
LIST OF PUBLICATIONS

Removal of Basic Dye from the Waste-Water
Using Silica as Adsorbent

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ABSTRACT

The kinetics of removal of Basic Blue 3 from a textile effluent was studied using silica as an adsorbent. The adsorption was found to follow a first order process. The influences on the rate of adsorption of various factors such as temperature, concentration of dye solution, pH of the system and the amount of adsorbent have been investigated. On the basis of the isotherm studies, the various thermodynamical parameters have been calculated. The effect of electrolytes and surfactants has also been seen on the removal of the dye from the waste-water.

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NOTATION

A	:	Adsorbent
b	:	Langmuir isotherm Constant (L mg^{-1})
C_e	:	Equilibrium concentration (mole L^{-1})
E_a	:	Energy of activation (Kcal mole^{-1})
f	:	Fraction of dye adsorbed onto surface (g g^{-1})
k	:	Specific reaction rate (min.^{-1})
k_F	:	Freundlich isotherm constant (L g^{-1})
K	:	Equilibrium constant
n	:	Freundlich isotherm constant
Q°	:	Langmuir isotherm constant (mg g^{-1})
t	:	Time (min.)
μ	:	Affinity of dye (Kcal mole^{-1})

INTRODUCTION

Textile industrial effluents are an important source of water pollution, because dyes in the waste-water undergo chemical as well as biological changes, consume dissolved oxygen from the stream and destroy the aquatic life. These dyes are mostly toxic in nature. (Ajmal and Khan, 1985 ; Walsh et al., 1980). It is therefore necessary to treat textile effluents prior to their discharge into the receiving water.

Adsorption has been found to be an efficient and economically cheap process (Allen et al., 1989 ; Gupta and Bhattacharya, 1985 ; Gupta et al., 1988b) to remove the pollutants such as colour, dyes and to control the BOD. Inorganic oxides such as alumina, silica and carbon have been used as adsorbents. Several workers (Allen et al., 1987 ; 1988a, b ; Gupta et al., 1988c, d ; McKay and Al-Duri , 1988 ; Nawar and Doma, 1989) have studied the removal of colours and dyes from the waste-water using various sorbents but the kinetics of adsorption have not been studied, probably because of the speed of adsorption ; the whole process is completed within a short interval of time. The aim of the present work was therefore to investigate the kinetics of the removal of Basic Blue 3, using silica as the adsorbent. The chief determinants of the adsorption have also been investigated.

EXPERIMENTAL METHODS

Chromatographic grade silica gel (Sisco Laboratory, Bombay, India) of 60-120 mesh size was treated with conc. HCl to remove surface impurities. It was washed thoroughly with hot water to remove the chloride ions and dried at 80°C for 12 h. Prior to its use in any experiment, the adsorbent was activated at 80°C for 12 h and allowed to cool in a desiccator (~ 4 h). The dye used in the present study was Basic Blue 3 (C.I. 51004) supplied by Chika Limited, Bombay, India. It was purified by dissolving it in ethanol.

An accurately weighed quantity of the dye was dissolved in double distilled water to prepare a stock solution (1.0×10^{-3} M). Experimental solutions of the desired concentrations were obtained by successive dilutions.

Kinetic studies

The procedure adopted for the study of kinetics of adsorption was reported by us earlier. (Ram and Prasad, 1982 ; 1985). A weighed quantity of the adsorbent was kept in contact with an appropriate concentration of the dye solution and measured volumes were withdrawn at different intervals of time. For this purpose, 0.5 g of silica gel was found to be suitable with 300 ml of dye solution of various concentrations (ranging from 1.0×10^{-5} M to 2.0×10^{-5} M). The adsorbent-

adsorbate system was kept in a thermostat at $30 \pm 0.1^\circ\text{C}$ and was shaken continuously using an electric device. At suitable time intervals shaking was arrested so that the necessary withdrawals of the sample solution (3 ml) could be made ; these were later used for the determination of the concentration remaining in solution. The progress of adsorption at various time intervals was measured by a spectrophotometer (Spectronic-20, Bausch and Lomb, U.S.A.). All the measurements were made at a wave length corresponding to the maximum absorbance. The amount present on the surface of the adsorbent was determined by the difference of the initial and remaining concentration of the dye solution. The experiments were carried out by varying the amount of the adsorbent, the temperature and the concentration of the dye solution as well as the pH of the solution.

Isotherm study

In order to study the adsorption isotherm 0.1 g of silica was kept in contact with 50 ml of dye solutions of different concentrations for 4 h, to attain equilibrium at constant temperature. The amount present on the surface of the adsorbent was determined by the difference of the two concentrations. The experiments were repeated at various temperatures in the range of $25-45^\circ\text{C}$.

RESULTS AND DISCUSSION

Effects of concentration

The plot of the amount of dye taken up at various intervals of time indicates that the removal of dye initially increases with time, but attains an equilibrium within 30 to 40 min. The process was found to be very rapid initially, and a large fraction of the total amount of the dye is removed within a few minutes. Adsorption of actual amount of dye increases with an increase in the concentration of the dye solution. Thus on varying the concentration of Basic Blue-3 from 1.4 to 2.0×10^{-5} M, adsorption increased from 2.86 to 3.99×10^{-3} g g⁻¹ using silica as an adsorbent (Table-1). This shows that the removal of dye is dependent upon the concentration of the dye solution. The time variation curves for dye removal (Fig. 1a) are smooth and continuous, indicating the formation of monolayer coverage on the surface of the adsorbent. The straight line plots of $-\log (1-f)$ Vs. time (plots are not given) is indicative of the first order process according to the equation.

$$-kt = 2.303 \log (1-f) \quad \dots\dots(1)$$

where 'f' is the fraction of the dye adsorbed onto the surface at various interval of time and k is the specific reaction rate. The values of k calculated from the above plots

were found to increase from 0.124 to 0.135 min.⁻¹, with an increase in the concentration of the dye solution from 1.4 to 2.0×10^{-5} M (Table-1). The corresponding linear plot given in Fig. 1b is the indicative of the formation of monolayer coverage in the concentration range studied.

Effects of Temperature

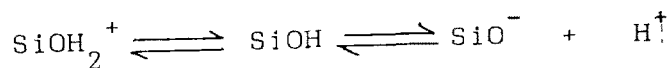
The nature of the time variation curve for the removal of dye from effluents was the same as described earlier, which shows that no change occurred due to variation of the temperature of the system. However, the uptake of dye was found to decrease with an increase in temperature, indicating that the process is exothermic in nature. (Ram and Prasad, 1982 ; Panday et al., 1984). This may be due to a tendency for the dye molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution. (Panday et al., 1984 ; Gupta et al., 1988a). Thus on increasing the temperature of the system from 20° to 50°C the adsorption of the dye decreased from 4.12 to 3.68×10^{-3} g g⁻¹ on silica. The values of the specific reaction rate k, calculated from the slope of straight line plots of -log (1-f) Vs. time (Fig. 2a) were found to increase from 0.129 to 0.145 min⁻¹ (Table 2).

The energy of activation calculated from the Arrhenious plot (Fig. 2b) is given in Table-2. Its low value shows

that adsorption of Basic Blue 3 is fast on the surface of silica. A low energy of activation has been reported by Singh et al., (1975) with adsorption of cationic dyes onto alumina and by McKay et al., (1980) with adsorption of dyes onto silica.

Influence of pH of the dye solution

The kinetics of removal of dye has been investigated at various pHs. The extent of adsorption increases from 3.80 to $4.15 \times 10^{-3} \text{ g g}^{-1}$, when the pH of the system is varied from 4.2 to 8.9. The specific reaction rate, k also increased from 0.109 to 0.141 min^{-1} over that range of pH (Table 3). The increase in adsorption, as well as its rate is dependent on the surface properties, as well as the dye structure. According to Onada and Fuerstanaue (1964) at lower pH the surface of silica becomes positively charged, whilst at higher pH it becomes negatively charged. This change is represented as follows :



At lower pH the adsorption of cationic dye should be less because of the lower dissociation of the dye molecules as well as the positively charged surface. At higher pH, both the dye as well as the surface will be dissociated, which

results in a higher adsorption through increased cation exchange capabilities. Similar results have also been described by Sethuraman and Rayamahashay (1975) with the adsorption of acidic and basic dyes on kaolinite and montmorillonite.

Influence of various amount of adsorbent on dye adsorption

A study of the kinetics of adsorption was made using various amounts of the adsorbent, whilst keeping the dye concentration constant, at constant temperature. The nature of adsorption was observed to be same as described above. However, a decrease in adsorption was obtained by increasing the amount of the adsorbent. Thus when the amount of silica varies from 0.3 g to 0.6 g the uptake decreased from 6.27 to $3.45 \times 10^{-3} \text{ g g}^{-1}$ at 30°C (Table 4). The corresponding k values were found to increase from 0.086 to 0.143 min^{-1} .

Adsorption Isotherm

The plots of the dye uptake against the equilibrium concentration (C_e) (Fig. 3a) indicates that adsorption increases initially with concentration, but then reaches saturation. The equilibrium data for the adsorption of Basic Blue 3 on silica fits the Freundlich adsorption isotherm according to the equation

$$x/m = k_F C_e^{1/n} \quad \dots (II)$$

where x/m is the amount adsorbed in $g\ g^{-1}$, k is a rough measure of the adsorption capacity, that is the intensity of adsorption, and C_e is the equilibrium concentration of the dye solution. The linear plot of $\log x/m$ Vs. $\log C_e$ (Fig. 4) indicates the applicability of the Freundlich adsorption isotherm, for the present system exhibits a monolayer formation of the coverage of the adsorbate on the outer surface of the adsorbent.

The values of k and $1/n$ calculated from the intercepts and the slopes of the log-log plot (Table 5) for all the temperatures were used for computing $\Delta\mu$ (i.e. the standard affinity of the dye). It is seen from the results that the values of $\Delta\mu$ decrease with an increase of temperature (Table 5) indicating greater adsorption affinity at lower temperatures. Similar results have been reported by Bird and Manchester (1955) with the adsorption of azo dyes onto secondary cellulose acetate.

The monolayer formation for the present system has further been confirmed by the linear plots of C_e/q_e Vs. C_e according to the Langmuir isotherm

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ}$$

: 10 :

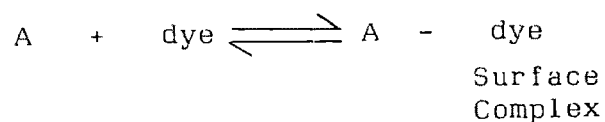
where Q° and b are the Langmuir constant related to the capacity and energy of adsorption respectively. The values of Q° and b calculated from the slopes and intercepts of the above plots are given in Table 5. The Q° values were found to remain constant over the concentration range studied.

Thermodynamic parameters

The change in standard free energy may be calculated using the following relationship.

$$\Delta G^\circ = -RT \ln K \quad \dots\dots(III)$$

where K is the equilibrium constant and can be determined as



where A is the adsorbent.

$$\text{Thus, } K = \frac{\text{Concentration of dye present on the surface}}{\text{Remaining concentration in solution}}$$

The change in enthalpy was determined from the slope of the linear plot of $\log K$ Vs. $1/T$ (Fig. 3b) and the entropy by,

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

The values for ΔG° , ΔS° and ΔH° are given in Table 6.

The negative values of ΔG° are indicative of a spontaneous process with a high affinity of a dye on the surface of the adsorbent. An exothermicity may be explained on the basis of negative values of the enthalpy (ΔH°) change in the adsorption of Basic Blue 3 on the silica surfaces. A negative entropy change (ΔS°) found in the present study could be understood in terms of restriction of the movement of molecules to two dimensions in the surface as against three dimensions in the bulk. In other words a decrease in entropy change is indicative of the decrease in the randomness of the system. Similar results have been reported by Wright and Pratt (1974) with adsorption of aromatic compounds onto oxide and carbon black.

Influence of Electrolytes and Surfactants

Uptake of a dye from a complex matrix such as an industrial effluent will certainly be different from that of a simple dye solution. Textile industrial effluents often contain sufficient concentration of electrolytes and surfactants. Therefore, adsorption experiments were carried out in the presence of electrolytes (Potassium chloride and Sodium chloride) and surfactants (CTAB, Brij 35 and SDS). In a typical experiment, when the concentration of KCl was increased

from 0.01N to 0.08N, adsorption of Basic Blue 3 on silica decreased from 2.26×10^{-3} to 1.29×10^{-3} gg^{-1} . Similar effect was observed in presence of NaCl and the surfactants. Such a behaviour is due to the interaction between surface and added solutes which may block some of the sorption active site, for the dye molecules.

Desorption of dye is important for economic regeneration of the adsorbent. It has been seen from some independent experiments that dyes adsorbed on the surface resist detachment when washed with water. However, preliminary column elution studies showed that adsorption of the dye can be brought about with relative ease by passing a dilute aqueous solution of an electrolyte such as potassium chloride. Detailed study of adsorption kinetics and economic regeneration of the adsorbent is under progress.

ACKNOWLEDGEMENTS

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Legend of Figures

- Fig. 1a : Time variation of adsorption of Basic Blue 3 on Silica with concentration of dye solution
- Fig. 1b : Variation of rate constant with concentration
- Fig. 2a : Variation of $-\log (1-f)$ with time for adsorption of Basic Blue on Silica.
- Fig. 2b : Plot of $\log k$ (rate constant) with $1/T$ for the adsorption of Basic Blue on Silica.
- Fig. 3a : Variation of adsorption of Basic Blue on Silica with equilibrium concentration at different temperatures.
- Fig. 3b : Plot of $\log K$ (equilibrium constant) with $1/T$.
- Fig. 4 : log-log plot of variation of adsorption with concentration at different temperatures.
- Fig. 5 : Plots of C_e/q_e Vs. q_e for the adsorption of Basic Blue on Silica.

Table - 1 : Time-rate study of adsorption on silica
with variation of concentration of dye
solution at $30 \pm 0.1^\circ\text{C}$

Concentra- tion of the dye solution (M) $\times 10^5$	(Amount adsorbed in g \bar{g}^{-1} adsorbent at equilibrium) $\times 10^3$	Specific reaction rate $k \text{ (min}^{-1}\text{)}$
1.4	2.86	0.124
1.6	3.26	0.128
1.8	3.60	0.132
2.0	3.99	0.135

Table - 2 : The influence of temperature on adsorption of Basic Blue 3 on Silica

Initial concentration of dye solution : $2.0 \times 10^{-5} \text{ M}$

Temperature	(Amount adsorbed in g g ⁻¹ adsorbent at equilibrium)	Specific reaction rate	Energy of activation
(°C)	$\times 10^3$	k (min ⁻¹)	Ea, Kcal mole ⁻¹
20	4.12	0.129	
30	3.99	0.135	0.68
40	3.82	0.140	
50	3.68	0.145	

Table - 3 : Time variation of adsorption with pH
of the dye solution at $30 \pm 0.1^\circ\text{C}$

Initial concentration of dye solution : $2.0 \times 10^{-5}\text{M}$

pH of the solution	(Amount adsorbed in g g ⁻¹ adsorbent at equilibrium) $\times 10^3$	Specific reaction Rate k (min ⁻¹)
4.20	3.80	0.109
5.45	3.93	0.122
7.80	4.08	0.131
8.90	4.15	0.141

Table - 4 : The influence of various amount of silica on adsorption of Basic Blue 3 at $30 \pm 0.1^\circ\text{C}$

Initial concentration of dye solution : $2.0 \times 10^{-5}\text{M}$

Amount of adsorbent (g)	Amount adsorbed in g g^{-1} adsorbent at equilibrium $\times 10^3$	Specific reaction rate $k (\text{min}^{-1})$
0.3	6.27	0.086
0.4	5.02	0.102
0.5	3.99	0.135
0.6	3.45	0.143

Table - 5 : Values of Langmuir and Freundlich Isotherms constants
calculated from the respective plots at different tem-
peratures

Tempera- ture (°C)	Langmuir constant $Q^{\circ}(\text{mg g}^{-1})$	Langmuir constant $b (\text{L mg}^{-1})$	Freundlich constant $k (\text{L g}^{-1})$	Freundlich constant $1/n (\text{Integer})$	Affinity $-\Delta \mu^{-1}$ (Kcal mole)
25	11.21	1.17	1.26	0.419	0.138
30	11.16	1.10	1.36	0.428	0.187
35	11.13	1.01	1.43	0.434	0.219
40	11.12	0.95	1.56	0.443	0.278
45	11.05	0.87	1.72	0.454	0.345

Table - 6 : Thermodynamic quantities calculated
from the adsorption isotherm

Tempera- ture (°C)	$-\Delta G^\circ_{-1}$ Kcal mole	Equilibrium constant K	$-\Delta S^\circ_{-1}$ Cal mole degree	$-\Delta H^\circ_{-1}$ Kcal mole
25	1.90	24.60	6.30	
30	1.87	22.28	6.30	
35	1.84	20.33	6.30	3.78
40	1.79	17.82	6.35	
45	1.77	16.54	6.32	

Figure No.-1a

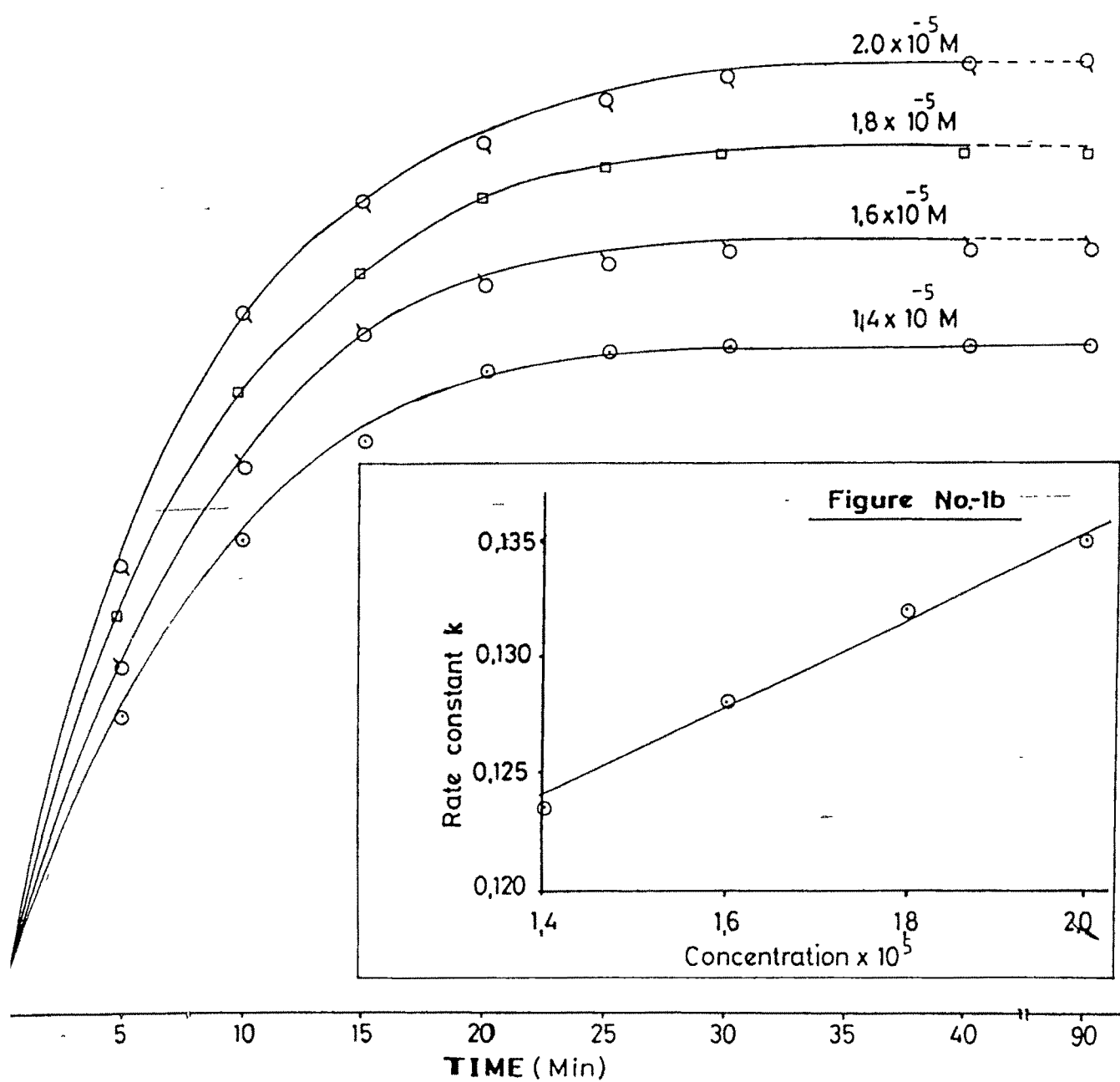


Figure No.-2a

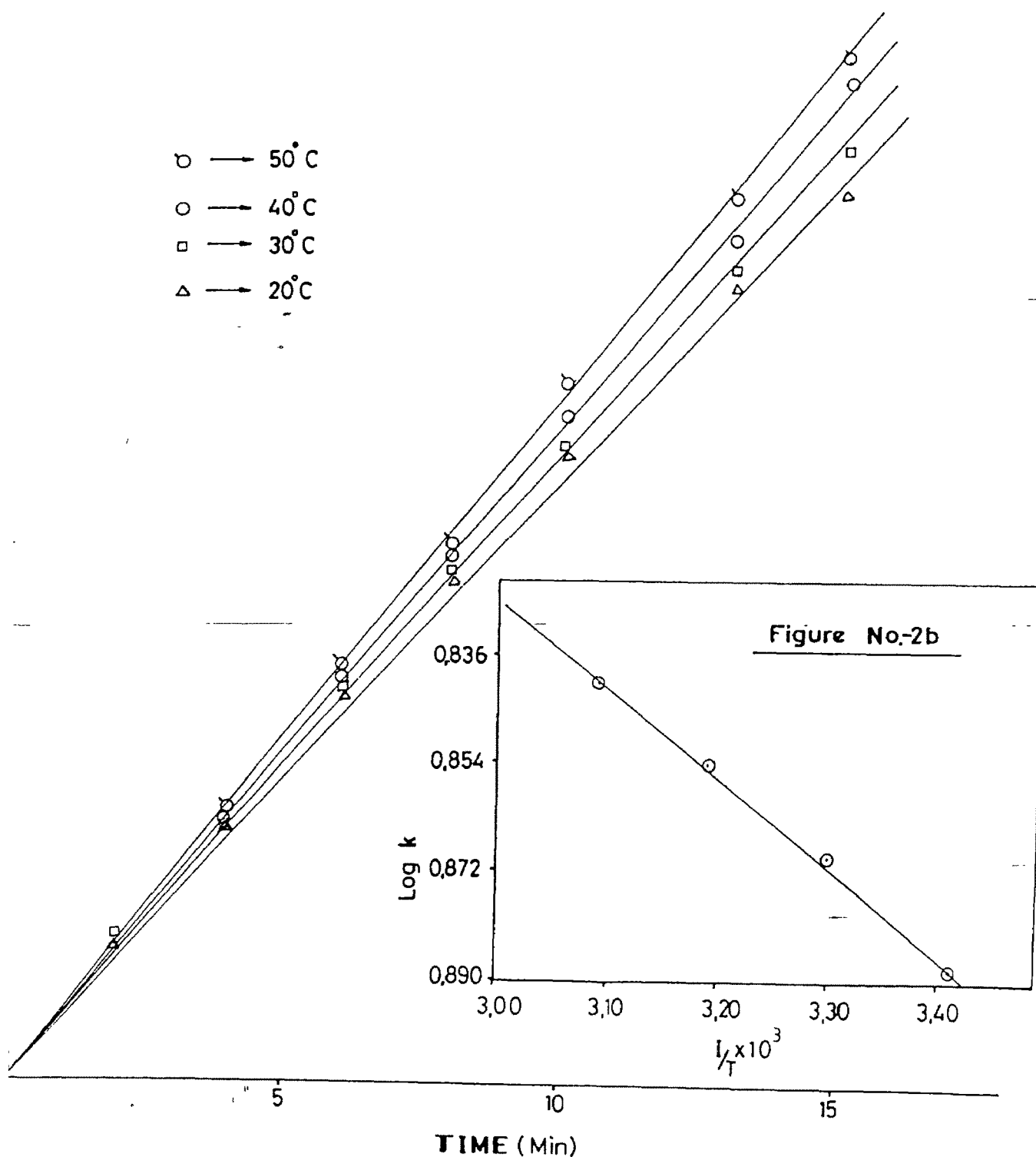


Figure No.-3a

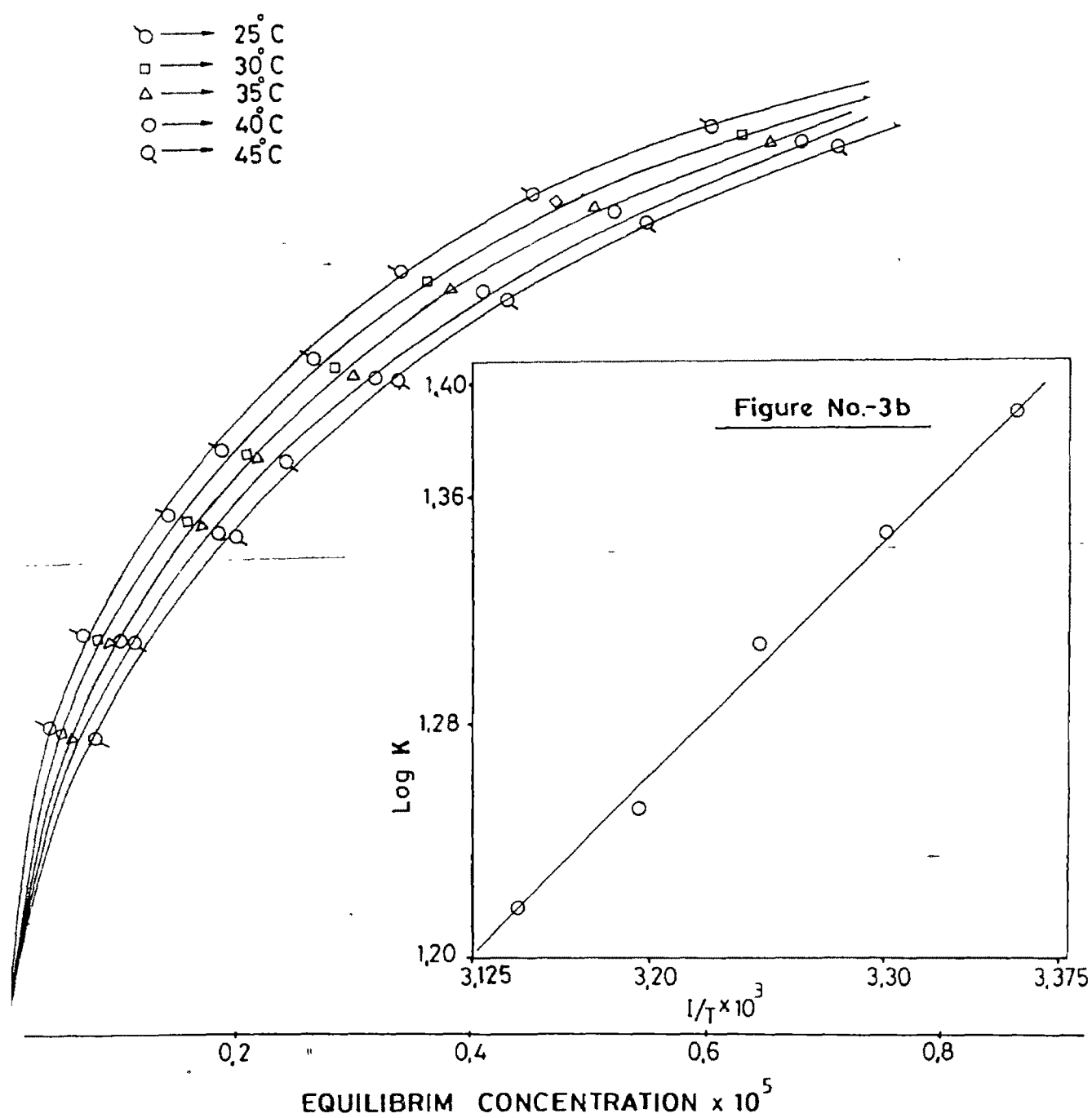
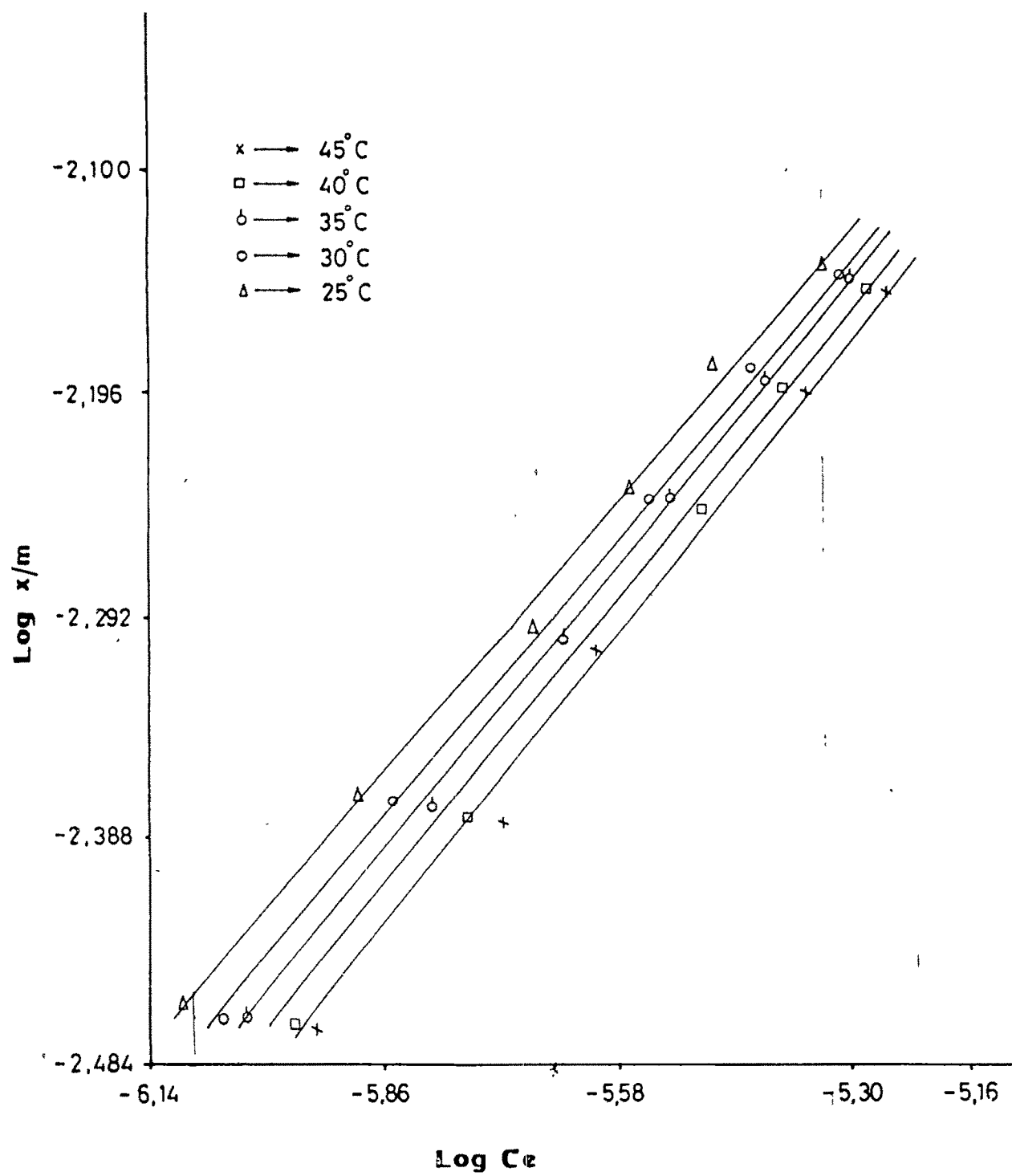
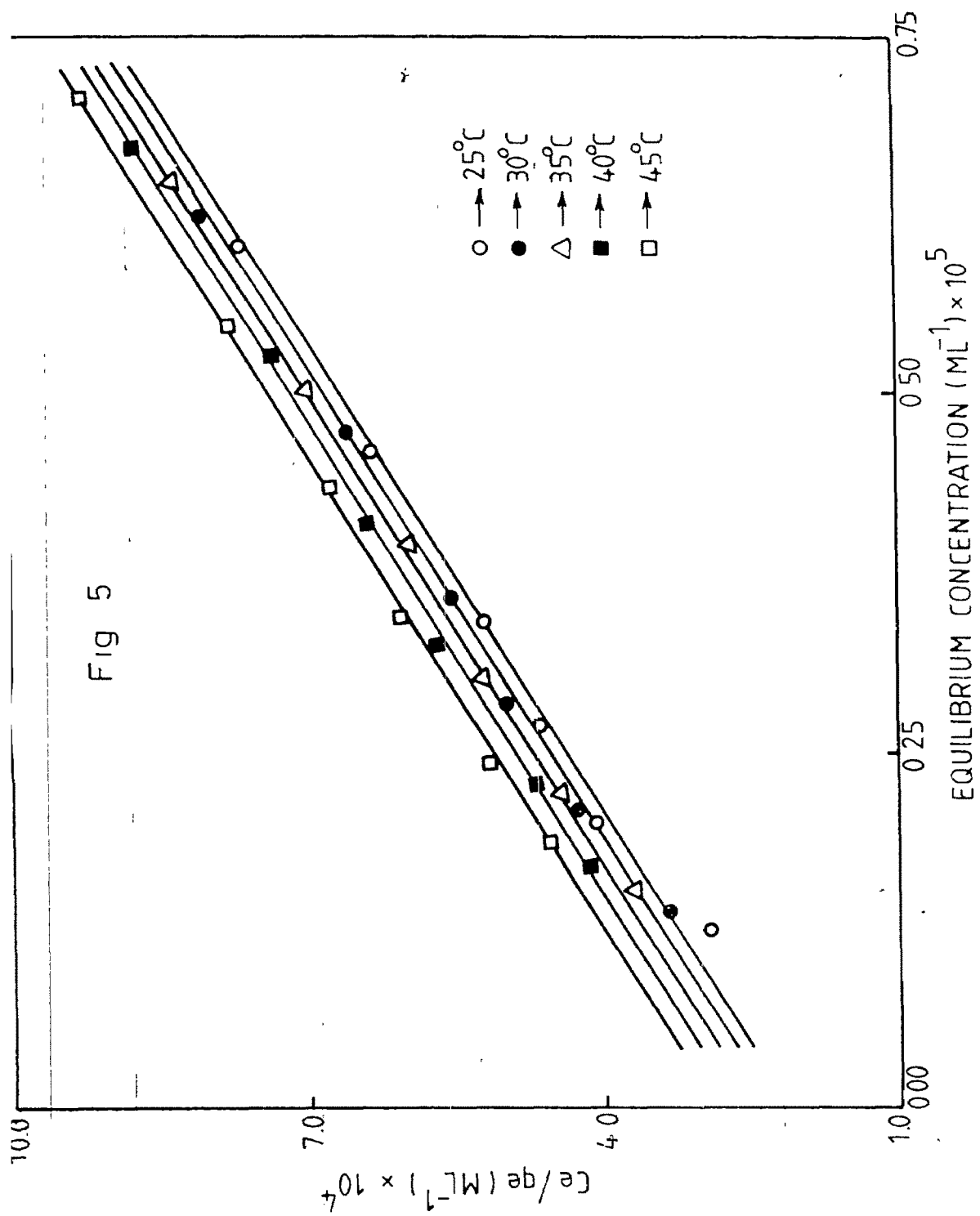


Figure No.-4





KINETICS OF REMOVAL OF BASIC VIOLET 1 FROM
AQUEOUS SOLUTION USING SILICA AS AN ADSORBENT

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ABSTRACT

The kinetics of removal of Basic Violet 1 from the aqueous solution was studied using adsorption process. The entire work consisted of the measurement of the time growth of adsorption as a function of the amount of adsorbent, pH and initial dye concentration as well as the temperature of the system. A large fraction of total amount of dye was found to be taken out using this process with a short span of time. The adsorption was found to follow the first order process. The adsorption data indicate that the process is spontaneous and exothermic in nature. On the basis of isotherm studies various thermodynamic parameters such as ΔG , ΔH & ΔS have been calculated. Freundlich and Langmuir isotherms are applicable for the present system, suggesting the monolayer formation of dye on the silica surface.