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Research Article

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Thermodynamics of adsorption of Pb (II) and Cd (II) metal ions from aqueous solution by *Punica granatum* L. husk

S. D. Deosarkar

School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431 606 (MS) India
S. F. S. College, Seminary Hills, Nagpur-444 006 (MS) India

ABSTRACT

Temperature effects on adsorption of Pb (II) and Cd (II) onto Punica granatum L. husk for optimized predetermined conditions has been studied by batch adsorption experiment for different contact time between adsorbate and adsorbent. The adsorption was found to increase with rise in temperature. Thermodynamic functions like equilibrium constant (K), free energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) for adsorption were estimated. The adsorption process was found to be endothermic with increase of randomness at solid-liquid interface.

Keywords: *Punica granatum*, batch adsorption, thermodynamics

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INTRODUCTION

A toxic heavy metal ion in industrial waste has attracted worldwide attention. Some metals have toxic or harmful effects on life [1]. Remove of the heavy metals from aqueous solutions by their adsorption onto the agricultural wastes is area of interest. Adsorption is collection of adsorbate on the surface of adsorbent due to force of attraction. Adsorption of toxic metals from aqueous solutions onto the agricultural waste is one of the economical and eco-friendly techniques.

Constituents like, phenolic punicalagins, gallic acid and other fatty acids [2] flavonols [3], flavones, flavonones [4] and anthocyanidins [5] are present in the *Punica granatum* pericarp. Therefore, we thought of using *Punica granatum* L. husk in natural state as an adsorbent for Pb (II) and Cd (II) metal ions. Adsorption of Cd (II) and Pb (II) from aqueous solutions onto activated alumina [6] agricultural byproducts [7], and functionalized sugarcane bagasse [8] has been studied. The adsorption of heavy metals has been studied by many workers [9-12].

Present work reports the adsorption of Pb (II) and Cd (II) metal ions on to *Punica granatum* L. at different temperatures and for different shaking times. The thermodynamics functions of adsorption have been estimated.

EXPERIMENTAL SECTION

Preparation of solutions

Pb (II) and Cd (II) salts ($PbCl_2$ and $CdCl_2 \cdot 2H_2O$) used for preparation of solutions were of analytical reagent grade. Demineralized distilled water was used for preparation of metal salt solutions. 100 mL solution of 3 mg/L of each metal salts was prepared in calibrated volumetric flasks by dissolving accurate amount of metal salt in water. Electronic balance was used for weighing (Model No.-CA-123, 0.001g, Contech Instruments Ltd.).

Preparation of adsorbent

Punica granatum L. husk were collected, exposed to sunlight for seven days and subsequently they were ground, sieved to pass through 100-mesh screen and then exposed to sunlight for 24 hours and were preserved in airtight bottles with cork. It was then dried in hot air oven, (Bio Techniques India).

Adsorption study

The adsorption of Pb (II) and Cd (II) metal ions from aqueous solutions was studied by batch adsorption method [13-14]. 300 mg of the adsorbent was weighed and added to the conical flasks containing 100 mL metal ion solution. The pH of mixtures was maintained at 6 and required temperatures were maintained constant. Flasks were corked and placed on shaker for desired time (60, 120 and 150 min). After 60, 120 and 150 minutes the mixtures were filtered using Whatman No. 40 filter paper and filtrates were analyzed for equilibrium metal ion concentration spectrophotometerically.

Experimental conditions

Experimental conditions were maintained throughout the experiment as:
Initial concentration of metal ions= 3 mg/L; dose of adsorbent= 3 g/L; pH= 6; contact time= 60, 120 and 150 min. and temperature= 298.15, 303.15 and 308.15 K.

RESULTS AND DISCUSSION

The percent adsorption (uptake) of metal (% X) was determined by following equation [15]:

$$\% X = \frac{C_o - C_e}{C_o} \times 100 \quad .....(1)$$

Where, C_o and C_e are initial and equilibrium concentration of metal ion solution (mg/L).

The values of equilibrium concentration and percent metal ion removal for different temperatures are reported in Table 1. The adsorption of metal ions onto pomegranate husk was studied at different temperatures for different shaking times (contact time between adsorbate and adsorbent) and variation of percent adsorption with temperature and shaking times for Pb (II) and Cd (II) is shown in Figure 1 and 2.

Fig. 1. Plots of percent metal removal versus temperature for different shaking times for Pb (II) metal ions

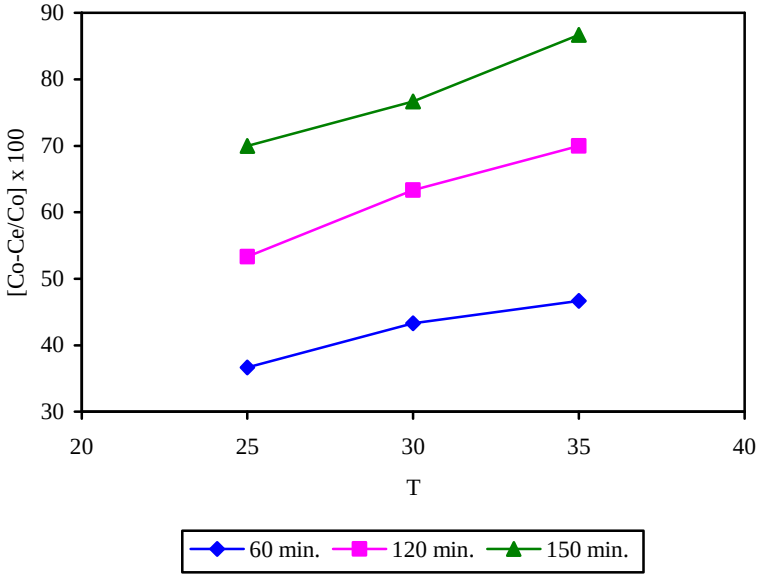
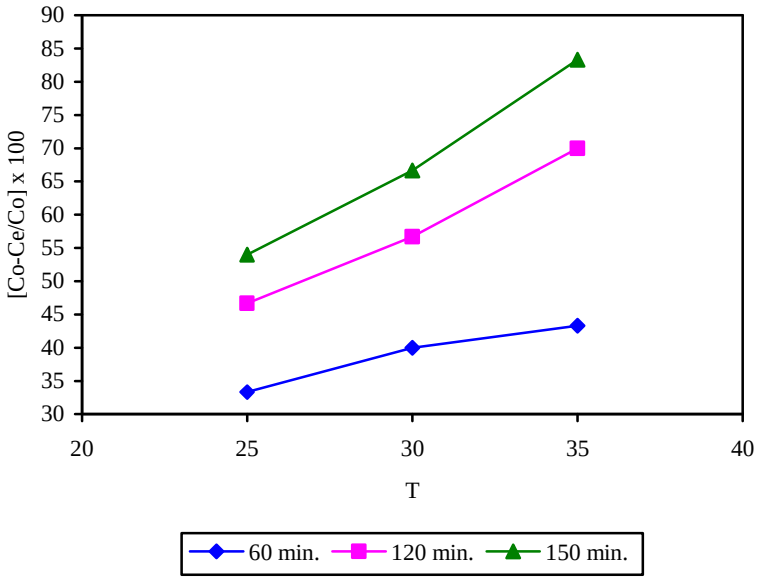


Table 1. Equilibrium concentration of metal ion and percentage of metal ion removal for different batch adsorption studies (C_0=3 mg/L)

T, K	*t, min.	C_e, mg/L		**$(C_o-C_e/C_o) \times 100$		log *K*	
		Pb (II)	Cd (II)	Pb (II)	Cd (II)	Pb (II)	Cd (II)
298.15	60	1.9	2.0	36.67	33.33	-0.2374	-0.3010
	120	1.4	1.6	53.33	46.67	-0.0580	0.0580
	150	0.9	1.38	70.00	54.00	0.3680	0.0696
303.15	60	1.7	1.8	43.33	40.00	-0.1165	-0.1761
	120	1.1	1.3	63.33	56.67	0.2374	0.1165
	150	0.7	1.0	76.67	66.67	0.5166	0.3010
308.15	60	1.6	1.7	46.67	43.33	-0.0580	-0.1165
	120	0.9	0.9	70.00	70.00	0.3680	0.3680
	150	0.4	0.5	86.67	83.33	0.8129	0.6990

**t=shaking (contact) time; **$(C_o-C_e/C_o) \times 100$= % adsorption*

Fig. 2. Plots of percent metal removal versus temperature for different shaking times for Cd (II) metal ions



It can be seen that the adsorption of both the metal ions increased with rise in temperature which indicates endothermic nature of the adsorption process [16]. This may be due to the increase in number of active sites on the adsorbent.

Thermodynamic functions

Equilibrium constant of adsorption process was calculated by using following equation [17]:

$$K = C_{solid} / C_{liquid} \quad .....(2)$$

Where, *K* is equilibrium constant; C_{solid} and C_{liquid} are solid phase and liquid phase concentration (mg/L) of metal ion at equilibrium. Log *K* values are reported in Table 2.

The free energy change (ΔG^0) associated with adsorption was calculated using following equations [18-19].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -2.303\,RT \log_{10} K \quad .....(3)$$

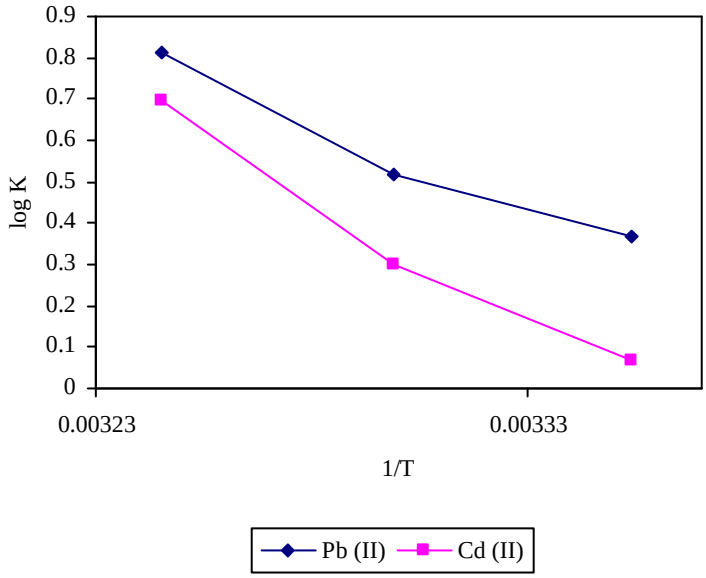
Where, R is gas constant (8.314 J/mol K) and T is temperature (K).

Entropy change (ΔS^0) and enthalpy change (ΔH^0) are related with *K* by following equation [20]:

$$\log_{10} K = \frac{\Delta S^0}{2.303\,R} - \frac{\Delta H^0}{2.303\,RT} \quad .....(4)$$

From the plot of log *K* versus 1/T, Figure 3 (vant Hoff plots), ΔS^0 was determined from intercept (ΔS= intercept × 2.303R) and ΔH^0 was determined from slope (ΔH= -slope × 2.303R) of the curve. The values of thermodynamic properties are reported in Table 2.

Fig. 3. Plots of log *K* versus 1/T for the estimation of thermodynamic functions



The positive values of ΔH^0 for both metal ions indicate endothermic nature of the adsorption onto pomegranate husk.

Entropy change is positive but negligible indicating small structural changes at active sites of the adsorbent during adsorption process.

Table 2. Thermodynamic parameters like free energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) change for optimized contact time

T (K)	t (min.)	ΔG^0 (kJ/mol)		ΔS^0 (kJ/mol)		ΔH^0 (kJ/mol)	
		Pb (II)	Cd (II)	Pb (II)	Cd (II)	Pb (II)	Cd (II)
298.15	150	-21.01	-3.97	2.63	3.64	781.15	1105.50
303.15	150	-29.99	-17.47				
308.15	150	-47.96	-41.24				

Free energy change is negative for all temperatures indicating spontaneity of process [21] and these values became more negative as temperature rises which is due to increase in spontaneity of the adsorption with rise in temperature.

CONCLUSION

Temperature and shaking time effects on adsorption of Pb (II) and Cd (II) metal ions from aqueous solutions by *Punica granatum* L. has been studied. The *Punica granatum* L. husk proved to be effective adsorptive material for Pb (II) and Cd (II) metal ions. For given temperature the adsorption has increased with shaking time. Rise in the temperature favored the adsorption of both the metal ions indicating it is an endothermic process.

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