Nickel, Lead, and Cadmium Removal Using a Low-Cost Adsorbent - Banana Peel

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ABSTRACT

Water pollution because of inorganic contaminants is a serious problem due to the acute toxicities and carcinogenic nature of pollutants. Recently, much attention has been focused on using natural and low-cost adsorbents, especially food residues, for removing toxic metal ions. Batch removal of nickel (Ni(II)), lead (Pb(II)), and cadmium (Cd(II)) from aqueous solution using a natural adsorbent is described in this study. Effects of various parameters on adsorption capacities such as pH, adsorbent dose, and stirring time were investigated by batch experiments. The maximum adsorption capacities for Ni(II), Pb(II), and Cd(II) ions were 1.6 mg g^{-1}, 125 mg g^{-1}, and 84 mg g^{-1}, respectively. Characterization of the surface modification was performed with FTIR measurements. FTIR spectra showed that chemisorption takes place at the surface of the adsorbent. The Freundlich and Langmuir adsorption isotherms were used to evaluate the equilibrium data. The characteristic parameters for each isotherm were determined. The Langmuir and Freundlich isotherm provided the best correlation for Ni(II), Cd(II), and Pb(II) using banana peel.

INTRODUCTION

Heavy metals, such as nickel (Ni), lead (Pb), and cadmium (Cd) are major toxic pollutants to the environment and for human health, because they tend to accumulate in the tissues of living organisms and are non-biodegradable (1-6). When they accumulate in the body, they can cause severe damage such as malfunction of the body's organisms, pathological states, as well as serious behavioral, developmental and learning problems, particularly in children (7,8). If these metals move into the ecosystem, they can be adsorbed by marine animals and enter the human food chain, resulting in high health risks to the consumer (8). For these reasons, removing heavy metals from aqueous solutions by accurate and economical techniques is of great importance. Generally, heavy metals like lead, cadmium, and nickel are present in low concentrations in water samples and are difficult to determine. Although a number of methods are currently employed to remove and recover the metals, some new and effective physicochemical methods as chemical oxidation and reduction, biosorption, chemical precipitation, ion exchange, flotation, membrane separation process, adsorption have recently been developed for their removal from various environmental samples (9-16). However, these techniques have some disadvantages, such as high capital investment and operational costs (17). Among these techniques, most use low-cost natural adsorbent adsorption techniques. Simple design and a wide range of applications are the advantages of adsorption in comparison to other methods. The main objective of this study has been to investigate the adsorption characteristics of banana peel for the removal of Ni(II), Pb(II), and Cd(II) from aqueous solutions.

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EXPERIMENTAL

Chemicals

Nickel sulfate, lead nitrate, cadmium sulfate, sodium hydroxide, hydrochloric acid, sodium citrate monohydrate, sodium dihydrogen phosphate, sodium tetraborate, glycine, and nitric acid were obtained from Merck (Darmstadt, Germany). All chemicals used were of analytical grade.

Preparation of Adsorbent

The bananas were purchased at a local market in Tunceli, washed with tap and distilled water to remove the dirt, then peeled. The peels were oven-dried at 60 °C until constant weight. The dried banana peels were ground in a blender, sieved to particles of <120 mesh, and stored in polyethylene bags at room temperature until use.

Preparation of Metals Solutions

A stock solution of 1000 mg L^{-1} each of Ni(II), Pb(II), and Cd(II) was prepared by dissolving an accurate quantity of $NiSO_4 \cdot 6H_2O$, $Pb(NO_3)_2$, and $3CdSO_4 \cdot 8H_2O$ in distilled water. Other concentrations varying from 1 mg L^{-1} to 400 mg L^{-1} were prepared from stock solutions by dilution.

Batch Adsorption Studies

In this investigation, all adsorption experiments were performed using Erlenmeyer flasks containing Ni(II), Pb(II), and Cd(II) synthetic solutions and an adsorbent at <120 mesh particle size was added to the solutions. The effect of initial metal

ion concentration (1–400 mg L^{-1}), pH (2–13) and contact time (10 to 180 minutes) were studied at room temperature. The pH was adjusted using hydrochloric acid and sodium hydroxide. A Jenco 6173 digital pH meter (Shanghai Jenco Electronics, Shanghai, China) was used for the pH measurements. The adsorbent was separated from the sample by filtering and the filtrate was analyzed using a PerkinElmer® AAnalyst™ 800 atomic absorption spectrometer. The instrumental operating conditions are listed in Table I. Each experiment was carried out in triplicate and the average results are given.

Characterization of Adsorbent

Fourier transform infrared (FTIR) spectra of the pretreated banana peel were compared with the FTIR of the banana peel spiked with Ni, Pb, and Cd. The spectra were recorded in the frequency range of 4000 – 500 cm^{-1} using an FTIR spectrophotometer (Thermo Nicolet iS10, Thermo Scientific, USA). The instrumental operating conditions are listed in Table II. The samples were analyzed with Attenuated Total Reflectance (ATR).

TABLE I
Instrumental Operating Conditions of AAnalyst 800 FAAS

Parameters	Ni	Pb	Cd
Wavelength (nm)	232	283.3	228.8
HCL current (mA)	20.0	-	-
EDL current (mA)	-	440.0	230.0
Flow rates: Air (L min^{-1})	17	17	17
Acetylene (L min^{-1})	2	2	2
Slit width (nm)	0.2	0.7	0.7

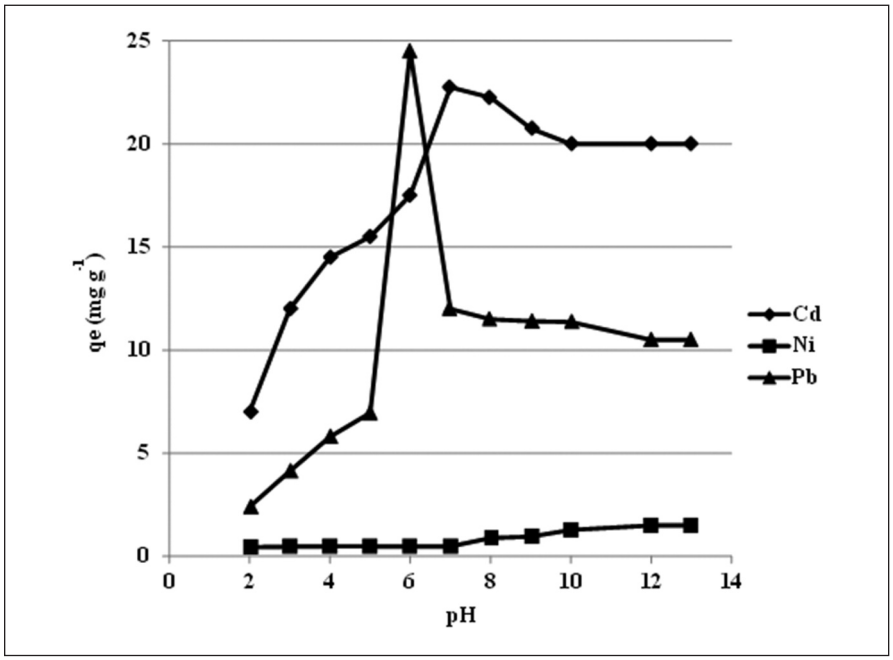

Fig 1. Effect of pH on adsorption capacity of nickel, lead, and cadmium on banana peel.

TABLE II
Instrumental Parameters for FTIR Analysis

Wavelength Range	4000 – 500 cm^{-1}
Sample to KBr Mass Ratio	1:100
Spectral Resolution	4 cm^{-1}

RESULTS AND DISCUSSION

Effect of pH

For pH optimization, about 0.25 g of banana peel adsorbent was added to metal solutions at different concentrations of Ni(II) 15 mg L^{-1}, Pb(II) 100 mg L^{-1}, and Cd(II) 400 mg L^{-1}, and then placed on a Radwag AS 220/C/2 (Radwag Balances & Scales, Poland) magnetic stirrer for 45 minutes. The pH was optimized in the range of 2–13. Citrate, phosphate, borate, and glycine buffers were used for the different pH ranges of 2–5, 6–7, 8–10, 11–13, respectively. It was observed that adsorption of these metals was maximum for Ni(II), Pb(II), Cd(II) at pH 12, 6, and 7, respectively. The results are given in Figure 1. The acid-base properties of the functional groups, mainly the carboxyl groups bound to the adsorbent surfaces, affect the relation between the metal uptake and the pH. The changing pH and adsorption values can be explained due to the competition between the metals ions and proton for the same functional groups, which results in a higher electrostatic attraction between metal and surface (18).

Different results were obtained for adsorbents by Carvalho et al. (19) by using silylated clays to remove Ni(II) from the aqueous effluents. They determined the maximum value of metal retention at approximately pH 6.0 and there was a decrease in the capacity of retention with a decreasing pH. In an another study (17), tea waste

was used as the adsorbent and the maximum adsorption of Ni(II) ions was obtained at pH 4.0. Jiang et al. (20) found that the adsorption of Ni(II) increased with an increase in pH from 2.0 to 8.0 on kaolinite clay.

Contact Time Studies

The influence of contact time on the adsorption of Ni(II), Pb(II), and Cd(II) on banana peel was evaluated from 10 to 180 minutes (Figure 2). The best contact time for Ni(II) was 90 minutes, for Pb(II) 30 minutes, and for Cd(II) 10 minutes.

Zuorro and Lavecchia (7) used black and green tea leaves as the adsorbent. In that study, about 0.5 g of this tea leave adsorbent was added to 50 mL of an aqueous solution at 0.1 g L^{-1} Pb concentration. The contact time was set to 2 hours and the temperature at 25 or 40 °C. A comparison of adsorbents such as used tea leaves and coffee grounds with regard to lead removal efficiency, it was found that they behave quite similar. Their average adsorption capacity was found to be 10.81±0.42 mg g^{-1} (at 40 °C) and 10.99±0.11 mg g^{-1} (at 25 °C).

Adsorbent Amount Study for Ni(II), Pb(II), and Cd(II)

The effect of adsorption of heavy metals ions on the amount of banana peel (from 0.1 to 1.0 g) was studied using 50 mL solutions with the optimum stirring time and pH. The adsorbed Ni(II) and Cd(II) amount increased with an increase in the adsorbent dose from 0.1 g to 0.25 g, while the adsorbed Ni(II) amount decreased with 0.25 g of adsorbent. The adsorbed Pb(II) amount increased with an increase in the adsorbent of 0.1 g, while the adsorbed Ni(II) amount decreased after 0.1 g of banana peel absorbent. The adsorption efficiency of Ni(II), Pb(II), and Cd(II) as a function of adsorbent dosage is shown in Figure 3.

During the adsorption reaction, many reasons such as incomplete saturation of the adsorption site and particle interaction can increase the amount of adsorbent used against a decline in q_e. A particle interaction, aggregation, can cause a reduction in the total surface area of the adsorbent (21).

Choksi and Joshi (22) studied Ni(II) removal from wastewater using natural adsorbents such as clay, starch, wood charcoal, and activated charcoal. They determined that for clay, the amount adsorbed increases from 0.09 g to 0.099 g per 0.25 g of adsorbent in relation to an increase in pH from 6.0 to 8.5, respectively. For clay, the adsorbed Ni(II) amount increases from 0.098 g per 0.2 g to 0.099 g per 1 g at 30 °C, and pH 7.5.

Effect of Final Volume

The final volume of metal solutions was studied (besides the other optimum conditions) in order to determine the use of appropriate volume for optimum adsorption. For this purpose, the adsorbent was interacted with heavy metal solutions at different concentrations: for Ni(II) 15 mg L^{-1}, for Pb(II) 150 mg L^{-1}, and for Cd(II) 100 mg L^{-1} but at different volumes (25-400 mL).

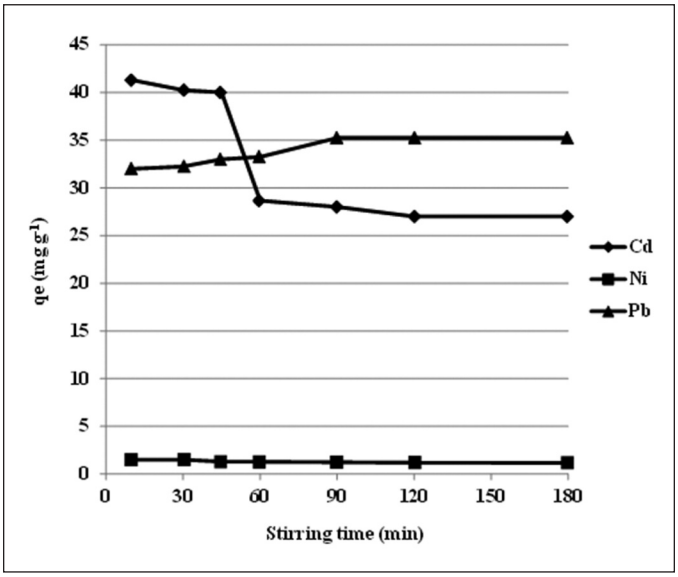

Fig. 2. Effect of stirring time on adsorption capacity of nickel, lead, and cadmium on banana peel.

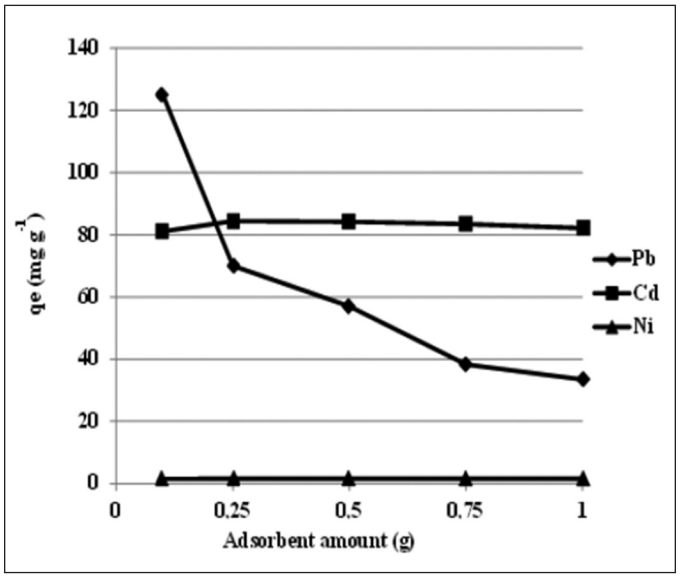

Fig. 3. Effect of adsorbent dose on adsorption capacity of nickel, lead, and cadmium on banana peel.

Figure 4 shows the optimum final volume required for the adsorption capacity of these elements. According to the obtained results, the solution volume has little effect on the adsorption capacity of the adsorbent. Adsorption capacities were about the same regardless of the difference in volume. The final volume for optimum adsorption capacity of banana peel for Ni(II) and Cd(II) was 50 mL solution, and for Pb(II) it was 250 mL solution.

Calculation of Metal Concentration

The amount of metals adsorption was calculated according to Equation 1:

$$q_e = ((C_0 - C_e) \times V) / m \quad \textbf{(Eq. 1)}$$

where q_e = The amount of Ni(II), Pb(II), and Cd(II) adsorbed by the banana peel adsorbent (mg g^{-1})

C_0 = The metal concentrations in the solution before adsorption (mg L^{-1})

C_e = The metal concentrations in the solution after adsorption (mg L^{-1})

V = The volume of the solution (L)

m = The mass of adsorbent used (g)

The metal adsorption capacity of the natural adsorbent used was calculated at optimum conditions. The q_e was calculated as 1.6 mg g^{-1}, 125 mg g^{-1}, and 84 mg g^{-1} for Ni(II), Pb(II), and Cd(II), respectively. According to the obtained results, Pb(II) has better adsorption on banana peel than Ni(II) and Cd(II).

Adsorption Isotherms

The isotherms of adsorption are the data calculated at the equilibrium point of the adsorbent. Isotherms were represented as positive, smooth, and concave. The amount of toxic metals was increased with the equilibrium concentration of toxic metals in solutions and showed that Pb(II) had better adsorption on the banana peel adsorbent than Cd(II) and Ni(II). Figure 5 shows the adsorption isotherms of Ni, Pb, and Cd in aqueous solution on banana peel. Because of the isotherm's shape, the data of adsorption were calculated according to the Langmuir and Freundlich equations and are given in Equations 2 and 3,

$$q_e = K_F C_e^{1/n} \quad \textbf{(Eq. 2)}$$

$$\frac{1}{q_e} = \frac{1}{K_L} + \frac{1}{Q_m} \quad \textbf{(Eq. 3)}$$

where q_e = The amount of toxic metals per unit weight of the banana peels (mg g^{-1}).

C_e = Equilibrium concentration of the metals (mg L^{-1})

K_F = Freundlich constant about adsorption capacity (mg g^{-1})

n = Freundlich constant about adsorption intensity

K_L = Langmuir constant about the intensity of the adsorption process (L mg^{-1})

Q_m = Constant relating to the surface area occupied by a monolayer of metals, reflecting the adsorption capacity (mg g^{-1})

Based on the data of q_e from the fittings of the pseudo-second order adsorption rate model, Q_m and K_L can be determined from its slope and intercept from a typical plot of $1/q_e$ versus $1/C_e$. In equation 2, the slope 1/n, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity. K_F is a constant for the system, related to the bonding energy. K_F can be defined as adsorption or distribution coefficient and represents

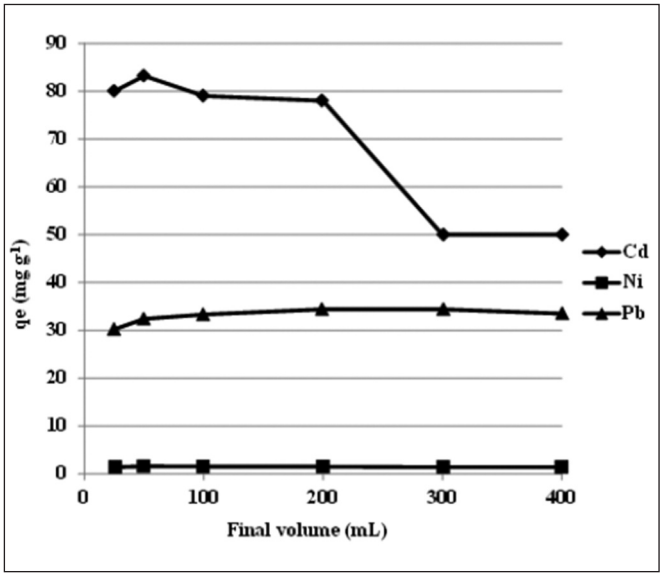

Fig. 4. Effect of final volume on adsorption capacity of nickel, lead, and cadmium on banana peel.

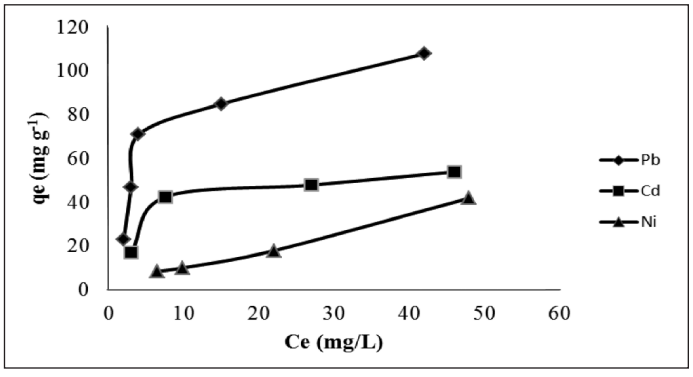

Fig. 5. Adsorption isotherms of nickel, lead, and cadmium in aqueous solution on banana peel.

the general capacity of toxic metals adsorbed onto the adsorbent for a unit equilibrium concentration. The results of the Freundlich and Langmuir isotherms fitted by using the data of adsorption capacity from the regression of Equation 3 (23). Obviously, it can be seen in Table III that the Langmuir model yields a somewhat better fit than the Freundlich model on the adsorption of Pb on banana peel, as reflected with correlation coefficients (R^2) of 0.98. At the same time, the values of K_L and K_F define a measure of the adsorption capacity. As indicated in Table III, the Freundlich model yields a somewhat better fit than the Langmuir model on the adsorption of Cd and Ni on banana peel.

TABLE III
Parameters in the Langmuir and Freundlich Adsorption Isotherm Models of Toxic Metals on Banana Peel

Toxic Metals	Langmuir Q_m (mg g^{-1})	Langmuir K_L (L mg^{-1})	Langmuir R^2	Freundlich K_F (mg g^{-1})	Freundlich n	Freundlich R^2
Pb	50.3	0.088	0.98	25.3	1.2	0.84
Cd	65.4	0.00009	0.16	40.8	6.48	0.37
Ni	49.0	0.0156	0.87	1.83	1.4	0.93

Fourier Transform Infrared Analysis of Adsorbents

The adsorption band at approximately 3300 cm^{-1} is attributable to the hydroxyl groups from the polyphenols originally present in banana peel. The C-H groups stretching vibrations for banana peel can be seen at 2900 cm^{-1}. The observed band around at 2851 cm^{-1} in Figures 6 (a - d) was assigned to the stretching vibration of C-H alkane groups. The C=O group of carboxylic acid or its ester peaks were seen at 1730 cm^{-1}. Symmetric and asymmetric stretching C=O or C=C aromatic vibration leads to a peak around 1604 cm^{-1}. The observed band around at 1240 cm^{-1} represents SO_3 stretching. At 1634 cm^{-1} it reflects carbonyl group stretching (amide) for the banana peel. All these functional groups show that quite likely these heavy metals are binding to this adsorbent. The shifts and intensity changes of the FTIR bands observed were rather weak, which is indicated by the dominance of the ion exchange over the precipitation/coprecipitation occurring during Ni(II), Pb(II), and Cd(II) sorption on adsorbent.

CONCLUSION

In the present study, a batch technique for the adsorption of Ni(II), Pb(II), and Cd(II) has been carried out using banana peel as the adsorbent. The important parameters for the batch technique such as pH, contact time, adsorbent dose, and final volume were studied for determining the adsorbent adsorption capacity. It was found that banana peel is a good adsorbent for heavy metals, especially for Pb(II) and Cd(II). The adsorption percentages are very high. This adsorbent is waste material, can easily be obtained, is eco-friendly and low cost.

This study is also important in terms of employing used adsorbent

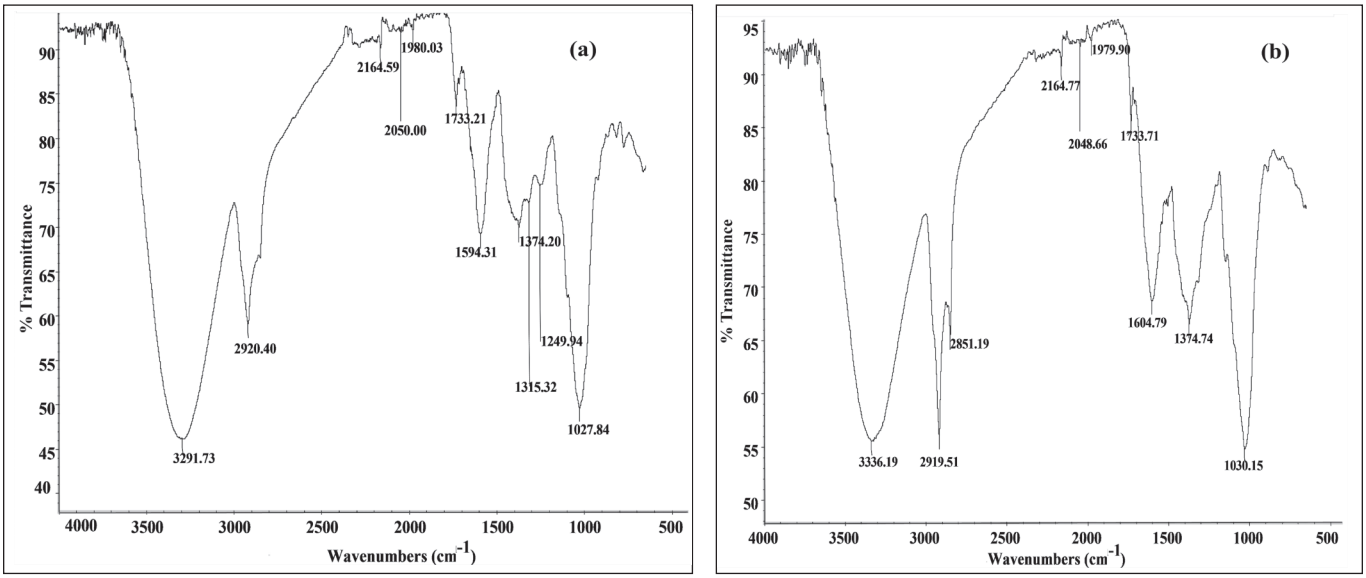

Fig. 6 (a and b). FTIR spectra of (a) banana peel and (b) Ni-loaded banana peel.

sources. The adsorbent is really a waste material but finds an ultimate final and important use for removing heavy metals to prevent harm to humans and the environment.

The results obtained with the Langmuir and Freundlich isotherm models are perfect applications for Ni, Pb, and Cd adsorption with a regression coefficient.

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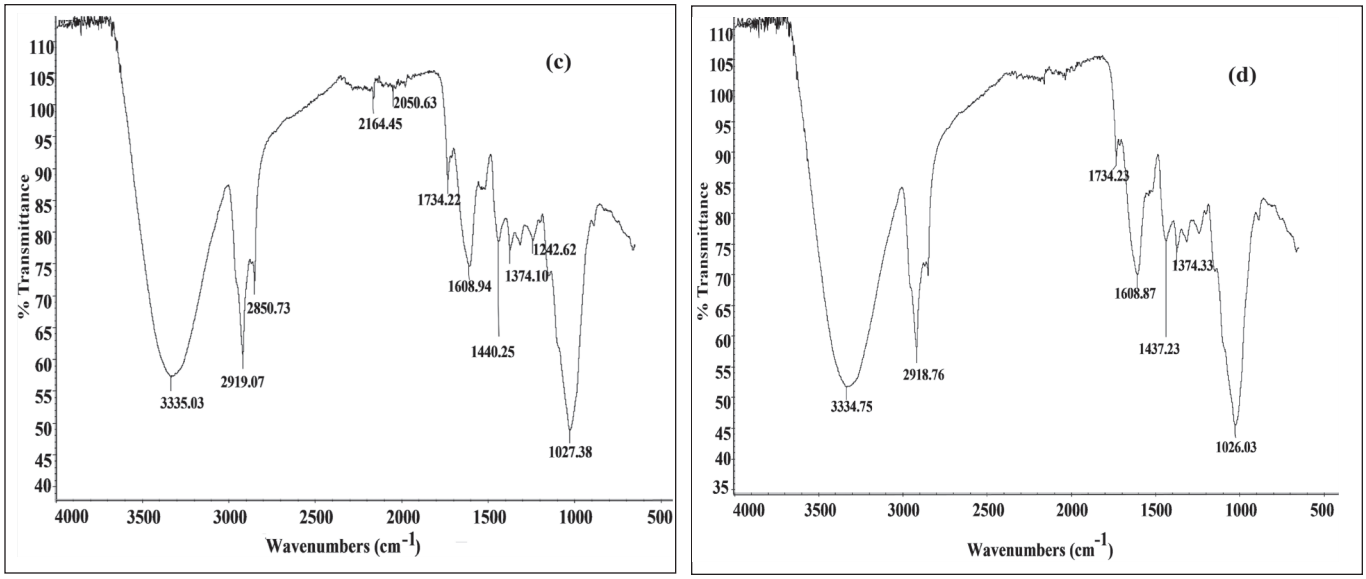

Fig. 6 (c and d). FTIR spectra of banana peel (c) Pb-loaded banana peel, (d) Cd-loaded banana peel.