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Biosorption of heavy metals from aqueous solutions by chemically modified orange peel

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ABSTRACT

Equilibrium, thermodynamic and kinetic studies were carried out for the biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solution using the grafted copolymerization-modified orange peel (OPAA). Langmuir and Freundlich isotherm models were applied to describe the biosorption of the metal ions onto OPAA. The influences of pH and contact time of solution on the biosorption were studied. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. According to the Langmuir equation, the maximum uptake capacities for Pb^{2+}, Cd^{2+} and Ni^{2+} ions were 476.1, 293.3 and 162.6 $mg\,g^{-1}$, respectively. Compared with the unmodified orange peel, the biosorption capacity of the modified biomass increased 4.2-, 4.6- and 16.5-fold for Pb^{2+}, Cd^{2+} and Ni^{2+}, respectively. The kinetics for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption followed the pseudo-second-order kinetics. The free energy changes (ΔG°) for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption process were found to be −3.77, −4.99 and −4.22 $kJ\,mol^{-1}$, respectively, which indicates the spontaneous nature of biosorption process. FTIR demonstrated that carboxyl and hydroxyl groups were involved in the biosorption of the metal ions. Desorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions from the biosorbent was effectively achieved in a 0.05 $mol\,L^{-1}$ HCl solution.

1. Introduction

Water pollution is a major environmental problem faced by modern society that leads to ecological disequilibrium and health hazards. Heavy metal ions such as copper, cadmium, lead, nickel, and chromium, often found in industrial wastewater, present acute toxicity to aquatic and terrestrial life, including humans. Thus, the discharge of effluents into the environment is a chief concern. Many methods, such as chemical precipitation [1], ion exchange [2], membrane processes [3] and adsorption onto activated carbon [4] etc., have been used to remove heavy metal ions from various aqueous solutions. However, the application of such processes is often restricted because of technical or economic constraints [5,6]. Biosorption of heavy metals is one of the most promising technologies involved in the removal of toxic metal ions from wastewater. It is a potential alternative to conventional processes for the removal of metals due to the low cost, easily obtained, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents and no nutrient requirements [7–9]. A great interest has recently been directed to the biosorption of heavy metals from solutions using different biomaterials as adsorbents. Among the various resources in biological wastes, both dead and live biomass, exhibit particularly interesting metal-binding capacities [10,11]. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean and cottonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, orange peel, and compost and leaves [12].

The use of orange peel (OP) as a biosorbent material presents strong potential due to its high content of cellulose, pectin (galacturonic acid), hemicellulose and lignin. As a low cost, orange peel is an attractive and inexpensive option for the biosorption removal of dissolved metals. Ajmal et al. [13,14] employed orange peel for metal ions removal from simulated wastewater. Some authors reported the use of orange waste as a precursor material for the preparation of an adsorbent by common chemical modifications such as alkaline, acid, ethanol and acetone treatment [15–19]. But through these methods, the adsorption capacity of biomass was not improved so much. Modification reactions including cross-linking and functionalization are commonly applied to enhance adsorption capacity and adsorbent stability of the components present in biomass. Since, the adsorption of metal ions takes place mainly on the biomass surface, increasing the adsorption active sites on the surface would be an effective approach to enhance the adsorption capacity. One efficient way to introduce functional groups on the biomass surface is the grafting of long polymer chains onto the biomass surface via direct grafting, or the polymerization of the monomer [20]. We have reported our preliminary findings that the

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preparation of a biosorbent (OPAA) from OP by means of hydrolysis of the grafted copolymer, which was synthesized by interacting methyl acrylate with cross-linking OP to examine its adsorption characteristics for copper (II) from aqueous solutions [21]. The objective of this study was to investigate the feasibility of using the modified orange peel (OPAA) by grafted copolymerization for the removal of Pb^{2+}, Cd^{2+}, Ni^{2+} ions from water by biosorption.

2. Materials and methods

2.1. Chemicals

All chemicals used in the present work were of analytical purity. The stock solution of Pb^{2+}, Cd^{2+} and Ni^{2+} was prepared in 1.0 g L^{-1} concentration using $Pb(NO_3)_2$, $3CdSO_4{\cdot}8H_2O$ and $Ni(NO_3)_2$ then diluted to appropriate concentrations. 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH were used for pH value adjustment. Preparation and characteristics of the modified orange peel (OPAA) by grafted copolymerization have been recently reported [21].

2.2. Biosorption experiments

Biosorption experiments were conducted at 30 °C by agitating 0.050 g of biosorbent with 25 mL of metal ion solution of desired concentration in 100 mL stoppered conical flask using a shaking thermostat machine at a speed of 120 rpm for 3 h except for the contact time experiments. The effect of solution pH on the equilibrium biosorption of metal ions was investigated under similar experimental conditions between pH 2.0 and 7.0. In the kinetic experiments, 50 mg L^{-1} Pb^{2+}, Cd^{2+} and Ni^{2+} ion solution were used. The sorption time was varied between 0 and 400 min. In the isotherm experiments, 0.050 g of biosorbent was added in 25 mL of Pb^{2+}, Cd^{2+} and Ni^{2+} ions solution at various concentrations (50–1200 mg L^{-1}). Once the pre-set contact time (3 h) reached, the samples were withdrawn and centrifuged at 4000 rpm for 5 min and the supernatant solutions were analyzed for the residual metal ion concentration by using Agilent model 3510 atomic absorption spectrophotometer. The amount of biosorption (q) was calculated by the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

The biosorption efficiency, A%, of the metal ion was calculated from:

$$A\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e are the initial and equilibrium metal ion concentrations (mg L^{-1}), respectively. V is the volume of the solution (L) and m is the amount of biosorbent used (g). All the biosorption experiments were conducted in duplicate, and the mean values were reported.

2.3. Desorption and regeneration tests

To investigate the possibility of repeated use of biosorbent, desorption and regeneration experiments were also conducted. The metal ions-loaded biosorbent was filtered, and metal ions content was measured. The biosorbent was then transferred to another conical flask and treated with 25 mL of 0.05 mol L^{-1} HCl solution for 2 h. It was again filtered and desorbed metal ions were determined in the filtrate. The biosorbent was washed several times with distilled water in order to remove excess acid. The biosorbent thus regenerated was used in further biosorption steps.

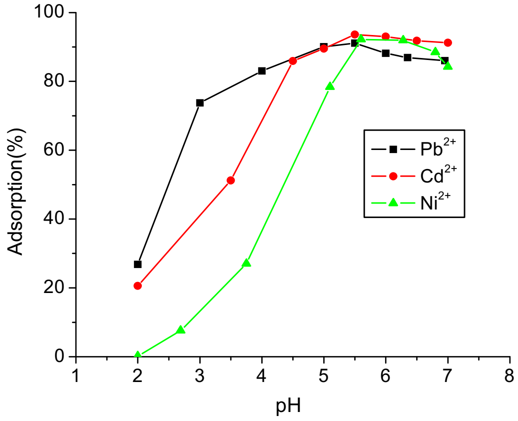

Fig. 1. The effect of pH on biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions.

2.4. FTIR spectroscopy

Spectra of the biosorbent before and after Pb^{2+}, Cd^{2+} and Ni^{2+} binding were recorded with a JASCO-410 model Fourier-transform infrared (FTIR) spectrophotometer using potassium bromide disks.

3. Results and discussion

3.1. Effect of pH on metal biosorption

It is well known that pH could affect the protonation of the functional groups on the biomass as well as the metal chemistry. The study of biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} on OPAA as a function of pH was accomplished; the results are presented in Fig. 1. As the pH of the heavy metal ions solution increased from 2.0 to 7.0, the biosorption yield of Pb^{2+}, Cd^{2+} and Ni^{2+} ions was changed. The percent biosorption is minimum at pH 2.0 and increases as the pH increases from 2 to 5.5. The minimum biosorption at low pH 2.0 may be due to the fact that high concentration and high mobility of H^+ ions, the hydrogen ions are preferentially adsorbed rather than the metal ions. At higher pH values, the lower number of H^+ and greater number of ligands with negatives charges results in greater metal ions biosorption. The weakly acidic carboxyl groups (R–COOH) are regarded as the main ligands involved in the metal uptake by OPAA. Because the pK_a value of R–COOH is in the range of 3.5–5.5 [22], more carboxyl groups will be deprotonated at pH over this range, and thus resulting in more negative binding sites. Consequently, the attraction of positively charged metal ions would be enhanced [23].

Another aspect that must be considered is the metal speciation in solution, which is also pH dependent. The speciation of Pb^{2+}, Cd^{2+} and Ni^{2+} ions was determined by using MINEQL+ [24], which showed that free Pb^{2+}, Cd^{2+} and Ni^{2+} ions were the predominant species at the pH values below 6, 8 and 7, respectively, for the three metals. At pH values higher than 6, 8 and 7 for Pb^{2+}, Cd^{2+} and Ni^{2+} respectively, several hydroxyl low-soluble species may be formed, such as $Pb(OH)_2$, $Ni(OH)_2$ and $Cd(OH)_2$. Maximum biosorption for Pb^{2+}, Cd^{2+} and Ni^{2+} by OPAA was achieved at pH 5.5 as no increases in metal uptake were observed above pH 5.5. For this reason, further metal sorption studies were carried out at pH 5.5, which is well below the pH levels where Pb^{2+}, Cd^{2+} and Ni^{2+} ions are precipitated.

3.2. Biosorption kinetics

Fig. 2 shows the kinetics of the biosorption of 50 mg L^{-1} Pb^{2+}, Cd^{2+} and Ni^{2+} ions at 30 °C by OPAA. The kinetic curve for heavy metal ions showed that the amount of biosorption sharply increases

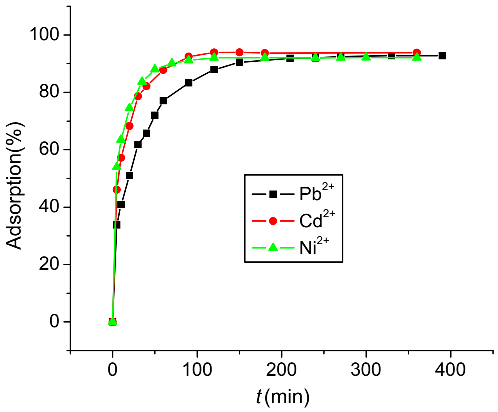

Fig. 2. Biosorptions kinetics of Pb^{2+}, Cd^{2+} and Ni^{2+} ions.

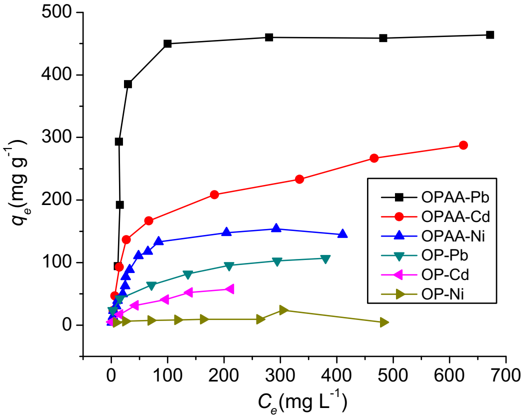

Fig. 3. Biosorption isotherms of Pb^{2+}, Cd^{2+} and Ni^{2+} ions on OPAA and OP.

with increasing contact time in the initial stage (0–30 min), and then gradually increases to reach an equilibrium value in approximately 150 min. A further increase in contact time had a negligible effect on the amount of biosorption. According to these results, the shaking time was fixed at 3 h for the rest of the batch experiments to make sure that the equilibrium was reached.

A good correlation of the kinetic data explains the biosorption mechanism of the metal ion on the solid phase [25]. In order to evaluate the kinetic mechanism that controls the biosorption process, the pseudo-first-order and pseudo-second-order models were applied for the biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions on the biosorbent.

Biosorption kinetic data of Pb^{2+}, Cd^{2+} and Ni^{2+} ions are analyzed using the Lagergren pseudo-first-order rate equation [26]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

where q_e and q_t are the amounts of biosorbed ($mg\,g^{-1}$) at equilibrium and at time t, respectively, and k_1 is the rate constant of pseudo-first-order biosorption (min^{-1}). The q_e and rate constants k_1 were calculated from the slope and intercept of the plot of $\log(q_e - q_t)$ vs. t (figure not shown). In fact, it is required that calculated equilibrium adsorption capacity values, q_e (cal.), should be in accordance with the experimental q_e (exp.) values [27]. Although the correlation coefficient values (R^2) are very high, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots (Table 1). This suggests that the biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions does not follow pseudo-first-order kinetics.

The biosorption kinetic data can also be described by pseudo-second-order equation [28]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where k_2 is the rate constant of pseudo-second-order biosorption ($g\,mg^{-1}\,min^{-1}$). The pseudo-second-order rate constant k_2 and q_e values were calculated from the slope and intercept of the plots t/q vs. t (figure not shown). It was found that the calculated q_e values agree well with experimental q_e values (Table 1). This suggests that the pseudo-second-order kinetic model based on the assumption that the rate-limiting step may be chemical sorption involving valance forces through sharing or exchange of electrons between heavy metal ions and the adsorbent provides the best correlation data for the heavy metal ions. Similar phenomenon has been observed in the adsorption of phosphate and thiocyanate on $ZnCl_2$ activated coir pith carbon [29,30].

3.3. Biosorption isotherms

Biosorption isotherms describe how adsorbate interacts with biosorbents and equilibrium is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during the surface biosorption. Equilibrium isotherms are measured to determine the capacity of the biosorbent for metal ions. The most common types of models describing this type of system are the Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and the biosorption of each molecule onto the surface has equal biosorption activation energy. While the Freundlich isotherm supposes a heterogeneous surface with a nonuniform distribution of heat of biosorption over the surface and a multilayer biosorption can be expressed. The Langmuir isotherms can be expressed as [31]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \qquad (5)$$

where q_{max} is monolayer capacity of the biosorbent ($mg\,g^{-1}$), and b is the biosorption constant ($L\,mg^{-1}$). The plot of C_e/q_e versus C_e should be a straight line with slope $1/q_{max}$ and intercept $1/q_{max}\,b$ when the biosorption follows the Langmuir equation.

The Freundlich equation can be expressed as [32]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (6)$$

where K_F and $1/n$ are Freundlich isotherm constants related to biosorption capacity and intensity of biosorption, respectively. If Eq. (6) applies, a plot of $\log q_e$ versus $\log C_e$ will give a straight line of slope $1/n$ and intercept K_F.

Fig. 3 presents the experimental biosorption isotherm of Pb^{2+}, Cd^{2+} and Ni^{2+} ions on OPAA at 30 °C. It could be seen that q_e

Table 1
Kinetic parameters for biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions on OPAA.

Metal ions	q_e (exp.) ($mg\,g^{-1}$)	Pseudo-first-order			Pseudo-second-order		
		q_e (cal.) ($mg\,g^{-1}$)	k_1 (min^{-1})	R^2	q_e (cal.) ($mg\,g^{-1}$)	k_2 ($g\,mg^{-1}\,min^{-1}$)	R^2
Pb^{2+}	23.19	14.45	0.0198	0.9959	24.28	0.068	0.9997
Cd^{2+}	23.46	11.87	0.0344	0.9951	21.53	0.0526	0.9956
Ni^{2+}	23.02	14.86	0.0539	0.9791	20.82	0.0542	0.9936

Table 2
The conform parameters of Langmuir and Freundlich equation for biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions on OPAA.

Metal ions	Langmuir model			Freundlich model		
	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_F	n	R^2
Pb^{2+}	476.1	0.056	0.9964	103.9	3.88	0.4974
Cd^{2+}	293.3	0.022	0.9886	20.36	2.15	0.8649
Ni^{2+}	162.6	0.032	0.9926	5.93	1.45	0.9450

increased initially with an increase in C_e until equilibrium was reached, after which q_e remained constant with further increase in C_e. The Langmuir and Freundlich biosorption constants evaluated from the isotherms with the correlation coefficients are listed in Table 2.

As it can be seen that the Langmuir isotherm gave better fits than the Freundlich isotherm, which illustrated that the biosorption on the surface of OPAA was a monolayer biosorption. According to the Langmuir equation, the maximum uptake capacity for Pb^{2+}, Cd^{2+} and Ni^{2+} ions were 476.1, 293.3 and 162.6 mg g^{-1}, respectively, which is respectively about 4.2, 4.6 and 16.5 time higher than that of the unmodified biomass (OP) and also much higher than some other biosorbents reported in literatures (Table 3).

3.4. *Biosorption thermodynamics*

Thermodynamic considerations of a biosorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG° is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. The change in free energy can be calculated from the thermodynamic equilibrium constant, K_D (or the thermodynamic distribution coefficient), which is defined as follows:

$$K_D = \frac{a_s}{a_e} = \frac{\nu_s q_e}{\nu_e C_e} \tag{7}$$

where a_s is the activity of the heavy metal ions biosorbed on the surface of OPAA, a_e is the activity of the heavy metal ions in solution at equilibrium, ν_s is the activity coefficient of the biosorbed heavy metal ions and ν_e is the activity coefficient of the heavy metal ions in solution at equilibrium. As the heavy metal ions concentration in the solution decreases and approaches zero, the activity coefficient ν approaches to unity. Eq. (7) may be written as:

$$\lim_{q_e \to 0} \frac{a_s}{a_e} = \frac{q_e}{C_e} = K_D \tag{8}$$

K_D can be obtained by plotting a straight line of $\ln(q_e/C_e)$ versus q_e (figure not shown) and extrapolating q_e to zero [38,39]. Its intercept gives the values of K_D.

Table 4
Equilibrium constant and Gibbs free energy changes for biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions on OPAA.

Metal ions	K_D	ΔG (kJ mol^{-1})	R^2
Pb^{2+}	4.46	−3.77	0.9079
Cd^{2+}	7.26	−4.99	0.9355
Ni^{2+}	5.34	−4.22	0.9820

The biosorption free energy changes (ΔG°) can be calculated according to

$$\Delta G^\circ = -RT \ln K_D \tag{9}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in Kelvin. The values obtained were shown in Table 4. The negative free energy changes in heavy metal ions–OPAA system are −3.77, −4.99 and −4.22 kJ mol^{-1} for Pb^{2+}, Cd^{2+} and Ni^{2+} ions, respectively, indicating the biosorption process is spontaneous at 30 °C, as observed.

3.5. *Recovery of the biosorbent*

Recyclability of an adsorbent is of crucial importance in industrial practice for metal removal from wastewater. To test the suitability and stability of the biosorbent, it was subjected to successive biosorption and desorption cycles. The procedure was carried out three times and 25 mL of 0.05 mol L^{-1} HCl was used as elution solution. The biosorbent was washed with water before each measurement. The results in Table 5 clearly show that OPAA can be used repeatedly at least three times without significantly loosing the biosorption capacity for Pb^{2+}, Cd^{2+} and Ni^{2+} ions.

3.6. *FTIR analysis*

The pattern of sorption of metals onto plant materials is attributable to the active groups and bonds present on them [33]. FTIR spectroscopy was, therefore, done for preliminary quantitative analysis of major functional groups present in OPAA used as biosorbent of Pb^{2+}, Cd^{2+} and Ni^{2+} ions in the present studies (Fig. 4a). FTIR spectra of metal (Pb^{2+}, Cd^{2+} and Ni^{2+} ions)-loaded OPAA were also obtained to determine correspondence of respective metal biosorption at the stretching and bending of active groups present in OPAA (Fig. 4b–d). The broad and intense absorption peaks at 3440 cm^{-1} correspond to the O–H stretching vibrations of cellulose, pectin, absorbed water, and lignin. The peaks observed at 2921 cm^{-1} can be attributed to the C–H stretching vibrations of methyl, methylene and methoxy groups. Peak observed at 1732 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 [40]. Asymmetric and symmetric stretching vibrations of ionic carboxylic groups ($–COO^-$), respectively, appeared at 1575,

Table 3
Biosorption capacities of various biosorbents.

Biosorbents	q_{max} (mg g^{-1})			References
	Pb^{2+}	Cd^{2+}	Ni^{2+}	
Rice husk	58.1	16.7	5.52	[33]
Sugar beet pulp	3.76	24.39	11.86	[34]
Corncobs	8.29	8.99	13.49	[35]
NaOH-modified biomass of *Solanum elaeagnifolium*	46.79	18.63	7.55	[36]
Solanum elaeagnifolium	20.60	18.94	6.50	[36]
Padina sp.	259.0	84.30	36.97	[37]
Sargassum sp.	240.4	85.43	35.80	[37]
Ulva sp.	302.5	65.20	17.02	[37]
Gracillaria sp.	93.24	33.72	16.43	[37]
Orange peel (OP)	113.5	63.35	9.82	This study
Modified orange peel (OPAA)	476.1	293.3	162.6	This study

Table 5
Results of Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption–desorption experiments.

Metal ions	Cycles	Amount before biosorption ($mg\,L^{-1}$)	Amount after biosorption ($mg\,L^{-1}$)	Biosorption (%)	Amount desorbed with 0.05 $mol\,L^{-1}$ HCl ($mg\,L^{-1}$)	Recovery (%)
Pb^{2+}	1	50	4.0	92.0	44.5	96.7
	2	50	3.9	92.2	44.5	96.5
	3	50	4.2	91.6	43.5	95.0
Cd^{2+}	1	50	3.2	93.6	45.5	97.2
	2	50	4.2	91.6	43.8	95.6
	3	50	4.0	92.0	43.1	93.7
Ni^{2+}	1	50	3.9	92.2	44.2	95.8
	2	50	4.1	91.8	43.8	95.4
	3	50	4.5	91.0	41.3	90.8

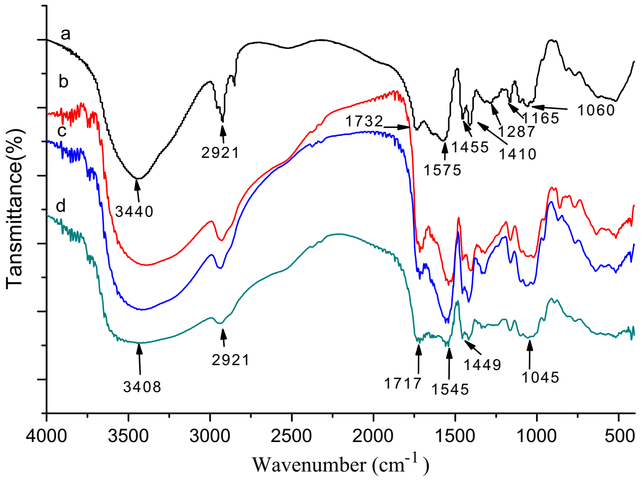

Fig. 4. FTIR spectrum of OPAA (a), OPAA–Pb^{2+} (b), OPAA–Cd^{2+} (c) and OPAA–Ni^{2+} (d).

and 1455 cm^{-1} [20]. The bands in the range 1300–1000 cm^{-1} can be assigned to the C–O stretching vibration of carboxylic acids and alcohols. It is well indicated from FTIR spectrum of OPAA 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 [41].

FTIR spectra of metal (Pb^{2+}, Cd^{2+} and Ni^{2+} ions)-sorbed OPAA showed that the peaks expected at 3440, 1732, 1575, 1455 and 1060 cm^{-1} (Fig. 4a) had shifted, respectively, to 3408, 1717, 1545, 1449, and 1045 cm^{-1} due to Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption (Fig. 4b–d). These shifts may be attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, are predominant contributors in metal ion uptake [41–43].

4. Conclusion

OPAA was prepared from hydrolysis of the grafted copolymer, which was synthesized by interacting methyl acrylate with cross-linking orange peel. Removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solution by grafted copolymerization-modified orange peel (OPAA) was found to be effective. Compared with the unmodified orange peel (OP), the biosorption capacity of the modified biomass increased 4.2-, 4.6- and 16.5-fold for Pb^{2+}, Cd^{2+} and Ni^{2+}, respectively. The results clearly show that OPAA is more effective than OP for the biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions. This may be due to the superior ion exchange capacity and chelating capacity of OPAA compared to OP because of the increasing number of carboxyl groups on OPAA after grafting of methyl acrylate on OP. Optimum pH for Pb^{2+}, Cd^{2+} and Ni^{2+} ions removal was found to be pH 5.5. Equilibrium biosorption data showed good fit to Langmuir isotherms. The biosorption equilibriums were reached at 150 min and biosorption processes followed pseudo-second-order kinetic model. The negative value of change in Gibbs free energy indicated the feasibility and spontaneous nature of the biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions on OPAA. The interactions between Pb^{2+}, Cd^{2+} and Ni^{2+} ions and functional groups on the surface of the biosorbent were confirmed by FTIR analysis and the spectra showed that carboxyl and hydroxyl groups are involved in Pb^{2+}, Cd^{2+} and Ni^{2+} ions binding to the OPAA. The adsorbed Pb^{2+}, Cd^{2+} and Ni^{2+} ions can be recovered using 0.05 $mol\,L^{-1}$ HCl solution and the spent biosorbent can be regenerated and reused making the biosorption process more economical. It can be concluded that the OPAA is an effective and alternative biomass for the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions from wastewater in terms of high biosorption capacity, natural and abundant availability and low cost.

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