

Mass Transfer Study for The Adsorption of Hexavalent Chromium Using Gas Stirring

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Abstract- The rate of mass transfer of adsorption of hexavalent chromium onto activated carbon (AC) in a bubble column using gas stirring as a mixing system was studied. Process parameters including the air flow rate, AC mass, initial chromium concentration and solution temperature were examined. The external and internal mass transfer were analysed based on external mass transfer and intraparticle diffusion models. The calculated external mass transfer coefficient, K_s increased with the increase in air flow rate and temperature while decreased with the increase in initial chromium concentration and mass of AC. The external mass transfer coefficient as function of the studied parameters can be given by equation $K_s = X (\text{variable})^Y$. The intraparticle diffusion coefficient, K_i was found to increase by the increase in air flow rate, initial chromium concentration and temperature and decreased with increase mass of AC. For the intraparticle diffusion the studied variables can be correlated by the equation $K_i = X (\text{variable})^Y$. The results revealed that air flow rate has more influence on increasing the rate of adsorption than effect of initial chromium concentration and mass of adsorbent or temperature.

Key words: Gas stirring ; hexavalent chromium ; activated carbon ; mass transfer ; intraparticle diffusion.

1. Introduction

In the recent years, growing concern about environmental issues has brought researchers to investigate appropriate processes for the removal of various pollutants. Among of these processes adsorption is found one of the more low-cost and effective processes to remove dangerous pollutants such as heavy metals (Ahna et al.,2009 ; Sharmaa et al.,2009). Chromium (VI) is found to be toxic to bacteria, plants, animals and people (Kozlowski et al.,2002). In addition, chromium(VI) is not biodegradable and tends to accumulate in living organisms, causing various diseases and disorders. Therefore, their presence in the environment, in particular in water, should be controlled. Little attention was given using bubble column adsorber using gas stirring. Few authors use gas stirring as mixing method to remove pollutants from waste water. (Nakseedee et.al., 2015, Nassar et.al., 2012; Nassar et al., 2007; Nassar and Yehia, 1999) . The previous studies proved that gas stirring is more economic (higher removal rates in shorter time at lower energy consumption) than mechanical stirring. The high efficiency of gas stirring compared to single phase flow was attributed to the ability of gas bubbles to induce radial momentum transfer for the whole bulk, as well as to create turbulence behind the wake of each gas bubble (Kast, 1962). In this study, the rate of mass transfer for adsorption of Cr(VI) ion onto activated carbon was investigated under the influence of some experimental conditions to explore the role of mass transfer in bubble column adsorber using gas stirring system.

2. Materials and methods

2.1 Adsorbate

Chromium was chosen as the target compound to represent the heavy metals found in industrial waste water. Stock solution of Cr(VI) at the desired concentration was prepared by dissolving $K_2Cr_2O_7$ salt (LOBA CHEMIE – 99.5% Assay – M.W.294.18) in bi-distilled water. The stock solution was diluted to give different initial concentrations. The concentration of free chromium ions in the stock solutions and unadsorbed Cr(VI) in the reaction medium was determined spectrophotometrically at 540 nm in a spectrophotometer using 1,5 diphenylcarbazide (OXFORD Laboratory Reagent – $C_{13}H_{14}ON_4$ – M.W. 242.28) as the complexing agent (Snell and Snell, 1959; and Arnold et al. 1992) .

2.2 Adsorbent

Activated carbon (AC) used as adsorbent in this study was prepared from cotton stalks by one-step chemical activation using ortho phosphoric acid. The detailed preparation procedure and the characterization of the activated carbon have been described elsewhere (Kelany, 2011).

2.3 Gas stirring system

Experimental set up for mass transfer study is shown in Fig. 1. The apparatus consists of a cell and air supply system. The cell is a vertical cylindrical jacketed glass column (30 cm height and 4.5 cm inside diameter). The column was fitted at its bottom with glass bubble distributor, which had an average pores diameter 5-10 microns, a ball valve was fixed to control air flow rate. Temperature was adjusted by passing hot water,

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thermostatically controlled, in the jacket around the column, the temperature was kept constant at 25°C. Before each run, the column was filled with 0.4 dm³ of fresh chromium solution at a certain concentration, followed by addition of a known mass of activated carbon and adjusting the air flow rate. The air flow rate was measured with a calibrated rotameter. Samples were taken at time intervals. The effects of air flow rate (250, 550, 800 and 1300 cm³/min), adsorbent mass (0.071, 0.118, 0.235 and 0.471 g), initial Cr concentration C₀ (10, 30, 75 and 100 mg/dm³) and temperature (15, 30, 40, 60 °C) were investigated. The pH of the solution was adjusted between 5 and 6. The amounts of Cr(VI) adsorbed were calculated from the concentration in solutions before and after adsorption. The chromium uptake by activated carbon was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)v}{m} \quad (1)$$

Where q_t is the amount of chromium sorbed on the surface of the activated carbon at any time t (mg/g), C₀, C_t are the initial and at time t chromium concentration in liquid phase (mg/dm³), v the volume of chromium solution (dm³) and m the mass of activated carbon (g).

1- Glass cylindrical column

2- Sintered glass for air distribution

3- Glass jacket

4- Solution level

5- Control valves

6- Rotameter

7- Air compressor

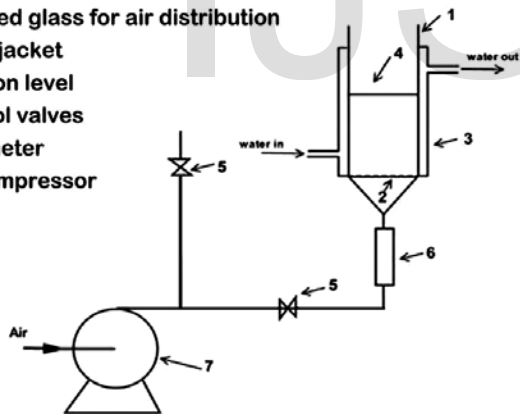


Figure 1. Gas stirring system

3. Results and discussion

3.1 External Mass Transfer Model

The model used for determining the external mass-transfer coefficient, K_s, is based on work by Furusawa and Smith (1973 a & b; 1974). They assume that the external mass transport of the chromium from the bulk solution across the boundary layer film to the external particle surface is rate-controlling in the early stages of the adsorption process.

In a well-agitated batch adsorber, the concentration of adsorbate in the liquid phase C_t and the concentration of

adsorbent particles in the liquid m_s (g/dm³) are assumed to be uniform throughout the vessel. Since at time t = 0, all the mass transfer resistance is restricted to the external layer of the particle, consequently, m_s can be determined according to the following equation

$$m_s = m/v \quad (2)$$

The change in chromium solution concentration (C_t) with time is related to the fluid-particle mass-transfer coefficient by the equation

$$\frac{dC_t}{dt} = -K_s S_s (C_t - C_s) \quad (3)$$

Where C_s is the saturation chromium concentration and K_s is the external mass transfer coefficient (cm/min), C_t = C₀ at t = 0

If the effective diffusion coefficient is neglected, then, since C_s approaches zero and C_t approaches C₀ as t → 0, equation 3 becomes

$$\left[\frac{d(C_t/C_0)}{dt} \right]_{t=0} = -K_s S_s \quad (4)$$

The external surface area of the particles, S_s, can be obtained from m_s by assuming that the particles are spherical of diameter, d_p, hence:

$$S_s = \frac{6m_s}{\rho_s d_p (1 - \epsilon_p)} \quad (5)$$

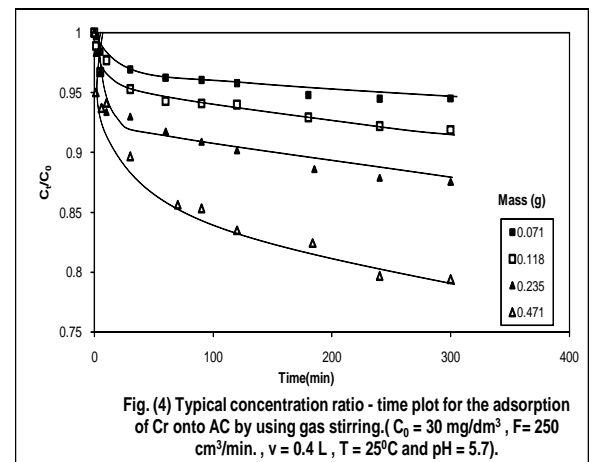
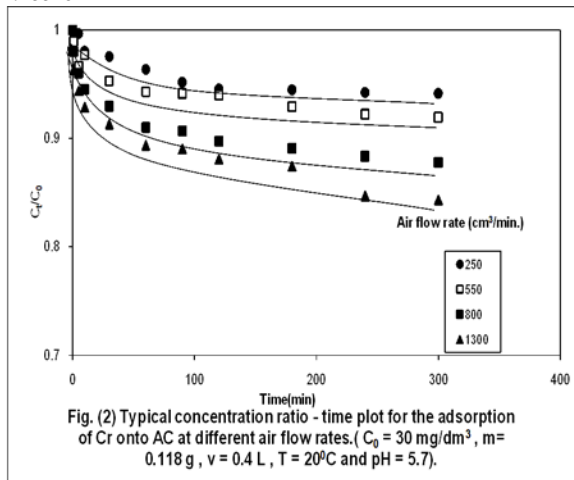
And the slope of equation 4 at t = 0 of a plot of (C_t/C₀) versus time is equal to (-K_sS_s) and K_s can be from such a slope and C.F is the correlation factor. The K_s value may be expressed by an equation of the general form:

$$K_s = X (\text{variable})^Y \quad (6)$$

3.1.1 Effect of air flow rate

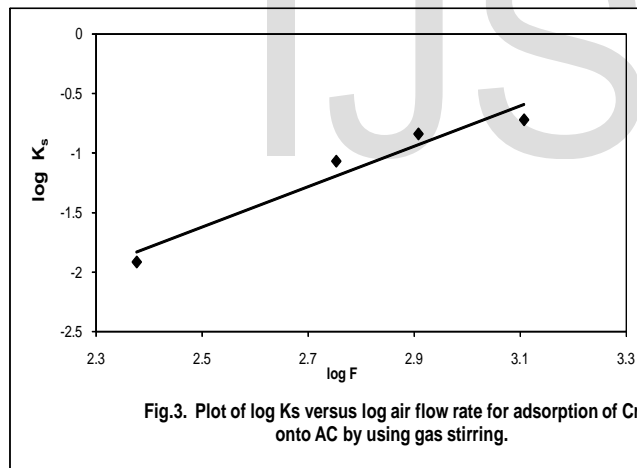
Effect of air flow rate on degree of chromium removal is shown in Fig 2, as variation of C_t/C₀ versus time t.

Four air flow rates were selected to study their effect on external diffusion of chromium. The results show that adsorption of chromium on activated carbon was faster at higher flow rate, and chromium concentration at each air flow rate was gradually approach the final equilibrium concentration after 200 min. Increase gas flow rate increases adsorption of chromium ions onto AC surface, this effect is due to decrease the boundary layer thickness by turbulence created gas flow. As gas flow increases more decrease of boundary layer resistance thickness



To estimate K_s the average C_t/C_0 values in the first min were used and the results have also been plotted as $\log K_s$ versus $\log F$ as shown in Fig. 3, linear variation was observed, which illustrates a linear relationship between $\log F$ and $\log K_s$ and can be expressed by the following equation

$$K_s = 1.377 \cdot 10^{-6} (F)^{1.695} \quad (7)$$



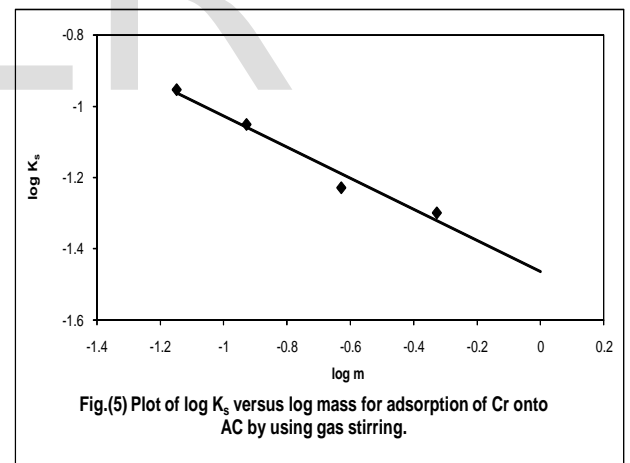
3.1.2 Effect of adsorbent mass :

Fig. 4 shows the effect activated carbon mass on the rate of adsorption of chromium at fixed air flow rate. As shown in this Figure the rate of solute removal increased with increasing activated carbon mass. The values of the corresponding external mass transfer coefficient were calculated from the initial gradients of these plots using equation (4) and following the same procedure carried out previously, K_s can be determined.

A linear relationship between $\log K_s$ and $\log m$ (Fig. 5) was obtained and can be represented by the following equation:

$$K_s = 0.0344 (m)^{-0.437} \quad (8)$$

The decrease in K_s with increasing activated carbon mass may be attributed to the obstruction effect exercised by increasing the activated carbon particles on the diffusion of chromium molecules, this gives rise to a decrease in the chromium effective diffusivity.



3.1.3 Effect of Initial Chromium Concentration

The influence of initial concentration of chromium was studied and the experimental results are shown in Fig. 6. It is evident that the rate of adsorption increase with time until it gradually approached a plateau due to the continuous decrease in the concentrations driving force at range of (10 – 100 mg/ dm³). Also by time the active sites on AC surfaces become saturated.

Table 1. External mass-transfer coefficient (K_s) at various variables using gas stirring technique.

Variables		K_s (cm/min)	X	Y	C.F
Air flow rate (Cm^3/min)	250	0.0122	$1.377*10^{-6}$	1.695	0.95
	550	0.0851			
	800	0.1439			
	1300	0.1906			
Mass (g)	0.071	0.1112	0.0344	-0.437	0.97
	0.118	0.089			
	0.235	0.059			
	0.471	0.0503			
Initial Concentration (mg/dm^3)	10	22.3438	163.79	-0.891	0.91
	30	6.4475			
	75	5.2247			
	100	2.1121			
Temperature ($^{\circ}C$)	15	0.0304	$3.408*10^{-4}$	1.706	0.96

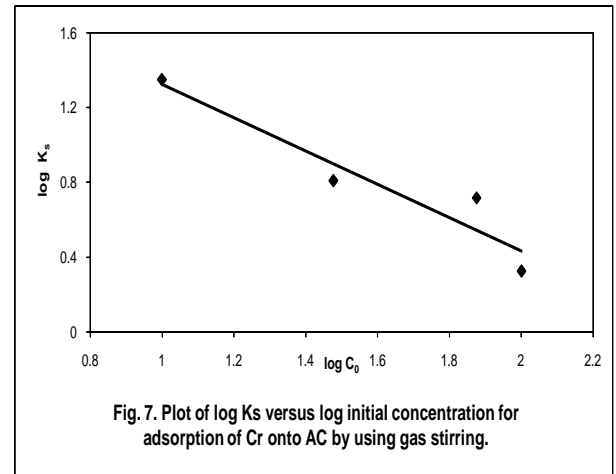


Fig. 7. Plot of $\log K_s$ versus $\log C_0$ for adsorption of Cr onto AC by using gas stirring.

Table 1. External mass-transfer coefficient (K_s) at various variables using gas stirring technique.

3.1.4 Effect of solution temperature

The uptake of Cr(VI) adsorption was studied as a function of temperature in the range of 15 – 60 $^{\circ}C$. The results obtained are presented in Fig. 8 as plot of C_t/C_0 against adsorption time. The results show that the maximum adsorption was found at 60 $^{\circ}C$ and there was a decrease in adsorption with decreasing temperature. This can be explained by the fact that at higher temperature viscosity of solution decreased leading to thinning of boundary layer thickness which leads to higher adsorption capacity. The

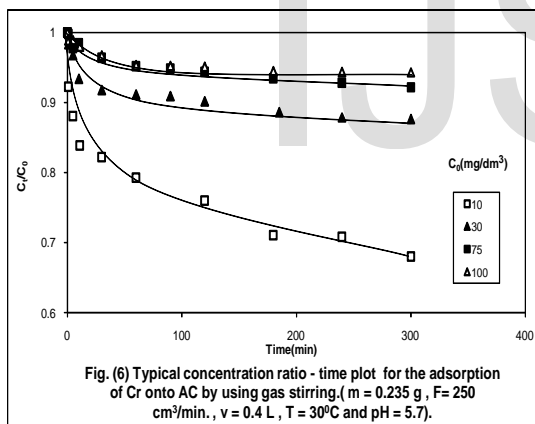


Fig. (6) Typical concentration ratio - time plot for the adsorption of Cr onto AC by using gas stirring. ($m = 0.235$ g, $F = 250$ $cm^3/min.$, $v = 0.4$ L, $T = 30^{\circ}C$ and $pH = 5.7$).

K_s was determined as shown before from the slope and plotted as $\log K_s$ against $\log C_0$ as shown in Fig. 7 and the data are tabulated in Table 1. The data given fit the equation:

$$K_s = 163.79 (C_0)^{-0.891} \quad (9)$$

The decrease of K_s with increase initial chromium concentration is due to the decrease of deriving force. The decrease of deriving force is due to accumulation of chromium ions onto activated carbon surface.

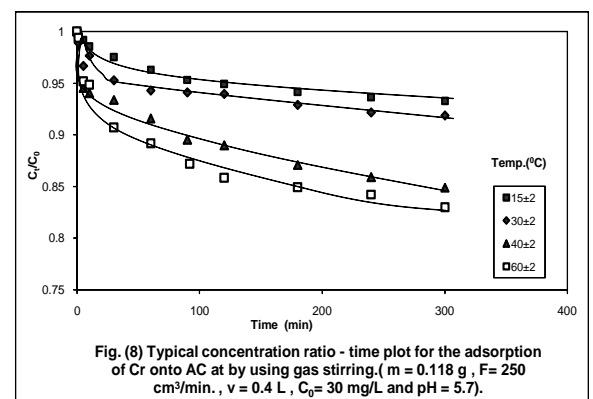
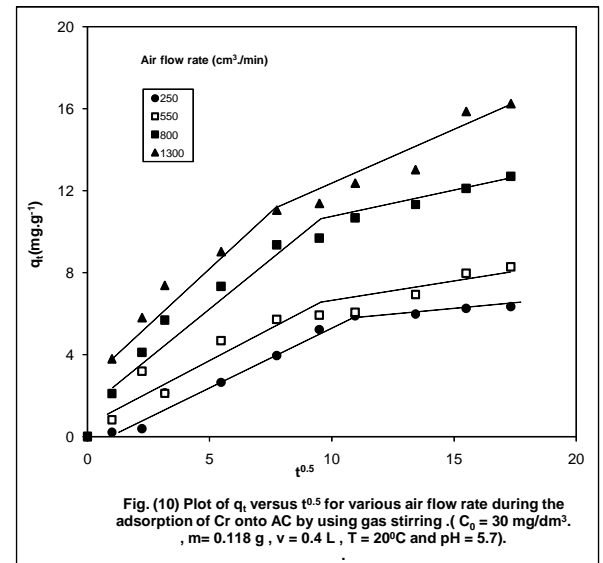
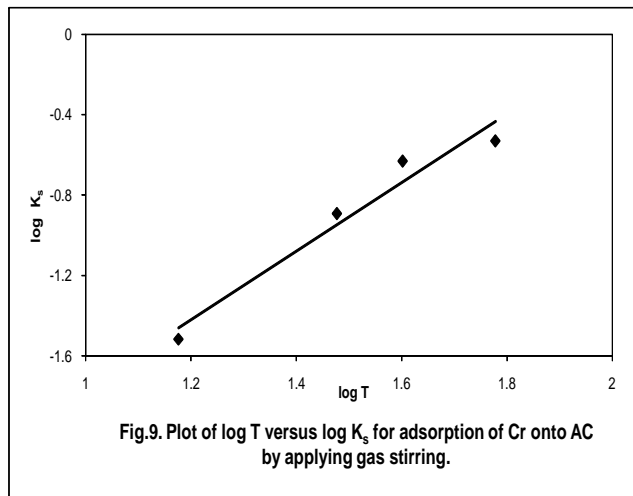


Fig. (8) Typical concentration ratio - time plot for the adsorption of Cr onto AC by using gas stirring. ($m = 0.118$ g, $F = 250$ $cm^3/min.$, $v = 0.4$ L, $C_0 = 30$ mg/L and $pH = 5.7$).

relationship between K_s and the temperature shown in Fig. 9 was correlated by equation (10) in the range (15 – 60 $^{\circ}C$):

$$K_s = 3.408*10^{-4} (T)^{1.706} \quad (10)$$



Data in Table 1 shows that in case of external mass transfer, mass of AC is more important followed by temperature while effect of gas flow rate is coming as the third effect variable.

3.2 Intraparticle Diffusion Model

Assume that the mass transfer is based on intraparticle diffusion which is the only rate controlling step for adsorption. The possibility of intraparticle diffusion resistance affecting was explored by using intraparticle diffusion model (Weber and Morris, 1963) as:

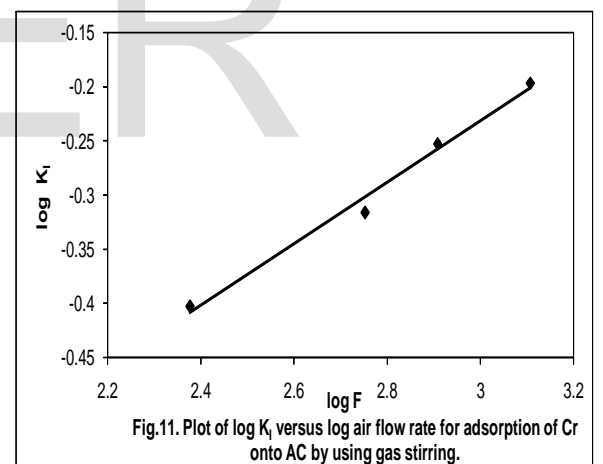
$$q_t = K_1 t^{0.5} \quad (11)$$

Where K_1 ($\text{mg/g.min}^{0.5}$), is the intraparticle diffusion coefficient and is defined as the gradient of linear portion of plot solid phase concentration q_t ; versus the square root of adsorption time, $t^{0.5}$. Weber and Morris, 1963, stated that if intraparticle is the rate controlling step, uptake of the adsorption varies in proportion to the square root of time. When the linear plot of q_t versus $t^{0.5}$ passes through the origin, then the intraparticle diffusion may be only the rate limiting step in the adsorption process.

3.2.1 Effect of Air Flow rate

On studying the plots of q_t versus $t^{0.5}$ for adsorption chromium onto activated carbon (Fig. 10), indicating that three steps took place. The first, was attributed to the diffusion of chromium through the solution to the external surface of adsorbent, or the boundary layer diffusion of solute molecules not shown in the figure.

The second portion described the gradual adsorption stage, where intraparticle diffusion was rate limiting step. The third portion was attributed to the final equilibrium stage for which the rate of intraparticle diffusion started to slow down. This is caused by the depletion of chromium in the bulk solution.



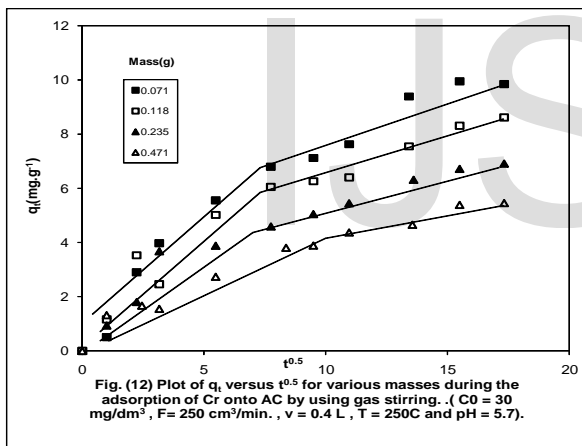
The intraparticle diffusion coefficient values, K_1 , have been determined from the slope of the linear portions of Fig. 10 at various levels of air flow rate. The value of K_1 is increased in linear form with the increase in the air flow rate, Fig. 11. This can be explained by the fact that the adsorption process is a two-step mechanism involving external-mass transfer as well as intraparticle diffusion. Enhanced air flow rates will increase turbulence through the radial and axial

mixing that resulted in decrease in the film resistance around activated carbon particles, enabling the chromium ions to move faster and to concentrate more rapidly at the particle surface and consequently there will be a greater driving force for intraparticle diffusion and thus higher K_I values. Similar results were reported by Nassar et al.,(2001). The K_I values were correlated in terms of (F) by equation 12 using air flow rate range of (250 – 1300 cm³/ min.) and the liner plot of log k_I against log F is shown in Fig. 11, fit the following equation:

$$K_I = 0.0824 (F)^{0.2844} \quad (12)$$

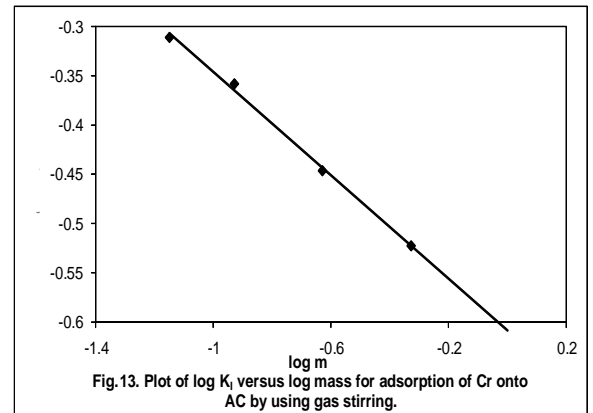
3.2.2 Effect of adsorbent Mass

Fig. 12 shows the plot of chromium uptake, q_t , against $t^{0.5}$ at various masses for the adsorption of chromium onto activated carbon.



The macropore rate parameters, K_I , have been determined as before for different adsorbent masses in the range of (0.071 – 0.471 g) and then plotted as log K_I against log m as shown in Fig. 13. A straight line has been obtained and the data are listed in Table 2. In general, the K_I value decreases with increasing mass of activated carbon can be explain based on that by increasing mass of activated carbon they will causes obstruction to each other and thus decrease the area at constant points and also the rate of diffusion of chromium. The K_I values were correlated in terms of adsorbent mass (m) by equation 13.

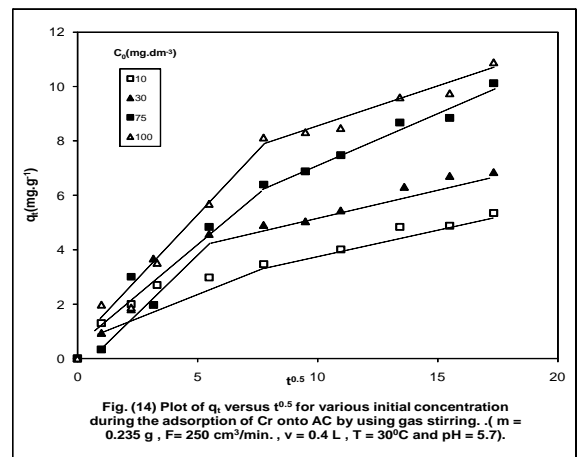
$$K_I = 0.2465 (m)^{-0.262} \quad (13)$$



3.2.3 Effect of Initial Chromium Concentration

The effect of initial chromium concentration is shown in Fig. 14 as a plot of q_t versus $t^{0.5}$ using fixed air flow rate at different initial concentrations. The values of the intraparticle diffusion coefficient, K_I , have been determined from the slope of the linear portion as discussed before. The relation between K_I and C_0 is linear and can be put as in the following form:

$$K_I = 0.055 (C_0)^{0.514} \quad (14)$$



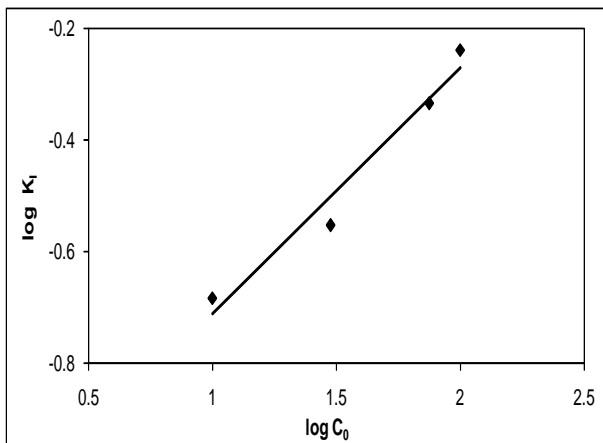


Fig.15. Plot of $\log K_1$ versus \log initial concentration for adsorption of Cr onto AC by using gas stirring,

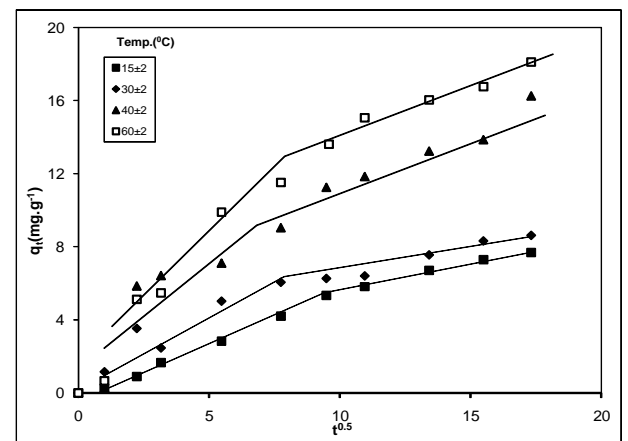


Fig. (16) Plot of q_t versus $t^{0.5}$ for various temperatures during the adsorption of Cr onto AC by using gas stirring. ($m = 0.118$ g, $F = 250$ cm³/min., $v = 0.4$ L, $C_0 = 30$ mg/dm³ and pH = 5.7).

The increase in K_1 with an increase in initial chromium concentration, indicating that increasing the bulk liquid concentration increases the driving force of solute from the bulk onto and then into the pores of AC particles. A rise in the concentration gradient caused faster diffusion and quicker adsorption (Mane, et al., 2007, Ponnusami et al., 2008).

3.2.4 Effect of temperature

Fig. 16 shows the plots of chromium uptake, q_t , against $t^{0.5}$ at various temperatures for the adsorption of chromium onto activated carbon.

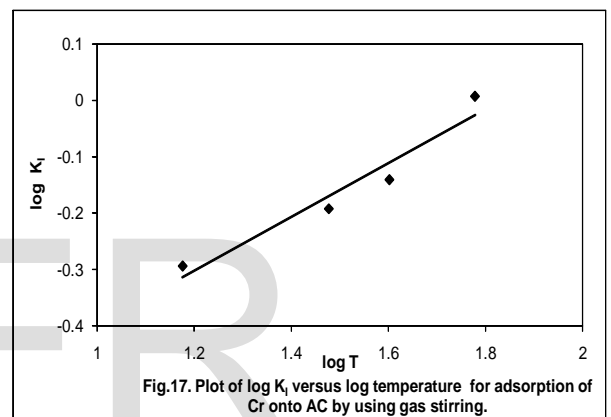


Fig.17. Plot of $\log K_1$ versus \log temperature for adsorption of Cr onto AC by using gas stirring.

Table 2: Macropore rate parameter (K_1) at various variables using gas stirring technique.

Variables		K_1 (mg/g.min ^{0.5})	X	Y	C.F
Air flow rate (Cm ³ /min)	250	0.396	0.0824	0.2844	0.98
	550	0.483			
	800	0.559			
	1300	0.636			
Mass (g)	0.071	0.489	0.2465	-0.262	0.99
	0.118	0.438			
	0.235	0.358			
	0.471	0.3003			
Initial Concentration (mg/ dm ³)	10	0.208	0.055	0.514	0.84
	30	0.281			
	75	0.463			
	100	0.577			
Temperature (° C)	15	0.509	0.1329	0.4782	0.94
	30	0.643			
	40	0.723			
	60	1.016			

The macropore rate parameters, K_1 , have been determined as before and have been plotted as $\log K_1$ against \log temperature as shown in Fig.17 and Table 2. It is observed that there is a gradual increase in K_1 with an increase in temperature as shown in Table 2, this may be explained that increasing of temperature decrease the viscosity of solution thus decrease of boundary layer resistance around adsorbent particle which leads to greater driving force for intraparticle diffusion and thus higher K_1 values.

A correlation derived for the adsorption of chromium onto activated carbon as shown by the following equation:

$$K_1 = 0.1329 (T)^{0.4782} \quad (15)$$

Table 2 shows that mass of AC is still the important factor, while effect of gas flow rate become the second important

4. CONCLUSION

The high efficiency of gas stirring in chromium removal from aqueous solution was attributed to the ability of gas

bubbles to induce radial and axial momentum transfer inside the whole bulk solution. Adsorption process of chromium onto activated carbon was controlled by external mass transfer in the early stage of adsorption process and then followed by intraparticle diffusion until process reach equilibrium. The air flow rate has more effect on external mass transfer during adsorption of chromium onto AC surfaces than by diffusion inside the pore (intraparticle).

5. References

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