Turkish Journal of Chemistry

Volume 23 | Number 2 Article 10

1-1-1999

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Recommended Citation

TEKER, MURAT; İMAMOĞLU, MUSTAFA; and SALTABAŞ, ÖMER (1999) "Adsorption of Copper and Cadmium Ions by Activated Carbon From Rice Hulls," *Turkish Journal of Chemistry*: Vol. 23: No. 2, Article 10. Available at: https://journals.tubitak.gov.tr/chem/vol23/iss2/10

Turk J Chem
23 (1999) , 185 – 191.

Adsorption of Copper and Cadmium Ions by Activated Carbon From Rice Hulls

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Received 05.01.1998

The removal of copper (II) and cadmium (II) ions from aqueous solutions, by adsorption on activated carbon prepared from rice hulls (ACRH), was investigated depending on pH, activated carbon dosage, contact time, initial metal concentration and solution temperature. The optimum values of pH, ACRH dosage and contact time were determined to be 5-8, 0.5 g ACRH/25 mL solution an 60 minutes respctively for the adsorption of Cu (II) ions and 5-8, 1.5 g ACRH/25 mL solution and 60 minutes for the adsorption of Cd (II) ions. From the initial concentrations, the constants for the Freundlich and Langmuir isotherm were calculated at 293 K and 313 K. The adsorption of Cu (II) and Cd (II) ions from aqueous solutions was found to be exothermic [$\Delta H°$=-13.474 KJ/mol for Cu (II) and $\Delta H°$=-2.302 KJ/mol for Cd (II)]. Furthermore, the other thermodynamic data for $\Delta G°$ and $\Delta S°$, were also calculated at 293 K and 313 K.

Key words: Adsorption, heavy metal, activated carbon, rice hulls.

Nomenclature

C = concentrate of absorbate ions at equilibrium
$\Delta G°$ = Gibbs free energy of adsorption (kJ/mol)
$\Delta H°$ = enthalpy f adsorption (kJ/mol)
k and n = Freundlich isotherm coefficient
K = equilibrium constant (L/mol)
m = the amount of adsorbent (g)
r = correlation coefficient
$\Delta S°$ = entropy of adsorption (kJ/mol)
x = the amount of absorbate ions (mg)
x_m = the adsorption maxima (mol/g)

Introduction

The presence of heavy metals in the environment is a major concern due to their toxicity for many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into hamless end products. Therefore, the elimination of heavy metals from water and waste water is important to protect pblic health. Thus, treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume followed by recovery or secure disposal.

Removall of heavy metal pollutants at hih concentrations from water can be readily accomplished by chemical precipitation or electrochemical methods. At low concentrations, removal of such pollutants is more effective by ion-exchange or adsorption on solid sorbents such as activated carbon[1,2], activated carbon from rice hulls[3] and coal fly ash[4,5]. Some inestigators have studied the removal of inorganic metal ions, namely, cadmium (II)[6,9] and copper (II)[10−12]. The activated carbon from rice hulls has been used for separation of air by adsorption[13].

In this study, ACRH which is a solid waste matter was used as an adsorbent for the removal of copper (II) and cadmium (II) ions from water. The aim was to investigate the optimum conditions of metal uptake and to calculate the adsorption capacity and some thermodynamic constants at two different temperatures.

Experimental

Apparatus and Chemicals

A Varian Spectra AA-20 flame atomic absorption spectrometer was used for the determination of copper and cadmium. An air-acetylene flame was used for these elements. A Schott-Gerate CG-840 model pH meter equipped with a combination pH electrode was used to measure the pH of all solutions. All the chemicals were of analytical-reagent grade. Standard stock solutions of mentioned elements were prepared from Titrisol concentrates (Merck). Reference solutions were prepared as required by further dilution with distilled water.

Preparation of Activated Carbon from Rice Hulls (ACRH)

The rice hulls were obtained from Lider Çeltik Factory, İstanbul, Turkey. A 500 mL $ZnCl_2$ solution containing 1.100 g $ZnCl_2$ per 100 mL of water was prepared. 50 g rice hulls was exposed to this solution for 24 hours. At the end of this time, the solution was filtered and dried. The rice hulls were activated in a closed ceramic vessel under N_2 atmosphere at 1023 K for 2-3 hours. The ACRH was boiled in solution of HCI which is diluted with water in the ration of one third and filtered again. After filtration through the filter paper, ACRH was washed with tap water first, then distilled water and dried at 105 °C[14].

The surface area of ACRH was determined to be 319 m^2/g by BET methods using N_2 gas adsorption. The composition of the ACRH determined by the standard methods[15] is given as moisture 11.85 %, loss on ignition 59.42 % SiO_2 25.35 %, $ZnCl_2$ 0.63 % and other oxides 2.75 %.

Adsorption Experiments

Batch adsorption experiments were carried out in which aliquots of 25 mL of Cu (II) and Cd (II) solutions of known concentration were poured into beaker glasses (100 mL) containing accurately weighed amounts of the adsorbents. The ACRH weight ranged from 0.3 to 1.0 g per 25 mL of solutions. The beaker glasses were shaken at 200 rpm using an electric shaker for a prescribed length of time to attain equilibrium at 293

K and 313 K separately. The adsorbent was then removed by filtration. After filtration through the filter paper the solution were analyzed for residual metal content by AAS.

Adsorption Model

To quantify the adsorption capacity of ACRH for removal of Cu (II) and Cd (II) from aqueous solutions, the Freundlich equation[16] in the form,

$$log\frac{x}{m} = logk + \frac{1}{n}log$$

and the rearranged Langmuir equation[17] in the form,

$$\frac{C}{x/m} = \frac{1}{K.X_m} + \frac{C}{X_m}$$

were applied where K was the assumed equilibrium constant or bonding energy[18]. Langmuir and Freundlich isotherms were obtained from the experiments at 293 K and 313 K.

Results and Discussion

The effect of pH on the adsorption process is presented in Fig. 1.

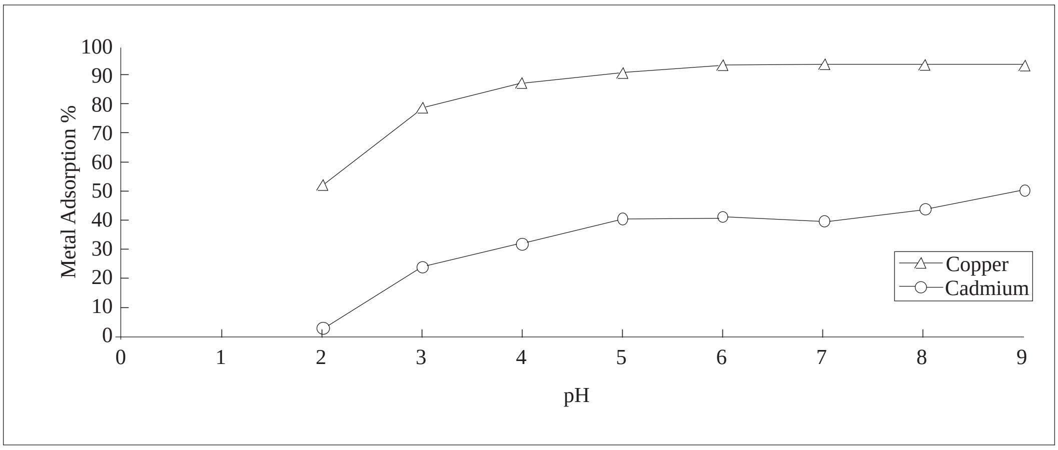

Figure 1. Effect of pH on adsorption of Cu (II) and Cd (II) at 293 K. (15 ppm, 0.3 g AC/25 mL solution, contact time 60 min. for copper and 15 ppm, 0.3 g AC/25 solution, contact time 60 min. for cadmium).

The removal of metal ions from aqueous solution by adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate[11]. As seen in Fig. 1, the adsorption percentage of Cu (II) and Cd (II) almost the same, in the pH range 5-8.

The dependence of adsorptions of Cu (II) and Cd (II) on ACRH dosage is given in Fig. 2.

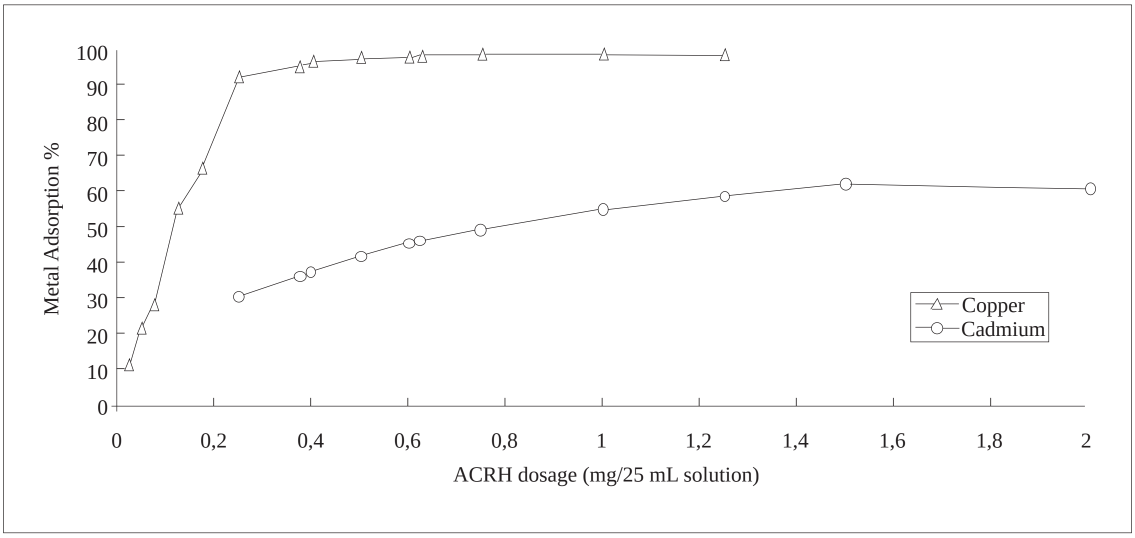

Figure 2. Effect of ARCH dosage on adsorption of Cu (II) and Cd (II) at 293 K (15 ppm, pH of 5.30, contact time 60 min. for Cu (II) and 15 ppm, pH of 6.90, contact time 80 min. for Cd (II)].

Figure 2 indicates that the adsorption increased with increasing ACRH dosage up to a certain value and then there was no further increase in adsorption for either metal ions. Therefore, the optimum ACRH dosages were selected as 0.5 g/25 mL for copper and 1.5 g/25 mL for cadmium.

The effect of the contact time on the adsorption of copper and cadmium are shown in Fig. 3.

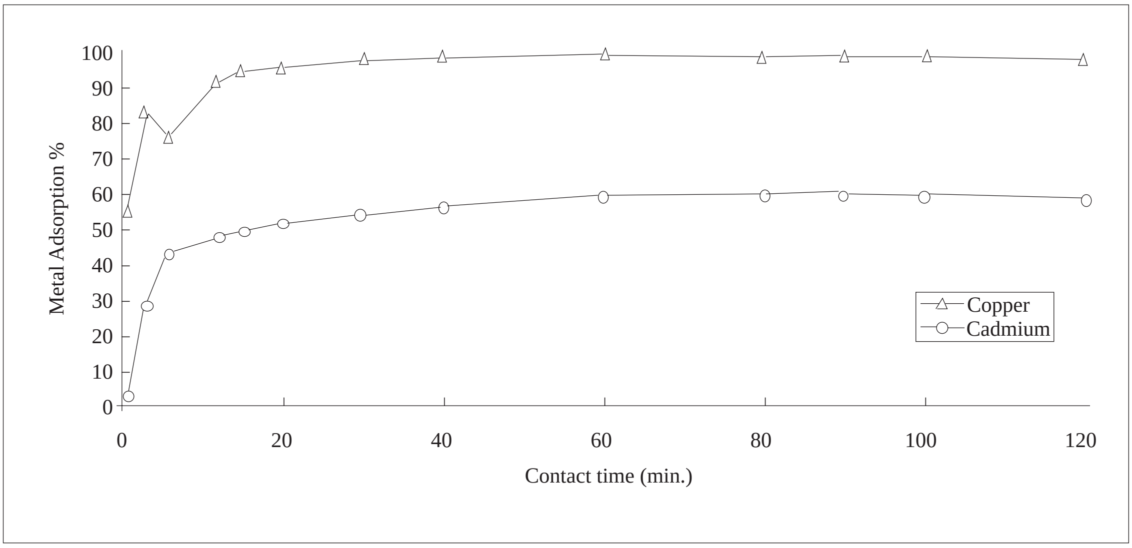

Figure 3. Effect of contact time on adsorption of Cu (II) and Cd (II) at 293 K. (15 ppm, pH of 5.30, dosage 0.5 g/25 mL for copper and 15 ppm, pH of 6.90, dosage 1.0 g/25 mL for cadmium).

The equilibrium was attained after shaking for 60 min. for Cu (II) and 80 min. for cd (II). Therefore in each experiment the shaking period was selected as 60 min. for copper and 80 min. for cadmium. As seen in Figure 3, Cu (II) exhibited a greater affinity than Cd (II).

The effect of intial concentration and temperature on adsorption for copper and cadmium ions are given in Figures 4 and 5.

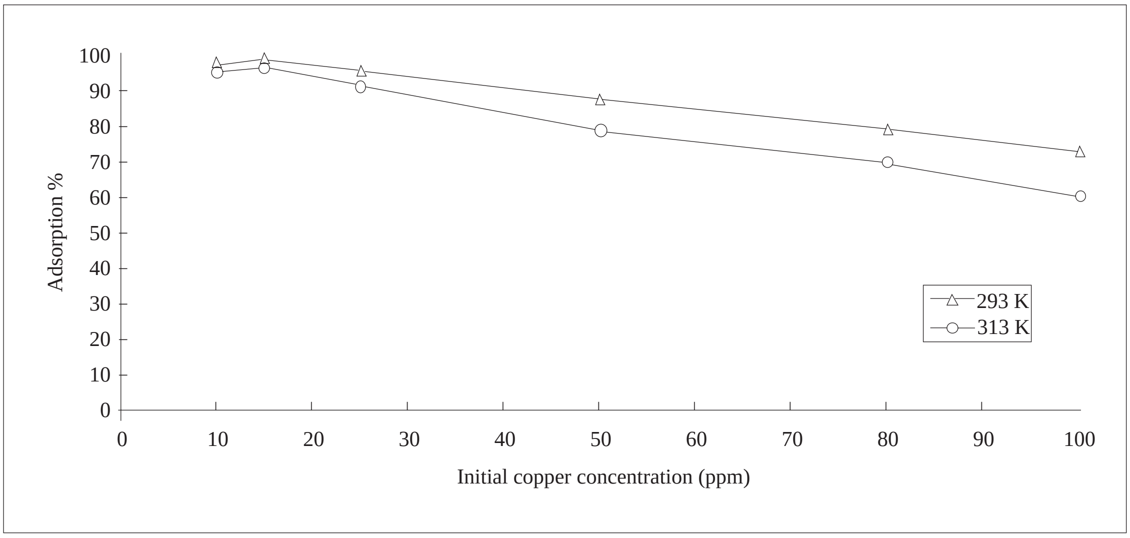

Figure 4. Effect of initial concentration and temperature on Cu (II) adsorption. (pH= 5.30, ACRH dosage 0.5 g/25 mL solution, and contact time 60 min).

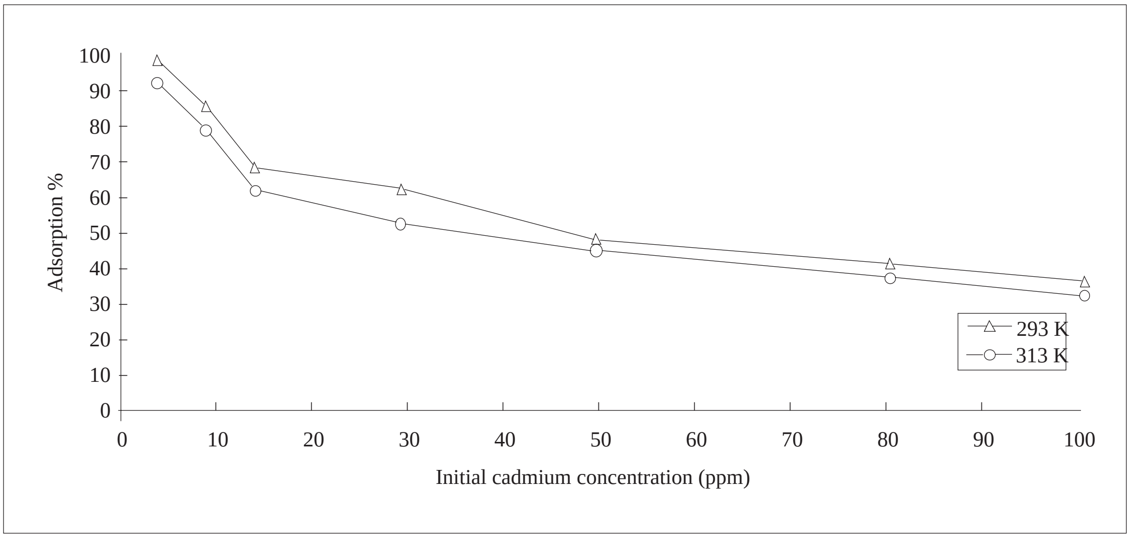

Figure 5. Effect of initial concentration and temperature on Cd (II) adsorption. (pH= 6.90, ACRH dosage 1 g/25 mL solution, and contact time 80 min).

As seen in Figures 4 and 5, the adsorption of Cu (II) and Cd (II) on ACRH decreased from 98.00 % and 77.62 % to 48.33 % and 19.36 % by increasing the Cu (II) and Cd (II) concentrations from 5 ppm to 100 ppm respectively. These results show that the removal of copper and cadmium are highly concentration dependent.

The adsorption data obtained with the adsorbent correlates well with the Freundlich and Langmuir adsorption models. Freundich constants calculated from the adsorption data are given in Table 1. The values of k decreased as temperatures increased, indicating that adsorption decreased with increasing temperatures.

Table 1. Values of Freundlich constants for Cu (II) and Cd (II) ions.

Metal ion	k		1/n		r(corr.coeff.)	
	313 K	293 K	313 K	293 K	313 K	293 K
Cu (II)	7.46×10^{-1}	9.77×10^{-1}	0.3986	0.4116	0.985	0.978
Cd (II)	7.57×10^{-2}	8.94×10^{-2}	0.4931	0.4783	0.996	0.995

Langmuir constants and thermodynamic parameters calculated from the adsorption data are shown in Table 2. Standard molar or Gibbs free energy for the process is calculated as $\Delta G°$=-RTlnK and the standard enthalpy change is calculated from the values of K at 293 K and 313 K respectively.

$$ln\frac{K_1}{K_2} = \frac{-\Delta H^0}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

K_1 and K_2 the respective constants at these temperatures are derived from Langmuir plots. Standard entropy change $\Delta S°$ for the process was calculated from the equation $\Delta G° = \Delta H° - T\Delta S°$.

Table 2. Values of Langmuir and thermodynamic parameters for Cu (II) and Cd (II) ions.

Metal ion	Adsorption Maxima X_m(mol g^{-1}		K values related to equilib. constant (L mol^{-1})		$\Delta G°$ (kJ mol^{-1})		Mean $\Delta H°$ (kJ mol^{-1})	Mean $\Delta S°$ (kJ mol^{-1})
	313 K	293 K	313 K	293 K	313 K	293 K		
Cu (II)	5.10×10^{-5}	6.14×10^{-5}	1.59×10^{4}	2.14×10^{4}	25.17	24.29	-11.45	0.1438
Cd (II)	6.76×10^{-6}	7.47×10^{-6}	5.96×10^{3}	6.26×10^{3}	22.62	21.29	-1.85	0.0664

The adsorption capacity (X_m) of ACRH for the uptakes of Cu (II) and Cd (II) decreased from 6.14×10^{-5} and 7.47×10^{-6} to 5.10×10^{-5} and 6.76×10^{-6} with increasing temperature from 293 to 313 K indicating that the process is exotermic (Table 2). The negative Gibbs free energy values indicate the feasibility of the process and the spontaneous nature of adsorption, the order of preference being Cu (II) $>$ Cd (II) (on the basis of x_m values at 293 K). The amount of adsorption decreased with temperature and the negative $\Delta H°$ values indicate the exothermic nature of the process.

A positive entropy of adsorption also reflects the affinity of adsorbent material for Cu (II) and Cd (II) ions under consideration.

Conclusions

Rice hulls, which are a waste substance, were converted into a carbonaceous adsorbent material. This product exhibits very good adsorption for copper and cadmium from aqueous solution. Adsorption of copper and cadmium by ACRH was shown to depend significantly on the pH, ACRH dosage, contact time and initial metal ions concentration.

The data thus obtained will be helpful in the design and performance of a fixed-bed adsorber.

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