REMOVAL OF CHROMIUM FROM WASTEWATER BY ADSORPTION

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ABSTRACT

The aim of the present research is to study the removal of chromium from industrial wastewater by using activated carbon as adsorbent.

Two systems were studied (batch and continuous systems). Experiments were done using Box Wilson method to study the effect of effluent concentration and solution pH on the performance of activated carbon.

The results of the continuous system indicated that the adsorption rate increased with increasing effluent concentration, bed height, solution pH and solution temperature.

A mathematical relation (for the effect of influent concentration and solution pH onto effluent concentration) was found using non-linear regression analysis

$$Y = -71.72 + 48.86\,x_1 - 0.23\,x_2 - 3.34\,x_1^2 + 7.17 \times 10^{-4}\,x_2^2 + 1.62 \times 10^{-2}\,x_1 x_2$$

INTRODUCTION

Adsorption is used for dealing with the increasing problems of drinking water preparation and wastewater treatment. The practical use of adsorptive processes depends on the availability of suitable adsorbent and regeneration processes$^{(1)}$. The porous solid generally used for adsorption are silica gel, activated alumina, activated carbon and molecular sieves$^{(2, 3)}$.

The ability of activated carbon to adsorb various organics and inorganics from solution is well recognized. Inorganics removal by activated carbon adsorption is seen in practice in three general areas: metallurgy, analytical chemistry, water and wastewater engineering$^{(4, 5)}$.

Many experiments$^{(1)}$ were carried out to study the effect of pH on Cr (VI) and Cr (III) adsorption by activated carbon. The results indicated that Cr (VI) is more readily removed than Cr (III) by at least two times. The optimum pH for adsorptive removal is 5.5-6 for Cr (VI) and for Cr (III).

Chromium compounds may be present in industrial wastes from a wide variety of processes including: electroplating, surface treatment of metals, the tanning of leather, the manufacture of pigments, coloring of glass. It is also found in some cements$^{(6)}$.

The Langmuir adsorption model$^{(5)}$ is valid for a single layer adsorption whereas the Brunauer Emmett Teller (BET) model represents multilayer adsorption$^{(5)}$. The Langmuir's equation is:

$$q_e = \frac{A\,bc}{1 + bc} \qquad (1)$$

The Freundlich equation is basically empirical and generally agrees well with Langmuir equation and experimental over a moderate range of concentration$^{(7)}$.

$$\log q_e = \log k_f + \frac{1}{n}\log c \qquad (2)$$

EXPERIMENTAL WORK

Materials

Activated carbon (supplied by Norit Verkoop Center, Amsterdam, Holland) was used as an adsorbent in the present work. Its physical properties are: bulk density = 0.4 x 10^3 kg/m^3, particle density = 1.4 x 10^3 kg/m^3, void fraction of bed = 0.4, surface area = 950 x 10^3 m^2/kg and internal porosity of particle = 0.4. The shape of activated carbon was cylindrical shape (height = 2.6 mm and diameter = 0.68 mm, equivalent diameter 1.22 mm).

Chromium trioxide (CrO_3) properties are dark red crystals, decomposed as agent Cr_2O_3 and oxygen at 250 °C; easily soluble in water; specific gravity (2.7).

Experimental Arrangement [8]

Two types of experiments were carried out in the present research (batch system and continuous system).

Batch system

A continuously mixed batch system used (electric shaker) according to Box Wilson Method(9) to study the effect of influent concentration and solution pH onto the effluent concentration. The solution (1.5×10^{-4} m^3) total was prepared by placing 1×10^{-5} m^3 1 M NaCl and various amount of chromate at different concentration (0.1 – 0.7 kg/m^3) mixed with 0.01 kg activated carbon in volumetric flask. The various initial pH values of the solution were adjusted by adding strong acid or strong base. The solution pH was designated (2 – 10). The samples were mixed for (3 hr). The samples were filtered and the amount of chromium absorbed was determined (using a Shimadzu Model UV – 160 A ultraviolet/visible spectrophotometer).

Column system (Continuous system)

A fixed bed activated carbon adsorber was constructed to determine the characteristics of the adsorption Figure (1). The major equipment used are:

1. Three QVF spherical containers each 0.1 m^3.
2. The adsorber was made of QVF glass column 7.2×10^{-2} m I.D. and 1.2 m height and packed with activated carbon.
3. Two calibrated rotameters were used to measure the liquid flow rate. all pipes, values and pumps were chemical resistant (QVF).

RESULTS AND DISCUSSION

Batch System

Twelve experiments done using Box-Wilson Method. The influent concentration (0.1 – 0.7 kg/m^3) and solution pH (2 – 10) were used. Table (1) shows that the chromium is removed most effectively in an acidic environment and adsorption capacity increases with decreasing pH. This is due to the fact that the surface function groups such as C_xO or C_xO_2 were formed during heating and activation of raw carbon materials.

Using non-linear regression analysis to find the effect of influent concentration (X_2) and solution pH (X_1) onto effluent concentration (Y) as in the equation below:

$$Y = A_0 + \sum B_i X_i + \sum C_i X_i^2 + D X_1 X_2 ; \quad i = 2$$

where $A_o = -71.22$, $B_1 = 48.86$, $B_2 = -0.23$, $C_1 = -3.34$, $C_2 = 17 \times 10^{-4}$, $D = 1.62 \times 10^{-2}$.

Table (1) Optimum conditions of influence concentration and pH

Y	X_1	X_2
0.091	3.17	0.188
0.226	3.17	0.612
0.107	8.83	0.188
0.282	8.83	0.612
0.158	6	0.4
0.164	6	0.4
0.003	2	0.4
0.186	10	0.4
0.194	10	0.4
0.001	2	0.4
0.367	6	0.7
0.064	6	0.1

Continuous System

Effect of the influent concentration

Five experiments were carried out at different chromium concentration (0.1, 0.2, 0.3, 0.5 and 0.7 kg/m^3) respectively. These experiments were conducted at flow rate 0.0138×10^{-3} m^3/sec., pH = 2, bed height = 0.1 m and temperature = 288 K.

The breakthrough curves for the above experiments were obtained by plotting effluent concentration against time Figure (2). To show the adsorption rate at different influent concentration, the adsorbed versus time were plotted Figure (3). This figure showed a linear portion existed for each curve at the early period of the experiments. With increasing influent concentration the linear segment of the curves extended over a shorter period of time. Deviation from linearity occurred because increasing influence of interparticle transport on the overall rate of mass transfer as each run progressed. This observation is considered by Weber(10).

The rate of adsorption was low at low concentration compared with that of high concentration. This can be explained by increasing the influent concentration would lead to increase driving force and consequently increasing the adsorption rate.

Langmuir and Freundlich isotherms

The plot of (c_{eq}/q_e) versus C_{eq} shows a straight line Figure (4). This means that the equilibrium data correlated well with Langmuir's equation, and can be represented by Equation (3).

$$q_e = \frac{0.426\, c_{eq}}{1 + 3.23\, c_{eq}} \tag{3}$$

The plot of ($\log c_{eq}$) against ($\log q_e$) shows a straight line Figure (5). This means that the equilibrium data for the adsorption correlated well with Freunlich's equation, and can be represented by Equation (4).

$$q_e = 0.11\, c_{eq}^{0.5} \tag{4}$$

Referring to Figures (4, 5) it can be seen that the Langmuir and Freundlich equations were both fit the experimental data. This was due to the moderate range of concentrations used in the present research.

Effect of flow rate

Five experiments column were carried out at different flow rates (1.388, 2.083, 2.77, 3.47 and 4.16) x 10^{-6} m^3/sec. All other conditions were kept the same (influent concentration = 0.5 kg/m^3, pH = 2, bed height = 0.15 m, temperature = 288 K). The breakthrough curves were plotted Figure (6). Examining this figure it can be seen that there is a marked increase in the rate of adsorption and the capacity of the activated carbon with decreasing flow rate Figure (7). Also Figure (6) showed that the lower flow rate the longer the linear portion of the curve, indicating that film diffusion remains rate limiting for longer periods.

Effect of bed height

Five experiments column were carried out at different bed heights (0.05, 0.1, 0.15, 0.2 and 0.25 m). All other conditions were kept constant (influent concentration = 0.5 kg/m^3, flow rate = 0.01388 x 10^{-3} m^3/sec, pH = 2, temperature = 288 K). The breakthrough curves were plotted Figure (8). Examining this figure it can be seen that it required a longer period of time to reach the equilibrium as the bed height was increased. Also the total quantity of pollutant removed from solution at any period of time increased with increasing the bed height. When increasing bed height, the total surface that is available for adsorption for adsorption will increase. Also when increasing the bed height, the empty bed contact time will also increase with increase the capacity of the activated carbon Figure (9).

Effect of solution pH

Four experiments column were(3) carried out with different solution pH (2, 4, 6 and 8). All other conditions were kept constant (influent concentration = 0.5 kg/m^3, flow rate = 0.01388 x 10^{-3} m^3/sec, bed height = 0.15 m, temperature = 288 K). The breakthrough curves were plotted Figure (10). From this figure it can be seen that the total amount of pollutant removed from the solution at any time increased with decreasing pH. This is due to the fact that the(4) surface function groups such as C_xO or C_xO_2 where formed during heating and activation of raw carbon materials.

Effect of solution temperature

Five experiments column were carried out with different temperatures (288, 293, 298, 303 and 308 K) respectively. The breakthrough curves were plotted Figure (11). From this figure it can be seen that the total quantity of pollutant removed from solution at any time increased as the temperature decreased. This phenomenon was applicable for most exothermic system. The effect of temperature on the adsorption capacity of activated carbon was shown in Figure (12) in which the capacity increased as the temperature decreased.

COCLUSIONS

1. The equilibrium isotherm for the system chromium activated carbon was a favorable type. The Langmuir and Freundlich's equations constants were found.
2. The adsorption capacity of the chromium by activated carbon was determined. The important characteristics of the activated carbon were specific surface area and surface acidity.
3. The adsorption rate was found to be increased with increasing the influent concentration.
4. The capacity of activated carbon increased with increasing influent concentration and bed height, while it increased with decreasing flow rate, solution pH and solution temperature.

NOMENCLATURE

A	Mass of solute absorbed per mass of adsorbent	kg/kg
b	Langmuir equilibrium parameter	m^3/kg
c	Adsorbate concentration in the bulk of solution	kg/m^3
c_{eff}	Effluent concentration	kg/m^3
c_{eq}	Equilibrium concentration	kg/m^3
k_f	Freundlich equilibrium parameter	kg/kg
q_e	Concentration of adsorbate in solid phase at equilibrium	kg/kg
Q	Flow rate	m^3/sec

REFERENCES

1. Cheremisinoff, P., Ellerbusch, F., "Carbon Adsorption on Activated Carbon", Pittsburg, Pennsylvania, 1976.
2. Avery, D. A. and Bolston, D. A., "Industrial Wastewater Treatment", Chemical Engineering, 8, 65, 1965.
3. Sulaymon, A. H. and Mahdi, A. S., Spherical Zeolite Binder Agglomerates, Trans. I. Chem. E., V 77, Part A, 1999.
4. Nemerow, N. L., "Industrial Pollution Control", Addison Wesley Publishing Co., 1978.
5. Kasser, N. L., Sulaymon, A. H., Modeling of Dynamic Behavior of Non-Isothermal Multicomponent Adsorption in Adiabatic Fixed Bed, Jordan International Chemical Engineering Conference III, 1999.
6. Huang and Min Hwang Wu., Water Research, 11, 7, 1977.
7. Hutchins, R. A., "New Method Simplifies Design of Activated Carbon System" Chem. Eng. 1973.
8. Al-Timimy, H. M., M.Sc. Thesis, University of Baghdad, 1997.
9. Box, George, E. P., William, G. Hunter, and J. Stuart, Hunter, "Statistic for Experiments, John Wiley and Sons U.S.A, 1978.
10. Weber, J. W. Jr. "Physicochemical Process for Water Quality Control", John Wiley and Sons, New York, 1972.

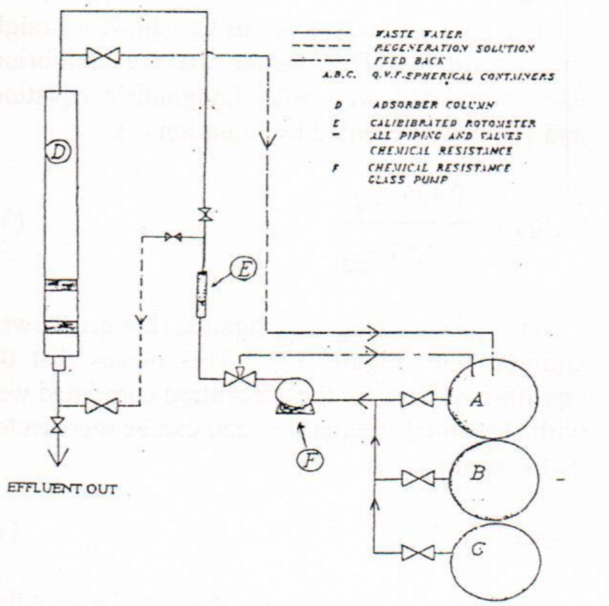

Fig. (1) Schematic diagram of the experimental equipments

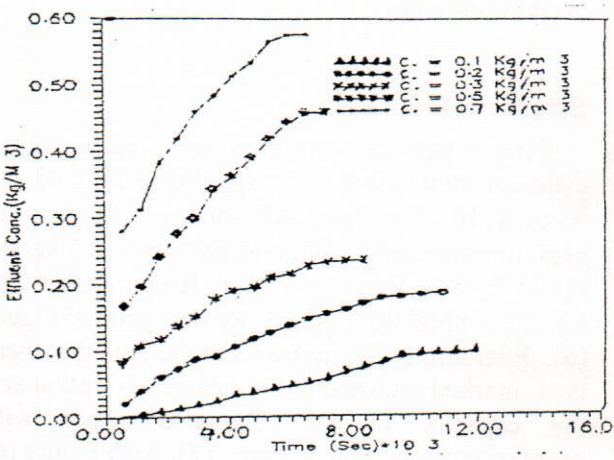

Fig. (2) Breakthrough curves for isothermal adsorption at different concentration

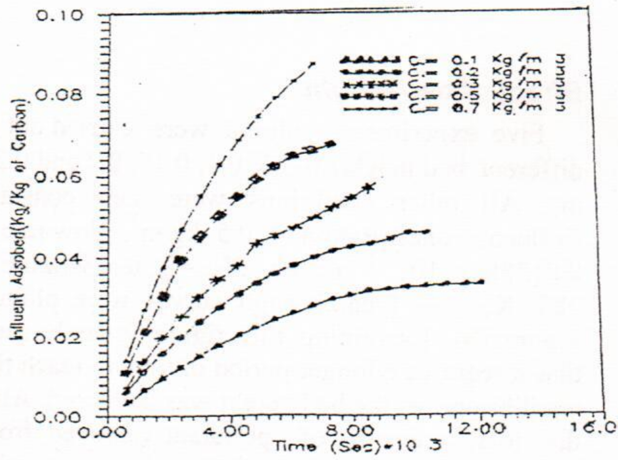

Fig. (3) Cumulative adsorption at different concentrations

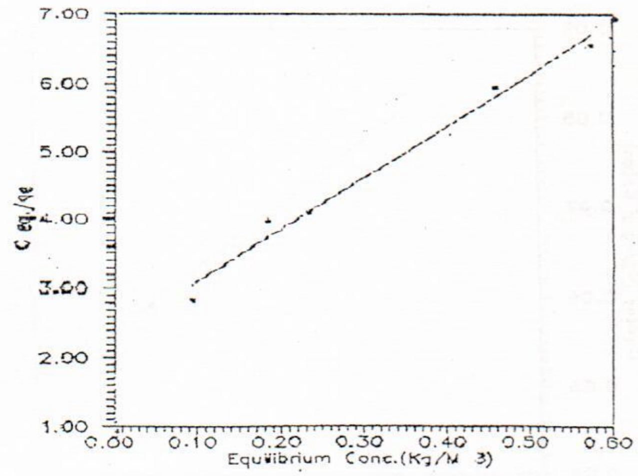

Fig. (4) Plot of $C_{eq.}/qe$ vs. C_{eq} for determination of Langmuir constants for chromium

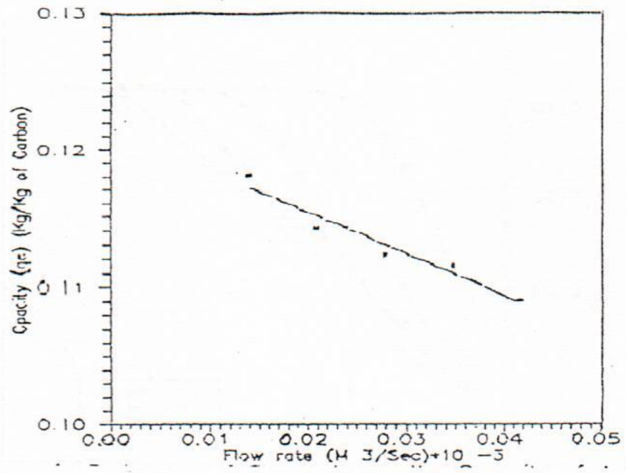

Fig. (7) Effect of flow rate on the capacity of activated carbon for isothermal adsorption of chromium

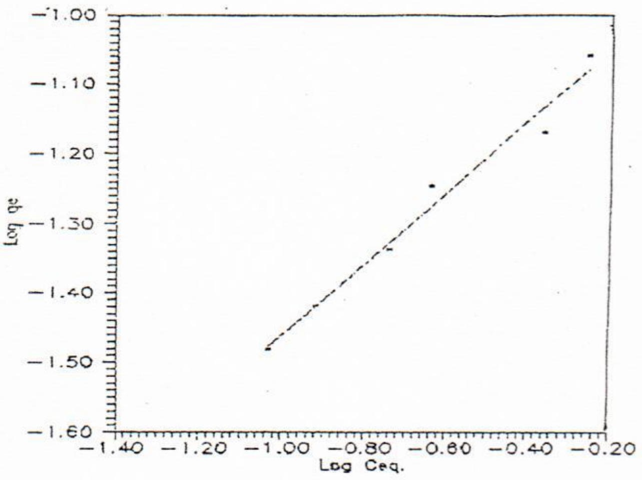

Fig. (5) Plot of log(qe) vs. Log(C_{eq}) for determination of Freundlich constant for chromium

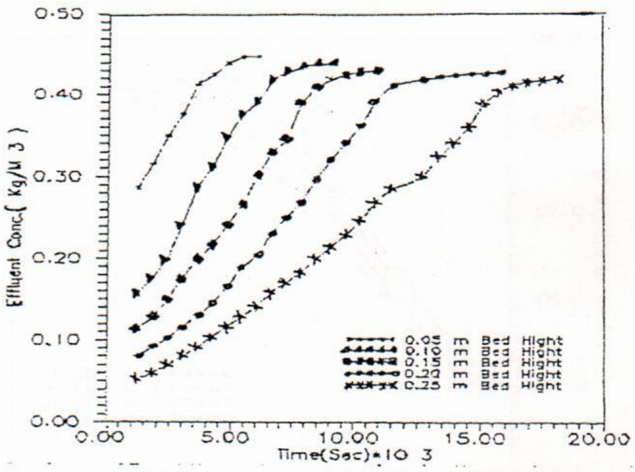

Fig. (8) Breakthrough curves for isothermal adsorption at different bed height

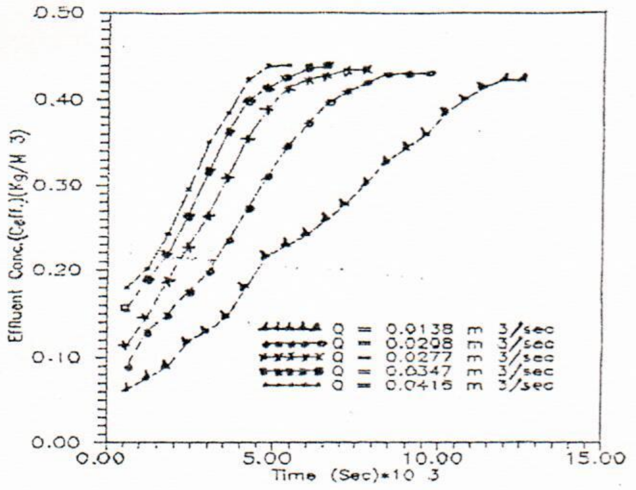

Fig. (6) Breakthrough curves for isothermal adsorption at different flow rate

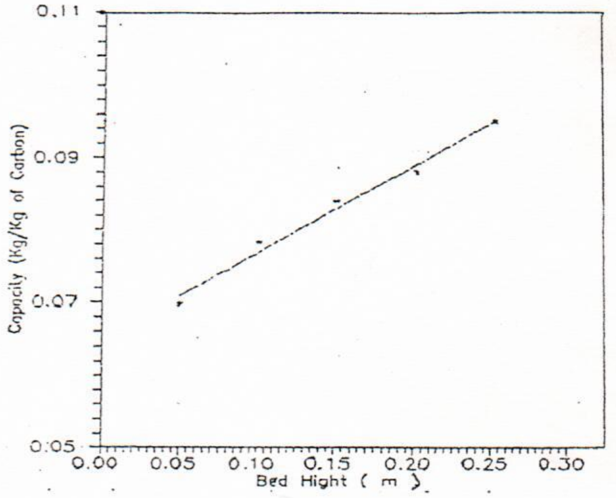

Fig. (9) Adsorption isotherm for chromium onto activated carbon

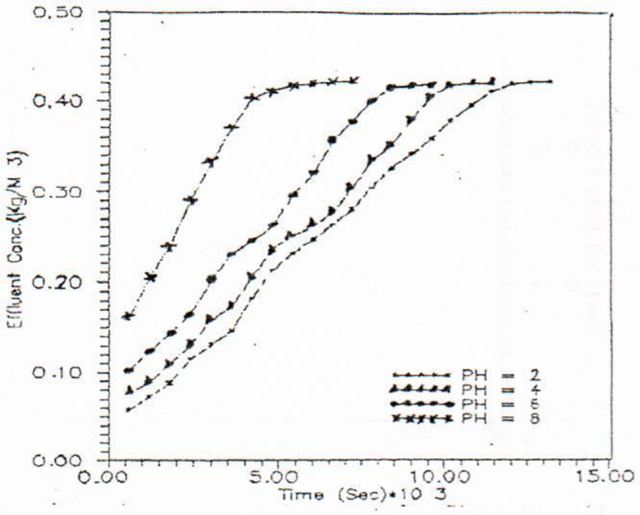

Fig. (10) Breakthrough curves for chromium at different solution pH

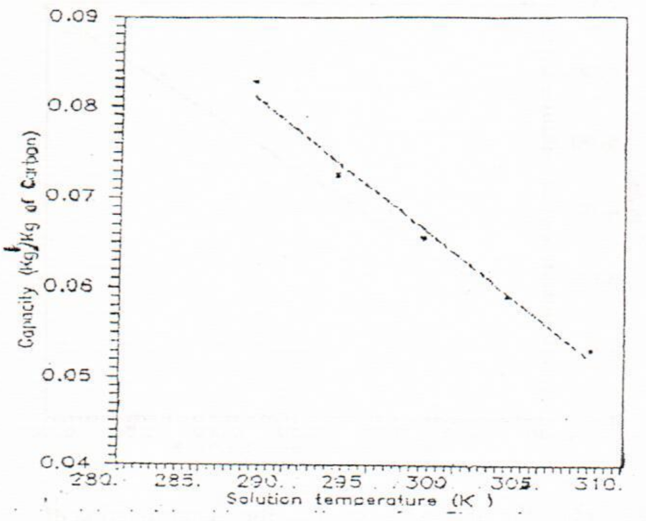

Fig. (12) Adsorption isotherm for chromium onto activated carbon

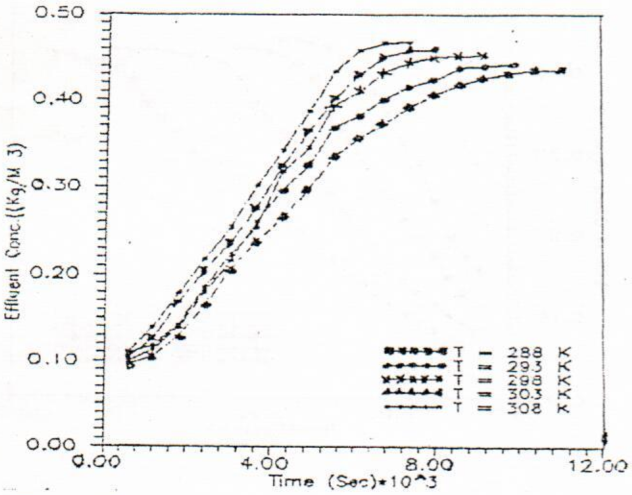

Fig. (11) Breakthrough curves for isothermal adsorption at different solution temperature