

STUDY OF CADMIUM ADSORPTION FROM AQUEOUS SOLUTION ON ACTIVATED CARBON FROM SUGAR BEET PULP

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ABSTRACT

The adsorption ability of activated carbons from sugar beet pulp to remove the cadmium from aqueous solutions has been investigated. Optimum temperature and time for carbonization of sugar beet pulp were determined as 700 °C and 120 min. The results of adsorption experiments show that pH for effective removal of cadmium was 6.3 or greater. The maximum removal percentage of cadmium were found to be 99.0, 78.2 and 57.0 by using 2.5 g l⁻¹ adsorbent dosage for initial cadmium concentration of 100, 250 and 500 mg l⁻¹, respectively, at optimum pH and 20 °C for a contact time of 120 min. Langmuir and Freundlich adsorption models were applied to the isotherm data. The free energy change of process was found to be -18.03 KJ mol⁻¹.

Key words: Cadmium removal, sugar beet pulp, carbonization, adsorption, adsorption isotherm.

INTRODUCTION

Toxic metals in the environment are harmful to humans and other organisms in small quantities. Since toxic metals do not degrade into harmless end-products, they are accumulated in the food chain, thereby posing the greatest danger to organisms [1]. Cadmium is one of the toxic metals and has received a great deal of attention. It is primarily present in wastewaters from metallurgical alloying, ceramics, metal plating, photography, pigment works, textile printing industries and lead mine drainage [2] and sewage sludge [3]. The removal methods of cadmium from wastewaters with high cadmium concentration include its precipitation as hydroxide [2,4] and carbonate [5]. In recent years, adsorption techniques have been investigated for the removal of cadmium from wastewaters. Adsorbents used in the cadmium adsorption process are activated carbon obtained from some agricultural by-products [6], commercial activated carbons [7,8] and bituminous coal [9]. Some various cellulosic materials such as coconut shell and raw rice husk [9], water hyacinth [10], nut and walnut shells, and waste tea [11] have also been used. Activated carbon adsorption appears to be a particularly competitive and effective process for the removal of cadmium and other toxic metals at trace quantities.

Active carbon used in this study was prepared by carbonizing sugar beet pulp in a constant flow rate of carbon

dioxide at different temperatures and times. After characteristics of the samples were determined, the influences of carbonization temperature and time, and adsorption parameters such as contact time, pH and temperature of solution, initial concentration of cadmium and dosage of activated carbon were investigated on the adsorption of cadmium from aqueous solution.

MATERIALS AND METHODS

Material

Sugar beet pulp used in preparation of activated carbons was provided from sugar plant located in Elazig Turkey. The sugar beet pulp was dried to obtain minimum humidity and stored in polyethylene bags until use. The activation process was carried out by heating 50 g portions of dried pulp at temperatures ranging from 350-750 °C in a constant flow rate of carbon dioxide (1.5 l min⁻¹) for different periods of time (15-120 min). Activated carbon samples so obtained have been denominated as A-time-temperature, e.g. A-120-700, where the letter A represents activated carbon samples, time and temperature are carbonization time (min) and temperature (°C), respectively. The activated carbons were ground and sieved to obtain -200 mesh fraction. The fraction was stored in a CaCl₂ desiccator until use in

adsorption experiments.

The ash content of these samples were determined by incinerating them in air at 600 °C. The pH values of aqueous suspensions of activated carbons were measured using pH meter (Mettler Delta 350 model) after 1 g portions of carbon were shaken mechanically with 20 ml of carbon dioxide-free distilled water for 48 hours at 25 °C [12].

To determine the iodine number (IN) of activated carbons, 0.5 g of each samples was added to 100 ml aqueous solution of iodine (2.7 g I₂ l⁻¹) and shaken at 25 °C [13]. After shaking for a period of 45 min, the suspension was filtered and the concentration of residual iodine was determined by titrating the supernatant with 0.1 N sodium thiosulphate solution. The gram amount of iodine adsorbed per gram carbon was taken as the iodine number.

Preparation of solutions

A stock solution of cadmium (1000 mg l⁻¹) was prepared by dissolving Cd(NO₃)₂·4H₂O (analytical grade) in distilled water. All working solutions were prepared by diluting stock solution with distilled water. Other reagents used in this work were of analytical grade. The pH of solutions was adjusted with either sodium hydroxide or nitric acid.

Adsorption experiments

Adsorption experiments were carried out using a continuously mixed batch system. To do this, various amounts of cadmium solution was added to a 100 ml glass bottle and diluted with distilled water and sodium hydroxide (0.01 M) or nitric acid solution (0.01 M) to obtain cadmium concentrations ranging from 200 to 700 mg l⁻¹ and initial pHs varying from 1.5 to 7.0. These solutions were transferred to

the flasks (150 ml) containing a certain amount of activated carbon (0.1-0.6 g) and the pH of mixtures were measured. The flasks were shaken at a constant rate (500 cycle min⁻¹) using a flask shaker (Stuart Scientific, SF1 model) in a temperature controlled water bath for predetermined contact time. At the end of required reaction period, the final pH values of suspensions were recorded and solutions were separated by filtration. Cadmium concentrations in the supernatants were analysed by atomic absorption spectrophotometry (Perkin Elmer, 370 model). The uptake of cadmium was calculated by the difference in their initial and final concentrations.

RESULTS AND DISCUSSION

Characterization of active carbons

Some characteristics of the active carbons are listed in Table 1. The yield of activated carbon decreases depending on the rise in time and temperature of carbonization process. The ash content of activated carbons is very high, which may be a disadvantage from the point of view of their technical use. In a previous study, the ash content of raw sugar beet pulp has been determined as 3.66 % [14]. The removal of volatile substances decomposed during the carbonization process causes an increase in ash content of carbonized material. The pH values of aqueous suspensions of activated carbons are basic. The presence of these suggests that the activated carbons obtained in this study will be suitable adsorbents for metal ions and other cationic constituents. The basicity of samples increases with time and temperature of carbonization.

The data related to iodine number (IN) of activated carbon obtained at different temperature are presented in Table 2.

Table 1. Some characteristic of activated carbons from sugar beet pulp.

Activated carbon samples	Yield (%)	Ash content (%)	pH of suspension	Activated carbon samples	Yield (%)	Ash content (%)	pH of suspension
A-15-350	38.8	15.5	8.55	A-15-400	33.8	18.2	9.39
A-30-350	38.4	16.2	8.68	A-30-400	33.0	18.6	9.41
A-60-350	38.3	17.5	8.85	A-60-400	32.4	19.0	9.56
A-90-350	37.9	18.3	9.35	A-90-400	31.9	19.4	9.60
A-120-350	35.2	18.6	9.38	A-120-400	30.7	19.8	9.64
A-15-500	29.2	21.4	10.05	A-15-600	26.4	22.3	10.15
A-30-500	28.4	21.5	10.08	A-30-600	25.0	22.7	10.22
A-60-500	27.7	21.8	10.11	A-60-600	24.7	23.0	10.27
A-90-500	27.3	22.1	10.11	A-90-600	23.2	23.8	10.30
A-120-500	27.0	22.1	10.12	A-120-600	22.8	24.2	10.32
A-15-700	22.0	25.2	10.32	A-15-750	20.6	26.4	10.38
A-30-700	21.5	25.4	10.30	A-30-750	19.2	28.3	10.40
A-60-700	21.0	25.4	10.27	A-60-750	18.9	30.4	10.55
A-90-700	21.0	25.3	10.37	A-90-750	18.2	31.4	10.92
A-120-700	20.6	25.8	10.40	A-120-750	16.4	33.2	11.00

Table 2. The variation of iodine number ($\text{mg I}_2 \text{ g}^{-1}$ adsorbent) with carbonization time and temperature.

Carbonization time (min)	Carbonization temperature ($^{\circ}\text{C}$)					
	350	400	450	500	600	750
15	367.5	397.3	374.5	275.3	207.0	219.8
30	386.4	403.1	372.6	274.5	196.8	207.7
60	384.1	406.8	361.0	222.3	191.3	289.6
90	394.2	410.0	337.5	212.0	184.6	324.2
120	399.0	417.2	281.9	191.6	180.4	324.6

It can be seen that the INs do not show a regular change when these values are compared considering their carbonization time and temperature. While the INs of samples obtained at lower temperatures ($350, 400^{\circ}\text{C}$) increase with a rise in carbonization time, those of samples at $450, 500$ and 600°C have a decreasing trend. The INs of samples obtained at the temperature higher than 600°C increase with time of carbonization. The adsorption of iodine molecules by activated carbons may be expressed in two ways; the formation of chemical bonds between iodine molecules and functional groups of sugar beet pulp, and the physical adsorption of these molecules in the pores. At lower temperatures, the formation of chemical bonds is more predominant compared to physical adsorption. At the temperatures of $450, 500$ and 600°C the number and size of opening pores is not sufficient to adsorb the molecules physically. A rise in carbonization temperature leads to a decrease in the amount of functional groups and an increase the size and number of pores, hence, physical adsorption is

predominant at 700 and 750°C .

Cadmium adsorption

The effect of carbonization temperature and time

The effect of carbonization temperature on the removal of cadmium was examined by contacting 0.25 g samples carbonized at different temperature for two hours with 100 ml cadmium solutions of various initial concentrations. The data related to the experiments are illustrated in Figure 1. As expected, the weight loss increased with temperature (Table 1) due to the removal of volatile substance from sugar beet pulp. This situation causes the carbonization products to have a larger surface area and more suitable adsorption site. By increasing carbonization temperature from 350 to 700°C the removal percentage of cadmium increased from $35.0, 20.2$ and 7.9 to $99.0, 78.2$ and 57.0 for initial cadmium concentrations of $100, 250$ and 500 mg l^{-1} respectively.

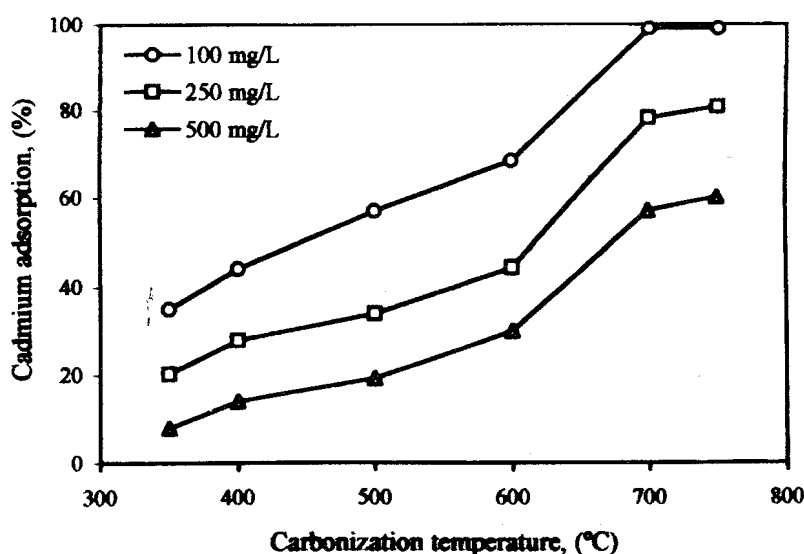


Figure 1. Effect of carbonization temperature on the adsorption of cadmium by activated carbons (Conditions: adsorbent dosage, 2.5 g l^{-1} ; contact time; 120 min , initial pH, 6.3 ; contact temperature 20°C).

However, the removal yields corresponding to 700 and 750 °C do not show a significant differences, because the carbonization of sugar beet is likely to be completed at these temperatures. For that reason, the subsequent experiments were carried out by using the samples carbonized at 700 °C .

To investigate the effect of carbonization time on the removal of cadmium, activated carbons prepared at 700 °C and different periods of time were used. The results obtained are given in Figure 2. The adsorption yield (%) increased with carbonization time. The maximum removal was attained by using activated carbon from sugar beet pulp carbonized for 120 min, therefore, to optimize the other adsorption parameters, activated carbon prepared at these conditions

(A-120-700) was used in subsequent experiments.

Effect of pH

Since the surface charge of an adsorbent can be modified by changing the pH of solution, the pH is one of the most important parameters affecting the adsorption process of ions. In order to know the influence of this parameter on the adsorption of cadmium, the A-120-700 samples were contacted with the cadmium solution pH of which varies from 1.5 to 7.0 for two hours. The results of these experiments are given in Figure 3. As seen, adsorption percentage are very low at strong acidic medium. After pH 4.5, adsorption yields

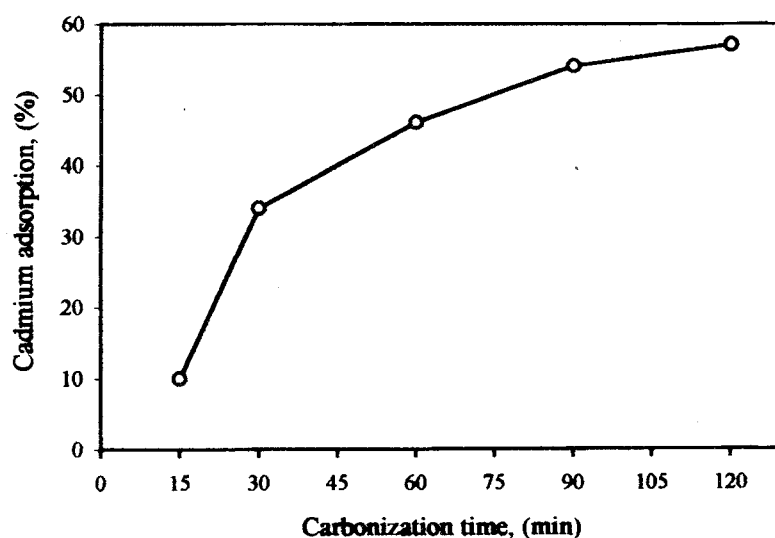


Figure 2. Effect of carbonization time on the adsorption of cadmium by activated carbons (Conditions: Adsorbent dosage: 2.5 g l⁻¹; contact time, 120 min; initial pH, 6.3; contact temperature, 20 °C).

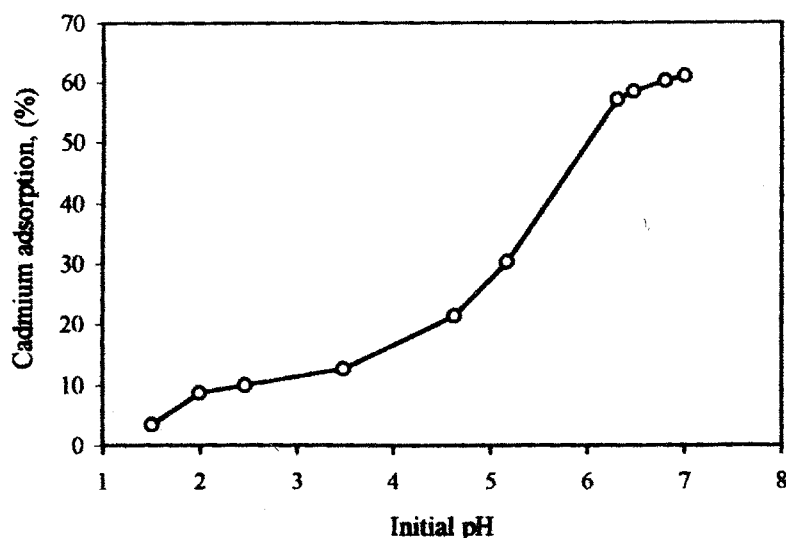
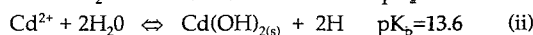
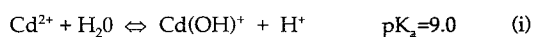


Figure 3. Effect of initial pH on the adsorption of cadmium by activated carbons (Conditions: Activated carbon samples: A-120-700; adsorbent dosage, 2.5 g l⁻¹; contact time, 120 min; contact temperature, 20 °C).

increase sharply up to pH 6.3 and thereafter they stay almost constant for greater pHs. The optimum pH for cadmium adsorption from aqueous solutions by activated carbons from almond shells, olive and peach stone has been reported as 5.0 [6]. In other work carried out by Girdih coal, the optimum pH was 6.6 [9]. These results are in a good agreement with our work. The uptake of cadmium can be explained as an H^+ - Cd^{2+} exchange reaction at pH range mentioned above. It has been pointed out that the cadmium ions may be hydrolyzed in aqueous solution, represented by [7]:



The hydrolysis extent of cadmium ions (initial concentration 500 mg l^{-1}) is unimportant over the pH range examined. But, above pH 8.0, cadmium ions can be precipitated as $Cd(OH)_2$ and the adsorption of ions masked by precipitation. For that reason, cadmium adsorption was not examined at pHs greater than 7.0.

Although all experiments were performed in distilled water, the presence of complexing agents and ionic composition of solution to be treated may affect the uptake of cadmium by adsorption. Since cadmium ions form strong complexes with some ions such as Cl^- and CN^- , its adsorption efficiency may reduce. In the case of real samples, the adsorption parameters must be reoptimized.

Effect of contact time

The percentage of cadmium removed by activated carbon (A-120-700) as a function of time is presented in

Figure 4. The adsorption of cadmium increase with time up to 120 min corresponding to 57.0 % removal. A time of 120 min was selected as a suitable contact time.

Effect of adsorbent dosage

The effect of activated carbon dosage on the removal of cadmium was studied by varying the dosage from 1 to 6 g l^{-1} at pH 6.3 for 120 min. The adsorption densities, q (mg g^{-1}), were plotted versus adsorbent dosages (Figure 5). The adsorption density increased with increasing dosage to a maximum value and then declined with further increase in dosage. 2.5 g activated carbon per liter of solution is a suitable dosage for this process, to give a maximum adsorption density corresponding to 114.0 mg g^{-1} .

Adsorption isotherms

The equilibrium data for the adsorption of cadmium by activated carbon were analyzed using both Langmuir and Freundlich equations. The linearized form of Langmuir and Freundlich equations may be described by the following:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_{\text{ads}}} + \frac{C_e}{q_{\max}} \quad (iii)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (iv)$$

where q_e represents the amount of adsorbate adsorbed at

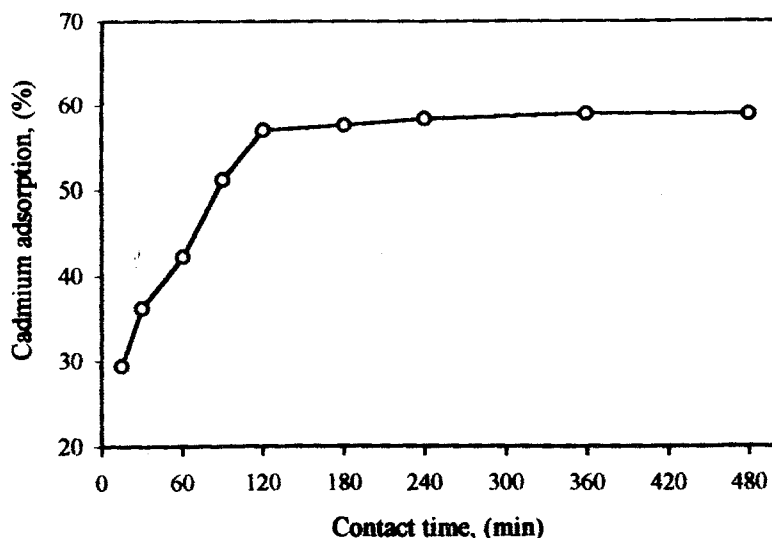


Figure 4. Effect of contact time on the adsorption of cadmium by activated carbons (Conditions: Activated carbon samples: A-120-700, Adsorbent dosage: 2.5 g l^{-1} , Initial pH: 6.3, Contact temperature: 20°C).

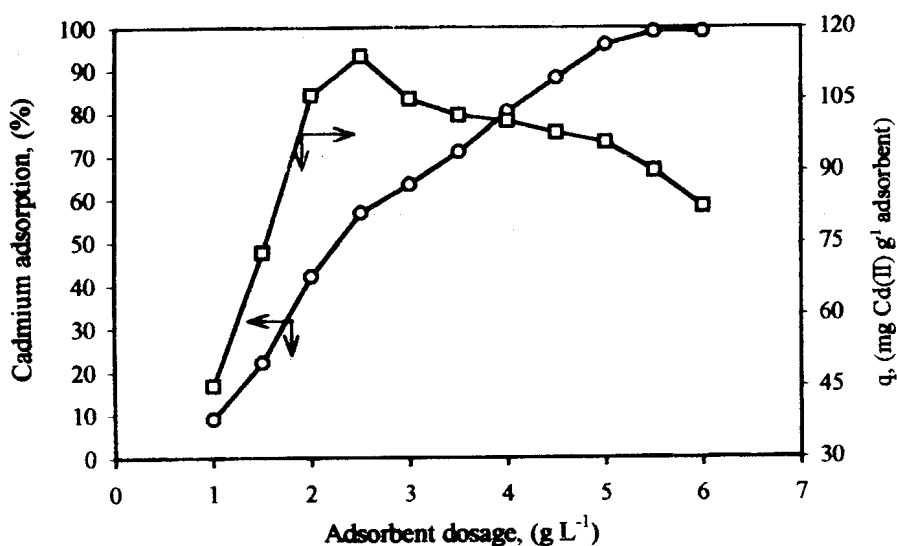


Figure 5. Effect of adsorbent dosage on the adsorption of cadmium by activated carbons (Conditions: Activated carbon samples: A-120-700; contact time, 120 min; initial pH, 6.3; contact temperature, 20°C).

equilibrium (mg g^{-1}), C_e is equilibrium concentration (mg l^{-1}), q_{max} is the maximum surface density or adsorption capacity and has same unit with q_e . K_{ads} (l mg^{-1}), can be related to the equilibrium constant or bonding energy. K_f and n are Freundlich constants. When C_e is plotted versus C_e/q_e , q_{max} is equal to the inverse of slope and K_{ads} is determined from the slope and intercept. The values K_f and n may be calculated from intercept and slope of line obtained by plotting $\ln q_e$ versus $\ln C_e$. The isotherm equations obtained for the process, by correlating equilibrium data for initial cadmium concentration ranging from 200 to 700 mg l^{-1} at pH 6.3 and different temperatures are presented in Table 3. The free energy change ΔG° given in Table 3 was calculated using following equation,

$$\Delta G^\circ = -RT \ln K_{\text{ads}} \quad (\text{v})$$

It can be seen that the adsorption data follow both Langmuir and Freundlich isotherms to a large extent, since the correlation coefficients (r^2) were found to be higher than

0.965. The maximum adsorption capacity of activated carbon (A-120-700) for uptake of cadmium increases from 149.0 to 150.6 mg g^{-1} with rise in temperature from 20 to 40 °C. The increase in values of K_f , which is a measure of adsorption capacity, with a raise of temperature is more outstanding compared to the values of q_{max} . The values of K_f are 19.4 and 35.8 mg g^{-1} , respectively. All these results indicated that the process is endothermic. Knoke and Hemphill [15] have stated that the increase in uptake of adsorbate with temperature may be due to the changes in the size of the pores and enhanced rate of intraparticle diffusion of adsorbate. It has been pointed out that the adsorption capacity will increase with rise in temperature of solution when pore diffusion is the rate-limiting step [16]. In all cases, the values of n calculated from Freundlich equation are higher than 1 and increase with temperature. The situation $n > 1$ is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density [7]. The values of ΔG° calculated at different temperature are negative, which indicates the process is spontaneous.

Table 3. Isotherm equations and free energy change of cadmium adsorption.

Temp. (°C)	Langmuir equation	r^2	Freundlich equation	r^2	$-\Delta G$ (kJ mol^{-1})
20	$C_e/q_e = 0.4593 + 6.71 \times 10^{-3} C_e$	0.991	$\ln q_e = 2.986 + 0.318 \ln C_e$	0.981	18.03
40	$C_e/q_e = 0.2857 + 6.64 \times 10^{-3} C_e$	0.981	$\ln q_e = 3.577 + 0.226 \ln C_e$	0.968	20.47
60	$C_e/q_e = 0.1880 + 6.40 \times 10^{-3} C_e$	0.982	$\ln q_e = 3.870 + 0.189 \ln C_e$	0.965	22.83

The free energy change decreased with rise in temperature, showing that the adsorption effectiveness will increase at higher temperature.

CONCLUSIONS

Based on the present study the following conclusions can be drawn.

The ash content of activated carbons prepared at different conditions varies from 15.5 to 32.2 %. The basicity of aqueous suspensions suggests that the activated carbons from sugar beet pulp are suitable adsorbent for cationic constituents. The most effective activated carbon for

cadmium adsorption was obtained by carbonizing sugar beet pulp at 700 °C for 120 min. The adsorption of cadmium is a function of pH. Maximum removal was achieved at a pH of 6.3 or greater. At pH 6.3, 99.0 % of cadmium was removed from a solution concentration which is 100 mg l⁻¹ by using an adsorbent dosage of 2.5 g l⁻¹. The results indicated that equilibrium in adsorption of cadmium on activated carbon was reached in contact time of 120 min. The data of adsorption equilibrium were applied to Langmuir and Freundlich isotherm equations. Cadmium adsorption capacities of activated carbon increased with rise in temperature, indicating the process to be endothermic. The negative change in free energy shows that adsorption process is spontaneous.

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