.21 meq g^{-1} of Cd^{2+} was sorbed, while a sum of 1.197 meq g^{-1} of Ca^{2+}, Mg^{2+}, K^+, Na^+ and H^+ was replaced. From a similar concentration of Pb^{2+}, sorption of the metal was 0.94 meq g^{-1} against the total replacement of 0.937 meq g^{-1} of alkali, alkaline earth metals and protons H^+. The results presented in Table 6 show that out of 0.94 meq g^{-1} removal of Pb^{+2} by MPW, 0.877 meq g^{-1} (93.29%) was removed by ion exchange mechanism with Ca^{2+}, Mg^{2+}, K^+ and Na^+. The remaining 6.38% of Pb^{2+} removal may be attributed to ion exchange with H^+ proton, since pH decrease was observed after sorption at equilibrium (Fig. 7). For Cd^{2+}, on the other hand, out of 1.21 meq g^{-1} removal of Cd^{2+} by MPW, 0.927 meq g^{-1} (76.61%) was accounted by direct exchange of Cd^{2+} with alkali and alkaline earth metals and 0.29 meq g^{-1} (22.31%) with H^+ proton. A decrease in pH was also

Table 4

Comparison between the sorption of Cd^{2+} and Pb^{2+} by mango peel waste and other agrowaste materials reported in literature as metal sorbents

Sorbent	Cd^{2+} uptake		Pb^{2+} uptake		Reference
	mg g^{-1}	meq g^{-1}	mg g^{-1}	meq g^{-1}	
Black gram husk	39.99	0.711	49.97	0.48	[4]
Cassava waste	14.3	0.254			[33]
Coffee husks	6.9	0.123			[34]
Corncob	55.7	0.991			[35]
Grape stalk waste	13.94	0.248	49.9	0.479	[25]
Hazelnut shells	5.42	0.096	16.23	0.156	[36]
Jackfruit peel	52.08	0.926			[37]
Jute			17.18	0.165	[8]
Jatropha oil cake	14.6	0.259			[38]
Maize corncob	18.1	0.322			[38]
Olive cake	10.56	0.188	19.53	0.188	[28]
Olive stone waste	8.99	0.16	14.50	0.14	[22]
Olive pomace	7.0	0.124			[39]
Orange peel			114.07	1.1	[9]
Papaya wood	17.22	0.306			[40]
Peanut hull	6.0	0.107			[41]
Sugar beet pulp	46.1	0.82	43.5	0.419	[3]
Sugarcane bagasse	14.8	0.263			[38]
Rice husk	14.4	0.256	54.0	0.521	[17]
Wheat bran	0.7	0.012			[42]
Waste tea leaves	31.48	0.56			[43]
Mango peel waste	68.92	1.226	99.05	0.956	This study

Table 5
Major cations released by mango peel waste on acidification with 0.1 M HCl

Wash medium and the number of washings	Cations released (meq g^{-1})				
	Ca^{2+}	Mg^{2+}	K^+	Na^+	Total cations released
Washing with 0.1 M HCl					
First	0.581	0.159	0.373	0.038	1.151
Second	0.027	0.012	0.033	0.002	0.074
Third	0.006	0.002	0.005	0.000	0.013
Sum of the three washings[a]	0.614	0.173	0.411	0.040	1.238[a]
Washing with deionized water (control)					
First	0.078	0.036	0.108	0.021	0.243
Second	0.008	0.007	0.007	0.001	0.023
Third	0.005	0.001	0.002	0.000	0.008
Sum of the three washings[b]	0.091	0.044	0.117	0.022	0.274[b]
Net cations released on acidification (a–b)	0.523	0.129	0.294	0.018	0.964

Table 6
Release of Ca^{2+}, Mg^{2+}, K^+ and Na^+ after sorption of Cd^{2+} and Pb^{2+} by 2.5 g l^{-1} mango peel waste from 500 mg l^{-1} initial metal concentration, initial pH 5.0, during shake flask at 100 rpm for 60 min at 25 ± 2 °C

Metal ions	Total metal sorbed (meq g^{-1})	Net amount of cations and protons released (meq g^{-1})					
		Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+	Sum
Cd^{2+}	1.21	0.513	0.118	0.283	0.013	0.27	1.197
Pb^{2+}	0.94	0.506	0.123	0.237	0.011	0.06	0.937

observed after the sorption of Cd^{2+} at equilibrium (Fig. 7). It may be concluded that the sorption process for both Pb^{2+} and Cd^{2+} on MPW occurs mainly through ion exchange mechanism involving replacement of alkali and alkaline earth metals and, to a lesser extent, with H^+ protons bound to native carboxylate groups and the concomitant complexation with –OH groups of polysaccharide components [30]. Similar type of ion exchange mechanism has been suggested for other agrowaste materials [25,31]. For further confirmation of the involvement of ion exchange process during the sorption of heavy metals by MPW, desorption of heavy metals with 0.1 M HCl was also investigated. For the purpose, both Cd^{2+}- and Pb^{2+}-loaded MPW were contacted with 0.1 M HCl for 60 min and the release of heavy metal ions in the supernatant was determined by atomic absorption spectrometry. About 99% of both the metal ions were noted to be eluted in the acidic desorption solution by means of exchange of H^+, confirming the results presented in Table 6 that metal uptake by MPW was mainly due to an ion exchange process.

3.9. Energy dispersive X-ray (EDX) analysis

Further confirmation of the involvement of ion exchange process in the uptake of heavy metals by MPW was done by energy dispersive X-ray (EDX) analysis. Fig. 8 shows the typical EDX pattern for MPW, before and after the sorption of Pb^{2+}. The EDX pattern (Fig. 8a) for the unloaded (native) MPW, did not show the characteristic signal of Pb^{2+}, whereas for the Pb^{2+}-loaded MPW (Fig. 8b) a clear signal of the presence of Pb^{2+} was observed. Furthermore, the presence of Ca^{2+} and K^+, which have been shown to be involved in the ion exchange with Pb^{2+} (Table 6), was indicated in the spectra of unloaded (native) MPW. After the adsorption of the Pb^{2+} onto MPW, however, these cations were not detected in the EDX spectrum of Pb^{2+}-loaded MPW. These findings on EDX analysis indicate the involvement of ion exchange mechanism for the removal of metal ions by MPW.

3.10. Metal desorption and regeneration of MPW

In order to make the sorption process more economical through repeated use of the sorbent, desorption and regeneration potential of MPW was investigated. HCl was used as the desorbing agent for the recovery of sorbed Cd^{2+} and Pb^{2+} from metal-loaded MPW. The usefulness of HCl as an efficient metal desorbent has been previously reported for other agrowaste sorbents [32]. For the study of metal desorption-sorbent regeneration, 1 g MPW loaded with maximum Cd^{2+} (67.21 mg g^{-1}) and Pb^{2+} (97.07 mg g^{-1}) was contacted with the desorption agent (0.1 M HCl) for 60 min and shaken at 100 rpm. The amount of Cd^{2+} and Pb^{2+} desorbed in acidic solution was then determined using atomic absorption spectrophotometer. Desorption of Cd^{2+} and Pb^{2+} from the metal-laden MPW for the first cycle resulted in 98.23% and 99.07% metal recovery, respectively. The desorption efficiency for both the metals remained almost unchanged during the five sorption–desorption cycles (Table 7). The sorption efficiency of MPW for Cd^{2+} and Pb^{2+} during these repeated cycles is also shown in Table 7. In the first cycle, the metal removing efficiency of MPW was 67.21 and 97.07 mg g^{-1}, for Cd^{2+} and Pb^{2+}, respectively. In the second cycle, 3.6% and 8.15% increase in the sorption capacity of MPW was noted for Cd^{2+} and Pb^{2+}, respectively. After the second cycle, a non-significant decrease in the sorption capacity of MPW for both metals was observed. However, it was still higher than the amount of metal sorbed in the first cycle. The

Table 7
Adsorption and desorption efficiency of Cd^{2+} and Pb^{2+} by mango peel waste in five adsorption–desorption cycles

Cycle no.	Cd^{2+} Adsorption (mg g^{-1})	Cd^{2+} Desorption (mg g^{-1})	Pb^{2+} Adsorption (mg g^{-1})	Pb^{2+} Desorption (mg g^{-1})
1	67.21 ± 1.41	66.02 ± 1.19	97.07 ± 1.84	96.17 ± 1.51
2	69.64 ± 1.25	68.76 ± 1.51	104.98 ± 1.67	104.18 ± 1.92
3	68.21 ± 1.13	66.95 ± 1.07.	103.73 ± 2.07	102.55 ± 2.25
4	67.25 ± 1.54	65.91 ± 1.32	101.82 ± 1.32	101.13 ± 1.20
5	66.92 ± 1.67	66.30 ± 1.16	99.47 ± 2.19	98.40 ± 1.87

Table 8
Alkali and alkaline earth metal cations (AAEMC) present in native mango peel waste (MPW), after first cycle of Cd^{2+} and Pb^{2+} sorption, and after desorption-regenerated MPW sorption cycles from 2.5 g l^{-1} MPW, 500 mg l^{-1} metal solution, pH 5.0, 100 ml 0.1 M HCl desorbent, during shake flask at 100 rpm for 60 min contact time

	Ca^{2+} (meq g^{-1})	Mg^{2+} (meq g^{-1})	K^+ (meq g^{-1})	Na^+ (meq g^{-1})	Cd^{2+} or Pb^{2+} (meq g^{-1})	Total cations (meq g^{-1})
AAEMC, Cd^{2+} and Pb^{2+} present in native MPW	0.532	0.127	0.291	0.018	n.d.	0.968
After cycle-1 of Cd^{2+} adsorption						
AAEMC and Cd^{2+} present in MPW	0.027	0.011	0.023	0.002	1.196	1.259
AAEMC released in solution	0.505	0.116	0.268	0.016		
After cycle-1 of Cd^{2+} desorption						
AAEMC and Cd^{2+} released in desorbing solution	0.026	0.011	0.023	0.002	1.179	1.241
After cycle-2 of Cd^{2+} adsorption						
AAEMC released in solution	n.d.	n.d.	n.d.	n.d.		
Cd^{2+} adsorbed					1.239	1.239
After cycle-1 of Pb^{2+} adsorption						
AAEMC and Pb^{2+} present in MPW	0.042	0.013	0.041	0.001	0.937	1.034
AAEMC released in solution	0.49	0.114	0.250	0.016		
After cycle-1 of Pb^{2+} desorption						
AAEMC and Pb^{2+} released in desorbing solution	0.041	0.012	0.040	0.001	0.932	1.026
After cycle-2 of Pb^{2+} adsorption						
AAEMC released in solution	n.d.	n.d.	n.d.	n.d.		
Pb^{2+} adsorbed					1.013	1.013

n.d.: not detectable.

increase in the second cycle may be attributed to the release of remaining cations, such as Ca^{2+}, Mg^{2+}, Na^+ and K^+, during the first desorption cycle with 0.1 M HCl, which exposed more binding sites for the sorption of heavy metal ions in the second sorption cycle.

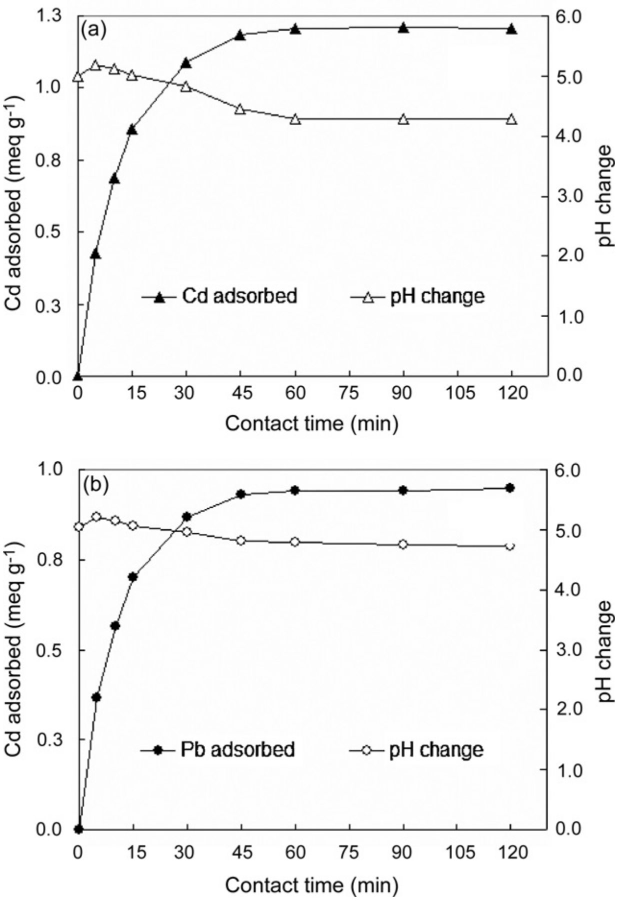

Fig. 7. pH change of metal solution during the sorption of (a) Cd^{2+} and (b) Pb^{2+} from 50 mg l^{-1} solutions by 2.5 mg l^{-1} mango peel waste during orbital shaking at 100 rpm at 25 ± 2 °C for 60 min.

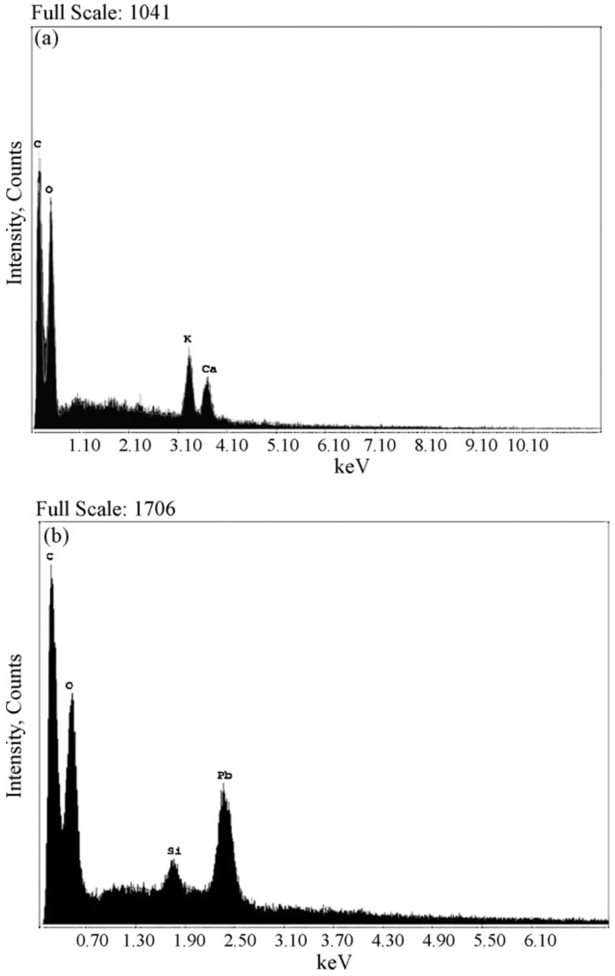

Fig. 8. Energy dispersive X-ray (EDX) analysis of mango peel waste (a) before and (b) after the sorption of Pb^{2+}.

These cations are likely to have remained intact on the surface of MPW during the first cycle of sorption owing to milder ion exchange forces, but were released in the desorption cycle due to abundant availability of H^+ protons of the desorbent HCl. These results conform to the results reported in Table 5 where the complete release of cations occurred after the second washing with 0.1 M HCl. For further confirmation of this hypothesis, the release of cations from MPW during the first two cycles of sorption–desorption was monitored, the results of which are given in Table 8. In the first cycle of sorption, out of 0.968 meq g^{-1} cations, 93.5% and 89.96%, respectively, were released due to the sorption of Cd^{2+} and Pb^{2+}. The remaining cations, which had remained intact on the surface of MPW, were released in the acidic medium along with the adsorbed metal ions during first sorption with 0.1 M HCl. This release of remaining cations resulted in an increase in the binding sites which ultimately increased the sorption capacity of MPW in the second and subsequent cycles. A good correlation exists between the total amount of alkali (K^+, Na^+), alkaline earth (Ca^{2+}, Mg^{2+}) metals and sorbed Cd^{2+} and Pb^{2+} metal ions (1.241 meq g^{-1} with Cd^{2+} and 1.034 meq g^{-1} with Pb^{2+}) released during the first desorption cycle and the amount of metal ions sorbed (1.239 meq g^{-1} for Cd^{2+} and 1.013 meq g^{-1} for Pb^{2+}) during the next sorption cycle (Table 8). These results additionally indicate that ion exchange was the main mechanism for metal sorption with MPW as the metal sorbent.

4. Conclusion

The present study reports the characteristics and mechanism of Cd^{2+} and Pb^{2+} sorption by a new sorbent (mango peel waste). Principal aspects investigated for the purpose included kinetics and adsorption isotherms modeling, FTIR and EDX spectra, chemical blocking of the expected binding sites and the release of alkali and alkaline earth metals and proton H^+ during the uptake of Cd^{2+} and Pb^{2+}. Sorption of metal ions was dependent on such experimental conditions as pH, sorbate and sorbent concentrations and sorbate–sorbent contact time. The pseudo-second order kinetics and Langmuir adsorption isotherm models were noted be fit to the experimental data. FTIR spectra showed that the principal functional sites taking part in the sorption process included carboxyl and hydroxyl groups. Chemical blocking of carboxyl and hydroxyl groups of MPW reduced the sorption of Cd^{2+} by 72.46% and 26.64% and of Pb^{2+} by 76.26% and 23.74%, respectively, which confirmed the involvement of these groups in the metal sorption process. Almost equal release (meq g^{-1}) of alkali and alkaline earth metals and proton H^+ during the uptake of Cd^{2+} and Pb^{2+} ions indicated that the process of sorption was exclusively ion exchange. EDX spectra of MPW, before and after the metal sorption, further supported the hypothesis of the involvement of ion exchange mechanism. Complete recovery of Cd^{2+} and Pb^{2+} from the metal-loaded MPW, and the reusability of desorbed-MPW in five repeated sorption–desorption cycles, showed that the material was an efficient sorbent. Complete desorption of the Cd^{2+} and Pb^{2+} ions also confirmed that the process involved was ion exchange. It may be concluded from the reported observations that MPW has the potential to be used as an efficient and cost-effective sorbent for the removal and recovery of Cd^{2+} and Pb^{2+} from aqueous solution.

Acknowledgements

We wish to thank Mr. Shane Billings, Lab Manager at Water and Environmental Research Centre, University of Alaska, Fairbanks, Alaska, USA for the FTIR analysis and Mr. Wilhelm Habicht, Institute of Technical Chemistry, Forschungszentrum Karlsruhe, Karlsruhe, Germany for SEM-EDX analysis.

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