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A. Özer , F. Tümen & M. Bildik

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Cr(III) REMOVAL FROM AQUEOUS SOLUTIONS BY DEPECTINATED SUGAR BEET PULP

A. ÖZER*, F. TÜMEN, M. BILDIK

Department of Chemical Engineering, University of Firat, Elazig 23279, TURKEY

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ABSTRACT

We report a study of the removal of Cr(III) from aqueous solutions by depectinated sugar beet pulp (DSBP) carried out at different initial concentration of Cr(III), pH and temperature of solution, particle size and adsorbent dosage. Removal percentage of Cr(III) was found to be 86 for inital concentration of 10 mg L^{-1} at 20 °C and 20 g L^{-1} adsorbent dosage. The optimum pH for the process was found to be 4.5. The process of uptake follows first-order adsorption rate expression and obeys Langmuir and Freundlich's adsorption models. Enthalpy change of adsorption was found to be -27.3 kJ mol^{-1}. Little fraction of Cr(III) was desorbed in strong acidic media.

Keywords: Cr(III) removal, sugar beet pulp, adsorption, thermodynamic parameters, desorption.

INTRODUCTION

In the wastewater treatment, adsorption has become a very important alternative to conventional precipitation of heavy metals. Active carbon is a standard adsorbent for the direct treatment of such micropollutants. Despite the efficiency of active carbon is very high in the removal of heavy metals from wastewaters, the high cost of active carbon has restricted its use and active carbon adsorption process is generally used as a final step in the treatment of heavy metals. Over recent years, this has a growing research interest into the production of low-cost alternatives to activated carbon from a wide range of organic and inorganic metarials. Various adsorbents and their some applications have well documented in an article [1].

Some agricultural wastes or by-products have long been recognized as starting materials for the preparation of active carbon [2-8]. Some of adsorbents to be used have been activated through simple ways without carbonization. Most of them are cellulosic and lignocellulosic in composition [9-14]. Consisting of mostly cellulosic substances, sugar beet pulp is a by-product of sugar industry and being utilized through various purposes, one of which is pectin extraction. It suggests that, after pectin extraction, the remaining pulp may be used as an activated sorption material to remove the heavy metals from wastewater streams. Thus, after recovering two valuable substances, sugar beet may be utilized for a third time. Starting with this idea, in this study, the adsorption of Cr(III) ions from aqueous solutions by depectinated sugar beet pulp (DSBP) was investigated.

MATERIALS AND METHODS

Material

Sugar beet pulp obtained from Sugar Plant, Elazig (TURKEY), was dried at 80 °C for 24 hours and then ground. The powdered material was passed through 50 mesh sieve and its pectin was extracted by means of HCl extraction [15]. After pectin extraction, the mixture was filtered by suction. Since pectin extraction was carried out in acidic media, the residual pulp was washed with distilled water (approximately 1 ml water per gram pulp) in order to remove excess acid. Depectinated sugar beet pulp (DSBP) was dried at 80 °C for 24 hours, ground and sieved to obtain -50 mesh fraction. The fraction was used in all adsorption experiments except that in the experiments where the effect of particle size was investigated.

Preparation of solutions

All reagents used were of analytical grade. Stock solutions of Cr(III) (1000 mg L^{-1}) was prepared by dissolving $Cr(NO_3)_3.9H_2O$ in distilled water. All working solutions were prepared by diluting the stock solution with distilled water.

Experiments

Batch adsorption experiments were carried out by shaking 1.0 g of depectinated sugar beet pulp with 50 ml of Cr(III) solutions in required concentration in the 100 ml flask. Immediately after the addition of DSBP, initial pH of solutions were adjusted with NaOH and HCl solutions using pH meter. The ionic strength of the solution was kept constant by addition of $NaClO_4$ (0.01 M). The mixtures were shaken (1100-1200 cycle min^{-1}) at required temperature and contact time in a temperature controlled-water bath. Stuart Scientific (SF1 model) flask shaker was used for shaking.

The effect of adsorbent dosage was performed on initial Cr(III) concentration of 10 mg L^{-1} and the adsorbent dosage were varied from 20 to 80 g L^{-1} for a contact time of 1 hour.

The adsorption isotherm studies were carried out by varying the initial Cr(III) concentration from 5 up to 30 mg L^{-1}.

Desorption studies were conducted by shaking 1.0 g of pregnant adsorbent containing 0.430 mg chromium with 50 ml distilled water at 20 °C and different pH.

In adsorption and desorption experiments, at the end of predetermined contact period, the reaction mixtures were centrifuged at 10,000 rpm for 10 min. Supernatants were analysed by Atomic Absorption Spectrometer (Perkin Elmer 370 Model) for chromium [16].

RESULTS AND DISCUSSION

Effect of pH

Figure 1 shows that the pH of solution is the most important parameter in the removal of Cr(III) ions by DSBP. As seen, the removal of Cr(III) ions increases with increasing pH to a maximum value and then declines with further increase in pH. Cr(III) ions are effectively removed at pH range 3.0-6.0. Since predominant species of Cr(III) is $Cr(OH)^{2+}$ at this pH interval, it can be stated that the adsorption of Cr(III) is governed by $Cr(OH)^{2+}$ species [17]. At pH 4.5, the Cr(III) removal is attained to a maximum which corresponds to 86 % yield. For that reason, subsequent experiments were carried out at this pH.

Huang and Wu [17] have reported that maximum removal occured within pH range from 2.8 to 6.0 in adsorption of Cr(III) ions onto activated carbon, a result which is in good agreement with our work.

Cr(III) ions tend to form precipitate at pHs higher than 5.0 [18], and therefore it is expected that Cr(III) adsorption can be masked by precipitation. However the large amount of Cr(III) ions remained in solution at the alkaline pH. This is probably due to amphoteric character of Cr(III) ions and complex compounds which may be formed in the reaction taking place between Cr(III) ions and organic substances leached out from DSBP during the adsorption process.

Effect of contact time and concentration

The effect of contact time was examined by treating 1 g DSBP with 50 ml Cr(III) solution at various initial concentrations. The results obtained are presented in Figure 2. It appears that a larger amount of Cr(III) ions are removed by DSBP in the first 5 min of contact time. At the end of contact time of 60 min the Cr(III) removal becomes nearly constant. At this point, the surface of adsorbent is saturated with Cr(III) ions, and thereafter the adsorption of chromium remains almost unchanged.

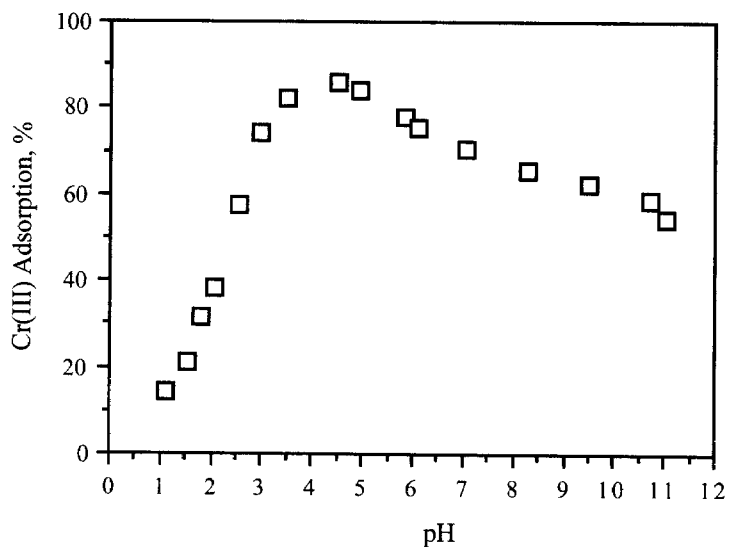

Figure 1. Effect of pH on Cr(III) adsorption by DSBP (Conditions: 50 ml 10 mg L^{-1} Cr(III) solution; contact time 60 min.; temperature 20 °C; 1 g DSBP; 0.01 M $NaClO_4$).

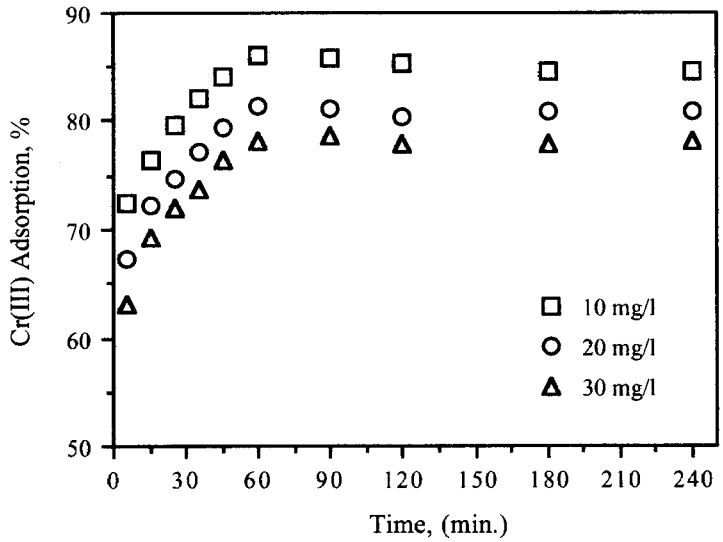

Figure 2. Effect of contact time on Cr(III) adsorption by DSBP at various initial concentrations (Conditions: pH 4.5; temperature 20 °C; 1 g DSBP; 0.01 M $NaClO_4$).

With the change in initial concentration of Cr(III) solution from 10 to 30 mg L^{-1}, the removal percentage of chromium decreases from 86 to 78 at 20 °C. At the lower initial concentration, the removal percentage of Cr(III) ions is higher, but the amount of chromium adsorbed per gram DSBP is lower in comparison with that of high initial concentration.

Effect of adsorbent dosage and particle size

The effect of adsorbent dosage on the removal of Cr(III) ions was studied for an initial concentration of 10 mg L^{-1} Cr(III) at pH 4.5. The results are shown in Figure 3. In all cases the removal efficiency of Cr(III) ions increases with increasing dosage of DSBP, but adsorption density decreases.

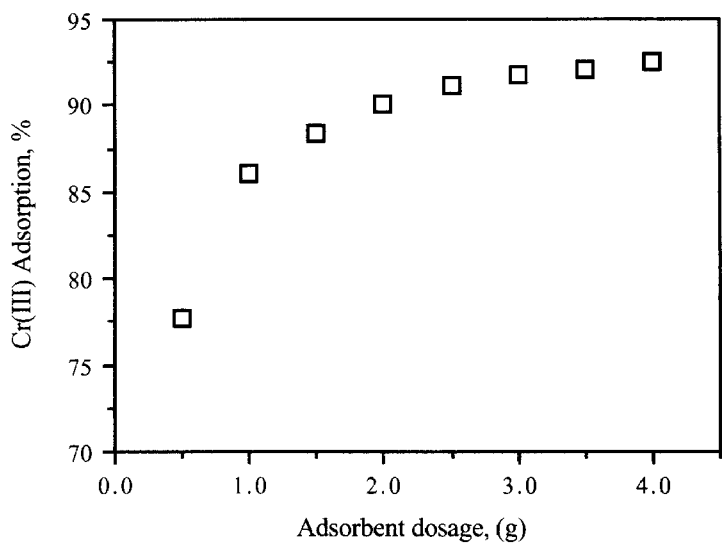

Figure 3. Effect of adsorbent dosage on Cr(III) adsorption by DSBP (Conditions: 50 ml 10 mg L^{-1} Cr(III) solution; contact time 60 min.; pH 4.5; temperature 20 °C; 0.01 M $NaClO_4$).

For example, by increasing the dosage from 20 to 80 g L^{-1}, the removal efficiency of Cr(III) was increased from 86 to 93 %, but adsorption density decreased from 0.430 to 0.116 mg g^{-1}. Sharma and Forster [19] pointed out that such a drop in adsorption densities originated in presence of unsaturated sites on the adsorbent surface during adsorption reaction.

Figure 4 shows the effect of DSBP having different particle size on the adsorption of Cr(III) ions as a function of contact time. The data indicates an increase in the uptake of Cr(III) ions as the particle size decreases. This observation is in agreement with the fact that the adsorption capacity of small particles is higher than the big ones since the small particles have a wider surface area.

Adsorption isotherms

The adsorption isotherms of Cr(III) ions on DSBP are shown in Figures 5 and 6. The data were analysed according to Langmuir and Freundlich isotherms.

$$C/(x/m)=1/bQ°+C/Q° \quad (i)$$

$$\ln(x/m)=\ln k_f+{}^1/_n \ln C \quad (ii)$$

Equation (i) and (ii) represents the linear form of Langmuir and Freundlich isotherms respectively. Where C is equilibrium concentration of adsorbate (mg L^{-1}), x/m is the amount adsorbed per gram adsorbent (mg g^{-1}), b and Q° are Langmuir's constants. k_f and ${}^1/_n$ are Freundlich's constants. The plot of C/(x/m) against C gives a straight line at each temperature (Figure 5) showing the applicability of Langmuir isotherm. The values of Q° (mg g^{-1}) and b (L mg^{-1}) determined from the slopes and intercepts of these lines are given in Table 1.The adsorption capacity of Cr(III) decreased with the raise in temperature. The values of k_f, which is a measure of adsorption capacity, and ${}^1/_n$ have been determined by the plot of ln(x/m) vs. lnC (Figure 6) and listed in Table 1. The intercept gives the value of $\ln k_f$ and ${}^1/_n$ is calculated from the slope. The correlation coefficients (r^2) for the Langmuir and Freundlich equations were found to be higher than 0.98, which indicates that there is a strong positive relationship in the data.

The effect of isotherm shape on whether adsorption is "favourable or unfavourable" has been considered. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant seperation factor or equilibrium parameter defined by Weber and Chakravorti [20] as follows:

$$R=1/(1+bC_o) \quad (iii)$$

The parameter indicates the shape of the isotherm accordingly;

R value	Type of the isotherm
R > 1	Unfavourable
R = 1	Linear
0 < R < 1	Favourable
R = 0	Irreversible

R values were found to be less than 1 and greater than zero, in the temperature range of 20 to 50 °C for the initial Cr(III) concentration of 30 mg L^{-1}. The R values at 20 and

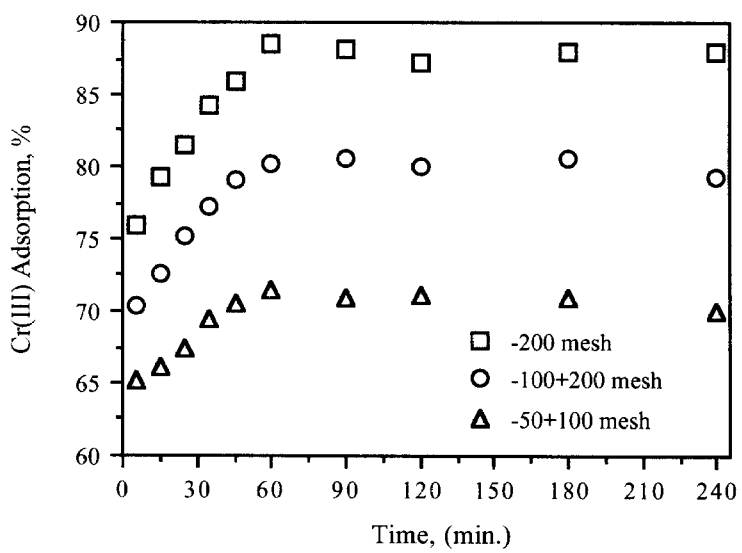

Figure 4. Effect of contact time on Cr(III) adsorption by DSBP heaving different particle size (Conditions: 50 ml 10 mg L^{-1} Cr(III) solution; pH 4.5 1 g DSBP at various fraction; temperature 20 °C; 0.01 M $NaClO_4$).

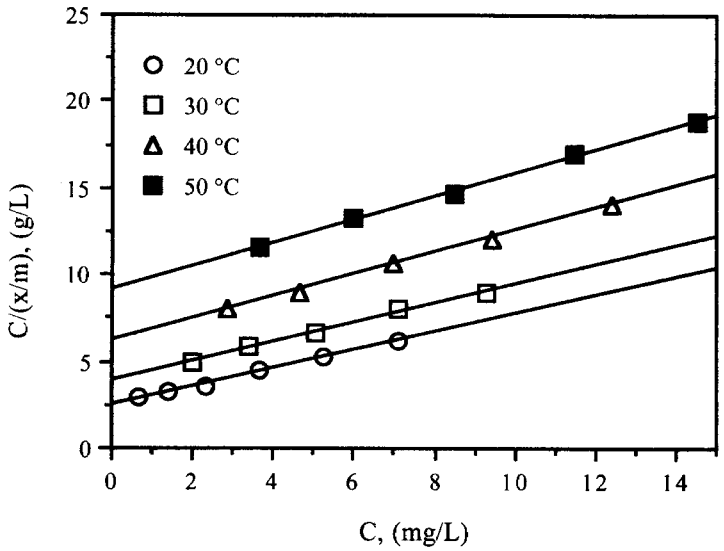

Figure 5. Langmuir plot of Cr(III) adsorption by DSBP (Conditions: pH 4.5; contact time 60 min.; 1 g DSBP; 0.01 M $NaClO_4$).

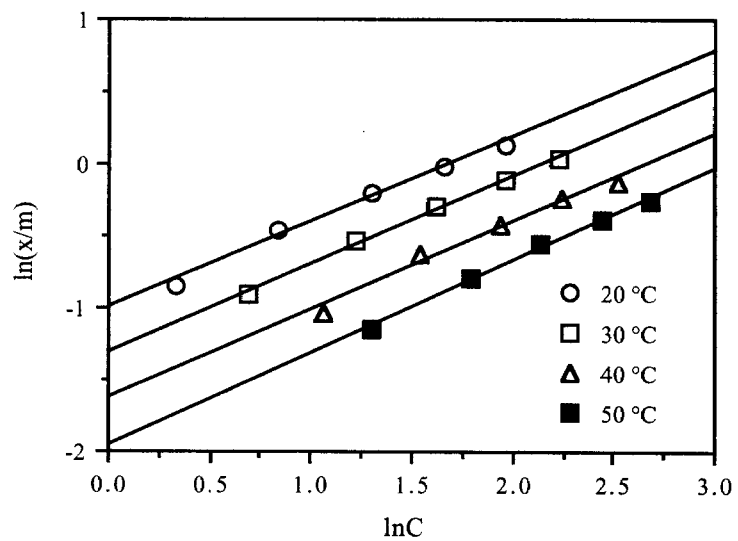

Figure 6. Freundlich plot of Cr(III) adsorption by DSBP (Conditions: pH 4.5; contact time 60 min.; 1g DSBP; 0.01 M $NaClO_4$).

50 °C are 0.139 and 0.313, respectively. These results show that Cr(III) adsorption onto DSBP is favourable at temperature range considered.

Effect of temperature

The data of adsorption at different temperatures indicated that there is significant change in the removal of Cr(III). When the temperature of solution is raised from 20 °C to 50 °C, the removal percentage of Cr(III) decreases from 86 to 63 at pH 4.5 for equilibrium time of 1 hour. The adsorption of Cr(III) did not change depending upon the temperature of solution by increasing the contact time of 1 hour. The values of Q° and b determined from Langmuir plots decrease with the raise in temperature. There is same trend for the values of k_f. These findings show that Cr(III) adsorption process by

Table 1. Langmuir and Freundlich constants.

	Langmuir constants			Freundlich constants		
Temp. (°C)	r^2	b (L mg^{-1})	Q° (mg g^{-1})	r^2	k_f(mg g^{-1})	$^1/_n$
20	0.997	0.206	1.919	0.990	0.369	0.594
30	0.998	0.140	1.814	0.984	0.269	0.615
40	0.998	0.104	1.569	0.990	0.195	0.613
50	0.998	0.073	1.493	0.996	0.140	0.647

DSBP is exothermic.

For the present system, the rate constants of adsorption (k_{ad}) and pore diffusion (K_d) were determined at various temperatures using equation (iv) [21] and (v) [22], respectively.

$$\log(q_e-q) = \log q_e - (k_{ad}/2.303)t \quad \text{(iv)}$$

$$q = K_d t^{0.5} \quad \text{(v)}$$

Where q_e and q (mg g^{-1}) are amount of Cr(III) adsorbed at equilibrium and any time, t, respectively. A straight line of $\log(q_e-q)$ vs. t (Figure 7) suggests the applicability of equation (iv), which called first order rate expression of Lagergren, for adsorption of Cr(III) onto DSBP. The values of k_{ad} at 20, 30 and 50 °C were found to be 4.71×10^{-2}, 4.63×10^{-2} and 4.07×10^{-2} min^{-1}, respectively. To determine the pore diffusion rate constants, q were fitted against to $t^{0.5}$ in Figure 8. The values of K_d determined from the slope of plots were tabulated in Table 2 .The values of K_d decrease with a raise in temperature of solution. However, the linear plots at each temperature do not pass through origin. A similar result has been interpreted as pore diffusion was not the only rate controlling step [23].

Activation energy of adsorption reaction of Cr(III) by DSBP were calculated to be -3.69 kJ mol^{-1} using the Arrhenius equation. The thermodynamic parameters such as free energy (ΔG), enthalpy (ΔH) and entropy changes (ΔS) for the adsorption processes have been determined using following equations and listed in Table 2.

$$\ln b = \ln b' - \Delta H/RT \quad \text{(vi)}$$

$$\ln(1/b) = \Delta G/RT \quad \text{(vii)}$$

$$\Delta S = (\Delta H - \Delta G)/T \quad \text{(viii)}$$

The enthalpy change of adsorption determined from the slope of lnb vs. 1/T was found to be -27.3 kJ mol^{-1}. The negative value of ΔH confirms that the process is exothermic. The negative values of ΔG at different temperatures are due to the fact that the adsorption process is spontaneous with high affinity of Cr(III) against to DSBP. The free energy

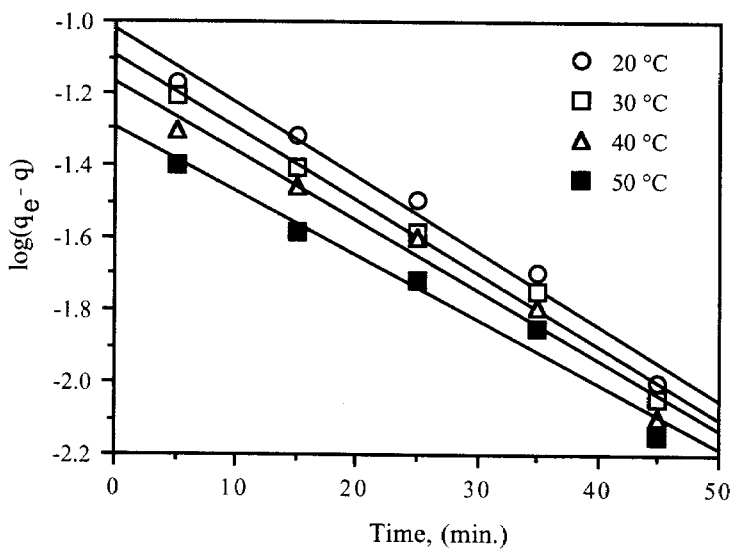

Figure 7. Lagergren plot for Cr(III) adsorption by DSBP(Conditions: 50 ml 10 mg L^{-1} Cr(III) solution; pH 4.5; 1 g DSBP ; 0.01 M $NaClO_4$).

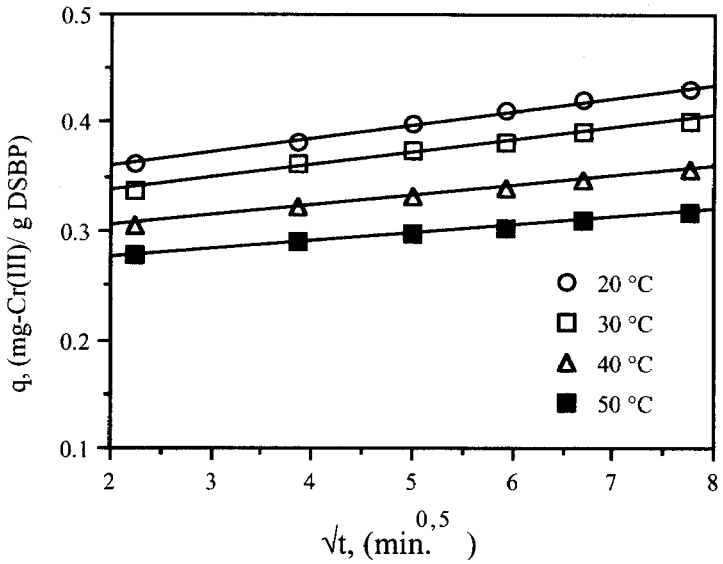

Figure 8. Plot of q vs. $t^{0.5}$ for pore diffusion rate constant (Conditions: 50 ml 10 mg L^{-1} Cr(III) solution; pH 4.5; 1 g DSBP ; 0.01 M $NaClO_4$).

Table 2. Thermodynamic parameters and pore diffusion rate constants.

Temp. (°C)	-ΔG (kJ mol^{-1})	-ΔS (kJ $mol^{-1}K^{-1}$)	K_d (mg $g^{-1}min^{-0.5}$)
20	22.6	$8.03x10^{-3}$	$1.27x10^{-2}$
30	23.4	$8.11x10^{-3}$	$1.12x10^{-2}$
40	22.3	$7.90x10^{-3}$	$0.92x10^{-2}$
50	22.1	$7.98x10^{-3}$	$0.71x10^{-2}$

change decreases with raise in temperature showing that the adsorption feasibility increases at higher temperature. The values of entropy changes are very small and negative for the present system.

Desorption studies

The time required for the desorption of Cr(III) is approximately 1 hour at pH 1.82. The desorption percentage of Cr(III) did not increase with further increase in contact time. It is expected that the desorption yield of positively charged Cr(III) ions is higher in acidic medium (Figure 9). The amount of desorbed chromium from 1.0 g DSBP containing 0.430 mg chromium is approximately 27 % at pH range of 1.0-2.0, thereafter it sharply decreases towards to alkaline medium. No chromium was found to be desorbed in the experiments carried out at pHs 3.4 and 5.3. It is possible that desorbed Cr(III) ions can be precipitated in the form of $Cr(OH)_3$ at above pH 5.0. Because of the amphoteric character of Cr(III), formed $Cr(OH)_3$ may be dissolved at alkaline media. However, desorption of chromium at alkaline pH has not been examined. It can be concluded that the Cr(III) ions tend to form strong bonds with organic groups in DSBP, therefore, its little fraction can be desorbed.

CONCLUSIONS

In this study, the waste pulp of sugar beet remaining from sequential extractions of sugar and pectin has been considered as a low-cost adsorbent. From the studies on the line Cr(III) adsorption characteristic of DSBP, the following conclusions can be drawn;

Adsorption of Cr(III) ions is highly pH dependent and the maximum removal is 86 % at pH 4.5 under the conditions of 20 °C and 20 g L^{-1} adsorbent dosage.

The kinetic studies indicated that equilibrium in the adsorption of Cr(III) on DSBP was reached in the contact time of 60 min.

The adsorption efficiency of Cr(III) increased with decreasing particle size of adsorbent and increasing of

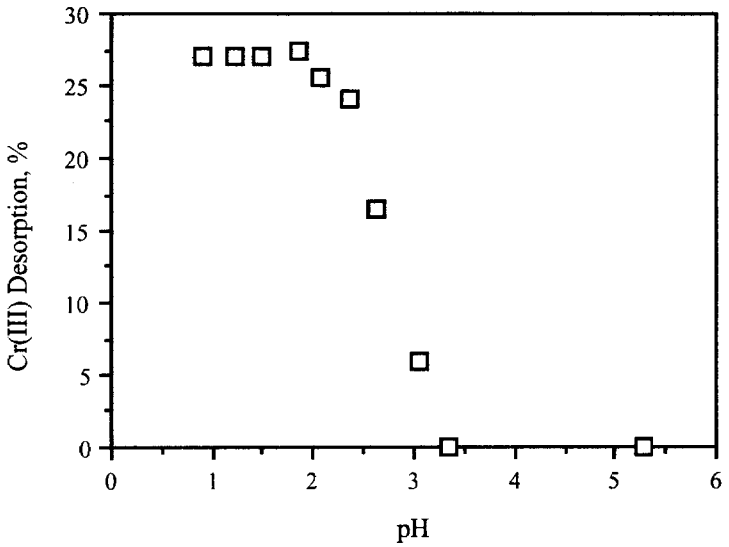

Figure 9. Effect of solution pH on desorption of Cr(III) (Conditions: 0.430 mg Cr(III) g^{-1} DSBP; temperature 20°C; contact time 60 min).

adsorbent dosage.

The first order reaction rate constant for Cr(III) adsorption on DSBP was found to be 4.71×10^{-2} min^{-1} at 20 °C, and it decreased with increasing temperature.

The negative change in enthalpy indicates that adsorption process of Cr(III) by DSBP is exothermic. Adsorption capacity decreases from 1.919 mg g^{-1} to 1.493 mg g^{-1} with an increase in temperature of solution from 20 °C to 50 °C.

Desorpable yield of Cr(III) ions is very low. This suggests that DSBP-Cr(III) bonds are very strong and adsorption of Cr(III) onto DSBP is a chemisorption process.

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