Pb(II) and Cd(II) removal from aqueous solutions by olive cake

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Abstract

The removal of heavy metals from wastewater using olive cake as an adsorbent was investigated. The effect of the contact time, pH, temperature, and concentration of adsorbate on adsorption performance of olive cake for Pb(II) and Cd(II) ions were examined by batch method. Adsorption of Pb(II) and Cd(II) in aqueous solution onto olive cake was studied in single component. After establishing the optimum conditions, elution of these ions from the adsorbent surface was also examined. The optimum sorption conditions were determined for two elements. Maximum desorption of the Pb(II) and Cd(II) ions were found to be 95.92 and 53.97% by 0.5 M HNO_3 and 0.2 M HCl, respectively. The morphological analysis of the olive cake was performed by the scanning electron microscopy (SEM).
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Keywords: Heavy metal; Adsorption; Olive cake; Lead; Cadmium

1. Introduction

Industrial wastewaters, which have heavy metals, are an important source of environmental pollution. Pb, Cd, Cu, Hg, Cr, Ni, and Zn are the main trace elements that are the most harmful for public health. These toxic metals are released into the environment in a number of different ways. Coal combustion, automobile emissions, mining activities, sewage wastewaters, and the utilization of fossil fuels are just a few examples [1]. However filtration, adsorption, reverse osmosis, solvent extraction, and membrane separation techniques are used for removal of heavy metals in aqueous solution, the chemical precipitation is a conventional technique. Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater and water supplies [2,3]. In the purification process, low cost adsorbents are preferred.

Activated carbon is the most common used adsorbent however it is relatively expensive [4]. Since the cost of this processes are rather expensive, the use of agricultural residues or industrial by-product have been studied for years and many references on this topic can be found in the literature. In recent years, number of agricultural materials such as palm kernel husk [5], modified cellulosic material [6], corn cobs [7], residual lignin [8,9], wool, [3,10], apple residues [11], olive mill products [3,12], polymerized orange skin and banana husk [13], pine bark [14], sawdust [15], etc., have been reported for the removal of toxic metals from aqueous solutions. In addition, peat, human hair, silk, and water hyacinth [16], marine algae [17] have also been used to remove heavy metals from wastewater. Adsorption of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compounds, which have metal binding functional groups, such as carbonyl, hydroxyl, sulphate, phosphate, and amino groups [18].

Olive cake is a waste of olive factory and usually used heating, fertilizer and feeding material. Its structure contains organic compounds like lignocellulosic material, polyphenols and also amino acid, protein, oil, and tannins [19]. Langmuir and Freundlich models are based on theoretical hypotheses that are hardly satisfied even for the ideal systems they were originally developed for gas adsorption onto planar surface. Furthermore, adsorption isotherms are commonly used for describing adsorption equilibrium for wastewater treatment.

The aim of this investigation is to determine the usability of olive cake as an adsorbent material for sorption of Pb(II) and Cd(II) ions from aqueous solutions.

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2. Experimental

2.1. Materials

All chemicals used were analytical reagent grade. $Pb(NO_3)_2$, $CdCl_2·2H_2O$, NaOH, CH_3COOH, HNO_3, and HCl were purchased from Merck. The olive cake which extracted by hexane was obtained from the Oil Factory, Belevi, Izmir, TURKEY.

2.1.1. Preparation of adsorbent

The olive cake washed with distilled water and dried at room temperature. This material was grinded with a grinding mill to obtained 212–132 μm particle size.

2.2. Instruments

The lead and cadmium concentration measurements were carried out using a Perkin-Elmer Optima 2000 DV ICP–OES. The pH of solution was measured with a Hanna P211 microprocessor pH-meter using a combined glass electrode. The shaking was carried out in a thermostated electronic shaker bath, Heidolph MR 3001 and centrifugation was performed on a Hettich EBA 20 centrifuge.

2.3. Method

Stock solutions (5000 mg L^{-1}) of Pb(II) and Cd(II) were prepared by dissolving $7.99 ± 0.01$ g of $Pb(NO_3)_2$ and $9.75 ± 0.01$ g of $CdCl_2·2H_2O$, respectively, in 1000 mL of ultrapure deionized water (18 MΩ cm). Standard solutions of the required Pb(II) and Cd(II) concentrations were prepared by appropriate dilution. Acetate buffer (0.1N) was prepared with dehydrate acetic acid and double distilled water. The required buffered pH was adjusted by adding 0.1N NaOH drop wise.

2.3.1. Uptake experiments

The sorption of lead and cadmium were performed by batch technique. For this aim a 50 mL of the test solutions, which adjusted to desire pH and concentration of these metal ions, were contacted with 1 g of olive cake. The experiments were conducted in a closed system, where no special attempts were made to exclude the dissolved carbonate. This mixture was stirred at low speed (750 rpm) for different contact times at room temperature. After an enough reaction time, the solution was separated from olive cake by centrifugation at 2500 rpm for 5 min using a Hettich EBA 20 centrifuge. ICP-OES has been used to perform for the determination of amounts of lead and cadmium in supernatants. The percentage adsorption of lead or cadmium from aqueous solution was computed as follows:

$$\text{Adsorption} (\%) = \frac{C_{int} - C_{fin}}{C_{int}} \times 100$$

where C_{int} and C_{fin} are the initial and final lead or cadmium concentrations, respectively.

Throughout the study, the contact time was varied from 5 to 300 min, the pH from 3.50 to 6.00, the initial lead or cadmium concentration from 2.5 to 50 mg/50 mL and temperature from 20 to 35 °C and also the adsorbent was used as $1.0 ± 0.01$ g in all test.

The adsorption isotherm for the Pb(II) and Cd(II) removal were obtained using initial concentrations of them between 2.5 and 50 mg/50 mL and 1 g of adsorbent at 30 and 35 °C, respectively.

2.3.2. Desorption experiments

Olive cake which is adsorbed at maximum concentration Cd(II) and Pb(II) ions were used for desorption studies. Desorption of metal ions was achieved using different concentrations of HCl and HNO_3. The olive cake carrying 18.14 mg Pb(II)/g and 9.05 mg Cd(II)/g were placed in this desorption medium and stirred at 750 rpm for 30 min at 30 and 35 °C for Pb(II) and Cd(II), respectively. The final metal ion concentration in the aqueous phase was determined by using ICP-OES. The desorption ratio was calculated from the amount of metal ions adsorbed on the olive cake and the final metal ions concentration in the desorption medium, using the following equation,

$$\text{Desorption ratio} (\%) = \frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}} \times 100.$$

3. Results and discussion

3.1. Analysis of olive cake by SEM

In order to know the structure sight of olive cake, morphological analysis of the olive cake was performed by scanning electron microscopy using a Jeol Jsm 5200. The working tension was 20 kV. Fig. 1 shows the intra structure of olive cake obtained by scanning electron microscopy (SEM). The figure indicates that olive cake has an extensive surface area and may be used as a sorbent material.
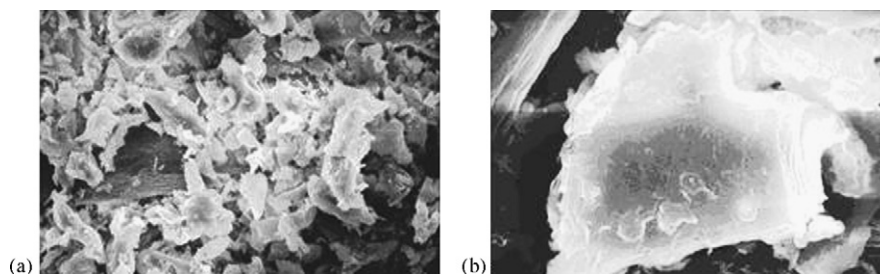

Fig. 1. Intra structure of olive cake: (a) general structure (×750, 10 μm) and (b) single particle (×3500, 5 μm).
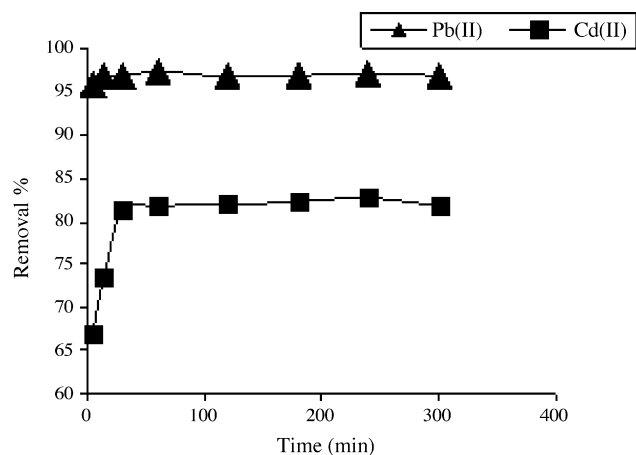
Fig. 2. Effect of contact time on the removal of Pb(II) and Cd(II) by olive cake at room temperature: [Pb(II)] = 5 mg/50 mL, [Cd(II)] = 5 mg/50 mL; 1 g adsorbent.

3.2. Effect of contact time

The chosen treatment periods of sample solutions with the adsorbent were 5, 15, 30, 60, 120, 180, 240, and 300 min at room temperature (20 °C). Note that the batch experiments were performed by using single (not mixed) solutions of the ions of interest. Initial pH were measured 4.89 and 5.18 for Pb(II) and Cd(II), respectively. Fig. 2 shows the effect of contact time on the adsorption of 5 mg/50 mL Pb(II) and Cd(II) at room temperature. According to the obtained data, the highest value of adsorbated Pb(II) ions on olive cake was reached at 60 min (97.34%). Nevertheless, there was no big difference between obtained data for 30 min (96.92%) and 60 min. As shown in Fig. 2, olive cake adsorbated Cd(II) ions with maximum value (82.9%) in 240 min contact time. With same reason as the above, 30 min contact time was chosen due to 81.3% adsorption value. These values show olive cake enabled rapid removal of lead and cadmium ions under these experimental conditions. Consequently, a contact time of 30 min was chosen for the later experiments.

3.3. Effect of initial pH

The acidity of solution (pH) is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. The initial pH of solutions varied from 3.5 to 6.00 with an increment of 0.50 pH units. In this group of experiments, the amount of adsorbent (1 g), the concentration of adsorbate [Pb(II) and Cd(II)] 5 mg/50 mL, and contact time (30 min) were kept constant.

The uptake of Pb(II) increased at pH 6.00 and removal percentage value reached up to 82.5 with 4.13% estimated error. A significant increase in Cd^{2+} uptake per unit weight of olive cake was noticed as the pH increased at pH 4.5 (Fig. 3). At pH below 3, the H^+ ions compete with Pb(II) and Cd(II) ions for the surface of the adsorbent. This could be due to the excess of H^+ ions surrounding the binding sites making sorption unfavorable. There was not studied above the pH 6.00 because in this pH range, Pb(II) and Cd(II) ions precipitation as a matter of fact hydroxide form. For Pb(II) and Cd(II), the effect of pH for removal
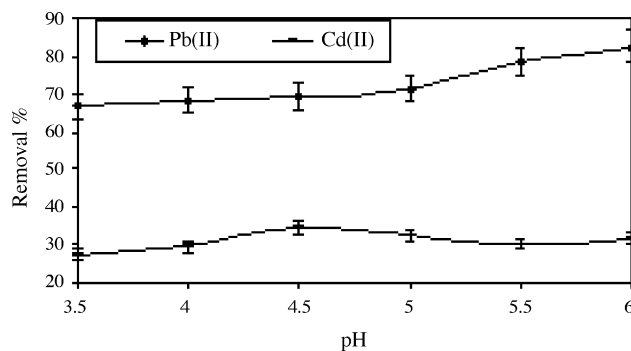

Fig. 3. Effect of pH on the removal of Pb(II) and Cd(II) by olive cake at room temperature: [Pb(II)] = 5 mg/50 mL, [Cd(II)] = 5 mg/50 mL; 1 g adsorbent; contact time, 30 min.

performance of olive cake changed significantly (Fig. 3). At the pH 6.00 (Pb^{2+}) and pH 4.50 (Cd^{2+}) sorption percentage values are approximately 82.5 with 4.13% at and 34.62 with 1.73% estimated errors, respectively.

Demirbaş showed that removal of Pb(II) on modified lignin from alkali glycerol delignificiation was completed at pH 5.00 [6]. Peterlene et al. studied Pb(II) with functionalized formic lignin from sugar cane baggase at pH 6.00 [2]. The same values were reported by Kadirvelu and Meena. Kadirvelu found that maximum pH for adsorption of both metals was 4.00 in the use of activated carbon and Meena found pH 6.00 for Pb(II), and pH 4.00 for Cd(II), using carbon aero-gel as an adsorbent [4,18]. In addition, similar behaviour with pH was reported by many authors [20,14,21].

3.4. Effect of temperature

The solutions with 5 mg/50 mL concentration of Pb(II) and Cd(II) ions were prepared in buffer solution. The temperature varied from 20 to 35 °C with an increment of 5.00 temperature units. The amount of adsorbent (1 g), pH 6.00 [Pb(II)], pH 4.50 [Cd(II)], and contact time (30 min) were kept constant. Fig. 4 shows the effect of temperature on the batch adsorption of 100 ppm Pb(II) and Cd(II), respectively. The rise in temperature
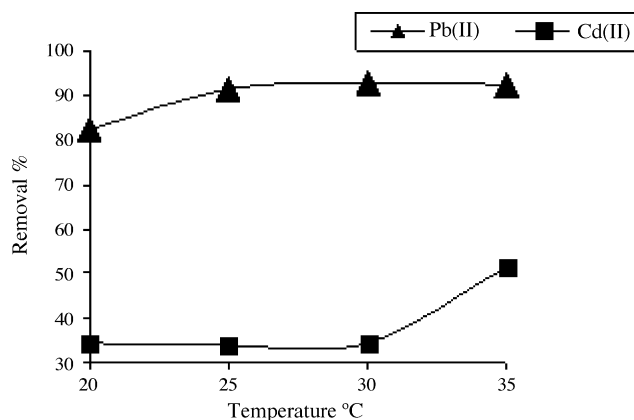

Fig. 4. Effect of temperature on the removal of Pb(II) and Cd(II) by olive cake: Pb(II) = 100 ppm, pH 6.00; Cd(II) = 100 ppm pH 4.50; 1 g adsorbent; contact time, 30 min.
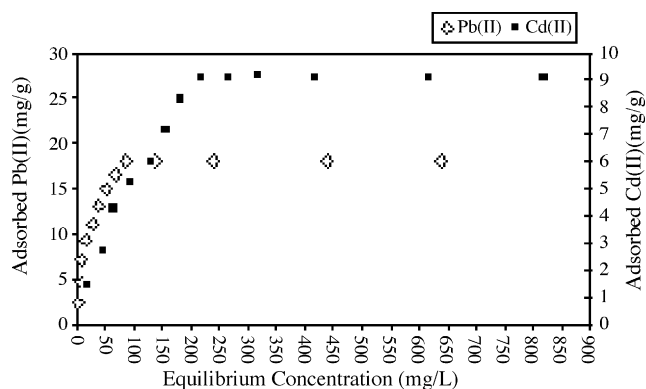
Fig. 5. Metal ion adsorption capacitiy on the olive cake: (Pb(II): pH 6.00; 1 g adsorbent; contact time, 30 min and temperature 30 °C. Cd(II): pH 4.50; 1 g adsorbent; contact time, 30 min; temperature, 35 °C).

Fig. 6. Langmuir plot for the adsorption of Pb(II) by selected adsorbent: (pH 6.00; 1 g adsorbent; contact time, 30 min; temperature, 30 °C).

caused to increase the percentage removal of Pb(II) 92.86% at 30 °C and for Cd(II) 51.40% at 35 °C.

3.5. Adsorption isotherms

Pb(II) and Cd(II) ions adsorption isotherms of olive cake are presented as a function of the equilibrium concentration of metal ions in the aqueous medium in Fig. 5 and adsorption conditions are also given in the figure legend. The amount of metal ions adsorbed per unit mass of olive cake (i.e. adsorption capacity) increased with the initial concentration of metal ions, as expected [2,3,22,23]. The initial concentrations were increased up to about 22.5 and 22.0 mg/50 mL for both Pb(II) and Cd(II) after this point assumed that adsorption values are constant. The maximum adsorption capacities are 18.14 and 9.05 mg per g of olive cake for Pb(II) and Cd(II), respectively. The maximum adsorption capacities in molar basis are 87.5 μmol Pb(II)/g olive cake and 80.5 μmol Cd(II)/g olive cake. The distribution of metal ions between the liquid and solid phases can be described by several mathematical model equations such as the standard Langmuir isotherm model and the Freundlich isotherm model [24]. The Langmuir and Freundlich models are widely used since they are simple and have an ability to describe experimental results in wide range of concentrations. Langmuir and Freundlich adsorption isotherms are also classical models to describe the equilibrium between metal ions adsorbed onto adsorbent and metal ions in solution at a constant temperature. Both isotherm models can be easily transformed into linear forms to obtain adjustable parameters just by linear regression analysis.

Adsorption isotherms of the type q_e versus C_e were used first to verify that adsorption was favorable for each element. For
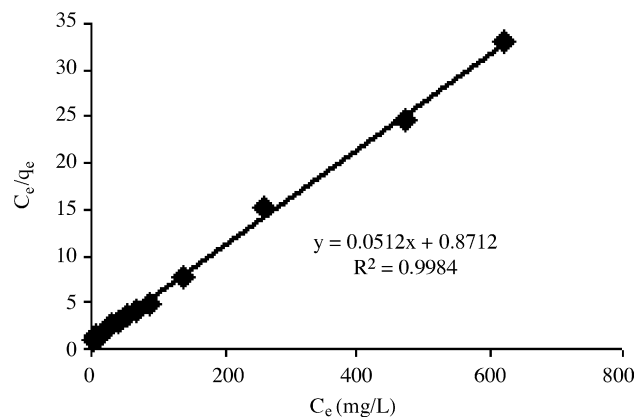
modeling of metal uptake from aqueous solutions of a single system, the classical isotherm equation of Langmuir and Freundlich were employed. These models could be summarized as below.

Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation is represented by the following equation [25]:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{1}$$

where C_e is the equilibrium concentration of adsorbate (mg L^{-1}), q_e the amount adsorbed at equilibrium (mg g^{-1} adsorbent), and Q (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the adsorption capacity and energy, respectively. When C_e/q_e is plotted against C_e, a straight line with slope $1/Q$ and intercept $1/Qb$ is obtained (Figs. 6 and 8), which shows that the adsorption of lead and cadmium follow Langmuir isotherm model. The Langmuir parameters, Q and b, are calculated from the slope and intercept of the graphs and are given in Table 1. These values may be used for comparison and correlation of the sorptive properties of the olive cake.

The Freundlich equation has been widely used and is applicable for isothermal adsorption. This is a special case for heterogeneous surface energies in which the energy term, b, in the Langmuir equation varies as a function of surface coverage, q_e, strictly due to variations in heat of adsorption [26]. The Fre-

Table 1
Values of Langmuir and Freundlich constants and thermodynamic parameters for the metal ions; Pb(II): pH 6.00, 30 °C and Cd(II): pH 4.50, 35 °C

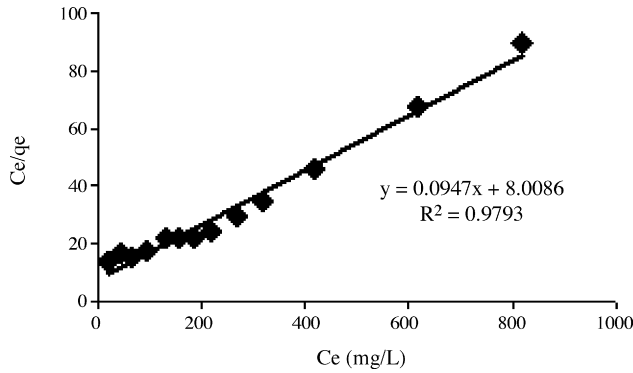| Metal ions	Langmuir model			Freundlich model					
	R^2	Q (mg g^{-1})	b (mg L^{-1})	R^2	K	n	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K)
Pb(II)	0.99	19.530	0.058	0.82	2.978	290	−15.855	44.530	0.199
Cd(II)	0.97	10.560	0.011	0.83	0.196	1.426	−9.574	31.584	0.133

Fig. 7. Langmuir plot for the adsorption of Cd(II) by selected adsorbent: (pH 4.50; 1 g adsorbent; contact time, 30 min; temperature, 35 °C).

undlich equation has the general form [27];

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{2}$$

where q_e is the amount of adsorbate adsorbed per unit weight (mg g^{-1} adsorbent), C_e is the equilibrium concentration (mg L^{-1}) of adsorbate, and K_f and n are the Freundlich constant. When $\log q_e$ is plotted against $\log C_e$, a straight line with slope $1/n$ and intercept $\log K_f$ is obtained. This reflects the satisfaction of Freundlich isotherm model for the adsorption of lead and cadmium ions. The intercept of line, $\log K_f$, is roughly an indicator of the adsorption capacity and the slope, $1/n$, is an indicator of adsorption intensity [28]. The Freundlich parameters for the adsorption of lead and cadmium ions are also given in Table 1.

The fit to the linear form of the models was examined by calculation of the linearity coefficient (R^2). It is noteworthy that the Langmuir model was found to describe adsorption successfully than Freundlich model according to linearity coefficients ($R^2 = 0.99$ and 0.98, respectively) were shown in Table 1 and Figs. 6 and 7.

Consequently, the sorption of metal ions on olive cake follows the Langmuir isotherm model where the uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules.

3.6. Thermodynamics of adsorption

The thermodynamics equilibrium constant obtained was used to calculate all other thermodynamic parameters (Figs. 8 and 9)
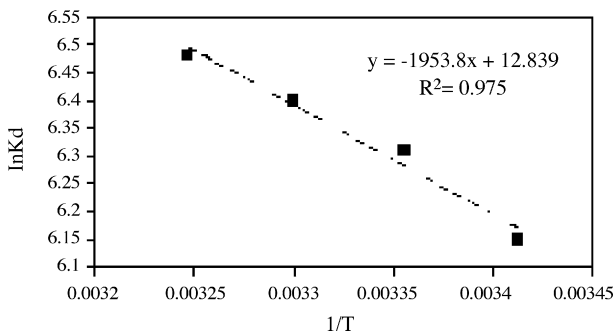

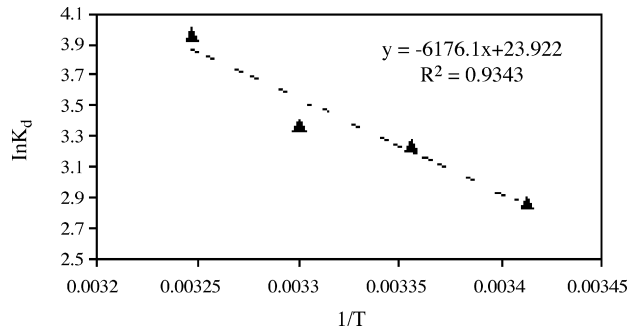Fig. 8. A plot against ln K_d to 1/T for removal of Pb(II).

for Pb(II) and Cd(II), respectively. The entropy, enthalpy and Gibbs free energy for the adsorption process were obtained at 30 °C for Pb(II) using Fig. 8 and Eq. (5) and also 35 °C for Cd(II) using Fig. 9 and Eq. (5).

The sorption capacity of the olive cake for both lead and cadmium increased with increasing temperature indicating that the sorption process was endothermic in nature. Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were determined using the following equations [29]:

$$\Delta G° = -RT \ln K_d \tag{3}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{4}$$

where $\Delta G°$ is the change in free energy (kJ mol^{-1}), $\Delta H°$ the change in enthalpy (kJ mol^{-1}), $\Delta S°$ the change in entropy (J mol^{-1} K^{-1}), T the absolute temperature K, R the gas constant (8.314×10^{-3}), and K_d is the equilibrium constant of adsorption.

From Eqs. (3) and (4), it can be rewritten as:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{5}$$

when $\ln K_d$ is plotted against 1/T, a straight line with slope $\Delta H°/R$, and intercept $\Delta S°/R$ is obtained (Figs. 8 and 9). The values of $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of the Van't Hoff plots of $\ln K_d$ versus 1/T (Figs. 8 and 9). The thermodynamic parameters for the adsorption process are given in Table 1.

Positive values of $\Delta H°$ suggest the endothermic nature of adsorption of lead and cadmium ions on the olive cake. The negative $\Delta G°$ values were obtained in this study. The negative Gibbs free energy indicates feasibility and spontaneous nature of adsorption of metal ions on the adsorbent. The positive values of entropy show the increased randomness at the solid/solution interface during the adsorption process. Positive entropy of adsorption also reflects the affinity of the adsorbent for lead and cadmium ions. These kinds of reactions are present in literature [18,22,29,30].

3.7. Desorption studies

In order to make the adsorption process more economical, it is important to desorb the spent adsorbent. The desorption

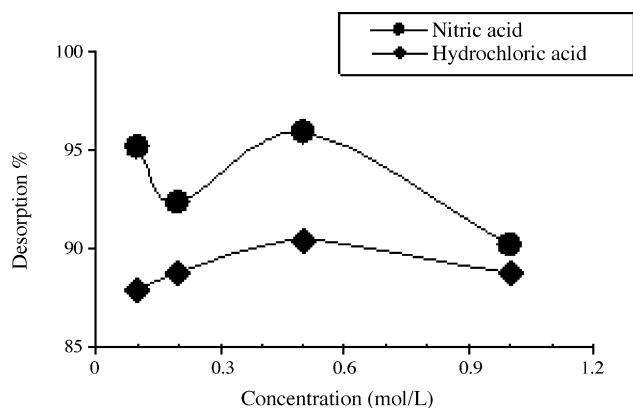Fig. 9. A plot against ln K_d to 1/T for removal of Cd(II).

Fig. 10. Desorption of Pb(II) from olive cake [Pb(II)] = 22.5 mg/50 mL; pH 6.00; 1 g adsorbent; contact time, 30 min; temperature, 30 °C.
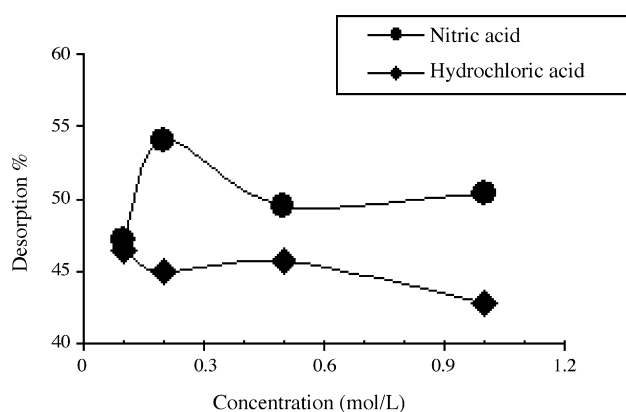

Fig. 11. Desorption of Cd(II) from olive cake [Cd(II)] = 22.0 mg/50 mL; pH 4.50; 1 g adsorbent; contact time, 30 min; temperature, 35 °C.

studies were carried out by batch process using HCl and HNO$_3$ solutions at different concentrations. Olive cake (1 g) loaded with maximum amounts of the Pb(II), 18.14 mg g^{-1}, olive cake and Cd(II), 9.05 mg g^{-1}, olive cake ions were placed within the desorption medium and stirred in 30 min. Then, the desorbed Pb(II) and Cd(II) amounts in different acid concentrations were determinated (Figs. 10 and 11). According to the results, the maximum desorption was achieved in 0.5 M HNO$_3$ for Pb(II) and 0.2 M HNO$_3$ for Cd(II) as 95.92 and 53.97%, respectively. The high level of desorption attained in these two cases could mean that surface adsorption was predominant on this adsorbent and there may be two mechanism; the ion exchange and the mono ion of sorption layer physical adsorption [14].

4. Conclusion

It is common to describe the goodness of fit in terms of R^2, which is the square of the correlation coefficient. As seen from Table 1, the Freundlich isotherm shows an inadequate fit of experimental data in the whole range of concentrations generally giving the R^2 values lower than 0.95. The poor ability of this model to represent the experimental data could have been due to the fact that the Freundlich isotherm does not take into account adsorbent–adsorbate interactions. The correlation of Langmuir

adsorption isotherm showed this isotherm yielded the best fitted to experimental data.

Olive cake has an aromatic ring containing a large number of hydrogen bonds with high content of phenolic components and prevalence of labile methoxy groups. These functional groups are known to serve as excellent binding sites as well as cation exchange sites for heavy metals [9].

The maximum adsorption capacities are 18.14 mg g^{-1} (80.62%) and 9.05 mg g^{-1} (45.25%) of the olive cake for Pb(II) and Cd(II), respectively.

Percentage of adsorption values both Pb(II) and Cd(II) in the study for capacity, more lower than percentage of adsorption values for optimum time. The chosen CH$_3$COOH/CH$_3$COO$^-$ buffer provides a constant pH in studies of capacity determination. Buffer ions may be formed in high ionic intensity so, adsorption values (%) were decreased.

Desorption of metal ions from adsorbent was performed in low acid concentrations so it may be shows that Pb(II) and Cd(II) ions are binding to olive cake with weak chemical bonds.

Heavy metals would be transferred from aqueous pollutants to the environment. In the aim of conservation of environment from transfer of these hazardous materials, there are many suggestion processes in literature. The olive cake loaded with heavy metals could be incinerate. Cementation, vitrification, pitch, polymerization, and pyrogenation techniques could be apply solidification to its fly ash then storage in waste containers /storage tanks and finally disposal in the suitable waste field [31–33].

The experimental studies showed that olive cake could be used as an alternative, inexpensive and effective material to remove high amount of toxic Pb(II) and Cd(II) ions from wastewaters.

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