



Heavy metals binding properties of esterified lemon

Hasan Arslanoglu, Hamdi Soner Altundogan, Fikret Tumen*

Department of Chemical Engineering, Firat University, 23279 Elazig, Turkey

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ABSTRACT

Sorption of Cd^{2+} , Cr^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} onto a carboxyl groups-rich material prepared from lemon was investigated in batch systems. The results revealed that the sorption is highly pH dependent. Sorption kinetic data indicated that the equilibrium was achieved in the range of 30–240 min for different metal ions and sorption kinetics followed the pseudo-second-order model for all metals studied. Relative sorption rate of various metal cations was found to be in the general order of $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$. The binding characteristics of the sorbent for heavy metal ions were analyzed under various conditions and isotherm data was accurately fitted to the Langmuir equation. The metal binding capacity order calculated from Langmuir isotherm was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$. The mean free energy of metal sorption process calculated from Dubinin–Radushkevich parameter and the Polanyi potential was found to be in the range of 8–11 kJ mol^{-1} for the metals studied showing that the main mechanism governing the sorption process seems to be ion exchange. The basic thermodynamic parameters of metals ion sorption process were calculated by using the Langmuir constants obtained from equilibration study. The ΔG° and ΔH° values for metals ion sorption on the lemon sorbent showed the process to be spontaneous and exothermic in nature. Relatively low ΔH° values revealed that physical adsorption significantly contributed to the mechanism.

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1. Introduction

Heavy metals are persistent pollutants because of non-degradable, accumulative and mobile character therefore they are of great concern. Due to the rapid increase in industrial and mining activities that are responsible for significant metal concentrations in surface and ground waters, heavy metal pollution of water bodies has become a serious problem. Since the stringent environmental regulations are established, environmental scientists have struggled for development of effective technologies on heavy metal removal from wastewaters for last two decades.

The chemical precipitation process has been traditionally employed for heavy metal removal from industrial wastewater, however, adsorption and ion-exchange methods have been evaluated as promising techniques. In order to find out cost-effective materials, numerous adsorbent and ion exchanging material have been tested for heavy metal removal in last decades. In this context, interests have also been focused to the investigation of agricultural by-products or wastes as adsorbents for the removal of heavy metal from wastewaters [1–3]. Since the adsorption capability of these materials has usually been limited, some mod-

ifications are desirable to enhance their removal efficiency. In this regard, various modification strategies such as incorporating some ion exchanging functional groups (i.e. carboxyl) on to complex polysaccharide matrix have been employed. In previous studies, various cellulosic wastes or by-products have been converted into ion-exchanger materials by modifying with poly carboxyl acids such as citric, tartaric, phytic acids and considerable improvements in metal binding have been reported [4–14].

In our recent study [15], as an introduction, a carboxyl groups-rich sorbent was developed from lemon which contains pectic-cellulosic substances and citric acid and the material obtained was characterised and tested for determining the sorption capacity and selectivity of divalent metal ions in a solution buffered with 0.07 M sodium acetate–0.03 M acetic acid system, pH 4.8. In above-mentioned study [15], we have reported that material prepared from lemon is effective especially for Pb and Cu removals. The objective of present study is to investigate the heavy metals binding properties of the sorbent mentioned. To do this, the sorption of selected heavy metal ions was studied by evaluating the influence of different experimental parameters on metal uptake, such as sorption time, metal concentration and temperature. The experimental data were correlated to isotherm and kinetic models and the characteristics related to binding capacity, selectivity and the mechanism of sorption are discussed.

* Corresponding author. Tel.: +90 424 2370000 5523; fax: +90 424 2415526.
E-mail address: ftumen@firat.edu.tr (F. Tumen).

2. Materials and methods

2.1. Preparation of sorbent

Lemon, grown in the Mediterranean region of Turkey, was purchased from local market. The yellow-coloured outer thin film of lemon was removed by grating and the lemons were chopped into small pieces less than 10 mm. Seeds were picked out. The material was placed on a glass tray and heated in an oven at 50 °C for 12 h. Resulting material was finally heated at 120 °C for 2 h. The brown-black material obtained was grinded in a coffee mill and sieved to $-150\ \mu\text{m}$. In order to remove unreacted citric acid and other soluble substances, material was subjected to washing. To do this, the powdered product was slurred in distilled water with a water/solid ratio of 20 and agitated for 30 min. The mixture was filtered and the same amount of water was added. The washing was repeated until the washing water does not give Pb-citrate precipitate with a tester solution prepared from $\text{Pb}(\text{NO}_3)_2$. The final product was dried at 105 °C for 24 h, cooled in a dessicator and stored in tightly capped jars during the experimental study. The characteristics of the sorbent prepared from lemon have been reported in our recent study [15].

2.2. Preparation of metal solutions

Two hundred and fifty millilitre stock solutions of metals were prepared in the concentration of 0.25 M by dissolving appropriate amount of metal salts ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$; $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ (x was found as 13.77); $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{Pb}(\text{NO}_3)_2$; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). Stock solutions were prepared with distilled water. In order to prevent precipitation of metals by hydrolysing, two to three drops of appropriate acid was added to the stock solutions.

Working solutions in the concentration range of 1–25 mM were prepared by diluting appropriate volume of 0.25 M stock metal solutions with buffer solution of 0.07 M sodium acetate–0.03 M acetic acid (pH 4.8 ± 0.2). The use of metal ion solutions prepared in this buffer system can set a standard in providing stable ionic strength to some extent. Sodium acetate and acetic acid were reagent grade chemicals.

In the study of pH effect, only, the pH of metal solutions was adjusted with 0.1 M HNO_3 and 0.1 M NaOH .

2.3. Experimental procedure

The experiments were conducted in 300-ml Erlenmeyer flasks containing 2.5 g of sorbent and 250 ml of metal solutions in varying concentrations from 1 to 25 mM. The flasks were agitated on an orbital shaker at 200 rpm and at constant temperature for different time. Samples were taken at pre-determined time intervals (5–360 min) for determination the residual metal ion concentrations in the solution. Before analysis the samples were filtered through the Advantec (No. 6) filter paper and the supernatant fraction was analyzed for the remaining metal ions. Blank experiments showed that the metal sorption of filter paper is negligible.

2.4. Analytical techniques

Metal analyses were performed using a PerkinElmer (Model PE-370) atomic absorption spectrophotometer. The amount of adsorbed metal was determined based on the soluble metal concentration measured after and before experiment. The amount of adsorption at any time, q (mmol g^{-1}), was obtained as follows:

$$q = \left(\frac{V}{m}\right)(C_0 - C_t) \quad (1)$$

where C_0 is the initial metal concentration (mmol l^{-1}) and C_t is the metal concentration (mmol l^{-1}) at any time; V is the volume of the solution (l); and m is the weight of the sorbent used (g).

All experiments were in duplicate and mean values were reported or taken for calculations. Controls without adsorbents were also run in parallel.

3. Results and discussion

In our recent study [15], it has been demonstrated that carboxyl groups can be attached to the cellulose skeleton by heating the lemon peel–internal pomace–lemon mixture and the resulting material shows enhanced removal of heavy metals from aqueous solution relative to lemon peel. The characteristics and proposal mechanism has been discussed in the above-mentioned preliminary study.

Sorption of metal ions on adsorbents is strongly dependent on solution pH. The pH of the aqueous medium not only affects the solubility of the metal ions but also the ionic form in which it will be present in the solution and the type and ionic state of the functional groups at the biosorbent surface [16,17]. In the low pHs, adsorption sites are more protonated and they are less attractive against to various cationic forms of metals. Depending on hydrolysis constant of a specific metal, in the solution having pHs more than a specified value, various aqueous speciation of metals such as $[\text{Me}(\text{OH})]^+$, $\text{Me}(\text{OH})_2$ forms due to hydrolysis, which will affect the approach of metal species. For example, concentration of various Cu hydroxyl species such as CuOH^+ , $[\text{Cu}_2(\text{OH})_2]^{2+}$, $[\text{Cu}(\text{OH})_4]^{2-}$, $\text{Cu}(\text{OH})_{2(\text{aq})}$ and $[\text{Cu}(\text{OH})_3]^-$, increases at $\text{pH} > 5.0$ in the solutions [18]. These phenomena may affect the sorption of metals by material.

The influence of pH on the sorption of metal ions on esterified lemon was studied. The results obtained with 10 mM initial metal concentration and $10\ \text{g l}^{-1}$ sorbent dosage at different pHs of about 2.5 and 3.5 (adjusted), and 4.8 (buffered) are given in Table 1. As seen, the sorption of metal ions sharply decreases with decreasing pH. For example, the amount of metals sorbed decrease in the range of 63–82% by decreasing the pH from 4.8 to about 2.5. This means that when the pHs lower than 3, active sites (e.g. carboxyl groups) become protonated and thus are no longer available to attract positive metal ions from solution. These significant decreases in metal removal by decreasing the pH suggest that the sorbent may be regenerated and thus metals may be recovered by applying a desorption process in which an appropriate acid is used.

Due to the results of pH study, further experiments were carried out in the solutions buffered with 0.07 M sodium acetate–0.03 M acetic acid system (pH 4.8). This may also provide a fixed ionic strength.

Fig. 1 shows the results of kinetic experiments conducted to determine the equilibrium time required for the removal of metal ions by sorbent. It is obvious from the figure that there is two-stage removal behaviour for all metals. A very rapid initial sorption is occurred over a few minutes thereafter a negligible fraction of

Table 1

pH effect on sorption of heavy metals in initial concentration of $10\ \text{mmol l}^{-1}$ (sorbent dosage: $10\ \text{g l}^{-1}$; temperature: 25 °C; contact time: 360 min).

Metal	q (mmol g^{-1}) at pH 2.5 ^a	q (mmol g^{-1}) at pH 3.5 ^a	q (mmol g^{-1}) at pH 4.8 (in buffer)
Cd	0.1245	0.3136	0.7183
Cr	0.1113	0.2992	0.5453
Cu	0.2752	0.5104	0.8244
Ni	0.2115	0.4517	0.7608
Pb	0.3149	0.5679	0.8594
Zn	0.1884	0.4190	0.6285

^a Approximate values of pH adjusted solutions.

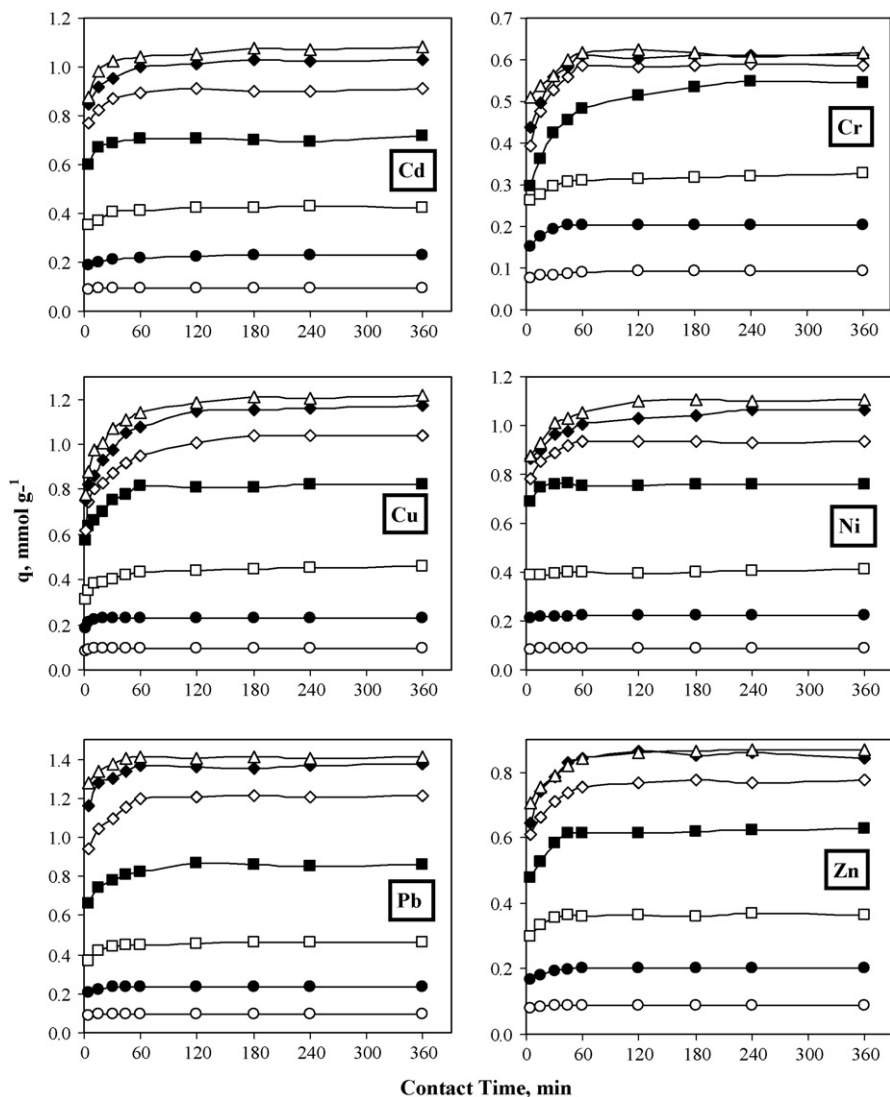


Fig. 1. Kinetic experimental studies of metal uptake (sorbent dosage: 10 g l⁻¹; C_i: 1–25 mmol l⁻¹; pH: 4.8). ((○) 1 mM; (●) 2.5 mM; (□) 5 mM; (■) 10 mM; (◇) 15 mM; (▲) 20 mM; (△) 25 mM).

metal is sorbed and a flat plateau is exhibited by all metal ions. The equilibrium time needed for the different metal–sorbent systems ranged from about 30 to 240 min for various initial metal concentrations. In general, about 90% of the total metal ion sorption was achieved within 60 min for the different metal–sorbent systems. To ensure that equilibrium condition was achieved, 360 min was chosen as the contact time for the calculations related to isotherm study.

In order to investigate the mechanism of adsorption kinetic models, experimental data are mostly tested for pseudo-first-order, pseudo-second-order and intraparticle diffusion equations.

The integrated form of pseudo-first-order rate model [19] is:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (2)$$

where q_e (mmol g⁻¹) and q (mmol g⁻¹) is the mass of metal adsorbed at equilibrium and at time t , respectively, k_1 (min⁻¹), is the first-order rate constant of adsorption. A straight line of $\log(q_e - q)$ vs. t suggests the applicability of this kinetic model. q_e and k can be determined from the intercept and slope of the plot, respectively.

The pseudo-second-order kinetic model [20] is expressed as:

$$\frac{t}{q} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e (mmol g⁻¹) and q (mmol g⁻¹) is the same as defined for Eq. (2), and k_2 (g mmol⁻¹ min⁻¹) is the pseudo-second-order rate constant of adsorption.

The intraparticle diffusion equation [21] can be written by the following equation:

$$q = k_i t^{1/2} + I \quad (4)$$

where q is amount of adsorbed metal concentrations (mmol g⁻¹) at time t , k_i is the intraparticle diffusion rate constant (mmol g⁻¹ min^{-1/2}). According to Eq. (4), a plot of q vs. $t^{1/2}$ should be a straight line with a slope k_i and intercept I when adsorption mechanism follows the intraparticle diffusion process. In a study on adsorption of acid dyes on chitosan, Cheung et al. [22] interpret that dye adsorption exhibits three-step process with various mechanisms, since they observe three distinct linear regions on $q-t^{0.5}$ graph. In our study, by the plots of q_t vs. $t^{0.5}$ of various metal ions in 10 mM concentration, two linear regions are observed in Fig. 2. This may indicate that more than one mechanism could govern the

Table 2

Kinetic parameters for the removal of heavy metals by esterified lemon sorbent (all kinetic evaluations were made for the initial concentration of 10 mM and specified equilibration time for different metals).

Metal	Equilibration time	$q_{e,exp}$ (mmol g ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	k_1 (min ⁻¹)	R^2
<i>Pseudo-first-order model (Lagergren model)</i>					
Cd	120	0.705	0.179	0.096	0.9903
Cr	240	0.550	0.213	0.015	0.9675
Cu	60	0.816	0.242	0.043	0.9840
Ni	45	0.764	0.110	0.104	0.9767
Pb	120	0.867	0.210	0.028	0.9819
Zn	60	0.493	0.305	0.063	0.9729
Metal	Equilibration time	$q_{e,exp}$ (mmol g ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	k_2 (g mmol ⁻¹ min ⁻¹)	R^2
<i>Pseudo-second-order model</i>					
Cd	120	0.705	0.710	1.653	1.0000
Cr	240	0.550	0.564	0.200	0.9992
Cu	60	0.816	0.827	0.569	0.9976
Ni	45	0.764	0.774	2.127	1.0000
Pb	120	0.867	0.883	0.364	0.9994
Zn	60	0.493	0.535	0.327	0.9957
Metal	Equilibration time	$q_{e,exp}$ (mmol g ⁻¹)	I (mmol g ⁻¹)	k_i (mmol g ⁻¹ min ^{-1/2})	R^2
<i>Intraparticle diffusion model</i>					
Cd	120	0.705	0.6099	0.011	0.6645
Cr	240	0.550	0.2919	0.020	0.8824
Cu	60	0.816	0.5424	0.036	0.9758
Ni	45	0.764	0.6641	0.016	0.8350
Pb	120	0.867	0.6448	0.022	0.9163
Zn	60	0.493	0.2250	0.036	0.9789

sorption process. It may be suggested that initial sorption with fast kinetics may result from the outer-surface sorption and a relatively slow sorption followed may be determined by particle diffusion.

The most suitable kinetic model can be determined with the regression analysis of data by comparing the actual and calculated q_e values. Although these kinetic evaluations have been made for all initial concentrations in Fig. 1, as example, calculated kinetic parameters and regression coefficients for three models have been given in Table 2 for all metal solutions having the initial concentration of 10 mM. Experimental q_e values included in the table are the values at the initial point of the flat plateau region in Fig. 2. As seen from table, pseudo-second-order kinetic model yielded best fits to the experimental data. Besides the highest regression coefficients, calculated q_e values are so close to actual values for this model. Also, according to calculated pseudo-second-order rate constants, it can be noted that the relative sorption rate of various metal cations is

to be in the general order of Ni²⁺ > Cd²⁺ > Cu²⁺ > Pb²⁺ > Zn²⁺ > Cr³⁺. Same results are valid for other initial concentration values.

In order to evaluate the effect of temperature, uptake of metals by sorbent was studied by a series of experiments conducted at the contact time, 360 min, for 10 mM initial metal concentrations by varying the temperature in the range of 25–55 °C. The results given in Fig. 2 reveal that the amount of sorbed metals slightly decreases with increasing the temperature, thereby indicating the process to be exothermic. Maximum decrease in metal sorption was observed for chromium, while the minimum decrease was observed for nickel (Fig. 3).

The equilibrium isotherms for heavy metals sorption are shown in Fig. 4 as plots of the amount of metal sorbed on the lemon sorbent vs. the metal concentration at equilibrium in solution. Regarding the influence of the initial concentration of metal ions, the equilibrium sorption capacity of the lemon sorbent increased with the initial metal concentrations. Experiments conducted with the solutions with the initial concentrations more than 20 mmol l⁻¹ showed

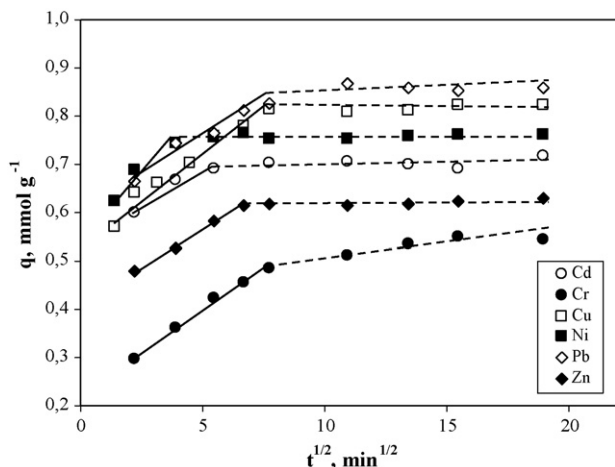


Fig. 2. The plot of intraparticle diffusion modeling of heavy metals onto esterified lemon sorbent (C_i : 10 mmol l⁻¹; pH: 4.8).

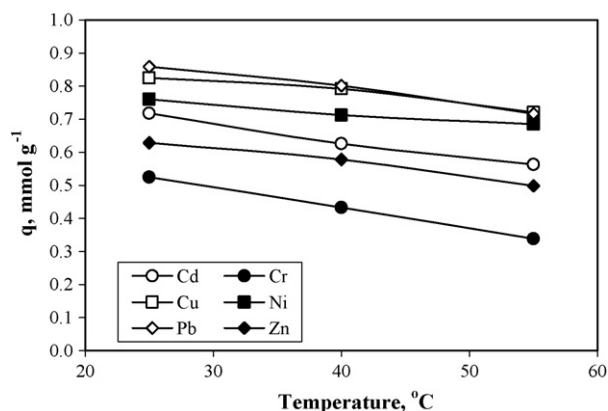


Fig. 3. Effect of temperature on the metal binding properties of esterified lemon sorbent (sorbent dosage = 10 g l⁻¹; C_i : 10 mmol l⁻¹; pH: 4.8; contact time: 360 min).

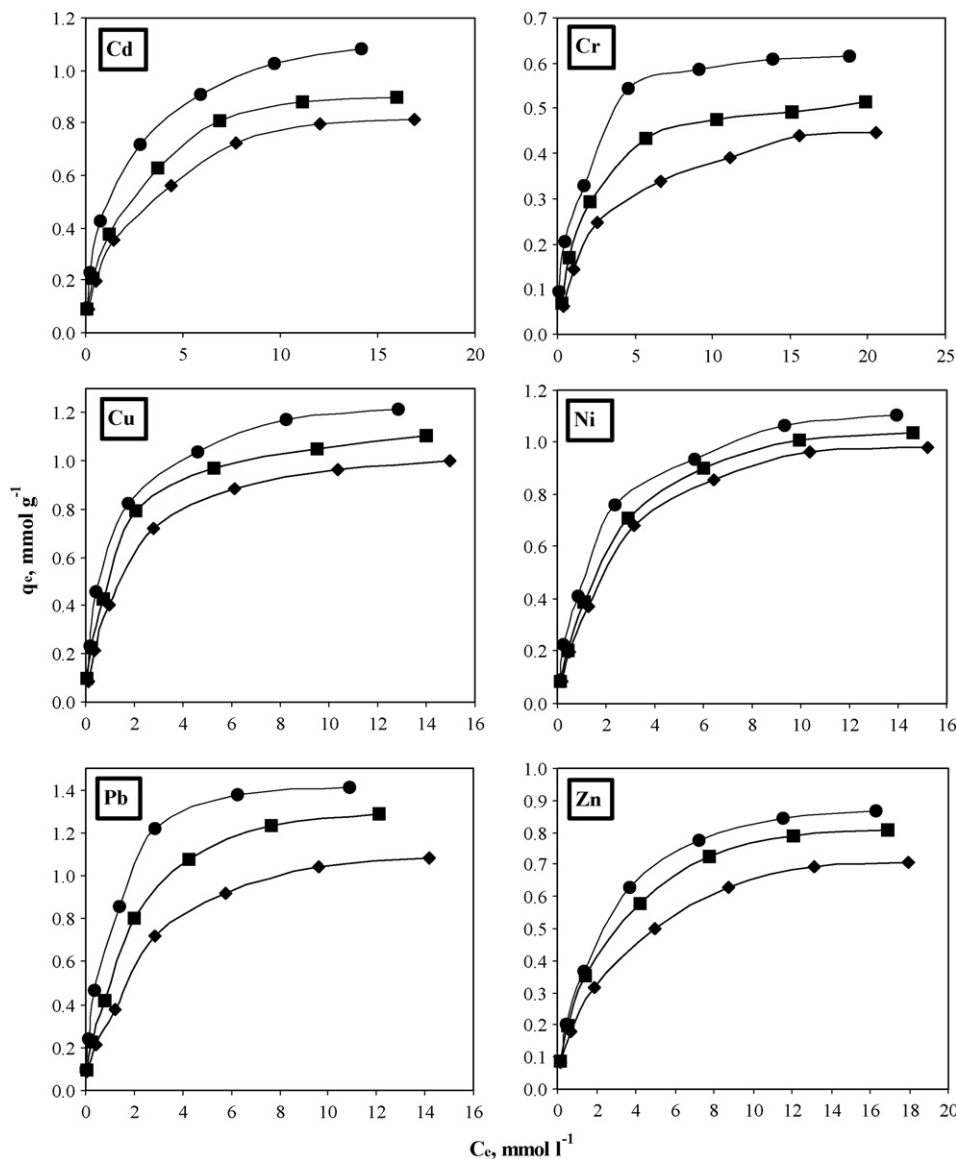


Fig. 4. Adsorption isotherms for binding of various metals by esterified lemon sorbent (sorbent dosage = 10 g l^{-1} ; C_i : $1\text{--}25 \text{ mmol l}^{-1}$; pH: 4.8; contact time: 360 min) (\bullet) 25°C ; (\blacksquare) 40°C ; (\blacklozenge) 55°C .

that the increase in equilibrium sorption capacity is slow. The sorption data for heavy metals at different temperatures were analyzed by fitting the Freundlich, Langmuir and Dubinin–Radushkevich isotherm models.

Freundlich isotherm [23] assumes that the uptakes of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The equilibrium data were analyzed using the following linearized equation:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (5)$$

where K_f is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. K_f and $1/n$ can be determined from the linear plot of $\ln q_e$ vs. $\ln C_e$. q_e is the amount of heavy metals adsorbed (mmol g^{-1}) on lemon sorbent at equilibrium; and C_e is the heavy metals concentration (mmol l^{-1}) of solution at the equilibrium. The calculated values of the Freundlich constants (K_f and $1/n$) at different temperatures for the metals studied are listed in Table 3.

The Langmuir model [24] assumes that the uptake of metal ions occurs on a homogenous surface by monolayer sorption without any interaction between adsorbed ions. It can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \quad (6)$$

where C_e is equilibrium concentration of the metals (mmol l^{-1}), q_e is the amount adsorbed per unit mass of adsorbent (mmol g^{-1}), q_{\max} is the maximum sorption capacity and has same unit with q_e . b (l mmol^{-1}) is a constant related to the affinity of binding sites or bonding energy. q_{\max} (mmol g^{-1}) represents a practical limiting sorption capacity when the surface of adsorbent is completely covered with adsorbate. Hence, a plot of $1/q_e$ vs. $1/C_e$ should be a straight line with a slope $1/bq_{\max}$ and intercepts $1/q_{\max}$, indicating that the sorption process follows the Langmuir model. The related parameters (Langmuir constants) for the fitting of Langmuir equation at different temperatures for heavy metals–lemon sorbent systems are summarized in Table 3.

The sorption equilibrium data were also modeled by Dubinin–Radushkevich (D–R) isotherm [25] which is widely

Table 3
Isotherm constants for metal removal by esterified lemon sorbent.

Metal	Temp. (°C)	Langmuir isotherm			Freundlich isotherm			D–R isotherm			
		q_{max} (mmol g ⁻¹)	b (l mmol ⁻¹)	R^2	K_f	$1/n$	R^2	q_m (mmol g ⁻¹)	E (kJ mol ⁻¹)	β	R^2
Cd	25	1.150	0.857	0.993	0.443	0.394	0.965	2.440	9.366	0.0057	0.999
	40	0.990	0.627	0.996	0.462	0.303	0.978	1.857	9.806	0.0052	0.999
	55	0.904	0.518	0.995	0.468	0.258	0.980	1.676	10.000	0.0050	0.998
Cr	25	0.649	1.035	0.997	0.343	0.263	0.974	0.992	11.043	0.0041	0.987
	40	0.564	0.509	0.998	0.455	0.161	0.917	1.090	9.285	0.0058	0.960
	55	0.507	0.348	0.999	0.479	0.124	0.948	0.937	9.449	0.0056	0.981
Cu	25	1.277	1.329	0.998	0.430	0.513	0.955	2.589	9.901	0.0051	0.981
	40	1.165	1.057	0.998	0.436	0.434	0.965	2.273	10.206	0.0048	0.985
	55	1.102	0.669	0.999	0.497	0.333	0.948	2.621	9.623	0.0054	0.987
Ni	25	1.211	0.722	0.999	0.494	0.379	0.967	3.181	8.392	0.0071	0.988
	40	1.195	0.492	0.999	0.545	0.310	0.964	2.873	8.704	0.0066	0.991
	55	1.142	0.443	0.998	0.554	0.280	0.960	2.778	8.980	0.0062	0.993
Pb	25	1.508	1.393	0.997	0.465	0.618	0.965	3.262	9.901	0.0051	0.997
	40	1.448	0.683	0.995	0.520	0.446	0.976	2.962	9.535	0.0055	0.982
	55	1.236	0.506	0.991	0.513	0.337	0.981	2.237	10.000	0.0050	0.972
Zn	25	0.960	0.578	0.997	0.474	0.282	0.973	1.880	9.054	0.0061	0.997
	40	0.898	0.535	0.997	0.470	0.258	0.976	1.711	9.535	0.0055	0.998
	55	0.800	0.418	0.995	0.478	0.209	0.983	1.462	9.713	0.0053	0.999

used to determine the nature of sorption. D–R model equation is given as:

$$\ln q = \ln q_m - \beta \varepsilon^2 \quad (7)$$

where q_m is maximum amount of ion that can be sorbed onto unit weight of sorbent (mg g⁻¹), β is the constant related to sorption energy (mol² kJ⁻²) and ε is the Polanyi potential which is equal to $RT \ln(1 + 1/C_e)$, where R and T are the gas constant (kJ mol⁻¹ K⁻¹) and the absolute temperature (K), respectively. The plot of $\ln q$ vs. ε^2 results a straight line. The slopes of the D–R plots give β constant and, q_m value is calculated from the intercept of the plot.

Comparison of correlation coefficient values (R^2) given in Table 2 show that the Langmuir isotherm model generally yielded the best fit for Cr, Cu, Ni and Pb, the D–R isotherm model fits the best to the experimental data for Cd and Zn. The Langmuir constant, b , which is related to the binding affinity, decreased with increasing temperature, suggesting that the sorption capacity is reduced at higher temperature for all metals.

The mean free energy of sorption can be calculated from D–R isotherm parameter β by [26]:

$$E = (2\beta)^{-1/2} \quad (8)$$

E is the energy required to transfer one mole of a sorbate to the surface from infinity in solution. The value of E is used to estimate the reaction mechanism occurring. If the magnitude of E is between 8 and 16 kJ mol⁻¹, the sorption process proceeds by ion exchange, while for values of $E < 8$ kJ mol⁻¹, the sorption process is of a physical nature [27,28]. In the present study, E values were calculated as about between 8 and 11 kJ mol⁻¹ at the temperature range of 25–55 °C for all metal ions studied. Thus, it may be concluded that the metal sorption mechanism is mainly governed by ion exchange.

In previous studies [29,30], authors have suggested that using a dimensionless separation factor is suitable for evaluation of sorption data. For the Langmuir type sorption process, the isotherm shape can be classified by a term r , dimensionless constant separation factor, which is defined as

$$r = \frac{1}{1 + bC_0} \quad (9)$$

where r is dimensionless separation factor, C_0 is initial metal concentration (mmol l⁻¹) and b is Langmuir constant (l mmol⁻¹). The

parameter r indicates the shape of the isotherm accordingly:

- $r > 1$ unfavourable
- $r = 1$ linear
- $0 < r < 1$ favourable
- $r = 0$ irreversible

The r values for metals sorption by sorbent prepared from lemon were representatively calculated for typical initial concentrations at 25 °C from Langmuir constants and given in Table 4. Since all r values are between 0 and 1, it can be stated that the metal sorption is favourable for all heavy metals studied.

As expected, higher sorbent/solution ratios are required to treat the solutions having higher metal removals. Unnithan and Anirudhan [31] have suggested Eq. (10) which the sorbent/solution ratio can be calculated from

$$\frac{m}{V} = \frac{(C_0 - C_e)(1 + bC_e)}{q_{max}bC_e} \quad (10)$$

where the m/V is sorbent/solution ratio (in other term, sorbent dosage) (g l⁻¹) and the C_0 is initial sorbate concentration (mmol l⁻¹). In order to have an idea about the required sorbent amount for higher metal uptake, calculated sorbent dosages to achieve the removal yields of 95% in the typical initial concentration of 10 mmol l⁻¹ for all metals by using Langmuir isotherm parameters obtained at 25 °C are shown in Table 5. As seen, the removal yield results obtained by using theoretical dosages are close to the value of 95% within the reasonable limits.

Table 4
Calculated r values for metal sorption by esterified lemon sorbent.

Metal	r values for various initial metal concentration at 25 °C		
	1 mmol l ⁻¹	10 mmol l ⁻¹	25 mmol l ⁻¹
Cd	0.429	0.104	0.045
Cr	0.491	0.088	0.037
Cu	0.429	0.070	0.029
Ni	0.581	0.122	0.052
Pb	0.418	0.067	0.028
Zn	0.634	0.147	0.065

Table 5

Calculated esterified lemon sorbent dosage to achieve the 95% removal yield and experimental results obtained using these dosages for heavy metals in initial concentration of 10 mmol l⁻¹.

Metal	Calculated <i>m/V</i> values (sorbent dosage) (g l ⁻¹)	Experimental removal yields (%)
Cd	27.5	93.41
Cr	43.0	97.02
Cu	18.6	95.70
Ni	29.6	93.63
Pb	15.3	96.14
Zn	44.1	93.18

Thermodynamic parameters such as enthalpy (ΔH°), free energy (ΔG°) and entropy (ΔS°) changes were also calculated using

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^\circ}{RT} \quad (11)$$

$$\ln b = \ln b_0 - \frac{\Delta H^\circ}{RT} \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

where *b* is Langmuir constant which is related with the energy of adsorption, *b*₀ is a constant, *R* the ideal gas constant (4.187 J mol⁻¹ K⁻¹) and *T* is temperature (K).

The enthalpy changes (ΔH°) of the process were determined from the slope of the line obtained by plotting $\ln b$ vs. $1/T$, as given in Fig. 5. The calculated values of thermodynamic parameters are given in Table 6. The negative values of ΔH° confirm exothermic nature of the process for all metals studied. ΔH° values are found in the range about from -8 to -29 kJ mol⁻¹. Since typically ΔH° for physical adsorption ranges from -4 to -40 kJ mol⁻¹ [32], it would be suggested that the physical adsorption is also contributing to the mechanism. The negative values of ΔG° at different temperatures are due to the fact that the sorption process is spontaneous with high preference of metal ions for the sorbent prepared from lemon. The positive values of ΔS° show increased randomness at the solid/solution interface with some structural changes in the sorbate (hydrated metal ions) and sorbent (esterified lemon), while the negative values suggest no structural changes during the sorption [33]. Also, negative value of entropy indicates a stable arrangement of metal ions on sorbent surface and adsorbed complex of metal ions on sorbent is in a more ordered form [34].

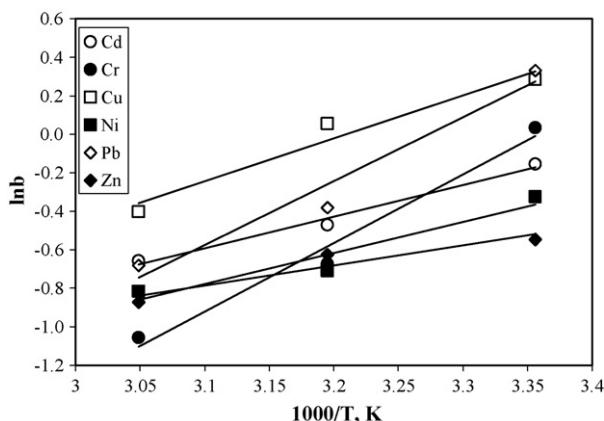


Fig. 5. $1/T - \ln b$ plots for various metals.

Table 6

Thermodynamic parameters for metals removal by esterified lemon sorbent.

Metal	Temperature (°C)	Thermodynamic parameters		
		ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
Cd	25		-16.732	0.010
	40	-13.659	-16.751	0.010
	55		-17.045	0.010
Cr	25		-17.203	-0.042
	40	-29.629	-16.220	-0.043
	55		-15.961	-0.042
Cu	25		-17.820	-0.002
	40	-18.502	-18.120	-0.001
	55		-17.740	-0.002
Ni	25		-16.310	0.010
	40	-13.360	-16.130	0.009
	55		-16.616	0.010
Pb	25		-17.935	-0.032
	40	-27.556	-16.983	-0.034
	55		-16.982	-0.032
Zn	25		-15.758	0.024
	40	-8.683	-16.349	0.025
	55		-16.462	0.024

4. Conclusions

In this paper, a sorbent prepared from lemon was used in batch sorption experiments to investigate sorption behaviours of the heavy metals Cd²⁺, Cr³⁺, Cu²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ in aqueous solutions. The analysis of experimental data led to the following results:

- The results show that the heavy metal sorption onto esterified lemon sorbent is highly dependent upon solution pH. Heavy metals removal sharply decreases with decreasing pH that is indicative that metals may be recovered by a desorption process.
- Kinetic tests demonstrated that sorption equilibrium is reached within 30–240 min for different metals. Moreover, a pseudo-second-order model has been successfully fitted to heavy metal uptake vs. time profiles. Relative sorption rate of various metal cations was found to be in the general order of Ni²⁺ > Cd²⁺ > Cu²⁺ > Pb²⁺ > Zn²⁺ > Cr³⁺.
- The sorption data are better fitted by the Langmuir and D-R adsorption isotherm models as compared to the Freundlich model. The monolayer capacity (*q*_{max}) was calculated using the Langmuir isotherm for the sorbent and the metal sorption capacity was found to be in the general order of Pb²⁺ > Cu²⁺ > Ni²⁺ > Cd²⁺ > Zn²⁺ > Cr³⁺.
- Free energy of sorption calculated from Dubinin–Radushkevich parameter lies in the range of energies (8–16 kJ/mol) characteristic for the ion-exchange mechanisms for all heavy metals studied.
- Calculated *r* values, all being in the range of 0–1, showed that the sorption process is favourable.
- The metal sorption capacities were found to decrease with increasing temperature, indicating the exothermic nature of the process. From the Langmuir parameters adsorption enthalpies were found to be in the range of -8.683 kJ mol⁻¹ for Zn²⁺ to -29.629 kJ mol⁻¹ for Cr³⁺ revealing that physical adsorption is contributing to the mechanism.
- From the basic thermodynamic analysis of data, negative values in free energy for metal sorption indicate the process is spontaneous and increases in the feasibility of adsorption at lower temperature.

Overall, the results of this study showed that the lemon, after converting to efficient sorption material, can be used as excellent sorbent to remove heavy metals from the aqueous solutions. Especially, lemons having low commercial values (e.g. damaged or spoiled lemons) may be utilized in such a way.

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