



Removal of anionic dye Wool Green 5 by neutral Alumina as a low-cost adsorbent: Kinetic and Equilibrium study

A. M. Zine¹, S. N. Thore², S. D. Pardeshi³, J. P. Sonar³, H. B Nagre

1Department of Chemistry, SunderraoSolankeMahavidyalaya,
Majalgaon, Dist. Beed 431131, Maharashtra, India.

2Department of Chemistry, Deogiri College, Station Road,
Aurangabad-431005, Maharashtra, India.

3Department of Chemistry, Vinayakrao Patil mahavidyalaya,
Vaijapur, Dist Aurangabad-423701, Maharashtra, India.

Zine.ashok@gmail.com

Abstract:

In the present paper, the adsorption of anionic dye Wool Green 5 from aqueous solution by alumina was studied in a batch adsorption system as a function of contact time and initial concentration. Several adsorption kinetic models like pseudo-first-order, pseudo-second-order, Elovich, and diffusion models (Weber-Morris and Dumwald-Wagner and Film diffusion) were used to investigate the adsorption mechanism. The experimental results have shown that the R² of both the pseudo-first-order and pseudo-second-order are about 99%, but the comparison of experimental and calculated values of adsorption capacity and statistical parameters of error analysis shows the better fitment of the pseudo-second order kinetic model over the pseudo-first order and Elovich model.

Keywords: Parthenium L, Wool Green 5, adsorption, kinetic, Diffusion models, Alumina.

1. Introduction

Synthetic dyes are extensively used in various industries like paper, textile, plastic, carpet, food, cosmetics and leather tanning¹⁻³. The unutilized and untreated dyes are released in industrial effluents leading to environmental pollution problem⁴⁻⁶. These dyes are of non-biodegradable in nature and may be toxic to aquatic life. It has carcinogenic and mutagenic effects causing problems to kidneys, liver, brain, the reproductive and central nervous system⁷⁻⁹. The removal of dyes from wastewater effluents is of great importance. A number of removal methods such as adsorption, advanced oxidation, aerobic coagulation, anaerobic microbial degradation, and membrane separation are used to remove dyes from wastewater. Amongst all these removal methods, adsorption is the most widely used due to its cost-effectiveness and efficiency. Activated carbon is a widely used adsorbent material because of its high adsorption capacity and microporous structure¹⁰. But it has limitation due to its high cost and limited commercial use. There is a need to try for other adsorbent having low cost, low toxicity, and abundance¹¹. Several abundant and low-cost adsorbents like coir pith^{12,13}, peanut hull¹⁴, rice husk¹⁵, baggas pith¹⁶, Vilaytitulsi¹⁷, carrot grass¹⁸⁻²⁰, wheat shells²¹, banana, and orange peels²² are tested for dye removal. As observed, many of the reported low-cost adsorbent materials show lesser adsorption capacity, thereby limiting their industrial use. New economical, easily accessible, environment-friendly and efficient adsorbents are required

The aim of the present study is to use neutral alumina a low-cost adsorbent for the removal of Wool Green 5 dye from aqueous solution.

2. Materials and methods

2.1 Adsorbate

Wool Green 5 (WG 5 – C₂₇H₂₅N₂NaO₇S₂) is an anionic azodye, was obtained from Aldrich Chemicals. The molecular weight of WG 5 is 576.63g and the structure is shown in Fig.1. WG 5 was used without further purification. The dye stock solutions were prepared by dissolving accurately weighed WG 5 in double distilled water to the concentration of 1 × 10⁻³ Molar. The experimental solutions were prepared by diluting dye stock solution in proper proportion.

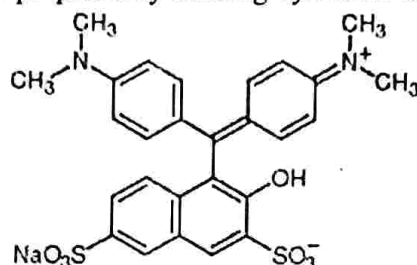


Fig. 1 Molecular structure of Wool Green 5

2.2. Preparation of adsorbent

The neutral alumina (active) of the chromatographic grade was made available from Glaxo Laboratories (India) Ltd., Mumbai, India. It was sieved for the particles of 100-140 mesh size and washed with boiling distilled water to remove surface impurity if any. It was then dried at about 85^oC for 16 hours, cooled in a desiccator at room temperature for 4 hours, the specific surface area of the alumina was found to be 129m²/g. then the alumina is used for the further kinetic studies.

2.3. Adsorption studies

The batch adsorption experiments were carried out in 500 mL Erlenmeyer flasks where 0.5 g of the adsorbent and 300 mL of the WG 5 solutions (5–25 mg/L) were added and agitated in an isothermal shaker at 100 rpm and 30^oC for 35 min to achieve equilibration. The concentration of the WG 5 in the solution after equilibrium adsorption was measured by a double beam UV–vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 634.5 nm. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g). Kinetic studies of adsorption were also carried out at various concentrations of the WG 5 wherein the extent of adsorption was investigated as a function of time. The amount of adsorption at time t , q_t (mg/g), was calculated by

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

3. Results and discussion

3.1. Effect of initial dye concentration on dye adsorption

The effect of the initial WG 5 concentration on the adsorption rate at the adsorbent dosage of 0.50 g and mixing speed of 100 rpm is shown in Fig. 2. It can be seen that the

adsorption at different concentrations is rapid in the initial stages and gradually slows down with the progress of adsorption until the equilibrium is reached. The amount of WG 5 adsorbed at equilibrium (q_e) increased from 2.70 to 10.40 mg/g as the concentration was increased from 5 to 25 mg/L. The initial concentration provides an important driving force to overcome all mass transfer resistances of the WG 5 between the aqueous and solid phases. Hence a higher initial concentration of dye will enhance the adsorption process.

3.2. Adsorption kinetics

3.2.1. Pseudo- first- order kinetics

A linear form of the pseudo-first-order model was described by Lagergren²³ in the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.302} t \quad (3)$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively (mg/g), k_1 is the rate constant of pseudo-first order adsorption

The rate constant is obtained by a linear plot of $\log(q_e - q_t)$ against time (Fig.3). The plot is found to be linear with good correlation coefficient, indicating that Lagergren's equation is appropriate to WG 5 adsorption on alumina. So, the adsorption process is a pseudo-first-order process. The Lagergren's first order rate constant k_1 and q_e determined from the model are presented in Table 1 along with the corresponding correlation coefficients. It was observed that the pseudo-first-order model does not fit well since the calculated and experimental values of adsorption capacity are different. This suggests that the adsorption of WG 5 does not follow first-order kinetics which is also supported by statistical error analysis (Table 3).

3.2.2. Pseudo-second-order kinetics

The pseudo-second-order kinetics may be expressed in a linear form as²⁴:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 is the pseudo-second-order rate constant of adsorption kinetics.

The equilibrium adsorption capacity (q_e), and the second order constants k_2 can be determined experimentally from the slope and intercept of plot t/q_t versus t (Fig. 4). The k_2 and q_e determined from the model are presented in Table 1 along with the corresponding correlation coefficients. The values of the calculated and experimental q_e are represented in Table 1. It can be seen from Table 1 that though the correlation coefficient values are high and the q_e experimental and q_e calculated values are in agreement for the pseudo-second-order model. Hence, the pseudo-second-order model fits better for the adsorption kinetics.

3.2.3. The Elovich equation

The Elovich equation was established by Zeldovich in his work concerning the adsorption of carbon monoxide on manganese dioxide²⁵. The Elovich equation was then employed for relating the adsorption of contaminants from aqueous solutions. The linear form of Elovich equation is expressed as,

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

where α is the initial adsorption rate and the parameter $1/\beta$ is related to the number of sites available for adsorption. The constants α and β were obtained from the slope and intercept of the linear plot of q_t versus $\ln(t)$ as shown in Fig. 5 and the values are presented in Table 1. From Table 1, the coefficient of determination of is lower than that of both the pseudo-first and second order models hence Elovich model do not fit better.

3.3. Adsorption diffusion models

3.3.1. Film diffusion model

The film diffusion mass transfer rate equation has been successfully applied to model several liquid/solid adsorption cases. However, when the transport of the solute molecules from the liquid phase up to the solid phase, boundary plays the most significant role in adsorption; the liquid film diffusion model²⁶⁻²⁷ may be applied as follows:

$$\ln(1 - F) = -k_{fd}t \quad (6)$$

where F is the fractional attainment of equilibrium $F = q_e/q_t$ and k_{fd} is the liquid film diffusion constant. The liquid film diffusion model linear plots of $-\ln(1 - F)$ versus time are presented in Fig. 6. From plots, the film diffusion parameters and coefficient of determination were obtained and given in Table 2. The zero intercept values show the significance of liquid film diffusion in the rate determination of the adsorption process.

3.3.2. Weber-Morris model

Several steps are involved in the sorption of sorbate by a sorbent. These involve transport of the solute molecules from the aqueous phase to the surface of the solid particulates and diffusion of the solute molecules into the interior of the pores, which is usually a slow process. In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber's intraparticle diffusion [48]. The kinetic results were analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism, which can be explained by Weber Morris model²⁸ as:

$$q_t = k_{id}t^{1/2} + C \quad (7)$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant, which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ as shown in Fig. 7. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step. The calculated intraparticle diffusion coefficient values are listed in Table 2. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin. This indicates that the intraparticle diffusion was not only rate controlling step.

3.3.3. Dumwald-Wagner model

Dumwald-Wagner proposed another intraparticle diffusion model²⁹. The simple form of the model can be written as

$$\log(1 - F^2) = -\frac{K}{2.303}t \quad (8)$$

Where K (min^{-1}) is the rate constant of adsorption.

The plot of $\log(1 - F^2)$ versus t is found to be linear and the rate constant of adsorption can be evaluated from it. The plots are shown in Fig. 8 and K values and coefficient of determination are presented in Table 2. Dumwald-Wagner model proved to be reasonable from the coefficient of determination values.

Comparing the results Table 2 of Weber Morris and Dumwald-Wagner intraparticle diffusion models with the coefficient of determination, Dumwald-Wagner intraparticle diffusion model and film diffusion model to be the best fit for the experimental diffusion data according to the diffusion constant which approves very well with the experimental data and coefficient of determination.

Graphs

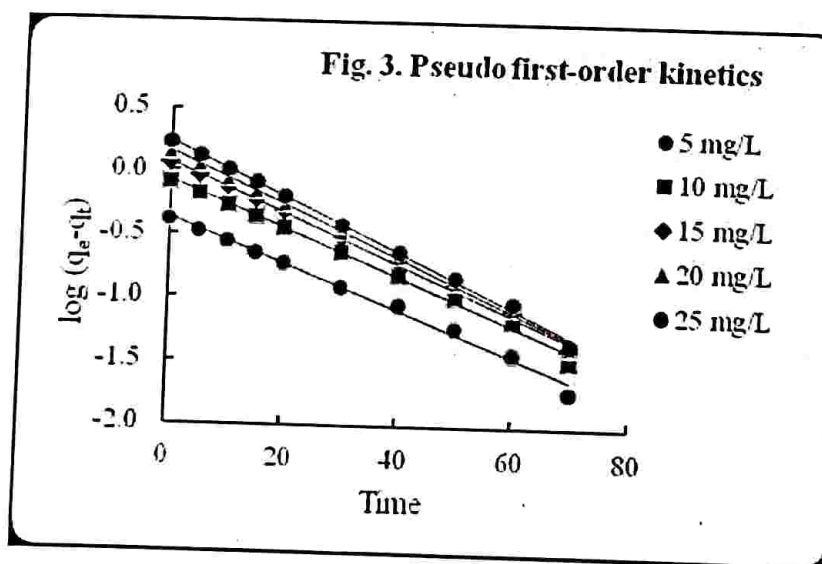
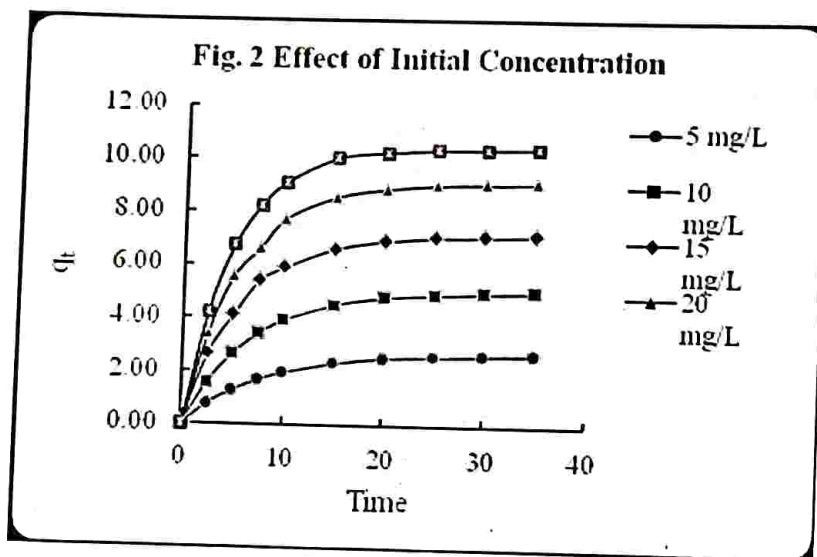




Fig. 4. Pseudo Second order kinetics

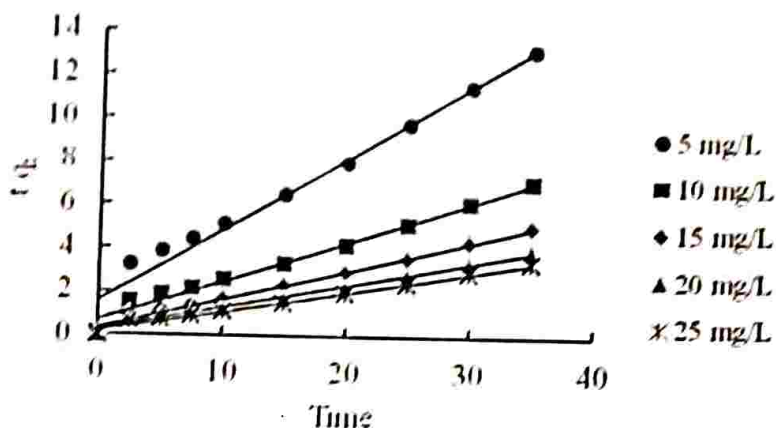


Fig. 5. Elovich kinetic model

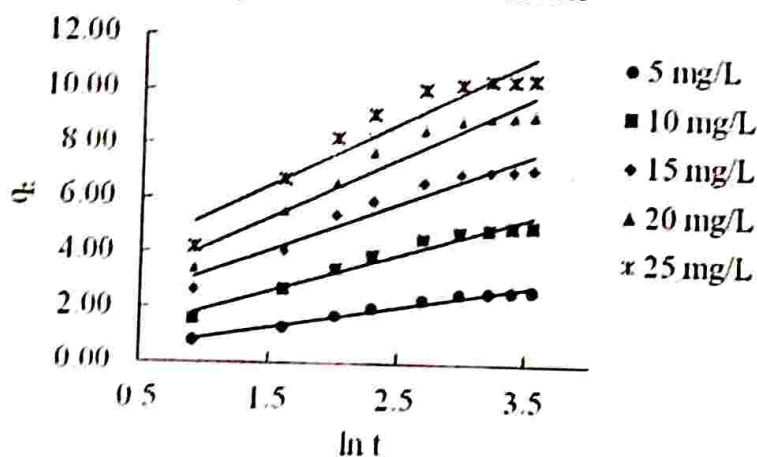
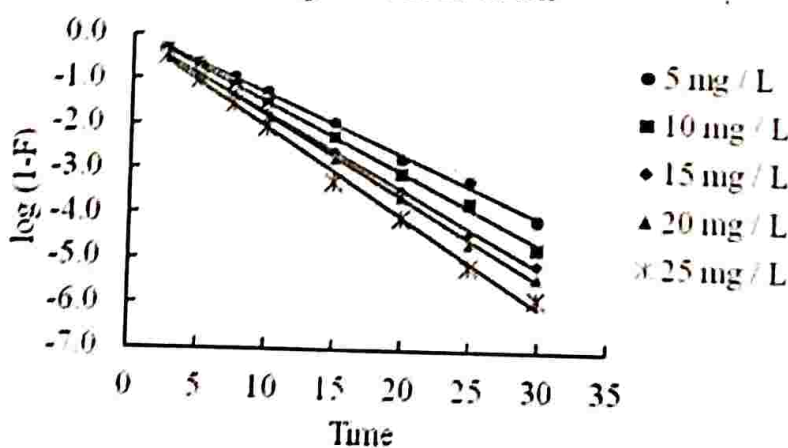
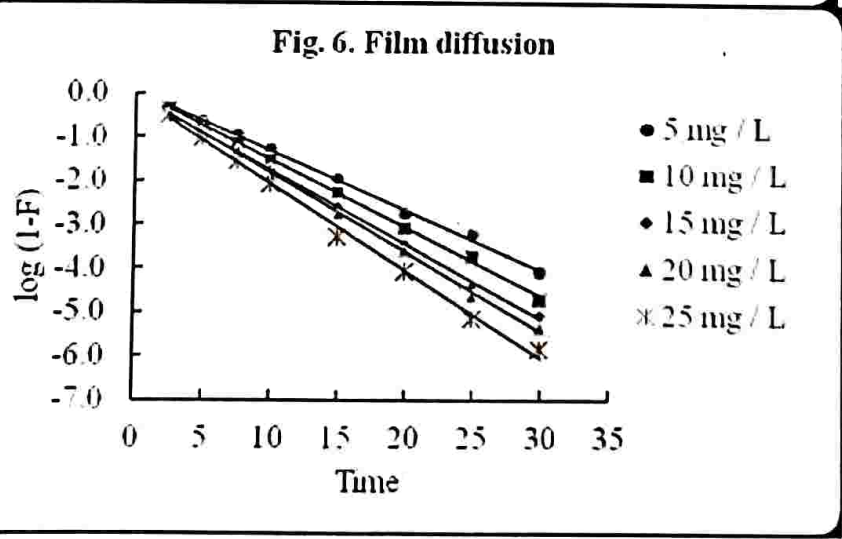
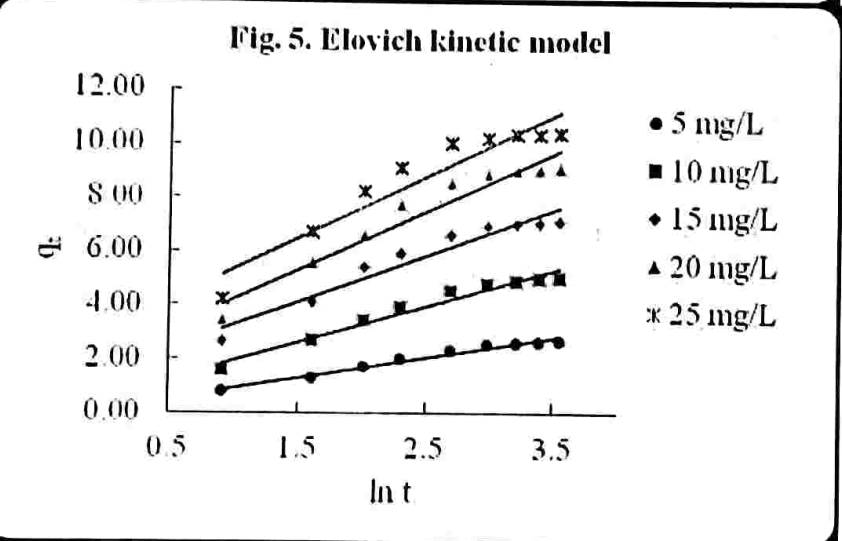
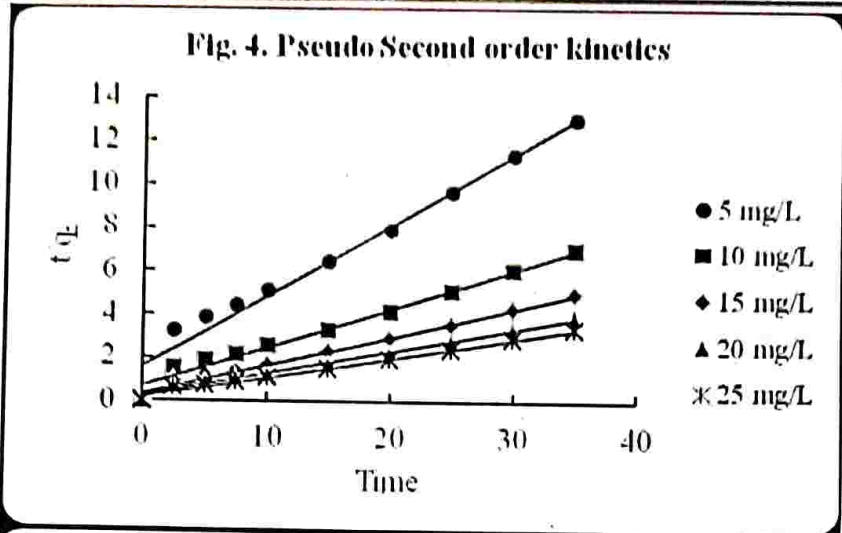
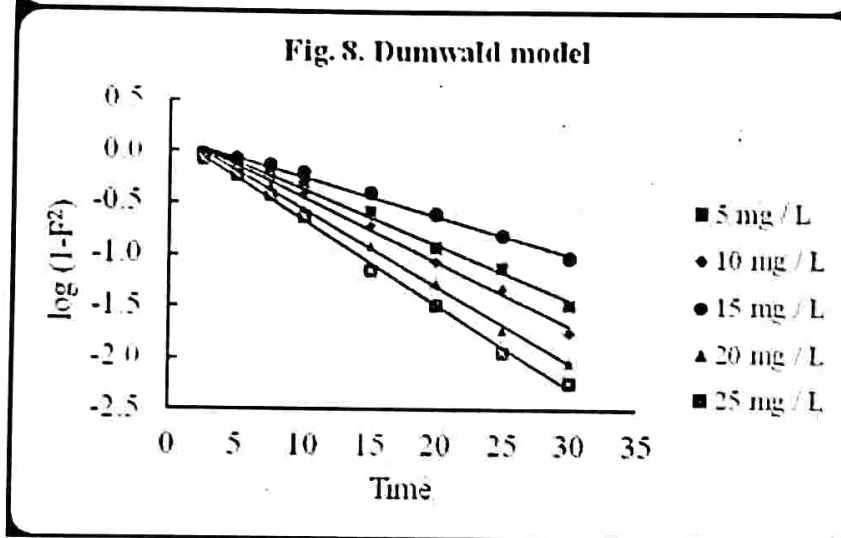
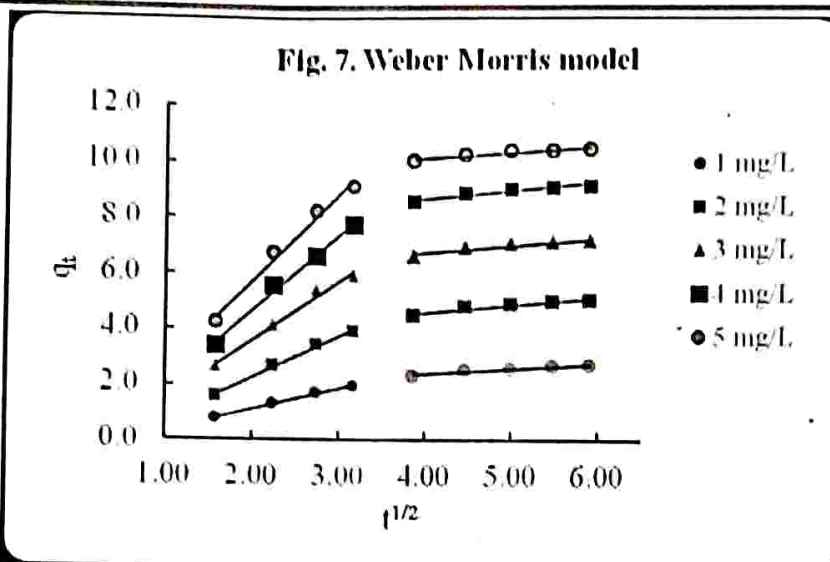


Fig. 6. Film diffusion







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