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Research Article

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Cu(II) Adsorption from Aqueous Solution by *Punica granatum* L. Husk

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ABSTRACT

Adsorption of Cu (II) metal ions onto Punica granatum L. husk was studied by batch adsorption experiments. In order to get conditions for maximum adsorption studies were carried out for different initial concentrations of metal (C_0), doses of the adsorbent (m), pH of solution, contact time(t) and temperature (T). Maximum adsorption was observed for 3 mg/L of initial concentration metal at pH=6 for 0.3 g adsorbent dose, 150 min contact time and 323.15 K. Thermodynamic functions such as free energy change (ΔG^0), entropy change (ΔS^0) and enthalpy change (ΔH^0) were estimated. Adsorption was found to be thermodynamically endothermic.

Keywords: *Punica granatum,* batch adsorption, thermodynamic functions.

INTRODUCTION

Adsorption has application for the removal of heavy metals from aqueous solutions. It shows collection of higher concentration of any molecular species or adsorbate on the surface of adsorbent due to the force of attraction. In adsorption the adsorbate adhere to solid surfaces. The adsorption of toxic metals onto the agricultural waste and waste materials provides economical and eco-friendly technique for metal removal from aqueous solutions.

E. P. Lansky and R. A. Newman have studied therapeutic applications of pomegranate [1]. The pericarp of pomegranate contains phenolic punicalagins, gallic acid and other fatty acids [2], flavonols [3], flavones, flavonones [4] and anthocyanidins [5]. Removal of metal ions by sawdust [6], activated sludge [7], hydrogels [8] as a biosorbents, bamboo wastes [9], and other agricultural solid wastes [10] have been proved. Chemically modified and unmodified agricultural adsorbents [11], maize leaf [12], orange mesocarp [13], okra wastes [14] were used for removal of heavy metal from water. A. Bhatnagar et al have used *Punica granatum* peel waste for removal of nickel [15]; S. D. Deosarkar has used the same material for removal of lead and cadmium from aqueous solutions [16]. Removal of Cu (II) from aqueous solutions by fly ash was studied by Panday et al [17].

Present paper reports adsorption of Cu (II) metal ions from aqueous solution using *Punica granatum* husk (pomegranate). Batch adsorption experiments were carried out for different initial concentration of metal ions, dose of adsorbent, pH, contact time and temperature.

EXPERIMENTAL SECTION

Metal salt used was of analytical reagent grade (Merk). Doubly distilled demineralized water was used for the preparation of solutions. Stock solutions of different concentrations (3.0-6.0 mg/L) of Cu (II) were prepared by dissolving accurate amount of metal salt in water. Weighing of solid salt was done on electronic balance (Model No.-CA-123, 0.001g, Contech Instruments Ltd.).

Punica granatum L. husk was collected and exposed to sunlight. It was then grounded, sieved to pass through 100-mesh screen and again exposed to sunlight and was preserved in airtight bottles with cork. It was dries in hot air oven, (Bio Techniques India, Model No.-BTI-30).

Batch adsorption method [18] was employed for the study of adsorption of Cu (II) onto adsorbent. The adsorbent was weighed and placed in each conical flask. The flasks were corked and placed for desired time. After attainment of the adsorption equilibrium the mixtures were filtered using Whatman No. 40 filter paper and filtrates were analyzed for equilibrium metal ion concentration. The pH of filtrates was measured and filtrates were preserved in airtight glass bottles. The changes in absorbance of metal ions before and after adsorption were measured. Initial and equilibrium concentration of Cu (II) was determined by using UV-VIS spectrophotometer. The pH of solution was maintained by adding required amounts of hydrochloric acid and sodium hydroxide stock solutions [19]. ELICO-L1-10 pH meter, precalibrated with 4.0 and 9.2 buffer solutions was used for measurement of pH of the solutions. Adsorption studies were carried for different initial concentration of metal ions, dose of adsorbent, pH and contact time in order to get the maximum adsorption.

RESULTS AND DISCUSSION

Table 1 represents initial and equilibrium concentration of metal ion and percent metal ion removal for different experimental conditions.

Percent adsorption of metal was determined by following equation [20-21]:

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

Where;

C_o =initial concentration of metal solution.

C_e=equilibrium concentration of metal solution.

Effect of initial concentration of metal ion

The batch adsorption experiment was carried out for different initial concentration of metal ions. The experimental data for dependence of percent of metal ion removal on initial concentration of metal ions is represented in Figure 1a. Percent removal was found to be maximum for low initial concentrations of metal ions (3 mg/L). It is 83.33 % for 3 mg/L metal concentration. For low initial concentrations of metal ions nearly all the metal ions get adsorbed due to availability of active adsorption sites. As the metal concentration increases active sites get occupied and hence the less adsorption [22].

Effect of dose of adsorbent

A variation in the percent of metal ion removal with dose of the adsorbent is shown in Figure 1b. The adsorption increased with increase in dose of the adsorbent from 0.1 to 0.3 g which is due to the increase in the surface area and hence available adsorption sites [23]. Then, it remained constant from 0.3 to 0.5 g. Therefore; 0.3 g dose was used throughout.

Table 1. Equilibrium concentration of Cu (II) ion and percent metal ion removal for different experimental conditions

C_0	C_e	$(C_o-C_e/C_o) \times 100$	t	C_e	$(C_o-C_e/C_o) \times 100$
3.0	0.50	83.33	60	0.80	73.33
3.5	0.60	82.86	150	0.70	76.67
4.0	0.80	80.00	240	0.70	76.67
4.5	1.30	71.11	**T**	**C_e**	**$(C_o-C_e/C_o) \times 100$**
5.0	1.50	70.00	303.15	0.50	83.33
5.5	1.70	69.09	313.15	0.40	86.67
6.0	2.10	65.00	323.15	0.20	93.33
pH	**C_e**	**$(C_o-C_e/C_o) \times 100$**	**m**	**C_e**	**$(C_o-C_e/C_o) \times 100$**
4.0	2.32	22.67	0.1	1.90	36.67
5.0	1.65	45.00	0.2	0.80	73.33
6.0	0.80	73.33	0.3	0.60	80.00
7.0	0.90	70.00	0.4	0.60	80.00
8.0	1.30	56.67	0.5	0.60	80.00

Foot note: *C_0 and C_e are in mg/L; m in g; t in min.; T in K.*

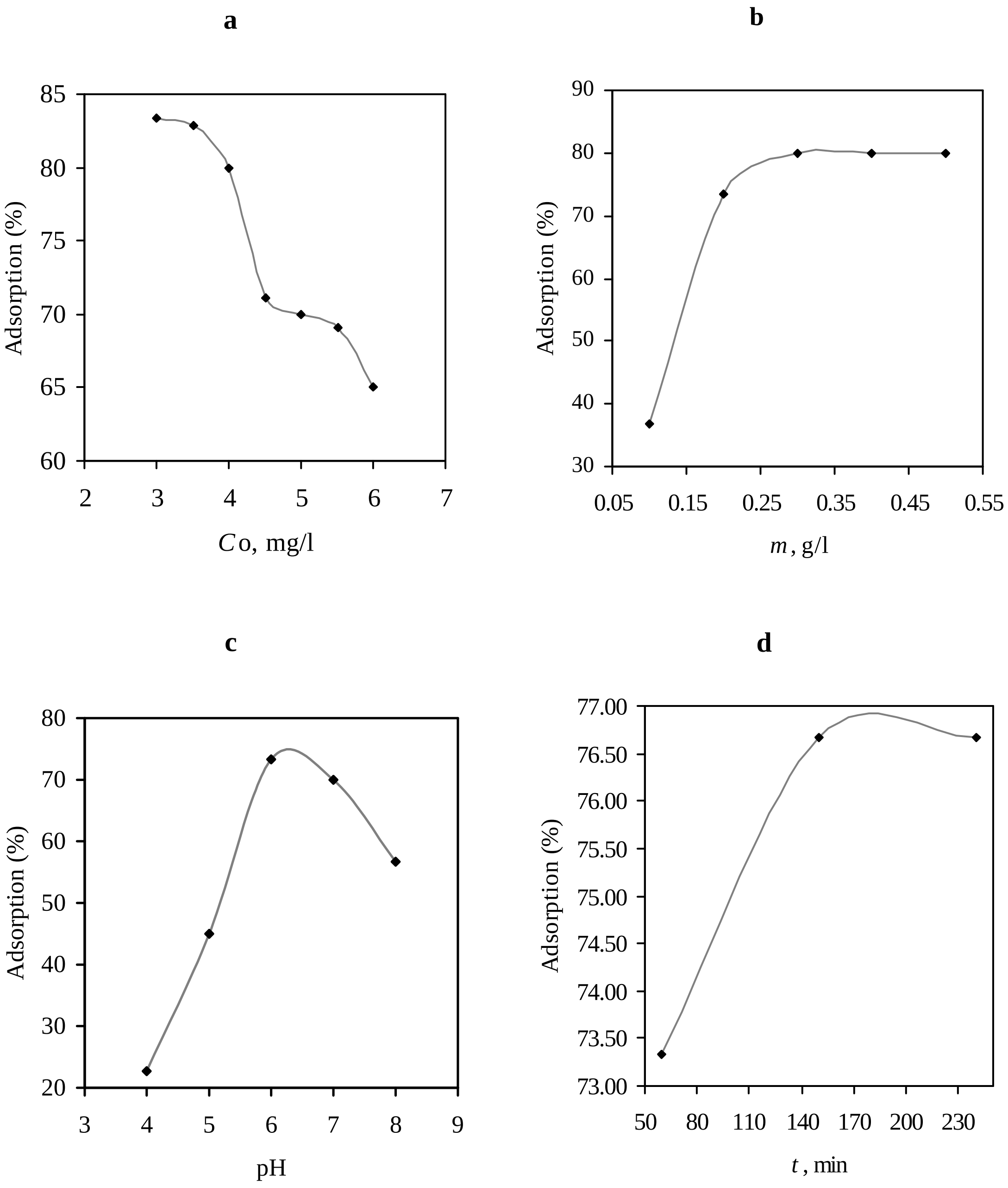
Effect of pH of solution

The pH affects solubility of metal and concentration of other ions present in functional groups of the adsorbent. It has significant effect on adsorption of metal [24]. The adsorption studies were carried out for selected pH values of the medium and results are presented in Figure 1c. It can be seen that adsorption increased with pH till pH 6 and then decreased which is due to the competition between OH^- and M^{n+} for adsorption [25].

Effect of contact time between adsorbate and adsorbent

Figure 1d represents experimental observations of effect of contact time between adsorbate and adsorbent on percent of metal removal. Maximum adsorption occurred at 150 min.

Figure 1. Graphical representation of percent metal ion removal with a) initial concentration of metal ion; b) dose of the adsorbent; c) pH of solution and d) contact time between adsorbate and adsorbent



Effect of temperature

It can be seen from Table 1 that percent Cu (II) metal ion removal increased with rise in the temperature. This indicates that the process is thermodynamically endothermic [21]. This is also graphically shown in Figure 2.

Figure 2. Graphical representation of percent metal ion removal with temperature

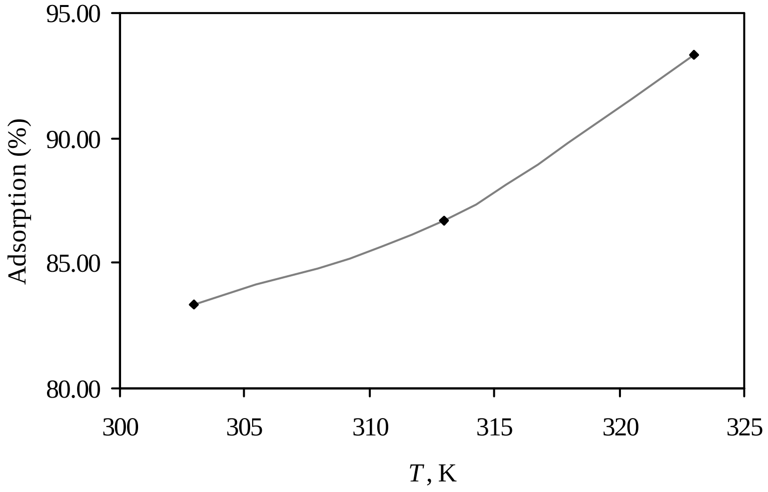
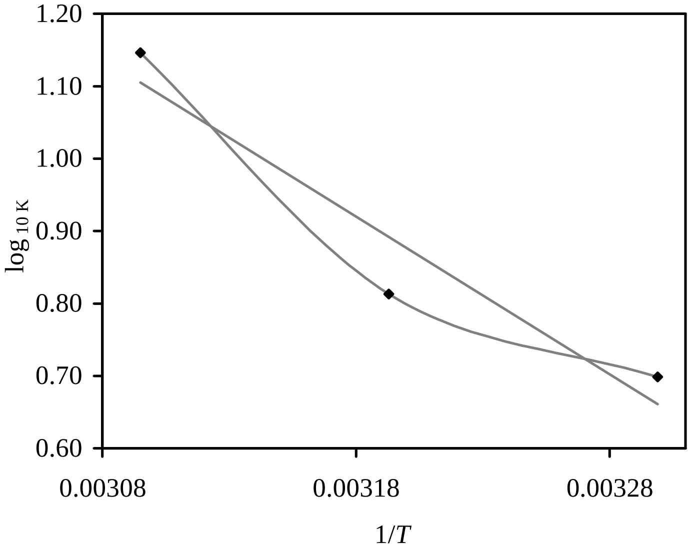


Figure 3. Plot of log *K* versus 1/*T* for the estimation of thermodynamic functions



The equilibrium constant of adsorption process was calculated from equation (2) and other thermodynamic functions such as free energy change (ΔG^0), entropy change (ΔS^0) and enthalpy change (ΔH^0) for adsorption process are estimated from equations (3 and 4) [26-27].

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

$$\Delta G^0 = -2.303RT\log_{10} K\text{.......(3)}$$

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

Where;
K= equilibrium constant.
C_{solid} = solid phase concentration (mg/L) of metal ion at equilibrium.
C_{liquid}= liquid phase concentration (mg/L) of metal ion at equilibrium.
R= gas constant (8.314 J/mol K).
T= temperature (K).

ΔS^0 and ΔH^0 were determined form the plot of log K versus 1/T (equation 4; Figure 3) as:

ΔS= intercept × 2.303R

ΔH= -slope × 2.303R.

Values of log K and other thermodynamic functions are reported in Table 2.

Table 2. Thermodynamic functions such as free energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) change for adsorption of Cu (II) metal ions

T	log K	ΔG^0(kJ/mol)	ΔH^0(kJ/mol)	ΔS^0(kJ/mol)
303.15	0.6990	-4.057	41.67	0.15
313.15	0.8129	-4.718		
323.15	1.1461	-6.653		

Spontaneity of process can be recognized from the negative values of free energy change for all temperatures [26] and process become more favorable as temperature rises. Positive enthalpy change indicates endothermic nature of the process. Entropy change is very negligible which suggests very little or no structural changes at adsorption sited.

CONCLUSION

Punica granatum L. husk proved to be effective adsorptive material for Cu (II) metal ions. Adsorption of Cu (II) onto *Punica granatum L.* husk is found to depend on initial concentration of metal ions, dose of adsorbent, pH, contact time, and temperature. Maximum adsorption was occurred for 3 mg/L initial metal ion concentration, 0.3 g dose of the adsorbent, pH 6, and 150 min. contact time and, 323.15 K temperature. From temperature dependence of adsorption the process is found to be endothermic and spontaneous at elevated temperatures.

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