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Removal of Lead from Aqueous Solutions by Biosorption on Pomegranate Skin: Kinetics, Equilibrium and Thermodynamics

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***Abstract*—**In this study, pomegranate skin, a material suitable for the conditions in Algeria, was chosen as adsorbent material for removal of lead in an aqueous solution. Biosorption studies were carried out under various parameters such as mass adsorbent particle, pH, contact time, the initial concentration of metal, and temperature. The experimental results show that the percentage of biosorption increases with an increase in the biosorbent mass (0.25 g, 0.035 mg/g; 1.25 g, 0.096 mg/g). The maximum biosorption occurred at pH value of 8 for the lead. The equilibrium uptake was increased with an increase in the initial concentration of metal in solution (Co = 4 mg/L, q_t = 1.2 mg/g). Biosorption kinetic data were properly fitted with the pseudo-second-order kinetic model. The best fit was obtained by the Langmuir model with high correlation coefficients ($R^2 > 0.995$) and a maximum monolayer adsorption capacity of 0.85 mg/g for lead. The adsorption of the lead was exothermic in nature ($\Delta H° = -17.833$ kJ/mol for Pb (II). The reaction was accompanied by a decrease in entropy ($\Delta S° = -0.056$ kJ/K. mol). The Gibbs energy ($\Delta G°$) increased from -1.458 to -0.305 kJ/mol, respectively for Pb (II) when the temperature was increased from 293 to 313 K.

***Keywords*—**Biosorption, Pb(II), pomegranate skin, wastewater.

I. Introduction

WATER pollution by heavy metal raises a great concern nowadays. Heavy metal ions such as cobalt, copper, nickel, lead, and zinc are detected in wastewater streams from different industrial settlements [1]. Therefore, the methods and technologies to treat this harmful effluent become one of research focuses in environment science [2]. Heavy metals have a harmful effect on human physiology and other biological systems when they exceed the tolerance levels [3]. Lead causes anemia, diseases of the liver and kidneys, brain damage, and ultimately death when the person is exposed [4]. Lead is a toxic element which is conservative and has cumulative characteristics. Lead is released into the environment from various industrial processes: industries engaged in lead acid batteries, petrochemicals, ceramics, metal, wood production and also combustion of fossil fuel, mining activity, automobile emissions [5]. The permissible limit of lead in drinking water is 0.05 mg/L. The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy, and hepatitis [6].

Numerous processes exist for removing the dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis. Among various treatment methods, ion exchange looks like the most attractive one when effective and low-cost ion exchangers are used. Generally, ion exchange and sorption are also preferred for the removal of heavy metal ions due to easy handling [7]-[8].

Many methods have been undertaken in the process to remove these unwanted contaminants such as physio-chemical methods, various biological methods, and nano-based techniques [9]. The methods that we have employed are purely based on the aim to achieve environmental sustainability by using household waste such as eggshells, banana peels and pumpkin which are cheap, easily available and a very effective adsorbent. Eggshells are a very reliable adsorbent due to its calcium carbonate content [9], [10]. Moreover, there is no scope of any organic compounds dissolving in the solution like pumpkin powder, banana peel powder, sago waste [11], peanut hull [12], hazelnut [13], bagasse [14], rice hull [15], sugar beet pulp [16], plants biomass and bituminous coal [17], pomegranate powder leaving the solution colorless [18], [19].

Some previous investigations on the removal of heavy metal ions with many agricultural by products have been reported [20], [21].

For the present study, a batch-contact-time method was used, and the equilibrium of Pb (II) adsorption onto pomegranate skin was investigated with the attempts to fit the data to Langmuir and Freundlich, and Temkin equations. The uptake of Pb (II) on pomegranate skin was examined as a function of temperature, initial lead concentration, mass adsorbent particle, pH, and contact time. The biosorption kinetic data of the biomaterial were tested by the pseudo-first-order and the pseudo-second-order kinetic models. The thermodynamics of the biosorption was also evaluated.

II. Materials and Methods

A. Preparation of the Biosorbent

The pomegranate skin was washed with boiling distilled water for 30 min. The pomegranate skin was then placed in a solution of NaOH (12%) for 15 min and washed again with tap water. They are whitened with bleach 12% for 3 h at

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ambient temperature after which the cords are rinsed with the distilled water for several times. Pomegranate skin was oven dried at 105 °C for 120 min, before being ground and sieved to remove the fraction of particles of diameter between 80 and 630 µm.

B. Lead Solution Preparation

All the chemicals used in the experiments were of analytical grade. $Pb(NO_3)_2$ (Reidel-deHaën. minimum assay 99%) was used as the source of Pb (II), and all solutions were made in double-distilled water. The solutions of Pb (II) were made from a stock solution containing 1000 mg of Pb (II) in 1 L. For experiments at different pH, the acidity of Pb (II) solution was adjusted by addition of drops of 0.1 M (HNO_3) and 0.1 M (NaOH) solution. Removal of lead from the solution was monitored by tracing the decrease of lead concentration. Lead concentrations were measured by using a flame atomic absorption spectrophotometer (Spectre AA 220). Each measurement of lead concentration was repeated three times.

C. Adsorption Studies

Adsorption studies for the evaluation of the Pomegranate skin adsorbent for the removal of Pb (II) from aqueous solutions were carried out using the batch contact adsorption. For these experiments, fixed amount of adsorbent 1 g were placed in a 500 ml glass Erlenmeyer flasks containing 300 ml of lead solutions 1, 2.5, and 4 mg/L, which were agitated for a suitable time 150 min from 293 to 313 K at pH 6. For a given contact time corresponding to equilibrium, we recover the filtrate solution for passing the flame atomic absorption spectrophotometer (Spectre AA 220).

Adsorption kinetic experiments were used to investigate the effect of contact time and determine the kinetic parameters. For these tests, 1 g of pomegranate skin was added to 300 ml Pb(II) solutions with different initial concentrations (1, 2.5, and 4 mg/L). The mixture was agitated on an electromagnetic stirrer at 298 K and 400 rpm. At predetermined time intervals (0 - 150 min), 10 ml samples were taken out and filtered. The same methods were used to determine the residual Pb (II) concentration. The adsorption amount at time t, q_t (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)\,V}{m} \quad (1)$$

where q_t is the amount of lead taken up by the adsorbent (mg/g); C_t (mg/L) is the concentration of lead solution at time, t (mg/L), C_0 (mg/L) is the initial concentration of Pb (II). V is the volume of Pb (II) solution (L), and m is the weight of adsorbent used (g).

III. Results and Discussion

A. Effect of pH on the Removal of Lead

Many studies suggest that pH is an important factor in the adsorption process [22], [23], and variations in pH could change the characteristics and availability of metal ions in solution as well as the chemical status of the functional groups responsible for biosorption. Some experiments were therefore performed at 313 K with 4 mg/L solutions to study the Pb (II) adsorption on pomegranate skin as a function of solution pH.

The results for the study of the effect of pH on lead adsorption are shown in Fig. 1. It is clear that a progressive increase in pH from 2 to 12 causes an increase in the adsorption capacity. This lead adsorption behavior can be explained by the fact that during the pH adjustment of the solution containing the lead, the pomegranate skin undergoes accordingly possible alteration of the ionic character of their surfaces and the aggregation state of the lead.

The ion exchange sites are mainly protonated and are less available for ion exchange. Within this pH range, the ion exchange process is the major mechanism for the removal of metal ion from the solution.

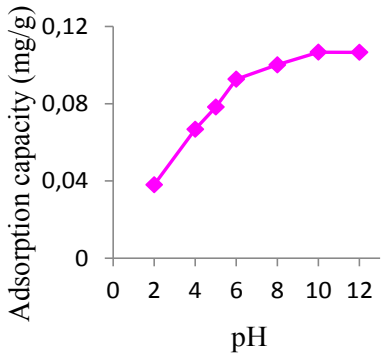

Fig. 1 Effect of pH variation on lead removal from 1mg/L solution through adsorption on pomegranate skin: V=120 ml, and T=313 K

B. Effect of the Mass of the Adsorbent

The influence of the mass of adsorbent was studied in the range between 0.25 and 1.5 g. Fig. 2 shows an increase in adsorption of Pb (II) as a function of the mass of pomegranate skin. The increase of the lead reduction rate with increasing the adsorbent mass is due to the availability of a large active surface site.

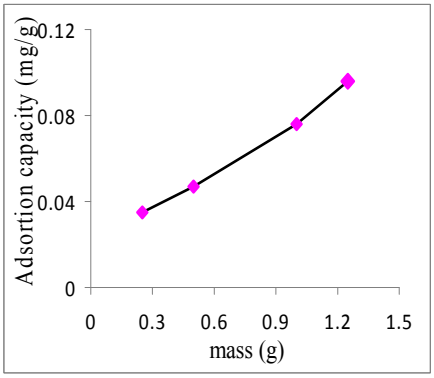

Fig. 2 Effect of the mass of the adsorbent on the adsorption of lead: particle size 0.08 ≤dp(mm) ≤ 0.63, V=120 ml, T=313 K, C_0 = 4 mg/L, and pH 7.2

C. Effect of Contact Time

Adsorption of Pb (II) was measured at given contact times for four different initial Pb (II) concentrations of 1, 2.5, and 4 mg/L. From Fig. 3, the plot reveals that the amount of lead removal is higher at the beginning. This is probably due to larger surface area of the pomegranate skin being available at the beginning for the adsorption of Pb (II) ions. As the surface adsorption sites become 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. The maximum amount of lead removal was nearly attained after about 150 min of shaking time at different initial concentrations. The increasing contact time increased the Pb (II) adsorption, and it remained constant after equilibrium reached in 40 min for different initial concentrations.

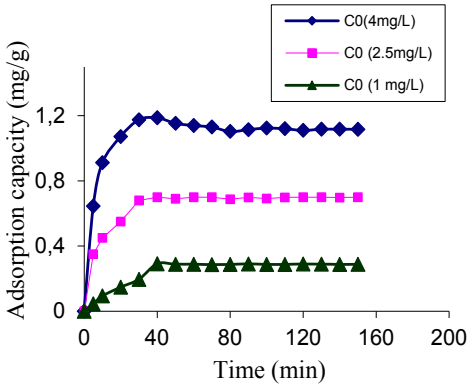

Fig. 3 Effect of Contact time on Pb(II) Removal onto pomegranate skin: pH 7.2, m = 1 g, 0.08 ≤ dp (mm) ≤0.63, V = 300 ml, and equilibrium time= 40 min

D.Effect of Initial Lead Concentration on Temperature Dependent Adsorption

The initial lead concentration provides an important driving force to overcome all mass transfer limitations of lead between the aqueous and solid phases.

Therefore, a higher initial lead concentration will enhance the adsorption process. Fig. 4 shows the effect of initial lead concentration on the equilibrium adsorption capacity (q_e) of lead on pomegranate skin at different temperatures. It was clear to see that the q_e values increase with the increase in the initial phenol concentrations or the solution temperatures. The maximum equilibrium (q_e) values were determined as 1.13, 1.15, and 1.20 mg/g for 4 mg/L initial lead concentrations at 293, 303, and 313 K, respectively.

The adsorption capacity for the system (Pb (II)/ pomegranate skin) increases with increasing the temperature from 293 to 313 K. The best removal efficiency (1.2 mg/g and 93.07%) was obtained at a temperature of 313 K. Work carried out by [24] to eliminate Cu (II) by the orange skin for increasing the temperature involves a decrease in the adsorbed amount; the elimination of copper adsorption capacity decreases (q_t = 0.999 mg/g) (q_t = 0.903 mg/g) when the temperature changes from 293 K to 333 K, respectively (exothermic) (C_0 10 mg/L and pH = 5.58), while our result for the system (Pb (II)/pomegranate skin) is greater than the Cu (II)/orange skin system.

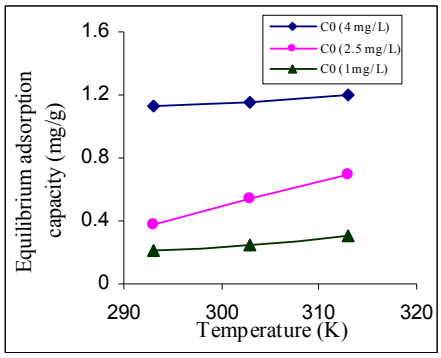

Fig. 4 Effect of temperature on the amount adsorbed by the pomegranate skin / Lead: pH 7.2, m = 1 g, 0.08 ≤dp(mm) ≤0.63 and V = 300 ml

E. Adsorption Isotherms

Adsorption isotherm models are widely used to describe the adsorption process and to investigate the mechanisms of adsorption. Adsorption isotherms were calculated based on the well-known Langmuir, Freundlich, and Temkin models. The Langmuir isotherm assumes that monolayer adsorption onto a surface contains a finite number of adsorption sites, by using uniform approaches for adsorption [25]. The linear form of the Langmuir isotherm equation is given as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (2)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_L the Langmuir adsorption constant (L/mg), and q_m is the theoretical maximum adsorption capacity (mg/g).

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter [26], R_L, defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

The value of R_L indicates the shape of isotherm to be either unfavorable (R_L>1) or linear (R_L= 1) or favorable (0<R_L<1) or irreversible (R_L = 0), [27]. The R_L values obtained (Table I) indicate favorable isotherm shape (0<R_L<1) for adsorption of Pb (II) on pomegranate skin the concentration range studied.

The Freundlich isotherm, on the other hand, assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [28]. The well-known logarithmic form of the Freundlich isotherm [29] is given by:

$$Log\,(q_e) = Log\,(k_F) + \frac{1}{n_F} Log\,(C_e) \quad (4)$$

where K_F (mg/g (L/mg)$^{1/n}$) and 1/n are the adsorption constants of Freundlich model generally related to the strength of interaction between adsorbate and sorbent.

Temkin's model rests on the assumption that during the adsorption gas phase, the heat of adsorption due to the interactions with the adsorbate decreases linearly with the recovery rate θ. From q_e plotted as a function of Ln C_e, B_T, and K_T values can be determined [30].

$$q_e = \frac{RT}{B_T} Ln\left(K_T . C_e\right) \quad (5)$$

where R is the perfect gas constant (8.314 J/(mol K)), T is the absolute temperature (K), B_T is the variation in energy of adsorption (J/mol), and K_T is the constant of Temkin (L/mg).

The plots of $1/q_e$ vs. $1/C_e$ for the adsorption of Pb (II) at 293, 303, and 313 K according to the linear form of the Langmuir isotherm are shown in Fig. 5. The adsorption isotherm constants of Pb (II) adsorption process on the pomegranate skin are listed in Table I.

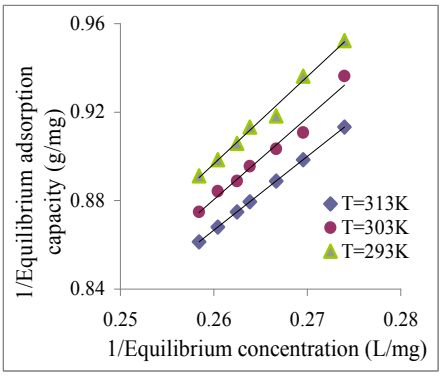

Fig. 5 Linearization of the Langmuir equation for adsorbing Pb(II)/pomegranate skin: pH 7.2, C_0=4 mg/L, V= 300 mL, and m=1 g

TABLE I
PARAMETERS OF DIFFERENT ADSORPTION MODELS FOR PB (II) / POMEGRANATE SKIN

Model parameters	System	Pb (II) / pomegranate skin		
	T (K)	293	303	313
	C_0 (mg/L)		4	
Freundlich	K_F	4.236	4.039	3.333
	$1/n_F$	0.940	0.81	0995
	R^2	0.991	0.971	0.989
Langmuir	qm (mg/g)	0.200	21.73	7.290
	K_L (L/g)	1.500	0.014	0.046
	R^2	0.999	0.984	0.995
	R_L	0.143	0.947	0.845
Temkin	K_T (L/g)	1.806	1.183	1.833
	B_T(kJ g/mol mg)	3.333	2.563	3.401
	R^2	0.928	0.972	0.963

From Table I, the values of 1/n were found to be less than 1. The low value of the linear correlation coefficient, R^2, indicated the unsuitability of Temkin isotherm model. The values of R^2 for Freundlich model (0.971, 0.989, and 0.991 at 293, 303, and 313 K, respectively) were high, indicating that this model can be used to characterize the equilibrium adsorption. However, Freundlich model was not the best model in this study. Langmuir models were fitting well with the isotherm data at various temperatures with the highest R^2 values, compared to Temkin and Freundlich models. The Langmuir fit is consistent with strong monolayer sorption onto specific sites. The maximum adsorption capacities (q_m) of pomegranate skin for Pb (II) were 1.13, 1.15, and 1.20 mg/g at 293, 303, and 313 K, respectively. The similar phenomena are also observed in adsorption of copper onto the orange skin [24] and in adsorption of copper and lead on tea waste [31].

F. Kinetics Studies

The rate constant for surface adsorption of Pb (II) ion onto pomegranate skin is also studied under the light of the pseudo-first-order rate expression of Lagergren model [32]. The integrated form of the Lagergren equation is given by:

$$Log(q_e - q) = Log q_e - \frac{k_1}{2.303} t \quad (6)$$

where q_e and q_t are the amounts adsorbed at equilibrium and at time, t (mg/g), and k_1 is the rate constant of the pseudo-first-order adsorption (1/min).

The pseudo-second-order kinetic model (7) can be represented in the following form [33]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where k_2 is the rate constant of the pseudo-second order adsorption (g/mg min).

The kinetics of adsorption of the adsorbate on the adsorbent was verified at different initial concentrations (1, 2.5, and 4 mg/L).

The validity of each model was determined by the sum of squared errors (SSE %), given by:

$$SSE = \frac{1}{N} \sqrt{\sum_N (q_{e,\exp} - q_{e,cal})^2} \quad (8)$$

where N is the number of trials. Low value indicates a better SSE smoothing.

The kinetic parameters for adsorption of lead presented in Table II were calculated from plots of log (q_e−q_t) vs. t and the plots of t/q_t vs t. For the first-order kinetic model, the obtained R^2 values were relatively low, ranging from 0.889 to 0.936, and the calculated $q_{e(cal)}$ were much larger than the experimental $q_{e(exp)}$. For the second-order kinetic model, the obtained R^2 values were between 0.996 and 0.999. Moreover, the experimental $q_{e(exp)}$ values agree well with the calculated

ones. These results indicate that the adsorption system of lead obeyed a pseudo-second-order kinetic model. The similar phenomena are also observed in adsorption of lead onto tree leaf powder [34] and in adsorption of copper and lead on tea waste [31].

TABLE II
PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETIC PARAMETERS FOR THE ADSORPTION OF PB (II) ONTO POMEGRANATE SKIN

Pseudo-first-order	System	Pb (II)/ Pomegranate skin		
	T(K)	313		
	C_0 *(mg/l)*	1	2.5	4
	$q_{e,exp}$ *(mg/g)*	0.301	0.760	1.200
	$q_{e,cal}$ *(mg/g)*	0.400	0.580	0.700
	K_1 *(min^{-1})*	0.048	0.047	0.046
	$q_{e,cal}/K_1$	8.300	12.340	15.220
	R^2	0.889	0.901	0.936
	SSE (%)	3.70	6.0	16.67
Pseudo-second-order	$q_{e,cal}$ *(mg/g)*	0.294	0.673	1.121
	K_2 *(g/mg.min)*	2.929	1.571	1.022
	$q_{e,cal}/K_2$	0.100	0.428	1.096
	R^2	0.999	0.998	0.996
	SEE (%)	0.74	2.90	2.63

G. Thermodynamic Parameters

The original concepts of thermodynamics assumed that in an isolated system, where energy cannot be gained or lost, the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change, ΔG°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity:

The value of ΔG° can be determined from:

$$\Delta G^0 = -R\,T\,Ln\,(k_L) \tag{9}$$

where K_L is the adsorption equilibrium constant, R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature.

A convenient form of the Van't Hoff equation then relates K_L to the standard enthalpy and entropy changes of adsorption, ΔH^o and ΔS^o, respectively [35]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10}$$

Equation (10) can be written as:

$$Ln(k_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\cdot\frac{1}{T} = -\frac{\Delta G^0}{R}\cdot\frac{1}{T} \tag{11}$$

where the values of ΔH° and ΔS° can be determined from the slope and intercept of the plot between Ln K_L vs (1/T) (Fig. 6). The values of ΔG°, ΔH°, and ΔS° for the biosorption of Pb (II) onto pomegranate skin at different temperatures (293, 303, and 313 K) are given in Table III. The negative values of Gibb's free energy changes approve a spontaneous nature of biosorption.

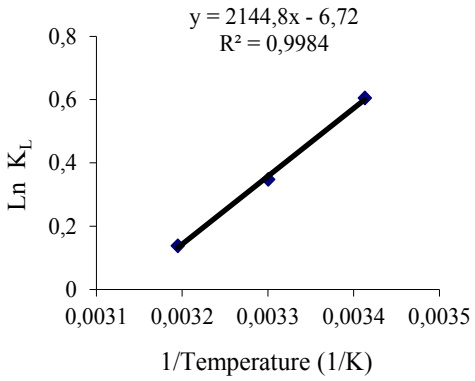

Fig. 6 Relationship between Langmuir sorption equilibrium constant and temperature for Pb (II) / Pomegranate skin; C_0= 4 mg/L

TABLE III
THERMODYNAMIC PARAMETERS OF THE ADSORPTION OF PB (II) ONTO POMEGRANATE SKIN AT DIFFERENT TEMPERATURES

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
293	- 1.458		
303	- 0.865	- 17.833	- 0.056
313	- 0.305		

The values of ΔH° and ΔS°, for the sorption processes are calculated to be - 17.833 kJ/mol and - 0.056 kJ/mol K, respectively. The negative ΔG° values indicate thermodynamically feasible and spontaneous nature of the Pb (II) biosorption on pomegranate skin [36]. The value of ΔH° is negative, indicating that the sorption reaction is exothermic. The negative ΔS° value suggests a decrease in the randomness at solid/solution interface during the biosorption of Pb (II) on pomegranate skin [33]. The ΔG° values obtained in this study for the Pb (II) ions are < - 10 kJ/mol, which indicates that physical adsorption was the predominant mechanism in the sorption process [37].

IV. CONCLUSION

This study shows that pomegranate skin, an abundant natural source, can be used effectively and efficiently for the removal of Pb (II) from aqueous solutions.

Equilibrium, kinetic, and thermodynamic studies were made for the adsorption of Pb (II) ions from aqueous solution onto pomegranate skin powder at pH 7.2. Equilibrium data were fitted to Langmuir, Freundlich, and Temkin isotherms, and the equilibrium data were best described by the Langmuir isotherm model (R^2 = 0.993), with a maximum monolayer adsorption capacity of 1.20 mg/g, at 40 min. The adsorption kinetics is best described by the pseudo-second-order (R^2 = 0.998).

The thermodynamic parameters for the adsorption of Pb (II) onto pomegranate skin were also determined. The negative sign of ΔS° shows the decreased randomness at the solid - solution interface during adsorption, and the negative sign of

ΔH° indicates that the adsorption process is exothermic. The negative sign of ΔG° confirms the spontaneous nature of the adsorption process, and physical reaction.

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REFERENCES

[1] N. A. Adesola et al, "Biosorption of lead ions from aqueous solution by maize leaf". Inter. J. Phy. Sci. Vol. 1 (1), pp. 023-026, 2006.
[2] J. L. Garde a-Torresdey, L. Tang, J.M. Salvador, "Copper Adsorption by Esterified and Unesterified Fractions of Sphagnum Peat Moss and Its Different Humic Substances", J. Hazard. Mater., 48: 191-206, 1996.
[3] M. Kobya, E. Demirbas, E. Senturk, M. Ince, "Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone". Bioresour. Technol. 96(13), pp. 1518–1512, 2005
[4] SK. Jain, P. Vasudevan, NK. Jha, "Removal of some heavy metals from polluted water by aquatic plants: studies on duckweed and water velvet", Biol. Wastes. 28: 115–126, (1989).
[5] P. S. Kumar, C. Vincent, K. Kirthika and K. S. Kumar, "Kinetics and Equilibrium Studies of Lead (II) Ion Removal from Aqueous Solutions by Use of Nano-Silversol-Coated Activated Carbon", Braz. J. Chem. Eng., vol. 27 (2), pp. 339-346, 2010.
[6] M. Sekar, V. Sakthi, S. Rengaraj, "Kinetic and Isotherm Adsorption Study of Lead (II) Onto Activated Carbon Prepared from Coconut Shell", J. Colloi. Interf. Sci., 279, pp. 307, 2004.
[7] I. Ghodbane, L.Nouri, L.Hamdaoui, M. Chiha, "Kinetic and Equilibrium Study for the Sorption of Cadmium (II) Ions from Aqueous Phase by Eucalyptus Bark", J. Hazard. Mater., 152, pp. 148, 2008.
[8] P. King, N. Rakesh, S. Beenalahari, Y.P. Kumer, V.S.R.K. Prasad, "Removal of Lead from Aqueous Solution using Sysigum cumini L.: Equilibrium and Kinetic Studies", J. Hazard. Mater. 142, pp. 340, 2007.
[9] B. R. Nurul Aimi, BAH Norhafizah, CS. Wong, "Removal of Cu(Ii) From Water by Adsorption On Chicken Eggshell". Inter. J. Eng. & Tech. Ijet-Ijens Vol: 13 No:01, (2013).
[10] SD. Renata, C. Laercio, F. Guilherme, MP. Pedro, JS. Margarida, "Banana Peel Applied to The Solid Phase Extraction of Copper and Lead from River Water: Preconcentration of Metal Ions with A Fruit Waste". Ind. Chem. Res., 2011.
[11] P. D. Johnson, M. A. Watson, J. Brown and I.A. Jefcoat, "Peanut hull pellets as a single use sorbent for the capture of Cu (II) from wastewater". Waste Management, vol. 22, No. 5, pp. 471-480, 2002.
[12] Z. Reddad, C. Gerente, Y. Andres and P. cloirec, "Adsorption of several metal ions onto a lowcost biosorbent: Kinetic and equilibrium studies". Env. Sci.d Techn., vol. 36, No. 9, pp. 2067-2073, 2002.
[13] S. Y. Quek, D.A.J. Wase and C.F. Forster, "The use of sago waste for the sorption of lead and copper". Water SA, vol. 24, No. 3, pp. 251-256, 1998.
[14] F. Pagnanelli, S. Mainelli, F. Veglio and L. Toro, "Heavy metal removal by olive pomace: biosorbent characterization and equilibrium modeling". Chem. Eng.g Sci., vol. 58, No. 20, pp. 4709-4717, 2003.
[15] S. Babel and T. A. Kurniawan, "Low-cost adsorbents for heavy metals uptake from contaminated water": a review. J. Hazard. Mat., vol. 97, No. 1-3, pp.219-243, 2003.
[16] K. C. Sekhar, C. T. Kamala, N.S. Chary and Y. Anjaneyulu, "Removal of heavy metals using a plant biomass with reference to environmental control". Intern. J. Mineral Process. vol. 68, No. 1-4, p. 37-45, 2003.
[17] QC. Charles, "Banana Peels May Help Filter Pollutants Out Of Water", 2011.
[18] AM. King'ori, "Eggshells and Shell Membranes". Inter. J. Poul. Sci. 10, pp. 908-912 (2011).
[19] D. Mohan, K. P. Singh, "Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste". Water Res., 36 (9), pp. 2304-18, 2002.
[20] S. Yoshihiro, T. Kametani, T. Maruyama, "Removal of heavy metals from aqueous solution by nonliving Ulva seaweed as biosorbent". Water Res., 39 (9), pp. 1803-1808, 2005.
[21] A. Nasruddin, "Biosorption of ions zinc from its aqueous solution using tempe". Ph. D. Thesis. Malaysia: University of Sains Malaysia, (2002).
[22] A. Kapoor, T. Viraraghavan, "Nitrate removal from drinking waterreview". J. Env. Eng.-Asce, 123(4), pp. 371–80, 1997.
[23] H. Song, Y. Zhou, A. Li and S. Mueller, "Selective removal of nitrate by using a novel macroporous acrylic anion exchange resin". Chin. Chem. Lett., 10.1016/j.cclet.2012.03.004, pp. 603-606, 2012.
[24] A. Khalfaoui, "Elimination of organic and inorganic pollutants by adsorption on natural materials: application to orange skin and banana", PhD Thesis, Constantine University, Algeria (2012).
[25] I. Langmuir, "The constitution and fundamental properties of solids and liquids", J. Am. Chem. Soc. 38, pp. 2221–2295, 1916.
[26] K. R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, "Pore and Solid-Diffusion Kinetics in Fixed Bed Adsorption Under Constant Pattern Conditions", Ind. Eng. Chem. Fundam., pp. 5212, 1966.
[27] P. Baskaralingam, M. Pulikesi, D. Elango, V. Ramamurthi, S. Sivanesan, "Adsorption of acid dye onto organobentonite"; J. Hazard. Mater., 128(2-3), pp. 138-44, 2006.
[28] T. W. Weber, R. K. Chakravorti, "Pore and solid diffusion models for fixed-bed adsorbers", AlChE J. 20, pp. 228–238, 1974.
[29] H. M. F. Freundlich, "Uber die adsorption in losungen (Over the adsorption in solutions", J. Phys. Chem. 57, pp. 385–470, 1906.
[30] M. J. Temkin, and V. Pyzhev, "Recent modifications to Langmuir isotherms". Acta Physicochim URSS, 12, pp. 217-222, 1940.
[31] B. M. W. P. K Amarasinghe and R. A. Williams, "Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater". Chem. Eng. J., 132(1-3), pp. 299-309, 2007.
[32] S. Lagergren, "Zur theorie der sogenannten adsorption gelöster stoffe, Kungliga Svenska Vetenskapsakademiens". Handlingar, 24 (4), pp. 1-39, 1898.
[33] G. Crini, "Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer", Dyes Pigm. 77, pp 415–426, 2008.
[34] P. Senthil kumar, R. Gayathri, "Adsorption of Pb(II) ions from aqueous solutions onto bael tree leaf powder: isotherms, kinetics and thermodynamics study". J. Eng. Sci. and Tech. Vol. 4, No. 4, pp. 381 – 399, 2009.
[35] Y. Seki, K. Yurdakoc, "Adsorption of Promethazine hydrochloride with KSF Montmorillonite", *Adsorption*, 12, pp. 89, 2006.
[36] J. R. Memon, S. Q. Memon, M. I. Bhanger, G. Z. Memon, A. El-Turki, G. C. Allen, "Characterization of banana peel by scanning electron microscopy and FT-IR spectroscopy and its use for cadmium removal". Colloi. Surf. B: Biointerfaces, 66(2), pp. 260-265, 2008.
[37] B. H. Hameed, A. T. M. Din, A. L. Ahmad, "Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies", J. Hazard. Mater. 141, pp. 819–825, 2007.
[38] N. T. Abdel Ghani and G. A. Elchaghaby, "Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ion from wastewater by adsorption". Int. J. Env. Sci. Tech., 4(4), pp. 451-456, 2007.