DETERMINATION OF SURFACE DIFFUSION COEFFICIENT FOR ADSORPTION PROCESS

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ABSTRACT

The aim of the present research was to find the surface diffusion coefficient which is necessary to calculate the transport mechanism for adsorption process. A batch isothermal adsorption process was carried out to study the adsorption of phenol onto the activated carbon. The effect of phenol concentration, activated carbon particle diameter and stirring speed on surface diffusion coefficient were investigated.

INTRODUCTION

Adsorption is a separation process based on the ability of certain solids to remove liquid or gaseous components preferentially from a flow stream (1). It is, in general, one of collecting soluble substances that are in solution on a suitable interface. Soluble organic compounds, which can be precipitated during chemical coagulation / flocculation processes, can be removed by adsorption (2). It involves the interface accumulation or concentration of substance at a surface or interface, the interface can be between the liquid and a gas, a solid, or another liquid (3). In the present research, only the case of adsorption at the liquid – solid interface will be considered.

Adsorption is probably one of the most common of the advanced wastewater treatment processes; and is finding increased use in wastewater treatment for removal of refractory, toxic substances, and color (4-7).

Diffusion into and within the adsorbent particles can be described by using the models by Carman (8), Crank (9), Foo (10), and Rice (11). They illustrated that a Fickian – type relationship, can describe the diffusion process. The classical analytical solution using cylindrical particles as adsorbent was (8):

$$1 - F = \sum_{n=1}^{\infty} \frac{4\lambda(1+\lambda)}{4(1+\lambda)+\lambda^2 q_n^2} \exp\left[-\frac{q_n^2 Dt}{R^2}\right] \quad (1)$$

Where q_n = constant of the solution and n =1,2 ($q_1 = 2.405$, $q_2 = 5.52$)[8]

EXPERIMENTAL WORK

Materials

The characteristics of the adsorption of phenol on activated carbon are studied. Phenol is a white, crystalline compound with a characteristic odor. The largest use for phenol is phenolic resins. Phenol properties (12) are listed in Table (1).

Table (1) Properties of Phenol

Stability	Crystals redden on exposure to air and light hastened by alkalinite
Molecular weight	94.144
Density	1.058 gm/ml
Specific gravity	1.0576 at 20°C
Solubility in : Water DMSO Ethanol and Acetone Ether and Benzene	50-100 mg/l at 19°C >100 mg/l at 19°C Very soluble
Melting point	41-43°C
Boiling point	182°C
Flash point	79°C
Flammability	Combustible

Activated carbon (supplied by N.V. Norit Verkoop Central, Amsterdam, Holland) was used as an adsorbent in the present work. Its physical properties are tabulated in Table (2).

Table(2) Properties of activated carbon

Dimension of the cylinder	2.6mm X 0.68mm
Bulk density	0.4×10^3 kg/m^3
Particle density	1.4×10^3 kg/m^3
Void fraction of bed	0.4
Surface area	950×10^3 m^2/kg
Internal porosity of particle	0.4

Activated carbon which was used in most of the experiments was of cylindrical shape (Height = 2.6mm and diameter = 0.68mm). In some experiments, the carbon was milled in a ball mill and then sieved into various particle size ranges, as shown in Table (3). For non spherical particles, the particle diameter (dp) may calculated from the geometric mean of the two consecutive sieve openings (13).

Table (3) Carbon particle size range

Shape	Particle Size Range (x 10^3m)	Particle Diameter (dp) (x 10^3m)
Cylindrical	2.6 x 0.68	1.22
Granular	0.9 – 0.7	0.8
Granular	0.7 – 0.57	0.63
Granular	0.57 – 0.4	0.48

Activated carbon was washed before being used with distilled water to remove fines and dried to a constant weight at 383K. Drying for 24 hours was usually sufficient to maintain constant weight, after which the carbon was kept in a desicator.

Equipment

The surface diffusion coefficient (D) was obtained by using a well-stirred batch contactor. In this method, a known amount of adsorbent is mixed with constant volume of well-stirred solution. The mount of solute adsorbed is measured by monitoring the solution concentration using UV-spectrophotometer. A well stirred cylindrical cell was used to estimate the surface diffusion coefficient. The cylindrical cell was constructed of Pyrex glass (0.095m diameter and 0.28m height) with a capacity of 2×10^{-3}m^3, fitted with a variable speed (0-2000 rpm) stainless steel stirrer type (Karl Klob). This stirrer was calibrated using stroboscope (type No.21, George Hill Electronics ltd., Japan).

The temperature of the solution was kept constant during the experiment by mean of a constant temperature water bath type (Decon Fs Zoob). An electronic balance (OHAUS model GT 800) was used for weighing purposes.

Experimental Procedure

An accurately weighed amount of activated carbon (3gm) was placed into the cylinder which contains (1.5 L) of an aqueous solution. The activated carbon was immediately mixed with the solution by means of the mechanical stirrer. Every 300 seconds, a sample was taken out periodically by means of pipette tube for analysis, until equilibrium was reached. Three different groups of experiment were carried out. First group: different stirring speeds (600, 800, 1000 and 1200 rpm). Second group: different initial concentration of Phenol (0.1, 0.15 and 0.2 kg/m^3). Third group: different activated carbon particle sizes (1.22×10^{-3} , 0.8×10^{-3} , 0.63×10^{-3} and 0.48×10^{-3}m).

RESULTS AND DISCUSSION

The diffusion coefficient (D) was obtained by plotting ln (1-F) versus time. The diffusion coefficient can be determined directly from the slope of the curve.

The diffusion coefficient is assumed to be constant towards the end of the adsorption process, so curve fitting was carried out for data up to approximately 70% saturation of adsorbent particles. This was because of slow down in the adsorption rate in the final stage of adsorption process.

Experiments were conducted to determine the stirring speed above which the rate process was independent of stirring speed, which means that the influence of film resistance ceased to play a role in the rate process and only intraparticle resistance is important. This is valid only in the limit when the film coefficient is large. The results are presented in Table (4), and shown in figure (1-5).

Table (4) Surface diffusivity for different stirring speeds

Stirring Speed (rpm)	Surface diffusivity (m^2/S)
600	0.447×10^{-12}
800	1.157×10^{-12}
1000	1.160×10^{-12}
1200	1.161×10^{-12}

Values of surface diffusivity were obtained for different adsorbate initial concentration (0.2, 0.15 and 0.10 kg/m^3). The results at a given stirring speed (1000 rpm) are listed in Table (5), and shown in figures (6-8).

Table(5) Surface diffusivity for different adsorbate initial concentrations

Adsorbate Initial Concentration (kg/m^3)	Surface Diffusivity (m^2/s)
0.2	1.160×10^{-12}
0.15	1.138×10^{-12}
0.1	1.114×10^{-12}

Values of surface diffusivity were obtained for different particle diameters (1.22×10^{-3}, 0.8×10^{-3} and 0.63×10^{-3} m). The results at a given stirring speed (1000 rpm) are tabulated in Table (6), and shown in figures (6,9,10).

Table (6) Surface diffusivity for different particle diameters

Adsorbent Particle Diameter (m)	Surface Diffusivity (m^2/s)
1.22×10^{-3}	1.160×10^{-12}
0.80×10^{-3}	1.090×10^{-12}
0.63×10^{-3}	0.974×10^{-12}

Within the present experimental results tables (5,6) showed that the surface diffusion coefficient should be invariant with the adsorbent particle diameter and initial concentration, and this is decidedly advantageous when compared with the models of Hiester and Vermulenn (14), and Keinath and Weber (15). However, several researchers have reported varying values for surface diffusion coefficient for the same solute on the same adsorbent of varying sieve size fraction. Mathews and Weber (16) obtained a value for surface diffusion coefficient of 1.34×10^{-12} m^2/s for phenol on Filtrasob 400 activated carbon using the size fractions passing U.S. sieve No. 35 and retained on U.S. sieve No. 40 (35/40). Crittenden and Weber (17), using the same carbon, but the size fraction 18/20, obtained a surface diffusion coefficient for phenol of 3.6×10^{-12} m^2/s. Mathews and Su(18), obtained a value of 3.8×10^{-12} m^2/s for phenol for the same carbon and size fraction used by Crittenden and Weber (17), thereby confirming their studies. Chudyk and Snoeyink (19), reported a value of 1.14×10^{-12} m^2/s for phenol for the same carbon but of size fraction 40/50. Foo and Rice (20), studied the concentration effect on the surface diffusion coefficient. They observed small difference in the surface diffusion coefficient over a fourfold change in concentration, and they found that the independence of surface diffusion coefficient on initial concentration appears to confirm that rate is not controlled by mass action at the adsorption site.

CONCLUSIONS

From the present study the following conclusions were made:

1. Equation (1) can be use to predict the surface diffusion coefficient for adsorption process with a good accuracy.
2. If surface diffusion coefficient must be determined experimentally the stirring speed must be exceed 1000 rpm.
3. It was found that the surface diffusion coefficient more or less constant at low concentrations, as well as for different particle size of adsorbent.

NOMENCLATURE

D	Surface diffusion coefficient	m^2/s
F	Fractional uptake	
K	Sorption equilibrium constant	
q_n	Constant in equation (1)	
R	Particle radius	m
t	Time	s
V_L	Volume of solution	m^3
V_P	Volume of particles	m^3
λ	Effective volume ration $\left(\dfrac{V_L}{V_P K}\right)$	

REFERENCES

1. Work, K. and Warner, C.F., *"Air Pollution, its Origin and Control"*, New York (1976).
2. Ademoroti, C.M., Water Research, Vol. 20, No.9, P.1105 (1986).
3. Metcalf and Eddy, *"Wastewater Engineering"* Mc Graw – Hill Book Company (1972).
4. Weber, J. W. Jr, *"Physicochemical Processes For Water Quality Control"* John Wiley and Sons, New York (1972).
5. Sulaymon, A. H. and Hasso, A. E., First International Engineering Conference, University of Jordan (2001).
6. Sulaymon, A. H. and Hadi, M. H., the Fourth Syrian – Egyptian Conference of Chemical and Petroleum Engineering (2001).
7. Kasser, N. W. and Sulaymon, A. H., Jordan International Chemical Engineering Conference III (1999).
8. Carman, P.C. and Haul, R. A. W., Proc. Roy. Soc., 222A, P.109 (1954).
9. Crank, J., *"The Mathematics of Diffusion"* Oxford University Press, London (1956).
10. Foo, S.C. and Rice, R. G., Ind. Eng. chem. Fundam. Vol. 18, No.1, P.68 (1979).
11. Rice, R. G., chem. Eng. Sci., Vol. 57, No.1, P.83 (1982).
12. Hawley, G. G., *"The Condensed Chemical Dictionary"*, Van Nostrand Reinold Company, New York (1981).
13. Allan, T., *"Particle Size Measurement"* Champman London (1968).
14. Hiester, N. K. and Vermeulen, T., chem. Eng. Prog., Vol. 48, P.505 (1952).
15. Keinath, T. M. and Weber, W. J. Jr., Water Pollution Control Federation J., Vol. 40, No.5, P. 741 (1968).
16. Mathews, A. P. and Weber, W. J. Jr., A. I. Ch. E. J., Symposium Series Vol. 73, No. 166, P.91 (1977).
17. Crittenden, J. C., and Weber, W. J. Jr., J. Environ., Eng. Div., ASCE, Vol. 104, EE2, P. 185 (1978).
18. Mathews, A. P., and Su, C. A., Envir. Prog., Vol. 2, P. 257 (1983).
19. Chundyk, W. A. and Snoeyink, V. L., A.I.Ch. E. J., Nov. 8-12 (1981).

Foo, S.C. and Rice, R. G. Ind. Eng. Chem. Fundam. Vol. 18, No.1, P.68 (1979).

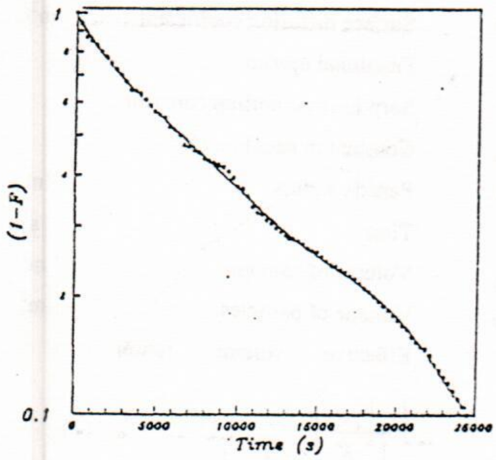

Fig. (1) Plot of ln(1-F) vs. time, stirring speed=600 rpm

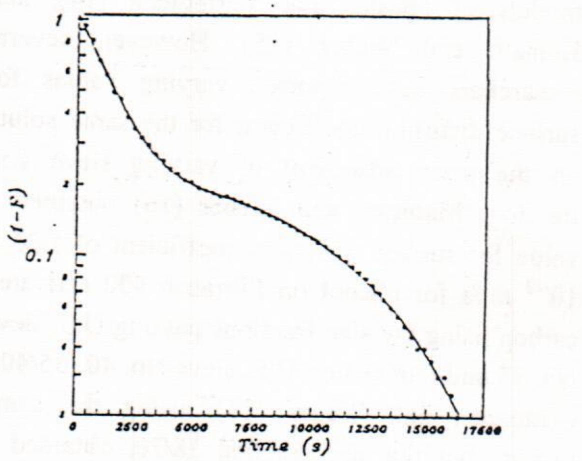

Fig. (2) Plot of ln(1-F) vs. time, stirring speed=800 rpm

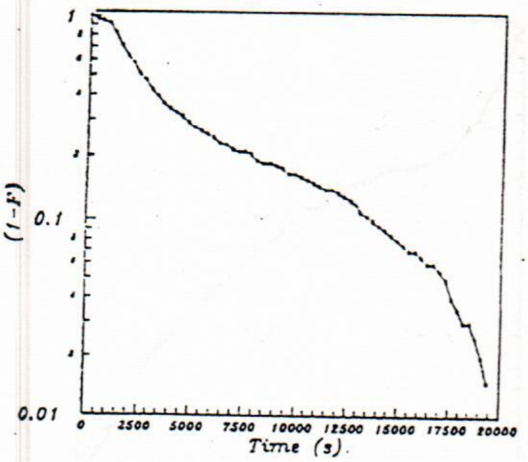

Fig. (3) Plot of ln(1-F) vs. time, stirring speed=1000 rpm

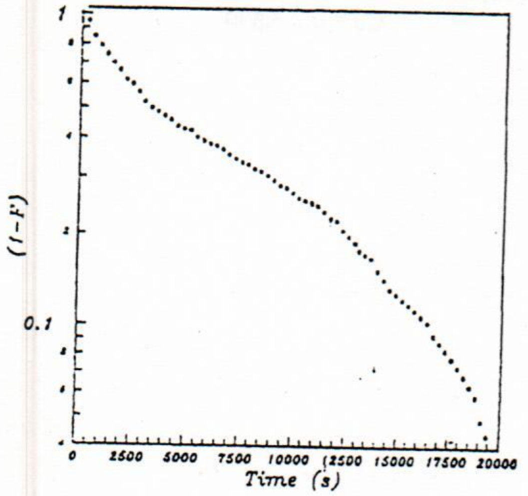

Fig. (4) Plot of ln(1-F) vs. time, stirring speed=1200 rpm

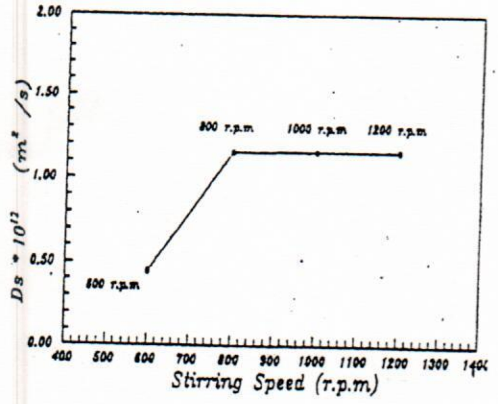

Fig. (5) Apparent particle diffusion coefficient at different stirring speeds

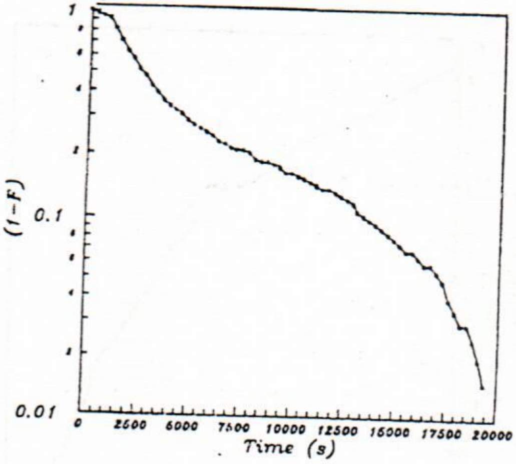

Fig. (6) Plot of ln(1-F) vs. time, dp=1.22×10^{-3}m, Co = 0.2 Kg/m^3

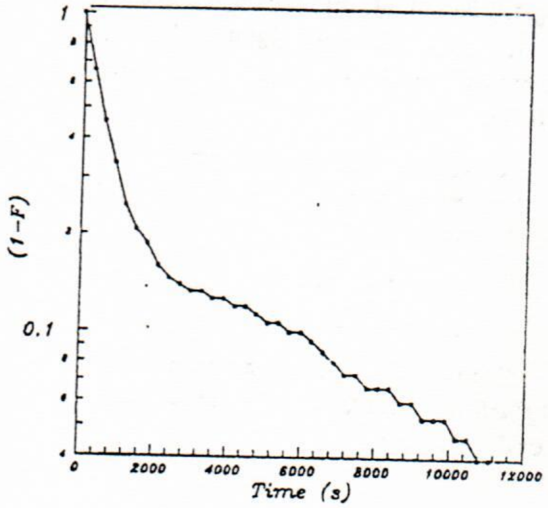

Fig. (7) Plot of ln(1-F) vs. time, dp= 1.22×10^{-3}m, Co = 0.15 Kg/m^3

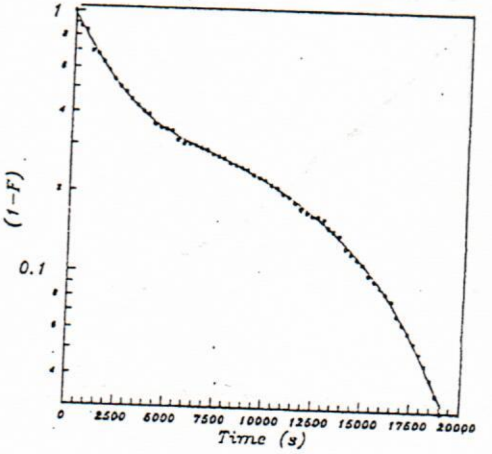

Fig. (8) Plot of ln(1-F) vs. time, dp=1.22×10^{-3}m, Co = 0.1 Kg/m^3

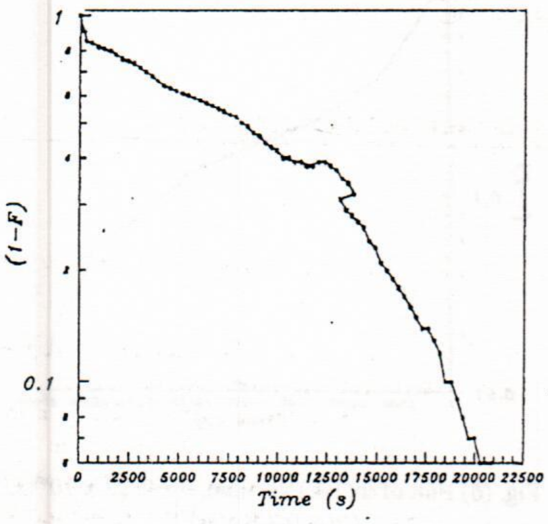

Fig. (9) Plot of ln(1-F) vs. time, dp= 0.8 x 10^{-3}m, Co = 0.2 Kg/m^3

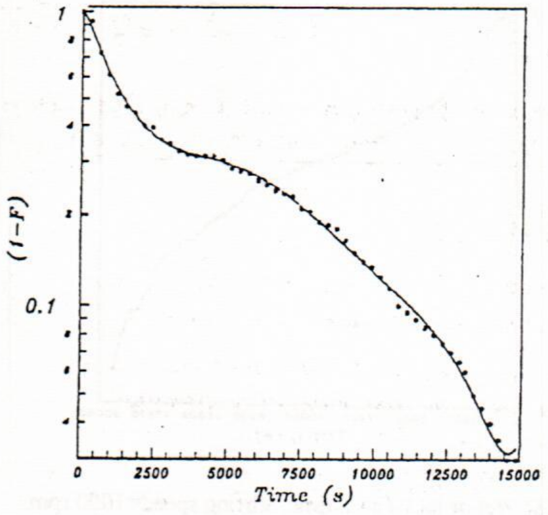

Fig. (10) Plot of ln(1-F) vs. time, dp= 0.63 x 10^{-3}m, Co = 0.2 Kg/m^3