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Adsorption of lead(II) ions from aqueous solutions by activated carbon prepared from biomass plant material of *Euphorbia rigida*

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Abstract

Adsorption of lead(II) ions onto activated carbon prepared from renewable plant material, which is *Euphorbia rigida*, was investigated with the variation in the parameters of pH, contact time, the amounts of adsorbent, lead(II) ions concentration and temperature. Adsorption data of lead(II) ions onto activated carbon by *E. rigida* obeys the Langmuir isotherm model. Maximum adsorption capacity ($q_{\max}$) of lead(II) ions onto adsorbent was 1.35×10^{-3} mol g^{-1} or 279.72 mg g^{-1} at 40 °C. Three kinetic models are the first-order, pseudo-second-order and intraparticle diffusion equations, were selected to interpret the adsorption data. Kinetic parameters such as the rate constants, equilibrium adsorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. It was indicated that the adsorption of lead(II) ions onto activated carbon by *E. rigida* could be described by the pseudo-second-order kinetic model and also followed the simple external diffusion model the initial 10 min and then by intraparticle diffusion model up to 50 min.

Keywords: Adsorption; Lead; *Euphorbia rigida*; Isotherm; Kinetics

1. Introduction

The presence of heavy metals in the aquatic environmental has been a big deal to scientists and engineers due to their increased discharge, toxic nature, and other adverse effects on receiving waters [1,2]. Metals, which can be toxic pollutants that are nonbiodegradable, public health, economic impact, include arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), copper (Cu), zinc (Zn), cadmium (Cd), nickel (Ni) and manganese (Mn), etc. Lead uses many industries such as acid battery manufacturing, metal plating and finishing, printing, photographic materials, explosive manufacturing, and tetraethyl lead manufacturing, and ceramic and glass industries. The main sources of lead in water are the effluents of processing industries. Lead poisoning in humans causes severe damage to the kidney, nervous system, reproductive system, liver, and brain and causes sickness or death. Severe exposure to lead has been connected with sterility, abortion, stillbirths, and neonatal death [3–5].

The permissible level for lead in drinking water is 0.05 mg L^{-1} according to the US Environmental Protection Agency (EPA). Therefore, a very low concentration of lead in water is very toxic [6]. The removal of such a heavy metal from contaminated water bodies has been attempted by several scientists employing a wide variety of techniques including chemical precipitation, ion-exchange, electroflotation, membrane filtration, reverse osmosis, etc. All these methods are generally expensive. For this reason, there is a need for developing economic and eco-friendly methods for waste minimization and fine tuning of the wastewater [7]. The most promising alternative method for the removal of metal ions is the adsorption. Although commercial activated carbon, with high surface area, microporous character and high adsorption capacity, has made its potential adsorbent for the removal of heavy metals from industrial wastewater, it is expensive, has relatively high operation costs. Thus, there is a growing demand to find low-cost and efficient, locally available adsorbent for the adsorption of lead such as activated carbon prepared by renewable biomass materials including coconut shell [1,3], sawdust [7], sugar cane bagasse [8], fruit stones [9], apricot stone [10], pyrolyzed coffee residues [11], pine bark [12], pecan shell [13], peanut shells [14], palm shell [15], nutshells (almond, walnut, pecan) [16], almond

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shells, olive stones, and peach stones [17]. There are two different ways for the preparation of activated carbon, which are physical and chemical activation. The chemical activation has two important advantages to compare with the physical activation. One is the lower temperature in which the process is achieved. The other is that the global yield of the chemical activation tends to be greater due to the fact that burn-off char is not required. Chemical activation consists of carbonization in the presence of a dehydrating agent (e.g., $ZnCl_2$, H_3PO_4, and H_2SO_4). These chemical agents may promote the formation of cross-links, leading to the formation of a rigid matrix that is further less prone to volatile loss and volume contraction upon heating to high temperatures [18]. In this study, the preparation of activated carbon from *E. rigida* impregnated with sulfuric acid was carried out. Sulfuric acid is more favored due to an inexpensive and non-volatile dehydrating agent than such as zinc chloride, due to problems of environmental contamination with zinc (Zn) compounds [19,20].

To our knowledge, compared with other biomass materials only little information exists on the use of activated carbon from biomass materials, as an adsorbent for the removal of lead(II) ions and also needs to research. One of these materials, *E. rigida*, which is biomass plant material, can be used as a source of activated carbon. *E. rigida* is a member of the Euphorbiaceae family and it grows abundantly in arid land regions in Anatolia, Turkey. This family of plants includes around 2000 species, ranging from small herbs to large trees. The most of them can produce milky latex, which yields wide range of chemical including rubber, oils, terpenes, waxes, hydrocarbons, starch, resins, tannins, and balsams of interest to various industries but not use for food production [21–23].

The study of adsorption equilibrium, isotherms and kinetics is essential in supplying the basic information required for the design and operation of adsorption equipments for wastewater treatment. Various isotherm models including Langmuir and Freundlich; and kinetic models such as the first-order, pseudo-second-order and intraparticle diffusion, have been put forward to describe or predict the adsorption isotherms and kinetics, respectively.

The objective of this research is to study the adsorption of lead(II) ions from aqueous solutions onto activated carbon from *E. rigida*. It is a renewable plant material and abundant and it was chosen as an adsorbent material due to a lack of information on its adsorption abilities. The effects of temperature, pH, contact time and concentration were examined. The adsorption isotherm and kinetic parameters were deduced from the adsorption measurements.

1.1. Equilibrium parameters of adsorption

Equilibrium data, mostly known as adsorption isotherms, are basic requirements to understand the mechanism of the adsorption. Well-known adsorption isotherm models, Langmuir and Freundlich, are used to describe the equilibrium between adsorbed lead(II) ions onto activated carbon from *E. rigida* (q_e) and lead(II) ions in solution (C_e) at a constant temperature.

The linear forms of the Langmuir [24] and Freundlich [25] adsorption isotherm equations can be written as following:

$$\text{Langmuir equation}: \quad \frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max}K_L}\right)\frac{1}{C_e} \tag{1}$$

$$\text{Freundlich equation}: \quad \ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{2}$$

where q_e is the equilibrium lead(II) ions concentration on the adsorbent (mol g^{-1}); C_e, the equilibrium lead(II) ions concentration in solution (mol dm^{-3}); $q_{\max}$, the monolayer adsorption capacity of the adsorbent (mol g^{-1}); K_L, the Langmuir constant (dm^3 mol^{-1}) related to the free energy of adsorption; K_F (dm^3 g^{-1}) and n (dimensionless) are the Freundlich constants. Hence a plot of $1/q_e$ versus $1/C_e$ for the Langmuir adsorption gives a straight line of slope $1/(q_{\max}K_L)$ and intercept $1/q_{\max}$; the plot of $\ln q_e$ versus $\ln C_e$ for the Freundlich adsorption isotherm was employed to generate K_F and n from the intercept and the slope values, respectively.

The effect of isotherm shape has been used [26] with a view to predict whether an adsorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter R_L is calculated using the following equation.

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

where K_L is the Langmuir constant (dm^3 mol^{-1}) and C_0 is the initial lead(II) ions concentration (mol dm^{-3}).

1.2. Adsorption kinetics

The first-order and pseudo-second-order kinetic models have been applied for the experimental data to predict to the adsorption kinetics. The first-order [27] and pseudo-second-order [28] equations are expressed as:

$$\text{first-order equation}: \quad \frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1 t} \tag{4}$$

$$\text{pseudo-second-order equation}: \quad \frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2}t \tag{5}$$

where q_t is the amount of the lead(II) ions adsorbed at various times t (mg g^{-1}); and k_1, the first-order rate constant (min^{-1}) of adsorption; q_1, the maximum adsorption capacity (mg g^{-1}) for the first-order adsorption; q_2, the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption; k_2, is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). Values of k_1 for the adsorption of first-order kinetic model can be calculated from the slope of the plots of $1/q_t$ versus $1/t$; values of k_2 and q_2 for the adsorption of pseudo-second-order kinetic model can be calculated from the plot of t/q_t against t.

Adsorption kinetics are generally controlled by different mechanism, of which the most limiting are the diffusion mechanisms, including the initial curved portion, attributed to rapid external diffusion or boundary layer diffusion and surface adsorption, and the linear portion, a gradual adsorption stage due to the intraparticle diffusion, followed by a plateau to the equilibrium where the intraparticle diffusion starts to decrease due to the low concentration in solution phase as well as fewer available adsorption sites [29].

In general, external mass transfer or external diffusion is characterized by the initial solute uptake [30,31] and can be calculated from the slope of plot of C/C_0 versus time. The slope of these plots can be calculated either by assuming polynomial relation between C/C_0 and time or it can be calculated based on the assumption that the relationship was linear for the first initial rapid phase [32]. In the present study, the second technique was used by assuming that the external mass transfer occurs in the first initial rapid step.

The intraparticle diffusion equation [33] can be written as follows:

$$q_t = k_p t^{1/2} + C \tag{6}$$

where C is the intercept, and k_p is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$).

The first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism and the kinetic results were then analyzed according to the intraparticle diffusion model. By using this model, the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) should be linear if the intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then the intraparticle diffusion is the rate-controlling step [34,35]. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The slope of linear portion from the figure can be used to derive values for the rate parameter, k_p, for the intraparticle diffusion.

2. Experimental

2.1. Preparation of activated carbon and lead(II) ions solutions

Euphorbia rigida, was used in this study a source of activated carbon, collected from nearby Afyon, Turkey. It was harvested between May and July, and then it was dried at room temperature and stored in a cool and dark room for 3 months. Production of activated carbon has involved by the carbonization of *E. rigida* in a negligibly ventilated atmosphere to drive out volatiles, leaving a porous carbon structure with a high surface area. Sulfuric acid as a chemical reagent added during the activation process help produce more effective adsorbent. The activation procedure was accomplished as: *E. rigida* was impregnated with 50% H_2SO_4 for 24 h and then filtered and the resulting chemical loaded *E. rigida* was placed in a furnace and heated (10 °C min^{-1}) to the final carbonization temperature of 850 °C for 30 min. In all experiments, the heating rate was kept constant. After cooling, the activated carbon was repeatedly washed with deionized water and dried at 110 °C. The carbonized material was sieved to <125 μm size and used for adsorption experiments.

Activated carbon was characterized with respect to the surface area was examined at 77 K by means of a standard BET procedure N_2 adsorption (Quantachrome Inst., Nova 2200e Surface Area Analyzer). BET equation was used to calculate the specific surface area. Before the measurements activated carbon was degassed at 300 °C for 3 h. The surface area of activated carbon is 741.21 m^2 g^{-1}.

A stock solution of lead(II) ions was prepared by dissolving an accurate quantity of $Pb(NO_3)_2$ in deionized water. Other concentrations prepared from stock solution by dilution varied between 50 and 200 mg dm^{-3} and the pH of the working solutions was adjusted to desired values with 0.1 M HCl or 0.1 M NaOH. Fresh dilutions were used for each experiment.

2.2. Batch adsorption studies

All batch experiments were conducted with adsorbent in erlenmeyer flasks closed with glass stoppers to avoid evaporation were stirred using a mechanical magnetic stirrer at 200 rpm to elucidate the optimum conditions of pH, adsorbent and lead(II) ion concentrations.

The effect of pH on the adsorption of lead(II) ions onto activated carbon from *E. rigida* was determined by equilibrating the adsorption mixture with dried adsorbent and 50 ml of 100 mg dm^{-3} lead(II) ions solution at different pH values between 1 and 6. The effect of adsorbent concentration was studied by using adsorbent the ranging from 0.2 to 1.0 g dm^{-3}.

For the assessment of the effect of metal ion concentration on adsorption, metal solutions ranging from 50 to 200 mg dm^{-3} were prepared and used. The optimum pH and adsorbent concentration were then determined as 5 and 0.8 g dm^{-3}, respectively, used throughout all adsorption experiments, which were conducted at various time intervals between 10 and 90 min and temperatures of 20, 30 and 40 °C. When the adsorption procedure completed, the solutions were centrifuged at 4500 rpm for 2 min and the supernatants were then analyzed for the residual lead(II) ion concentrations.

The adsorption of lead(II) ions onto activated carbon from *E. rigida* was evaluated at constant temperatures of 20, 30 and 40 °C for the adsorption isotherms as well as the first-order, pseudo-second-order and intraparticle diffusion kinetic models.

The final lead(II) ion concentrations of the solutions were determined by using an atomic absorption spectrophotometer (Varian AA250 Plus) with an air-acetylene flame. The instrument calibration was periodically checked by using standard metal solutions for every 15 reading.

3. Results and discussion

3.1. Effect of adsorbent concentration on metal removal

The results of the experiments with varying adsorbent concentrations are presented in Fig. 1. With increase in the adsorbent concentration, from 0.2 to 1.0 g dm^{-3}, the amount of adsorbed lead(II) ions removal increases from 47.00% to 99.80%. After

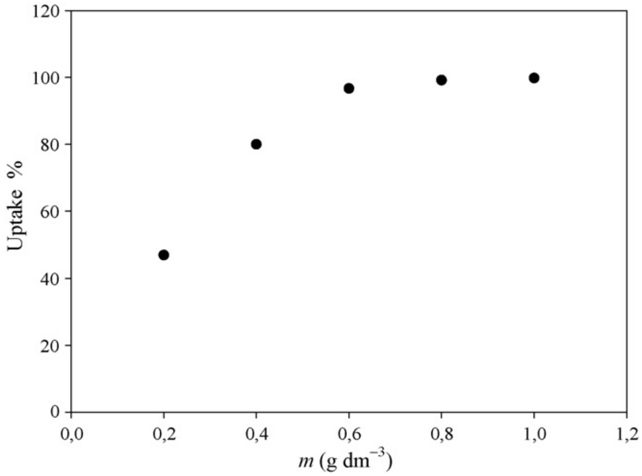

Fig. 1. Effect of adsorbent concentration for the adsorption of lead(II) ions onto activated carbon from *E. rigida* at 20 °C.

certain adsorbent dosage the removal efficiency is not increased significantly. It is evident that the optimum amount of activated carbon from *E. rigida* for further adsorption experiments was selected as 0.8 g dm^{-3} and the removal of lead(II) ions was found to be 99.2%. The removal efficiency at 1 g dm^{-3} of adsorbent dosage was not much higher than 0.8 g dm^{-3}. The variation in adsorption capacities between the various adsorbent dosages could be related to the type of surface group responsible for the adsorption of metal ions from solution. With increasing adsorbent dosage more surface area is available for the adsorption due to increase in active sites on the adsorbent and its availability for adsorption, making easier penetration of lead(II) ions to the adsorption sites and that increasing this number had also no effect after equilibrium was reached.

3.2. Effect of pH

The pH of solution has been identified as the most important variable governing metal adsorption on the adsorbent. Fig. 2 indicates the effect of pH on the removal of lead(II) ions onto activated carbon from *E. rigida* from aqueous solutions that the adsorption of metal ions was not observed for pH less than 3. The heavy metal-removal capacity increased very sharply with an increase in pH from 3 to 5. The low metal adsorption at pH 3.0 has been attributed to the competition that metal ions face from hydrogen ions for the available adsorption sites. The results showed that pH is an important parameter affecting the adsorption of heavy metals. At low pH (less than 4.0) heavy metal removal was inhibited, possibly as a result of a positive charge density on metal binding sites due to a high concentration of protons in solution. With an increase in the pH, the negative charge density on the activated carbon surface increases due to deprotonation of the metal binding sites and thus increases adsorption. Experiments were carried out with the pH values of 5 due to the fact that metal precipitation appeared at higher pH values and interfered with the accumulation or adsorbent deterioration [36,37].

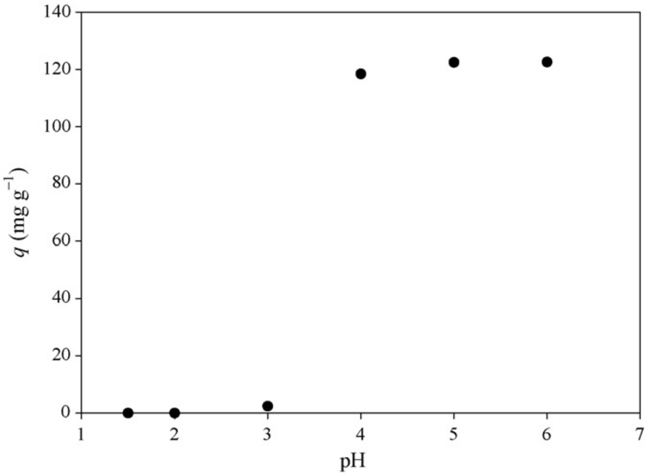

Fig. 2. Effect of pH for the adsorption of lead(II) ions onto activated carbon from *E. rigida* at 20 °C.

3.3. Effect of equilibrium contact time

The adsorption capacity of lead(II) ions removed by activated carbon from *E. rigida* versus contact time is illustrated in Fig. 3. It can be seen that the adsorbed amount of lead(II) ions increased with contact time up to 50 min, after that a maximum removal is attained. Therefore, 50 min was selected as the optimum contact time for all further experiments.

3.4. Effect of temperature on metal uptake

The temperature of the adsorption medium could be important for energy-dependent mechanisms in the metal adsorption by activated carbon from *E. rigida*. The equilibrium adsorption capacity of lead(II) ions onto activated carbon was favored at higher temperatures. This may indicate that adsorption of lead(II) ions onto activated carbon from *E. rigida* is chemical. An increase in the temperature from 20 to 40 °C leads to an increase in the adsorption capacity from 230.63 to 241.06 mg g^{-1} at an equilibrium time of 50 min and the concentration of 200 mg dm^{-3}. Below the equilibrium time, an increase in the temperature leads to an increase in the lead(II) ions adsorption, which indicates kinetically controlling process and endothermic in nature. After the equilibrium attained, the uptake increases with increasing temperature, this effect may be explained by availability of more in active sites of adsorbent at higher temperatures. Enhancement of adsorption capacity at higher temperature may be attributed to the enlargement of pore size and/or activation of adsorbent surface [38].

3.5. Adsorption isotherms

The equilibrium adsorption isotherms are one of the most useful data to understand the mechanism of the adsorption. Several isotherm equations are available and two important isotherms are chosen in this study, which are namely the Langmuir and Freundlich isotherms. The plots of linear form of Langmuir and Freundlich adsorption isotherms of lead(II) ions obtained at the temperatures of 20, 30 and 40 °C are illustrated in Figs. 4 and 5.

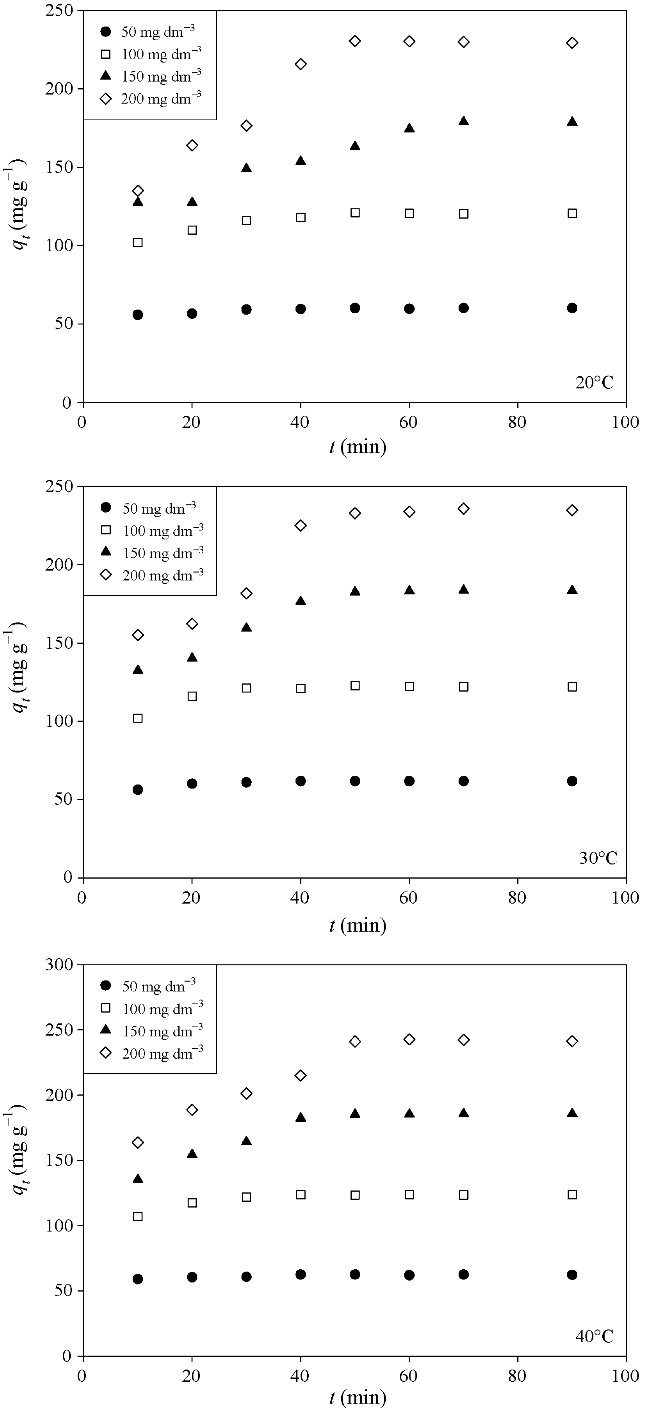

Fig. 3. Effect of contact time for the adsorption of lead(II) ions onto activated carbon from *E. rigida* at various temperatures.

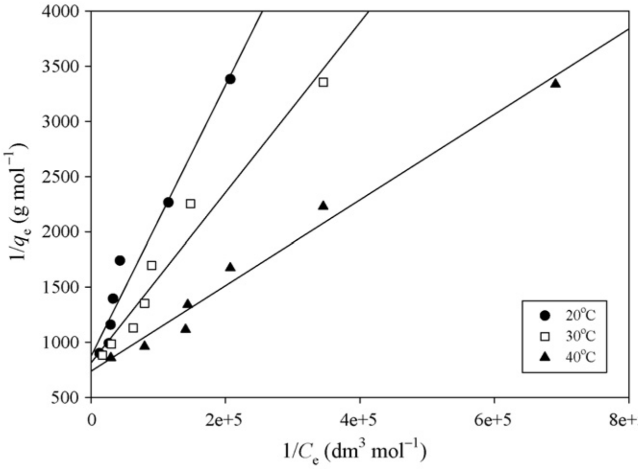

Fig. 4. Langmuir plots for the adsorption of lead(II) ions onto activated carbon from *E. rigida* at various temperatures.

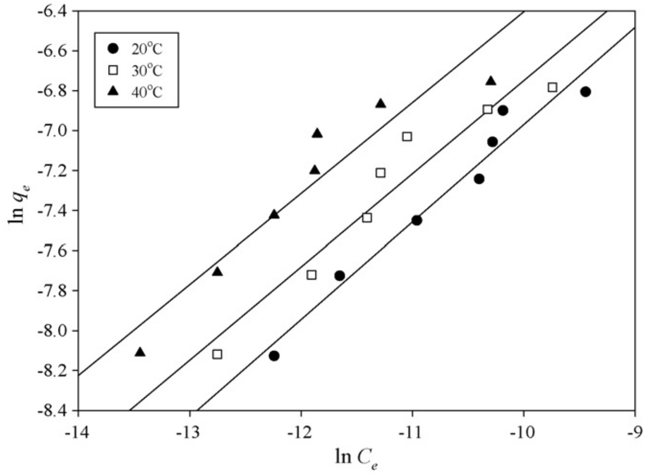

Fig. 5. Freundlich plots for the adsorption of lead(II) ions onto activated carbon from *E. rigida* at various temperatures.

All of the isotherm model parameters for the adsorption of lead(II) ions onto activated carbon from *E. rigida* are listed in Table 1. It is evident from these data, Langmuir model fits well compared with the r^2 values in Table 1.

The maximum adsorption capacity ($q_{\max}$) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorbent for lead(II) ions. The adsorption capacity of adsorbent increased on increasing the temperature. The highest value of $q_{\max}$ obtained at 40 °C is 1.35×10^{-3} mol g^{-1} or 279.72 mg g^{-1}. It appears to be the highest in comparison with the uptake obtained at the other temperatures (Table 1).

Table 1
Adsorption isotherm constants for the adsorption of lead(II) ions onto activated carbon by *Euphorbia rigida* at various temperatures

Langmuir				Freundlich			
t (°C)	$q_{\max}$ ($\times 10^{-3}$ mol g^{-1})	K_L (dm^3 mol^{-1})	r_L^2	R_L	K_F (dm^3 g^{-1})	n	r_F^2
20	1.15	7.11×10^4	0.958	1.44×10^{-2}	0.123	2.051	0.961
30	1.23	1.05×10^5	0.961	9.73×10^{-3}	0.124	2.145	0.927
40	1.35	1.90×10^5	0.981	5.41×10^{-3}	0.156	2.199	0.901

Table 2
Adsorption results of lead(II) ions from the literature by activated carbons obtained from various plants, agricultural and wood based materials and operating conditions

Activated carbon source	pH	t (°C)	Operating conditions		
			Initial concentration range (mg dm^{-3})	Adsorbent dosage (g dm^{-3})	Adsorption capacity (mg g^{-1})
Sawdust [7]	5.0	27	50–1000	2.0	200.00
Apricot stone [10]	6.5	25	–	2.0	22.85
Pecan shell [13]	4.8	–	104	0.5–10.0	64.2
Peanut shell [14]	4.8	–	1036–10360	10.0	152.91
Palm shell [15]	3.0 and 5.0	27	100–700	5.0	95.20
Coconut shell [40]	5.6	25	–	2.0	76.66
Bagasse pith [41]	4.0–8.0	30	100	–	200.00
Mature pods of *M. oleifera* containing seeds [42]	5.8	30	30	2.0	19.20
Coirpith waste [43]	4.0	–	25–100	–	263.00
Whole corncob [44]	3.8	–	–	0.5	154.36
Peanut husks [45]	6.0	20	31	0.6	113.96
Eichhornia crassipes [46]	3.0	–	15	0.8	16.61
Flax shive [47]	6.0	25	–	2.0	147.10
Date pits [48]	5.2	25	25–300	4.0	30.7
Rice straw [49]	5.0	23	518	10.0	36.05
Soybean hulls [49]	5.0	23	518	10.0	39.37
E. rigida H_2SO_4 impregnated (in this study)	5.0	40	50–200	0.8	279.72

When the temperatures increase, the K_L values calculated from Langmuir model also increase. This also indicates that the adsorption process is endothermic in nature.

The value of R_L calculated from Eq. (3) is incorporated in Table 1. As the R_L values lie between 0 and 1, the adsorption process is favorable [39]. Further, the R_L values for this study at all temperatures studied are between 5.41×10^{-3} and 1.44×10^{-2} therefore, the adsorption is favorable.

One of the Freundlich constants K_F indicates the adsorption capacity of the adsorbent and the values of K_F at equilibrium at all temperatures lie a range of 0.123–0.156 $dm^3\,g^{-1}$. The other Freundlich constant n is a measure of the deviation from linearity of the adsorption and the numerical values of n at all temperatures lie between 2.051 and 2.199 and are greater than unity, indicating that lead(II) ions are favorably adsorbed by activated carbon from *E. rigida* at all the temperatures studied.

The adsorption capacity of activated carbon from *E. rigida* by H_2SO_4 activation obtained from Langmuir isotherm equation for lead(II) ions in this study is comparable and was found to be the highest from many corresponding adsorbents reported in the literature (Table 2) [7,10,13–15,40–49].

3.6. Kinetics of adsorption

In order to understand the adsorption kinetics of lead(II) ions, three kinetic models, which are the first-order, pseudo-second-order and intraparticle diffusion, have been applied for the experimental data. The plots of linear form of the first-order, pseudo-second-order (Fig. 6) and intraparticle diffusion (Fig. 7) for the adsorption of lead(II) ions were obtained at the temperatures of 20, 30 and 40 °C. The kinetic parameters for the adsorption of lead(II) ions onto activated carbon from *E. rigida* are given in Table 3. The plots of

Table 3
Kinetic parameters for the adsorption of lead(II) ions onto activated carbon by *E. rigida* at various initial concentrations and temperatures

t (°C)	C_0 (mg dm^{-3})	k_1 (min^{-1})	q_1 (mg g^{-1})	r_1^2	k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})	r_2^2	k_p (mg g^{-1} $min^{-1/2}$)	C (mg g^{-1})	r_p^2
20	50.00	0.964	60.66	0.869	1.63×10^{-2}	60.75	0.999	1.189	51.86	0.923
	100.00	2.264	124.48	0.976	3.93×10^{-3}	123.93	0.999	4.825	87.77	0.975
	150.00	4.910	179.46	0.757	5.70×10^{-4}	196.71	0.994	9.860	91.81	0.897
	200.00	9.612	257.36	0.933	3.65×10^{-4}	262.88	0.991	24.83	52.77	0.966
30	50.00	1.156	63.08	0.966	2.11×10^{-2}	62.34	0.999	1.370	52.91	0.845
	100.00	2.405	127.86	0.951	5.52×10^{-3}	124.84	0.999	5.074	89.65	0.827
	150.00	5.201	194.05	0.875	8.28×10^{-4}	198.68	0.997	13.91	84.39	0.962
	200.00	7.092	250.24	0.800	3.94×10^{-4}	265.41	0.989	21.92	75.18	0.893
40	50.00	0.700	62.93	0.886	2.33×10^{-2}	62.93	0.999	0.933	56.10	0.937
	100.00	1.892	128.01	0.970	6.30×10^{-3}	126.01	0.999	4.237	96.26	0.865
	150.00	4.832	197.95	0.958	1.07×10^{-3}	197.86	0.998	13.27	93.94	0.980
	200.00	6.076	256.69	0.927	5.03×10^{-4}	265.58	0.996	18.48	103.97	0.971

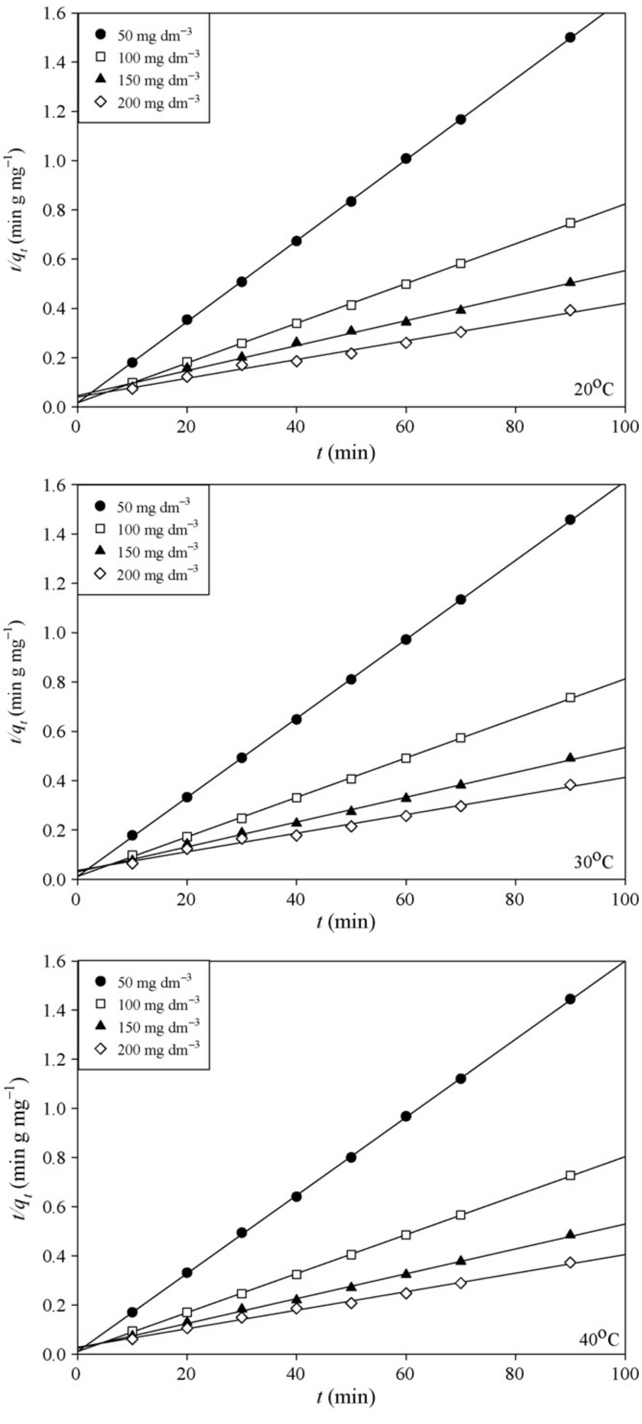

Fig. 6. Pseudo-second-order kinetic plots for the adsorption of lead(II) ions onto activated carbon from *E. rigida* at various temperatures.

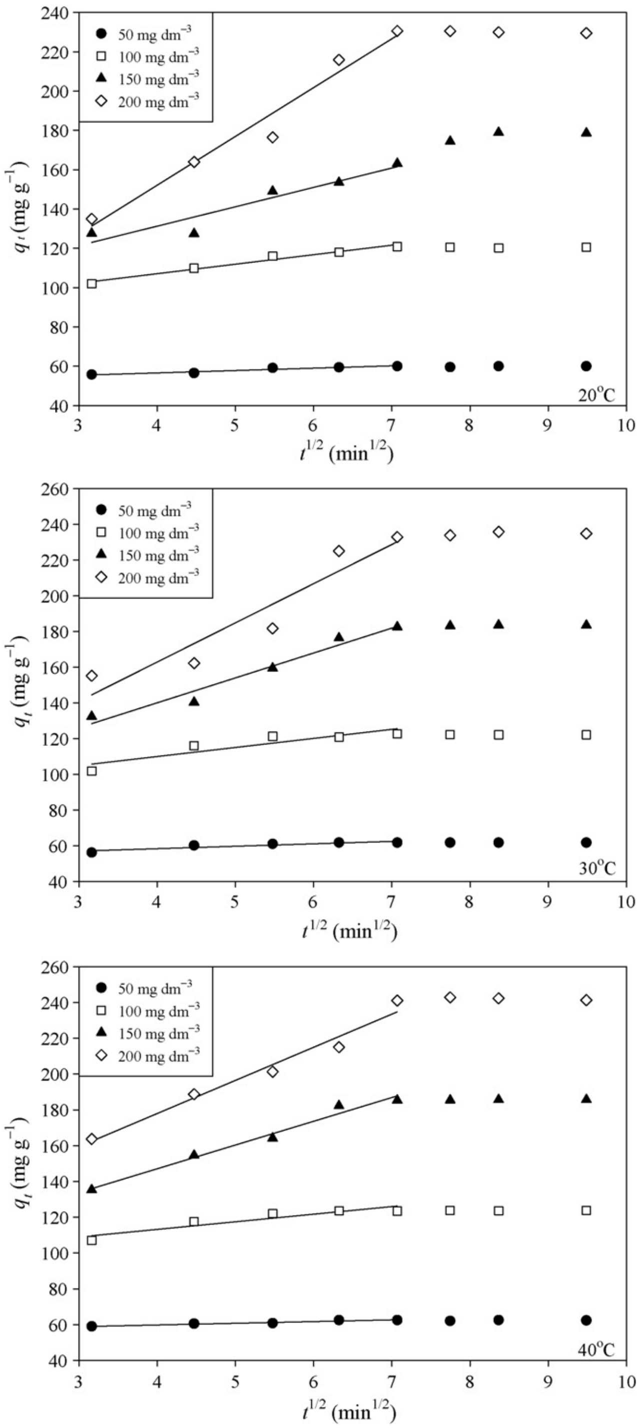

Fig. 7. Intraparticle diffusion plots for the adsorption of lead(II) ions onto activated carbon from *E. rigida* at various temperatures.

$1/q_t$ versus $1/t$ for the first-order equation are not shown as a figure since the calculated correlation coefficients are less than 0.977 for the first-order kinetic model, whereas the values of the correlation coefficient are greater than 0.988 for the pseudo-second-order kinetic model, therefore, the adsorption kinetics could be well explained and approximated more favorably by the pseudo-second-order kinetic model for the activated carbon from *E. rigida*. According to Table 3, these results suggest that the pseudo-second-order mechanism is predominant and that chemisorption might be the rate-limiting step that controls the adsorption process. The pseudo-second-order rate constants indicate a steady increase from 3.65×10^{-4} to 5.03×10^{-4} g mg^{-1} min^{-1} with an increase in the solution temperatures from 20 to 40 °C at a concentration of 200 mg dm^{-3}, indicating that the adsorption of lead(II) ions onto activated carbon from *E. rigida* is the rate-controlled.

There is an external mass transfer process that controls the early stages of the adsorption process. It can be supposed that the adsorption of lead(II) ions onto activated carbon from *E. rigida* follows mainly three steps of the external diffusion, intraparticle diffusion, and finally adsorption. Some of these steps can control the adsorption kinetics. In most cases, the adsorption occurs rapidly. Therefore, first two steps are important in the adsorption kinetics [35]. The first shaper linear stage being a rapid external mass transfer (external diffusion) and surface adsorption, and the second linear stage is a gradual adsorption stage, where the intraparticle is rate-limited. As shown in Fig. 7, the adsorption has three stages. The first and second steps are more valuable than the final step for the adsorption of lead(II) ions onto activated carbon by *E. rigida*.

The first stage is completed in about 10 min. Mass transfer coefficients for the adsorption of lead(II) ions onto activated carbon by *E. rigida* were quantified as $(C_{10\,\mathrm{min}}/C_0)/10$. The calculated average external mass transfer coefficient values for the adsorption of lead(II) ions onto activated carbon by *E. rigida* were found to be $2.71 \times 10^{-2}\,\mathrm{min}^{-1}$ at 20 °C, $2.40 \times 10^{-2}\,\mathrm{min}^{-1}$ at 30 °C and $2.06 \times 10^{-2}\,\mathrm{min}^{-1}$ at 40 °C, at a concentration range of 50–200 mg dm^{-3}.

The adsorption experimental data for the second stage were used only the range of 10–50 min of adsorption region to the calculate intraparticle diffusion coefficients. According to the Eq. (6), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_p and intercept C when adsorption mechanism follows the intraparticle diffusion process. The values of k_p as obtained from the slopes of straight lines are listed in Table 3. Because of the deviation of the curves from the origin and non-linear distribution of the plots, intraparticle diffusion cannot be accepted as the only rate-determining step for the adsorption of lead(II) ions onto activated carbon from *E. rigida*. Although the correlation coefficients for the intraparticle diffusion model are also lower than that of the pseudo-second-order kinetic model, this model indicates that the adsorption of lead(II) ions activated carbon from *E. rigida* may be followed by an intraparticle diffusion model up to 50 min.

4. Conclusions

This study has related that one of the biomass material *E. rigida*, can be used to remove lead(II) ions from aqueous solution. Experiments were performed as a function of pH, contact time and temperature. The maximum adsorption capacity of activated carbon from *E. rigida* for the removal of lead(II) ions was obtained at pH 5.

The Langmuir and Freundlich isotherm models were used for the mathematical description of the adsorption of lead(II) ions onto activated carbon depending on the temperature and the isotherm constants were evaluated from these isotherms. Results indicated that the adsorption equilibrium data fitted well to the Langmuir isotherm model in the studied concentration range at all temperatures. The kinetics of lead(II) ions adsorption onto activated carbon was based on the assumption of the pseudo-second-order mechanism and also followed the external diffusion model the first 10 min and then by the intraparticle diffusion model up to 50 min. The results show that the pseudo-second-order mechanism is predominant and that chemisorption might be the rate-limiting step that controls the adsorption process. This is consisted by the best agreement with the Langmuir isotherm model. The adsorption process was found to be endothermic, spontaneous and can be explained with the pseudo-second-order type kinetic model. Intraparticle diffusion should also be taken into account, but it was observed that intraparticle diffusion is not a rate-determining step. It may be concluded from above results that activated carbon from *E. rigida* can be used for the elimination of heavy metal pollution from wastewater since it is a low-cost, abundant and locally available adsorbent.

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