

Removal of Lead and Cadmium Ions from Aqueous Solution using Walnut Shells as Low-Cost Adsorbent Materials

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In this study dry walnut shells were used as adsorbent to remove of Pb(II) and Cd(II) ions from aqueous solution through batch adsorption of single component. An investigation was carried out to identify the effect of pH, initial concentration of the heavy metal's ions, contact time, dose and size diameter of adsorbent on the removal efficiency at 25 °C. Isotherm adsorption parameters were determined by using both Langmuir and Freundlich models. Two simplified kinetic models including a pseudo-first-order equation and pseudo-second-order equation were selected to follow the adsorption process. Results showed that the maximum removal efficiency of Pb(II) and Cd(II) ions are 86.16% and 72.35% respectively in the best conditions. The experimental data fitted better to the Langmuir isotherm model than to Freundlich isotherm model. The experimental data proved that the adsorption kinetic of Pb(II) and Cd(II) ions could be described by a pseudo-second order model.

Keywords: adsorption; equilibrium; isotherm; kinetics and agricultural by-products

The industrial developments cause an increasing in the concentrations of heavy metal ions from industrial effluent. This became one of the most difficult for the environmental protection, because metal ion can be toxic by entering the food chain [1]. Heavy metals are non-biodegradable materials, comparing with other pollutants, and accumulate in the living tissues [2]. The lead ions have effect on the physiological and biochemical processes of the most organisms, especially the humans, thus these ions can cause nephrotoxicity, neurotoxicity, and hypertension. As a result of the similarity in the size and charge, lead can substitute calcium and so it could be inserted in bones. Therefore, it is very dangerous for children, as they are especially susceptible to lead due to the high calcium level demand of the developing skeletal systems [3]. Previous studies on animals and humans have shown that chronic and acute exposure to cadmium ion may contribute to some forms of cancer in humans or can induce a variety of health disorders, including kidney damage. Exposure usually occurs by oral route and kidney is the target organ [4].

Many industries, such as metal industries, petroleum refining, battery manufacturing processes, the production of paints and pigments, tanning, photographic processing, ceramic and glass industries and electroplating are a major source for pollution of heavy metals [5]. All previous industries generate significant quantities of wastewaters containing heavy metals (such as nickel, chromium, zinc, lead, copper, cadmium, platinum, silver, titanium and vanadium) [6].

The methods most commonly applied to remove heavy metal ions from industrial waste water include: chemical precipitation, filtration, ion exchange, electrochemical, reverse osmosis, adsorption, flocculation, and membrane advanced systems [7-9]. Depending on the aqueous effluent flow rates and concentration of metal ion, also the industrial application of these processes is restricted

by the inefficiency and operating costs of the technique. Therefore, all these techniques have their inherent advantage and limitations in application [10].

Adsorption is found to be the most effective method for removing dissolved metal ions from wastes. Use of adsorption contacting systems for industrial and municipal wastewater treatment has become more prevalent during recent years [11]. Adsorption is often used at the end of a treatment sequence for pollution control due to high degree of purification that can be achieved.

Agricultural waste could be potentially used as low cost adsorbents to remove the heavy metal ions from solution, as it represents unused resources, low cost, widely available and environmentally friendly. The presence of cellulose and lignin are main components of most agricultural by-products. The presence of lignin signifies the existence of polar functional groups such as: carboxylic, alcohols, aldehydes, phenolic, ketones and ether groups attached on such adsorbents. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups on order to form complexes with the metal ions in solution [12].

There are many recent studies, focused to develop inexpensive and effective adsorbents from the plentiful sources of natural agriculture wastes in order to replace the conventional metal-removing available methods. Some papers studied the effect of experimental parameters such as the initial metal concentration, pH, contact time, adsorbent dose, agitation speed and temperature [13-20]. The removal of heavy metals have been done by using some of the low-cost natural materials such as: rice husk, rice straw [13], sawdust [14], pomegranate peel [15], peanut shells [16], green coconut shells [17], apple waste [18], wool fibers [19], orange peel, banana peel [20] and waste tea leaves [21].

The aim of this paper is to study the removal efficiency of dry walnut shells as adsorbents to remove lead and

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cadmium ions from aqueous solution in a batch adsorption of single component system. The effect of pH, initial concentration of heavy metal ions, contact time, dose and size diameter of adsorbent as well as isotherm models and kinetic models for this system were studied.

Experimental part

Materials and Methods

Adsorbent

Walnuts were collected from the local market, and then they were broken to obtain walnut shells. They were washed twice in distilled water to remove the dust, dried for 24 h at temperature 100 °C, ground using laboratory mill, sieved to 0.5–3 mm and stored in plastic containers ready for use.

Reagents

A stock solution of Pb(II) and Cd(II) ions at a concentration of (100 mg/L) for each ions were prepared by dissolving calculated amount of $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ from REACTIVUL® Company, Bucharest, Romania in distilled water. Lower concentrations were then prepared when required by further dilution of the stock solution with distilled water. The diluted solutions were kept at room temperature. Before the sorption process was initiated, the pH of solutions was adjusted to the required value by adding 0.1 M HCl and 0.1 M NaOH solutions.

Instrumentation

The equipment used for the experiments was:

- atomic Absorption Spectrometer: AAS (GBC 933 plus, Australia),
- shaker incubator, Heidolph, No.549-59000-0-0, Korea,
- pH bench meter (Cyberscan, PCD 6500), EUTECH INSTRUMENTS,
- electrical balance, TE 2145, Sartorius, Germany,
- FTIR, spectrophotometer, TENSOR 27, BRUKER, Germany,
- glass ware (beakers, conical flasks) and
- filter paper (Whatman 40 mm).

Working procedure and analytical methods

Sorption experiments

Batch adsorption of single component system of Pb(II) and Cd(II) ions experiments have been carried out at temperature 25 °C and stirring speed of 200 rpm to establish the optimal working parameters: pH, initial concentration, contact time, adsorbent dose and particles diameter. The procedure supposed to fill a 100mL flask with 50 mL of each heavy metal ions solution Pb(II) and Cd(II). Experiments were carried out at initial pH value ranging from 3 to 7; the initial concentration of heavy metal ions (10 – 100) mg/L, the contact time (10-180) min, adsorbent dose (0.125-1) g and particles diameter (0.5-3) mm. After equilibrium, was established samples (20 mL) were taken from the flask. These samples were filtered and the concentration of heavy metal ions in the solutions was determined by AAS. The removal efficiency (R %) was calculated using equation (1):

$$R\% = \frac{C_o - C_e}{C_o} * 100 \quad (1)$$

where: C_o and C_e are the initial and final concentration of the metal ions respectively (mg/L).

Sorption isotherm models

Sorption isotherms are very powerful tools for the analysis of an adsorption process establishing relationship between the equilibrium concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. Some of most widely used models Freundlich, and Langmuir are discussed here [22, 23]. Freundlich and Langmuir isotherm models showed that adsorption from solution could be described in by equations (2) and (3) respectively:

$$q_e = KC_e^{1/n} \quad (2)$$

where q_e is the adsorbed metal ions (mg/g), C_e is metal ions concentration in the solution at equilibrium (mg/L), K , (mg/g) (L/mg)^{1/n} and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where: q_e is the adsorbed metal ions (mg/g), q_m is the maximum sorption capacity for monolayer coverage (mg/g), b is the constant related to the affinity of the binding site (L/mg), and C_e is metal ions concentration in the solution at equilibrium (mg/L).

Sorption kinetic models

The kinetics of batch adsorption of single component system studies were performed for Pb(II) and Cd(II) ions at different initial concentrations (10, 25, 50, 75 and 100 mg/L) by suspending 0.5 g of sorbent in 50 mL of each metal ions solution and the pH was adjusted to 6 and stirred at 200 rpm. Samples were withdrawn at pre-determined time intervals (10, 30, 60, 90, 120, 150 and 180 min), and analyzed for residual metal ion concentration.

The kinetics of batch adsorption of single component system of Pb(II) and Cd(II) ions adsorption onto walnut shells was analyzed using pseudo-first-order and pseudo-second-order models [24, 25]. A linearized pseudo-first-order equation is described in equation (4):

$$\ln(q_{eq} - q_t) = \ln q_{eq} - k_1 t \quad (4)$$

where: q_{eq} is the amount of pollutant adsorbed at equilibrium (mg/g); q_t is the amount of pollutant adsorbed at time t (mg/g); and k_1 is the equilibrium rate constant of pseudo-first sorption (L/min). This pseudo-first-order equation could be applicable when a plot of $\ln(q_{eq} - q_t)$ against t is a straight line and then q_{eq} and k_1 could be determined from the slope and intercept, respectively. Adsorption data were analyzed with the following linearized pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \quad (5)$$

where k_2 is the rate constant of adsorption, (g/mg.min), q_{eq} is the amount of pollutant adsorbed at equilibrium, (mg/g), q_t is amount of adsorbate on the surface of the adsorbent at any time, t , (mg/g). k_2 and q_{eq} are the slope and intercept of the t/q_t vs. t plot, respectively.

FTIR analysis

The functional groups present in adsorbent were detected by FTIR analysis. Infrared spectra for Pb(II) and Cd(II) loaded adsorbent were also carried out to investigate the possible binding sites of these ions and to find out which functional groups are responsible for the adsorption process. Two flasks of 2000 mL were filled with 1000 mL of each metal solution 50 mg/L and 10 g of dried walnut shells. The flasks were then placed on a shaker and stirred continuously for 150 min at 200 rpm. Samples of each flask were dried in oven at 50 °C for 48 h.

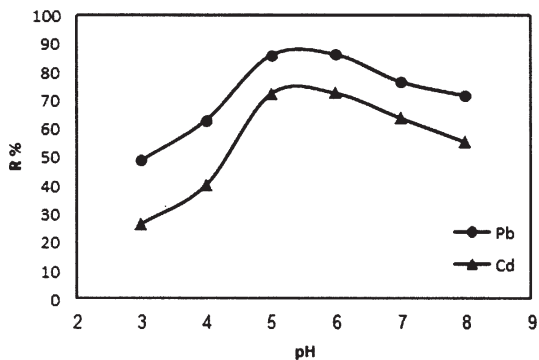


Fig. 1. Influence of pH on the adsorption efficiency of metal ions onto dry walnut shells at $C_0 = 50$ mg/L, agitation speed = 200 rpm, contact time = 150 min, adsorbent dose = 0.5 g/50 mL and temperature = 25 °C.

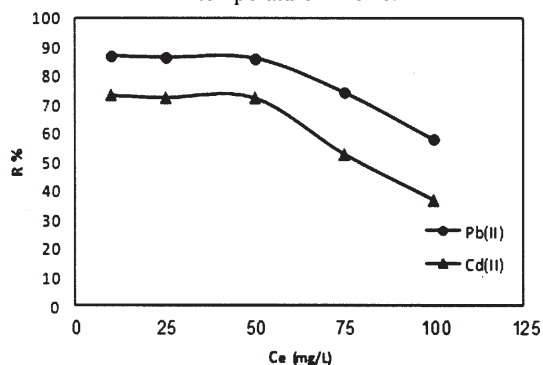


Fig. 2. Influence of the initial concentration on the adsorption efficiency of heavy metals onto dry walnut shells at pH = 6, stirring speed = 200 rpm, adsorbent dose = 0.5 g/50 mL, contact time = 150 min and temperature = 25 °C.

Results and discussions

Influence of various parameters (sorption stage)

Influence of pH

The pH value of the aqueous solution is an important variable which controls the adsorption and plays an important role in the precipitation and adsorption mechanisms. The experiments concerning the effect of pH on the adsorption were carried out in the range of pH not influenced by the metal precipitation as metal hydroxide which it occurs at a pH above 6 [26].

From figure 1 it could be observed that the removal efficiency of Pb(II) and Cd(II) are increases from 48.8 and 26.34 to 86.16 and 72.35%, respectively, with the increase in pH value from 3 to 6. Metal uptake increased at a pH around 6. At this pH, the functional groups onto adsorbent surface deprotonate and the adsorbent surface becomes negatively charged (i.e., increasing of OH⁻ groups), so in this region of pH metal ions could favorably be attracted onto the adsorbent [27]. When the pH values are higher than 6, the removal takes place by adsorption as well as precipitation, due to formation of metals hydroxide. This can be explained by the fact that, as the pH of the solution increased the OH⁻ ions concentration in the solution increases and they form some complexes with metal ions and precipitate as metals hydroxide.

Influence of initial metal concentration

The initial concentration of Pb(II) and Cd(II) provides an important driving force to outweigh all mass transfer resistance of metal between the aqueous and solid phases. Removal of these ions for various initial concentrations (10 to 100 mg/L) by dry walnut shells dose (0.5 g/50 mL) at 150 min contact time and at pH 6 is depicted in the figure 2. The removal efficiency of Pb(II) increased from 57.58 to 87.05% and for Cd(II) from 36.84 to 73.23%, with a

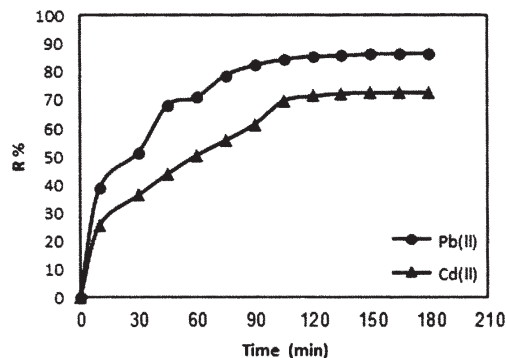


Fig. 3. Influence of the contact time on the adsorption efficiency of heavy metals onto dry walnut shells at $C_0 = 50$ mg/L, pH = 6, adsorbent dose = 0.5 g/50 mL, stirring speed = 200 rpm and temperature = 25 °C.

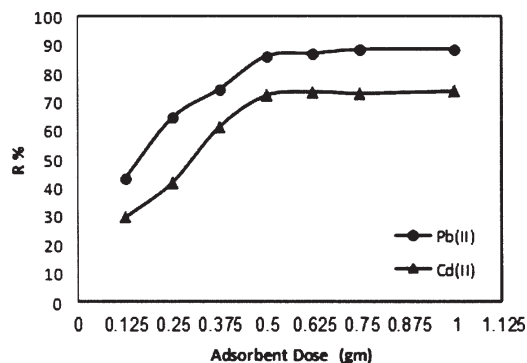


Fig. 4. Influence of the adsorbent dose on the adsorption efficiency of heavy metals onto dry walnut shells at $C_0 = 50$ mg/L, pH = 6, contact time = 150 min, stirring speed = 200 rpm and temperature = 25 °C.

decrease in initial concentration from 100 mg/L to 10 mg/L. The influence of initial metal concentration could be explained as follow: at low metal ion, adsorbent ratio, metal ion concentration adsorption involves higher energy binding sites. As the metal ion, adsorbent ratio increase (i.e., at higher initial concentration), the higher energy binding sites are saturated and adsorption begins on lower energy binding sites, resulting a decrease of the adsorption efficiency [28].

Influence of contact time

Contact time is an important factor for the removal efficiency of heavy metals using natural adsorbent materials. The effect of contact time on removal efficiency of Pb(II) and Cd(II) onto dry walnut shells for a contact time between 0 and 180 min are shown in figure 3. It was observed that the removal efficiency increases for Pb(II) from 0 to 87.01% and for Cd(II) from 0 to 72.17% as the contact time increases from 0 to 180 min. The results clearly revealed that rate of sorption is higher at the beginning and this is due to availability of a large number of active sites on the adsorbent. As these sites are exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [29]. Maximum removals were attained in the first 150 min of stirring time. There must not be seemed to be much benefit after 150 min.

Influence of the adsorbent dose

The effect of varying the adsorbent dose on the sorption of Pb(II) and Cd(II) ions is shown in figure 4. It is clearly observed that the removal efficiency increases for Pb(II) and Cd(II) ions from 43.45 to 88.64% and from 29.62 to 73.87%, respectively, as the dry walnut shells mass increases from 0.125 to 1 gm/50 mL. As the walnut shells

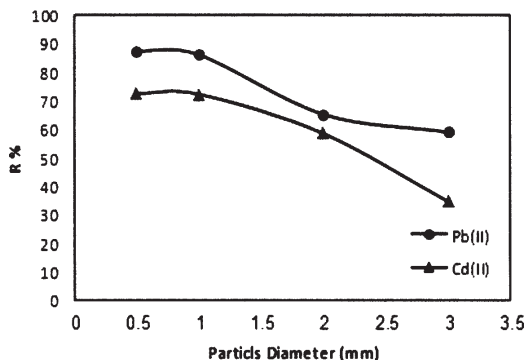


Fig. 5. Influence of the particles diameter on the adsorption efficiency of heavy metals onto dry walnut shells at $C_0 = 50$ mg/L, $pH = 6$, agitation speed = 200 rpm, adsorbent dose = 0.5 g/50 mL, contact time = 150 min and temperature = 25°C

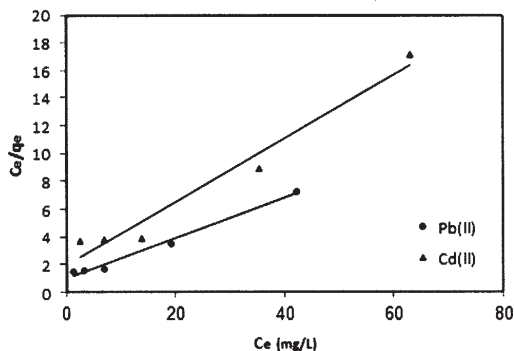


Fig. 6. Langmuir isotherm for batch adsorption of single component system for Pb(II) and Cd(II) ions onto dry walnut shells

mass increases the number of binding sites for the ions also increases. After some point, adsorption capacity was steady due to a screen effect between adsorbent, and solution such effect produced a block of the adsorbent active sites by an increase of adsorbate (heavy metal ions) in the system [28]. Similar observations were also made by other investigators [30]. The best dose of dry walnut shells was established at 0.5 g/ 50 mL and for Pb(II) and Cd(II) ions because of a slight difference in the removal efficiency when we use a larger quantities than the adsorbent dose.

Influence of particles diameter

The particles diameter of adsorbents material is another important variable during metal sorption process. The effect of particle diameter was investigated for Pb(II) and Cd(II) metal solutions at (0.5, 1, 2, 3) mm particles diameter, the pH kept at the best value and the concentration for metallic ions was 50 mg/L. Figure 5 shows the removal efficiency at different particles diameter of dry walnut shells. It was found that increase in the particles diameter from 0.5 mm to 3 mm, causes a decrease of adsorption efficiency for Pb(II) and Cd(II) from 87.56 to 59.17% and from 72.65 to 34.59%, respectively, which it would be

Model	Parameters	Pb(II)	Cd(II)
Pseudo-first-order Equation (4)	q_e (mg/g)	5.0505	7.2456
	K_1 (L/min)	0.0375	0.0383
	R^2	0.9775	0.8745
Pseudo-second-order Equation (5)	q_e (mg/g)	4.8614	4.5433
	K_2 (g/mg.min)	0.0106	0.0054
	R^2	0.9963	0.9815
	q_e (Experimental) (mg/g)	4.3080	3.6175

Table 1
ISOTHERM PARAMETERS OF BATCH ADSORPTION OF SINGLE COMPONENT SYSTEM FOR Pb(II) AND Cd(II) IONS ADSORPTION ONTO DRY WALNUT SHELLS

Model	Parameters	Pb(II)	Cd(II)
Freundlich Equation (2)	K (mg/g)(L/mg) ^(1/n)	1.0159	1.6656
	n	1.8436	1.9493
	R^2	0.8657	0.8039
Langmuir Equation (3)	q_m (mg/g)	6.8259	4.3572
	b (L/mg)	0.1553	0.1223
	R^2	0.9843	0.9658

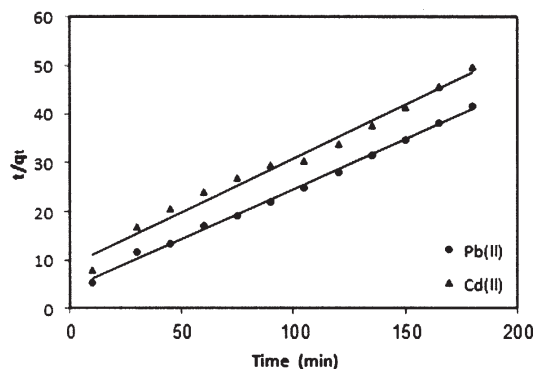


Fig. 7. Pseudo-second order kinetic model for batch adsorption of single component system for Pb(II) and Cd(II) ions onto dry walnut shells

anticipated with the decreasing the surface sites of ion exchange between the metals and particles.

Sorption isotherms

The adsorption for a single component systems of Pb(II) and Cd(II) ions onto dry walnut shells in batch experiments allows to determine the isotherms constants for each system using Langmuir and Freundlich isotherm models. The sorption isotherm constants are evaluated from isotherms and their correlation coefficients are presented. Table 1 shows that the data for the Langmuir model describe the sorption data slightly better than Freundlich model according to the value of correlation coefficients. The linearized Langmuir of Pb(II) and Cd(II) ions for sorbents are given in figure 6.

Kinetics models

Table 2 shows that the values of correlation coefficient (R^2) indicate a better fit of pseudo- second- order model with the experimental data compared to pseudo- first- order model. The values of q_e calculated from the second order kinetic model agreed very well with the experimental values, and the regression coefficients are over 0.98. Therefore, the second-order model can be applied for Pb(II) and Cd(II) sorption process (fig. 7). The first- order kinetic model was used for reversible reaction with an equilibrium

Table 2
KINETIC MODEL PARAMETERS Pb(II) AND Cd(II) IONS ADSORPTION ONTO WALNUT SHELLS OF BATCH ADSORPTION OF SINGLE COMPONENT SYSTEM

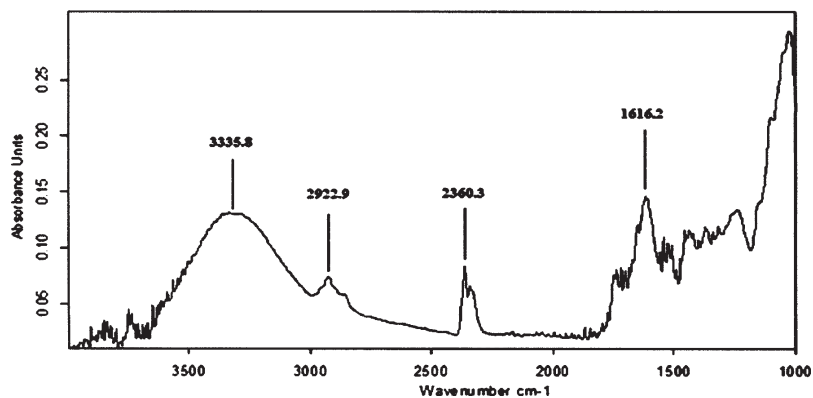


Fig. 8. FTIR analysis of dry walnut shells

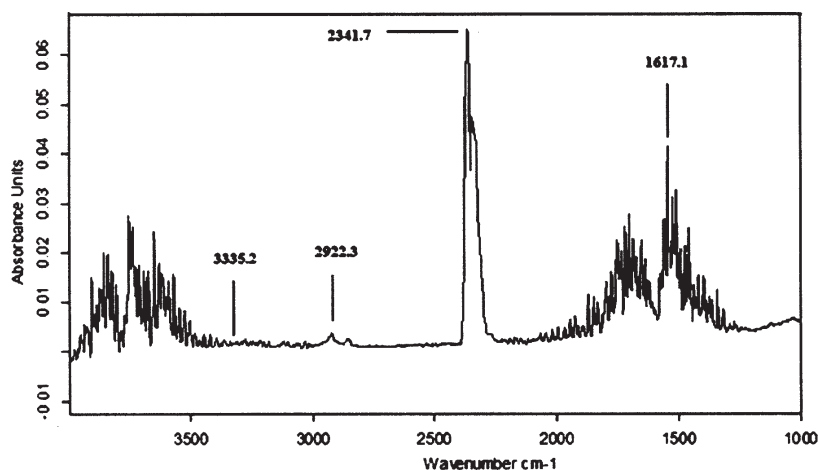


Fig. 9. FTIR analysis of dry walnut shells with adsorbed Pb(II) ion

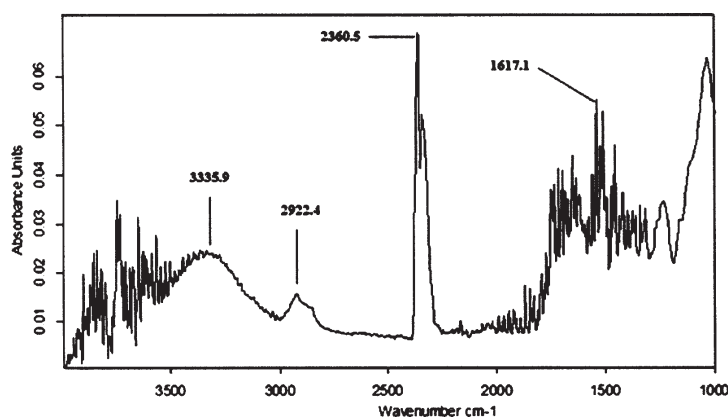


Fig. 10. FTIR analysis of dry walnut shells with adsorbed Cd(II) ion

being established between liquid and solid phases. Whereas, the second order kinetic model assumed that the rate limiting step could be the chemical sorption [31].

FTIR analyses of walnut shells

FTIR analysis of dry walnut shells have been carried out, in order to find out which chemical functional groups are responsible for adsorption of Pb(II) and Cd(II) ions. Figures 8-10 shows the spectra of raw material and these materials with adsorbed ions respectively.

The band displacement decreasing define the change in the structure with Pb(II) and Cd(II) imply the related functional groups to be responsible for the adsorption process. From these findings, it can be concluded that Pb(II) adsorbed more shifted than Cd(II). The figures 8-10 show also that the bands of hydroxyl, carbonyl, alkyl and aromatic groups shifted to higher transmission (bands of adsorption), and therefore it plays the major role in adsorption of these ions. Our finding are in accordance with the other studies [32].

Conclusions

In this study, it was observed that the dry walnut shells had a good adsorption efficiency to remove Pb(II) and Cd(II) ions in the batch adsorption of single component. Maximum removal efficiency of Pb(II) and Cd(II) ions are 86.16% and 72.35%, respectively, at $pH=6$, initial concentration of heavy metal ions was 50 mg/L, contact time 150 min, adsorbent dose of 0.5 g/50 mL of solution and 1 mm diameter size for the walnut shells. A Langmuir isotherm model gives the best fit to the experimental data in comparison to the Freundlich isotherm model. According to the Langmuir adsorption capacity parameter (q_m), the adsorption of metals was in the order of: Pb(II) > Cd(II). By applying the kinetic models to the experimental data, it was found that the sorption of Pb(II) and Cd(II) ions followed pseudo-second-order kinetics. From FTIR analysis it could be seen that the absorbance bands were shifted to new values due to sorption of the two heavy metal ions.

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