CHAPTER - 6

ISOTHERM STUDY

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6.1 ISOTHERM STUDY : ADSORPTION OF DYES ONTO OXIDES AND GRAPHITE SURFACES

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6.1.1 Introduction

Amongst the factors which determine the extent of adsorption, the concentration of the adsorbate solution is one of the chief determinant. Any change in this factor is seen to affect not only the extent but in some cases also the nature of the adsorption. The actual variation of the amount adsorbed with concentration (pressure in case of gases) at a constant temperature is expressed by a relation usually known as adsorption isotherm. The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate in the solution. Several such isotherms both obtained empirically as well as derived on theoretical basis have been proposed from time to time to represent the observed results. Many of these, despite their succesful adoption in specific cases, are found inadequate in systems of diverse nature or in simple cases also specially when applied over wide range of experimental parameters. Initially most of the isotherms were derived for the adsorption of gases onto solid surfaces [1] but they were also found successful in representing the other sorption processes, especially the adsorption of dyes onto solid surfaces [2,3].

The amount of solute adsorbed by one gram of the adsorbent, under a given set of condition, is expressed usually as

$$X = f(C) \quad \text{or} \quad f(P)$$

Where C is the concentration (P is pressure in case of gas) of the adsorbate solution. In the adsorption study from solution, various isotherms have been used to express adsorption behaviour. Among them Langmuir and Freundlich adsorption isotherms are frequently used by several workers [4-8]. A brief description of the commonly used adsorption isotherms are given below.

The Langmuir adsorption isotherm for adsorption from solutions is expressed as :

$$q_e = \frac{x}{m} = \frac{\overset{o}{Q} b C_e}{1 + b C_e}$$

Where the terms have their usual significance. A linear form of the above equation is expressed as :

$$C_e / q_e = \frac{1}{K} + \frac{b}{K} C_e \quad [\text{here } K = \overset{o}{Q} b]$$

The Freundlich [9] adsorption isotherm can be expressed by an empirical equation :

$$\frac{x}{m} = K_F C_e^{1/n}$$

Where K_F and n are isotherm constants ; the values of K_F and exponent 1/n depend on the actual system and experimental conditions. A linear form of the Freundlich adsorption isotherm is :

$$\log q_e = \log K_F + 1/n \log C_e$$

from which the constants K_F and 1/n can be calculated.

The modified form of Redlich-Peterson [10] isotherm can be expressed as :

$$q_e = \frac{KC_e}{1+a_R C_e^b}$$

Where K, a_R and b are constants. These can be determined from the linear plot represented by following equation :

$$\ln\left(K\frac{C_e}{q_e} - 1\right) = b\ln C_e + \ln a_R$$

A large amount of the experimental results of adsorption from solution have been expressed using these isotherms. The adsorption of dyes from aqueous solution has also been represented by these relations. Thus the adsorption of methyl red onto silica [11], basic dyes onto lignite [12], removal of tetramethyl thiuram disulfide (thiram) from aqueous solution by bentonite [13] are some examples where the results have been expressed simultaneously using these isotherms.

Some examples which show the applicability of Freundlich as well as Langmuir isotherms include the adsorption of phenol, chlorophenol and sodium dodecyl sulphate onto activated carbon [14], basic dyes onto hard wood [15] and peat [16]. In the study of acids on charcoal, metallic salts on silica, phosphate ions on hematite and gibsite and of dyes onto silk, Freundlich [17-20] adsorption isotherm was found suitable while in the adsorption of Cd(II) onto fly ash [21], the removal of mordant blue by fly ash [22] and chrome dye by mixed adsorbents [23] are some such examples, where Langmuir adsorption isotherm fits well. However several workers have noticed that the studies were applicable only for monolayer adsorption within the limited range of concentration [24-26].

The Brunauer - Emmett-Teller [27] model proposed for multilayer adsorption, was a direct extension of the Langmuir model. The equation adopted for this purpose is as follows :

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_o}$$

Where the terms have their usual meaning. Use of this equation has not only been limited exclusively to gaseous adsorption but has equally been extended to adsorpion from solutions also [28]. The equation was used by several workers [26,29-31], for the surface area measurement of commonly used adsorbents using dye adsorption from equeous solutions.

Another important model proposed by Frumkin and Slygin [32] is as follows :

$$\theta = \frac{1}{f} \ln C_o p$$

where θ is the fraction of the surface covered, P is the pressure of the gas and 'f' and C_o are constants.

The isotherm due to Herkins and Jura [33] is represented as

$$\log \frac{p}{P_o} = B - \frac{A}{V^2}$$

Where V is the volume of gas adsorbed at pressure p, p_o is the saturation pressure and A and B are constants. Another isotherm proposed by Temkin [34] is as follows :

$$\theta = C_1 \ln (C_2 KP_A)$$

where θ is the fraction of the surface covered by the gas, P_A is the pressure of the gas, C_1, C_2 are the constants related to enthalpy of adsorption and K is a constant.

These equations as well as several others [35-37] of similar type have found successful application largely in gaseous adsorption. From the consideration of the energetics of adsorption, Sips [38] proposed a relation which was adopted to represent several observations of importance. Some of the other relations which have shown better fit of the experimental data on many occasions and are worth mentioning here are the adsorption isotherms [39-43] of Gibbs, Elovich, Chakravarti and Dhar, Young and Crowell, Hayward and Trapnell, Zeise, and Magnus.

In the adsorption of dyes using various adsorbents of common use, it has been seen that the actual nature of the variation with concentration differs widely and is seen to be decided by both the nature of adsorbent and adsorbate and the concentration range studied. It was of interest therefore, to investigate this aspect i.e., the influence of dye concentration on adsorption from dilute solutions onto oxides and graphite surfaces and also to test the isotherm, suitable to represent the results obtaining under the conditions employed in the present study.

6.1.2 Experimental

The method adopted here for the preparation and the processing of the adsorbents is the same as described earlier (Chapter 2). Weighed quantities of the adsorbents were kept in contact with measured volume of dye solutions of different concentrations. These were maintained at a constant temperature for a suitable period during which the systems were shaken continuously using same procedure (Chapter 2). The time duration allowed was of 4 hours, a period sufficiently long as compared to that required for equilibrium in any of the systems studied for the kinetics. The amount of dye adsorbed was calculated from the difference in the initial and equilibrium concentrations of the solution measured spectrophotometrically. The concentration range selected here, was mostly near about the same concentrations which is employed for the kinetic study. This facilitated mutual correlation of the results, in addition to the available advantage in measurement of absorbance directly from the experimental solutions without any subsequent dilution which otherwise becomes necessary in the use of very high concentrations. Thus the concentration of dye used with silica and alumina were in the range of

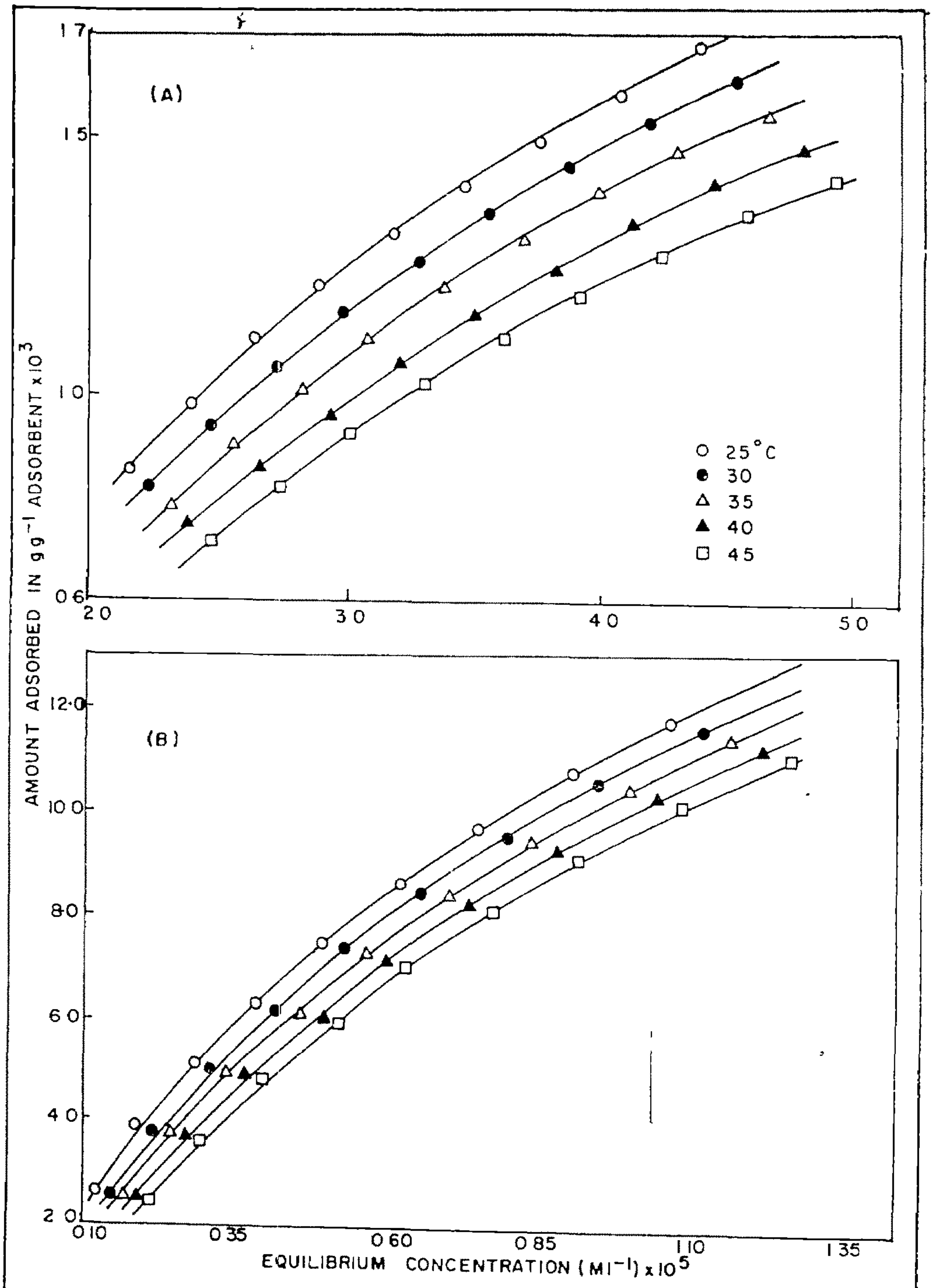

Fig 6 1 1 Variation of adsorption of (A) Basic Brown 4 on basic alumina and (B) Ketone Blue A on neutral alumina with equilibrium concentration at different temperatures

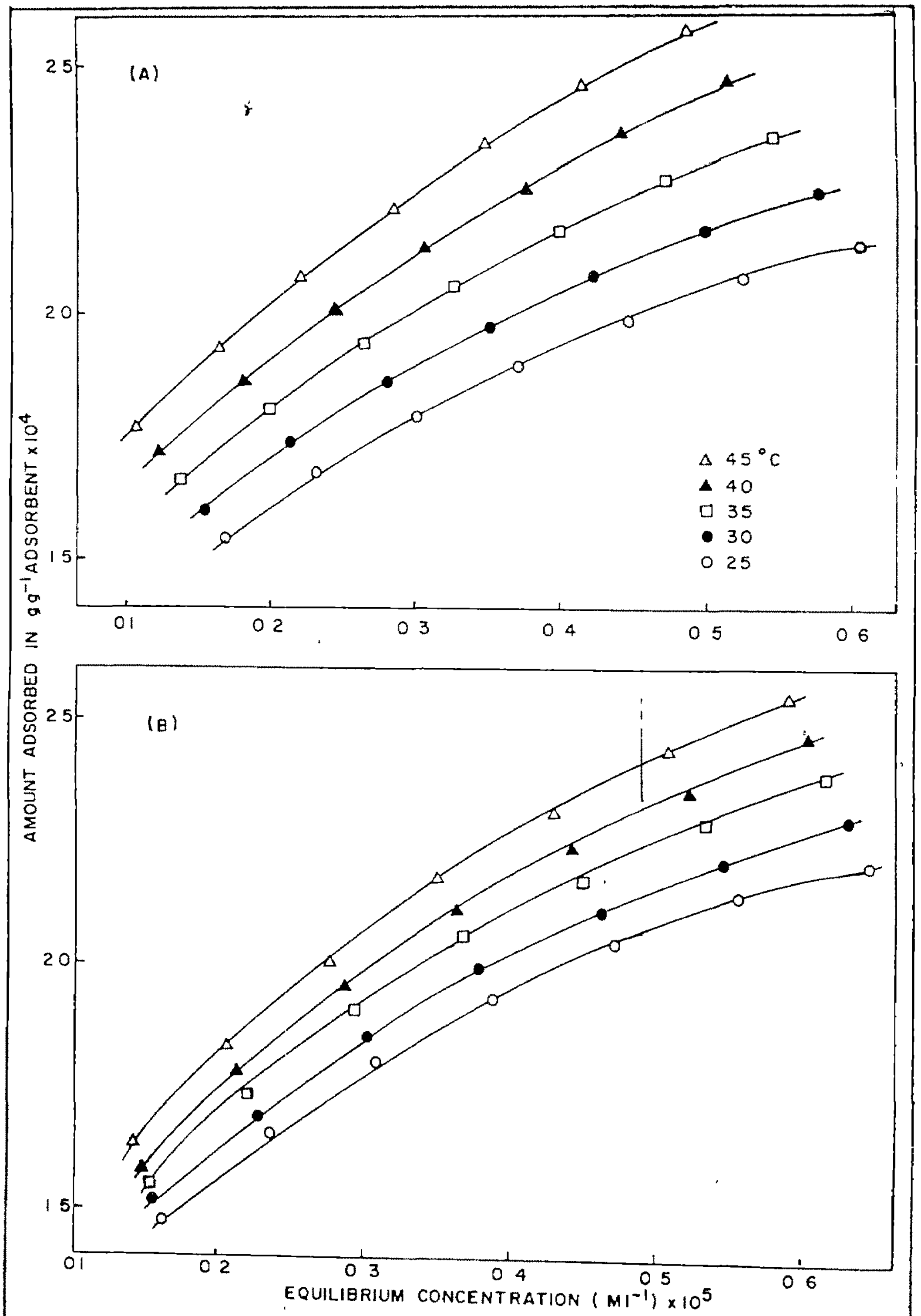

Fig 6 1 2 Variation of adsorption of (A) Basic Blue 3 and (B) Acid Green 25 on graphite with equilibrium concentration at different temperatures

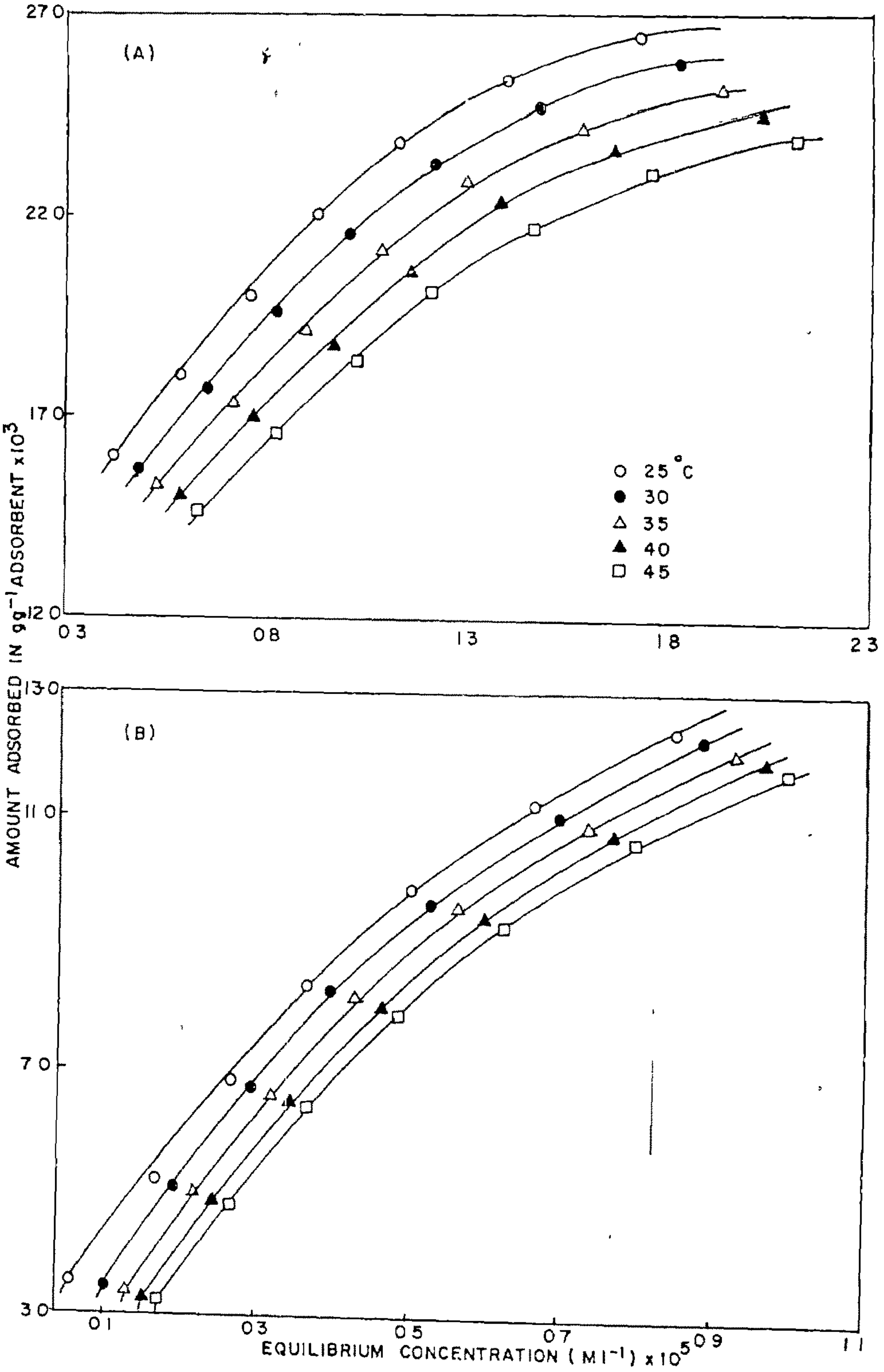

Fig 6 1 3 Variation of adsorption of (A) Acid Black 1 on neutral alumina and (B) Basic Violet 1 on silica with equilibrium concentration at different temp

1.0×10^{-5} to 5.0×10^{-5} M whereas with graphite the dye solutions were used in the range of 5.0×10^{-6} to 1.5×10^{-5} M. The amount of adsorbent and the volume of the dye solution, appropriate for any experiment, were different in different cases and dependent on the adsorbent-adsorbate system. Thus with all the systems 25 ml of dye solution was used with 0.25 g of graphite. In the system other than graphite, 50 ml of dye solution was used with suitable amounts of silica gel and alumina. Due to larger adsorption usually a lesser amount of silica was used as compared to that of alumina. The experiments were repeated at other temperatures also (ranging from 25^{o}-45^{o}C) though the results for graphite-ketone Blue A and neutral alumina-Ketone Blue A are given in Table 6.1.1 for all the temperatures. Due to similar nature in variation of adsorption the results are given only at one temperature i.e., at 30^{o}C for all the systems in Table 6.1.2 and the variation of some systems are shown graphically in Figures 6.1.1-6.1.3. The plots of log x/m Vs $\log C_e$ (Freundlich adsorption isotherm) are shown in Figures 6.1.4-6.1.5 and that of C_e/q_e Vs C_e (Langmuir adsorption isotherm) are shown in 6.1.6-6.1.7.

6.1.3 Results and discussion

It is evident from the curves in Figures 6.1.1-6.1.3 that the variation of adsorption with concentration at a given temperature increases rapidly at the initial stage but slows down thereafter indicating finally a tendency to approach

Table 6.1.1. VARIATION OF ADSORPTION OF KETONE BLUE A ONTO GRAPHITE AND NEUTRAL ALIMINA AT DIFFERENT TEMPERATURES.

(a) Adsorbent : Graphite

Initial dye concentration (M) × 10^6	Amount adsorbed at equilibrium in $gg^{-1} \times 10^4$				
	25°C	30°C	35°C	40°C	45°C
4.0	1.22	1.28	1.33	1.39	1.45
5.0	1.38	1.44	1.50	1.56	1.62
6.0	1.49	1.56	1.63	1.69	1.76
7.0	1.60	1.67	1.75	1.82	1.90
8.0	1.71	1.79	1.87	1.95	2.03
9.0	1.81	1.90	1.99	2.08	2.16
10.0	1.90	2.00	2.10	2.19	2.28

(b) Adsorbent : Neutral alumina

Initial dye concentration (M) × 10^5	Amount adsorbed at equilibrium in $gg^{-1} \times 10^3$				
1.0	2.62	2.56	2.50	2.44	2.38
1.5	3.93	3.86	3.79	3.72	3.65
2.0	5.17	5.09	5.00	4.92	4.84
2.5	6.37	6.27	6.17	6.08	5.98
3.0	7.56	7.45	7.35	7.25	7.14
3.5	8.69	8.57	8.46	8.34	8.24
4.0	9.80	9.67	9.55	9.42	9.29
4.5	10.87	10.73	10.59	10.45	10.31
5.0	11.98	11.74	11.59	11.45	11.30

Table 6.1.2. AMOUNT ADSORBED OF THE DYES AT EQUILIBRIUM ONTO OXIDES AND GRAPHITE IN THE STUDY OF ADSORPTION ISOTHERM AT 30°C.

1 System	2 Initial dye concentration (M) × 10^5	3 Equilibrium concentration (M) × 10^5	4 Amount adsorbed at equilibrium (gg^{-1})
Silica - Basic Green 1	1.0	0.1012	4.34×10^{-3}
	1.5	0.2000	6.27
	2.0	0.3228	8.10
	2.5	0.4744	9.78
	3.0	0.6660	11.27
	3.5	0.9074	12.51
	4.0	1.1765	13.63
Silica - Basic Voilet 1	1.0	0.1094	3.51×10^{-3}
	1.5	0.1957	5.14
	2.0	0.2917	6.73
	2.5	0.3970	8.28
	3.0	0.5285	9.74
	3.5	0.6915	11.06
	4.0	0.8793	12.29
Silica - Basic Brown 4	4.0	1.1698	6.53×10^{-3}
	4.5	1.3128	7.35
	5.0	1.4844	8.11
	5.5	1.6955	8.78
	6.0	1.8980	9.46
	6.5	2.1789	9.97
	7.0	2.4572	10.48
	7.5	2.7982	10.85
	8.0	3.1852	11.10
Silica - Basic Blue 3	1.5	0.0541	2.60×10^{-3}
	2.0	0.0859	3.44
	2.5	0.1408	4.25
	3.0	0.2131	5.01
	3.5	0.2863	5.78
	4.0	0.3600	6.55
	4.5	0.4745	7.24
	5.0	0.6250	7.87
Basic alumina-Basic Brown 4	4.0	2.2222	0.82×10^{-3}
	4.5	2.4638	0.94
	5.0	2.7187	1.05
	5.5	2.9851	1.16
	6.0	3.2755	1.26

Table 6.1.2 Continuation

	6.5	3.5714	1.35
	7.0	3.8777	1.44
	7.5	4.1899	1.53
	8.0	4.5300	1.61
Basic alimina-Basic Violet2	1.0	0.5273	1.73×10^{-4}
	1.5	0.6538	3.10
	2.0	0.8381	4.24
	2.5	1.0577	5.28
	3.0	1.3200	6.15
	3.5	1.6400	6.80
	4.0	2.0000	7.32
Neutral alumina-Acid Green 25	0.6	0.2195	0.22×10^{-3}
	1.0	0.3385	0.82
	1.4	0.5535	1.05
	1.8	0.8058	1.24
	2.2	1.0913	1.38
	2.6	1.4255	1.46
	3.0	1.7909	1.51
Neutral alumina - Ketone Blue A	1.0	0.1486	2.56×10^{-3}
	1.5	0.2182	3.86
	2.0	0.3103	5.09
	2.5	0.4167	6.27
	3.0	0.5232	7.45
	3.5	0.6511	8.57
	4.0	0.7860	9.67
	4.5	0.9351	10.73
	5.0	1.0986	11.74
Neutral alumina - Acid Black 1	3.0	0.4696	15.60×10^{-3}
	3.5	0.6444	17.60
	4.0	0.8243	19.58
	4.5	1.0038	21.55
	5.0	1.2088	23.37
	5.5	1.4806	24.78
	6.0	1.8281	25.72
Graphite - Acid Green 25	0.4	0.1571	1.51×10^{-4}
	0.5	0.2285	1.69
	0.6	0.3029	1.85
	0.7	0.3796	1.99
	0.8	0.4625	2.10
	0.9	0.5459	2.20
	1.0	0.6316	2.29

Table 6.1.2 Continuation

Graphite - Ketone Blue A	0.4	0.1875	1.28 x 10^{-4}
	0.5	0.2600	1.44
	0.6	0.3412	1.56
	0.7	0.4225	1.67
	0.8	0.5016	1.79
	0.9	0.5850	1.90
	1.0	0.6667	2.00
Graphite - Basic Blue 3	0.6	0.1560	1.60 x 10^{-4}
	0.7	0.2173	1.74
	0.8	0.2824	1.86
	0.9	0.3531	1.97
	1.0	0.4255	2.07
	1.1	0.5006	2.16
	1.2	0.5786	2.24
Graphite - Basic Green 1	1.0	0.3415	3.18 x 10^{-4}
	1.3	0.4804	3.96
	1.6	0.6312	4.68
	1.9	0.7891	5.36
	2.2	0.9465	6.05
	2.5	1.1372	6.58
	2.8	1.3355	7.07

towards saturation. Though this characteristic nature is observed in all the systems employed, the extent of approach towards saturation is seen to depend on the constituents of the system. In this respect the nature of the adsorbent is seen to put greater impact on the adsorption behaviour. An examination of the curves (Figs. 6.1.1-6.1.3) indicates that the present isotherms may be divided into two types. In the first, saturation appears to be very near at hand and in the second, it remains for ahead. The isotherms, obtained, in the use of graphite-dye systems, illustrate the former whereas those with silica gel and alumina indicate the latter. Furthermore, the type of variation (either the first or the second) found with any of the above adsorbents is obtainable uniformly with all the dyes. This is indicative of the predominant role of adsorbent over that of dye.

In the adsorption of dyes by commonly used solid adsorbents isotherms of different nature have been reported by several workers [30]. This includes even those showing regular increase upto a maximum followed by a decrease to a minimum and then sometimes a rise again, as well as those showing interrupted rise with well defined constant adsorption at intermediate stages. In the present study, however, the isotherms are all showing an increase in the amount adsorbed characteristically throughout. Figures 6.1.1-6.1.3 indicate that the process involved in dye adsorption is simple and uniform over the concentration range studied. It is thus free of any complication such as the multilayer formation of the adsorbed dye on the surface of the adsorbents.

In present study a small variation in temperature (i.e., 5 ^{o}C) is chosen for each run. Such a small change in temperature does not appear to affect the general nature of the isotherm though individual values of the amount adsorbed are seen to vary (Table 6.1.1). With oxides as adsorbents a lower temperature is favourable for larger adsorption whereas with graphite reverse is true (Table 6.1.1). Thus the amount adsorbed from 2.0×10^{-5} M solution of Ketone Blue A by neutral alumina decreases from 5.17×10^{-3} to 4.84×10^{-3} gg^{-1} as the temperature increases from 25^{o} to 45^{o}C ; the amount adsorbed onto graphite from 1.0×10^{-5} M solution of same dye are from 1.90×10^{-4} to 2.28×10^{-4} respectively at respective temperatures.

The amount adsorbed depends not only on concentration but also on the relative abundance of the available dye, is demonstrated from the results of additional experiments. In this series of experiments different volumes of dye solution of certain concentration were kept with same amount of adsorbents at a constant temperature at 30^{o}C. The amount adsorbed at equilibrium was found to increase with the volume of dye solutions. One representative set of results of the systems from each adsorbent are given in Table 6.1.3; those of other systems being similar in nature are not given here. Thus the amount adsorbed by silica gel from 1.0×10^{-5} M

Table 6.1.3 VARIATION OF ADSORPTION OF DYES WITH VOLUME OF DYE SOLUTION

Temperature : 30±0.1°C

1 System	2 Initial dye concentration (M) x 10^5	3 Volume of dye solution (ml)	4 Amount adsorbed at equilibrium (gg^{-1})
Silica-Basic Green1	1.0	25	2.35 x 10^{-5}
		50	4.34
		75	5.69
		100	6.59
		125	7.50
		150	8.30
Graphite-Basic Blue 3	1.0	25	2.07 x 10^{-4}
		50	2.30
		75	2.48
		100	2.65
		125	2.86
Neutral alumina-Acid Green 25	1.0	25	0.48 x 10^{-5}
		50	0.82
		75	0.93
		100	1.02
		125	1.11
Basic alumina-Basic violet 2	1.0	25	1.42 x 10^{-4}
		50	1.76
		75	2.01
		100	2.25
		125	2.42
		150	2.57

solution of Basic Green 1 varies from 2.35×10^{-3} to 8.30×10^{-3} gg^{-1} as the volume of the dye solution increases from 25 to 150 ml. Similar is the results with other systems (Table 6.1.3). It is important to note that inspite of the observed enhancement in adsorption, the general nature of variation remains sensibly unaffected.

The amount adsorbed is also found to depend on the amount of adsorbent used in the experiment. In this series of experiments different amount of adsorbent was kept in contact with fixed volume of dye solution of appropriate concentration. The amount adsorbed at equilibrium was determined using same method stated earlier. The amount adsorbed in gg^{-1} adsorbent is found to decrease with the amount of adsorbent. Thus the amount adsorbed from 1.0×10^{-5} M solution of Basic Green 1 decreased from 8.52×10^{-3} to 2.76-$\times10^{-3}$ gg^{-1} as the amount of graphite increased from 0.05 to 0.35g respectively. Similar is the result with other systems. One representative result for each adsorbent is given in Table 6.1.4

6.1.3.1 Applicability of Freundlich isotherm

The results obtained in the isotherm study is tested for the applicability of Freundlich adsorption isotherms. The linear form of the Freundlich equation is :

$$\log x/m = \log K_F + 1/n \log C_e$$

The straight line plots of log x/m against $\log C_e$ shows the applicability of Freundlich adsorption isotherm. The

6.1.4 VARIATION OF ADSORPTION OF DYES WITH AMOUNT OF ADSORBENT

TEMPERATURE : 30 ± 0.1 °C

1 System	2 Initial dye concentration (M) × 10^5	3 Amount of adsorbent (gm)	4 Amount adsorbed at equilibrium (gg^{-1})
Silica-Basic Blue 3	2.0	0.02	9.35 × 10^{-3}
		0.04	6.82
		0.06	5.27
		0.08	4.25
		0.10	3.44
Graphite-Basic Green 1	1.0	0.05	8.52 × 10^{-3}
		0.10	5.39
		0.15	4.26
		0.20	3.62
		0.25	3.21
		0.30	2.98
		0.35	2.76
Neutral alumina-Acid Black 1	3.0	0.02	27.34 × 10^{-3}
		0.04	18.90
		0.06	14.14
		0.08	11.06
		0.10	9.01
		0.12	7.57
		0.14	6.55
Basic alumina-Basic Brown 4	5.0	0.4	1.24 × 10^{-3}
		0.6	0.90
		0.8	0.71
		1.0	0.59
		1.2	0.52
		1.4	0.46
		1.6	0.42
		1.8	0.38
		2.0	0.36

graphical representations for some systems of Freundlich isotherm are shown in Figures 6.1.4-6.1.5; being similar in nature the plots of other systems are not given. The values for the Freundlich constants K_F and 1/n calculated from the intercepts and slopes of the above mentioned plots are given in Table 6.1.5. The values of 1/n is found to be dependent on the nature of both the adsorbent and the adsorbate ; the actual magnitude lies between the limits of 0 and 1. It is observed that (Table 6.1.5) the values of 1/n in all systems except that of graphite-Basic Green 1 increase with temperature. For example, with silica-Basic Green 1, the values are 0.432, 0.460, 0.486, 0.513 and 0.538 respectively at 25^o, 30^o, 35^o, 40^o and 45^o C. It is interesting to note that the 1/n values never becomes either 0 or 1 which is indicative of non-attainment of complete saturation on one hand and on the other no constant partition of dye between the surface and the solution.

6.1.3.2 Applicability of Langmuir isotherm.

The data obtained from the present isotherm study of most of the systems also fit well the modified Langmuir equation :

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

The linear plots of C_e/q_e Vs C_e at various temperatures suggest the applicability of the Langmuir isotherm. The values of Langmuir isotherm constant Q^o and b are determined

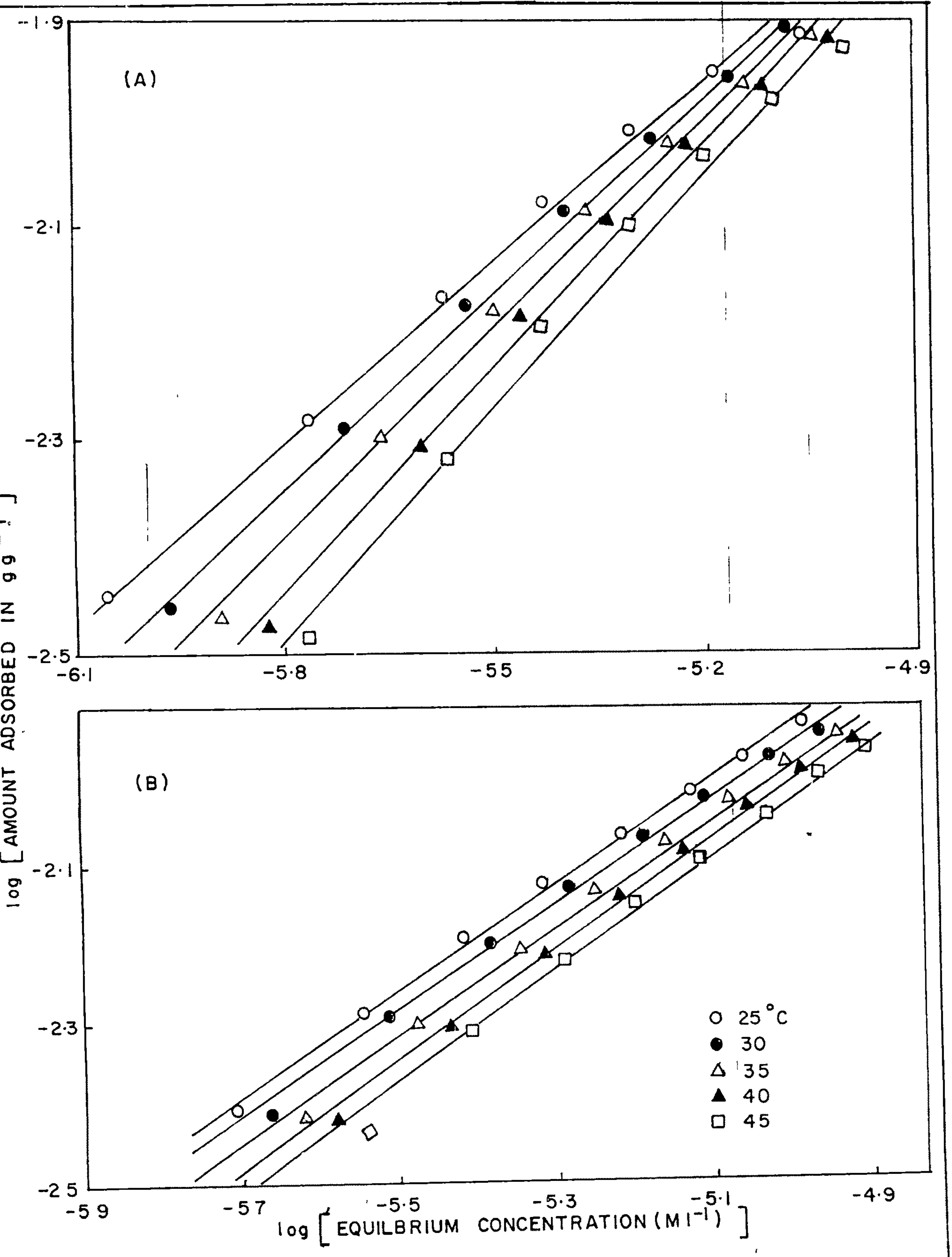

Fig 6 1 4 Plots of log x/m Vs log C_e with the adsorption of (A) Basic Violet 1 on silica and (B) Ketone Blue A on neutral alumina at different temperatures

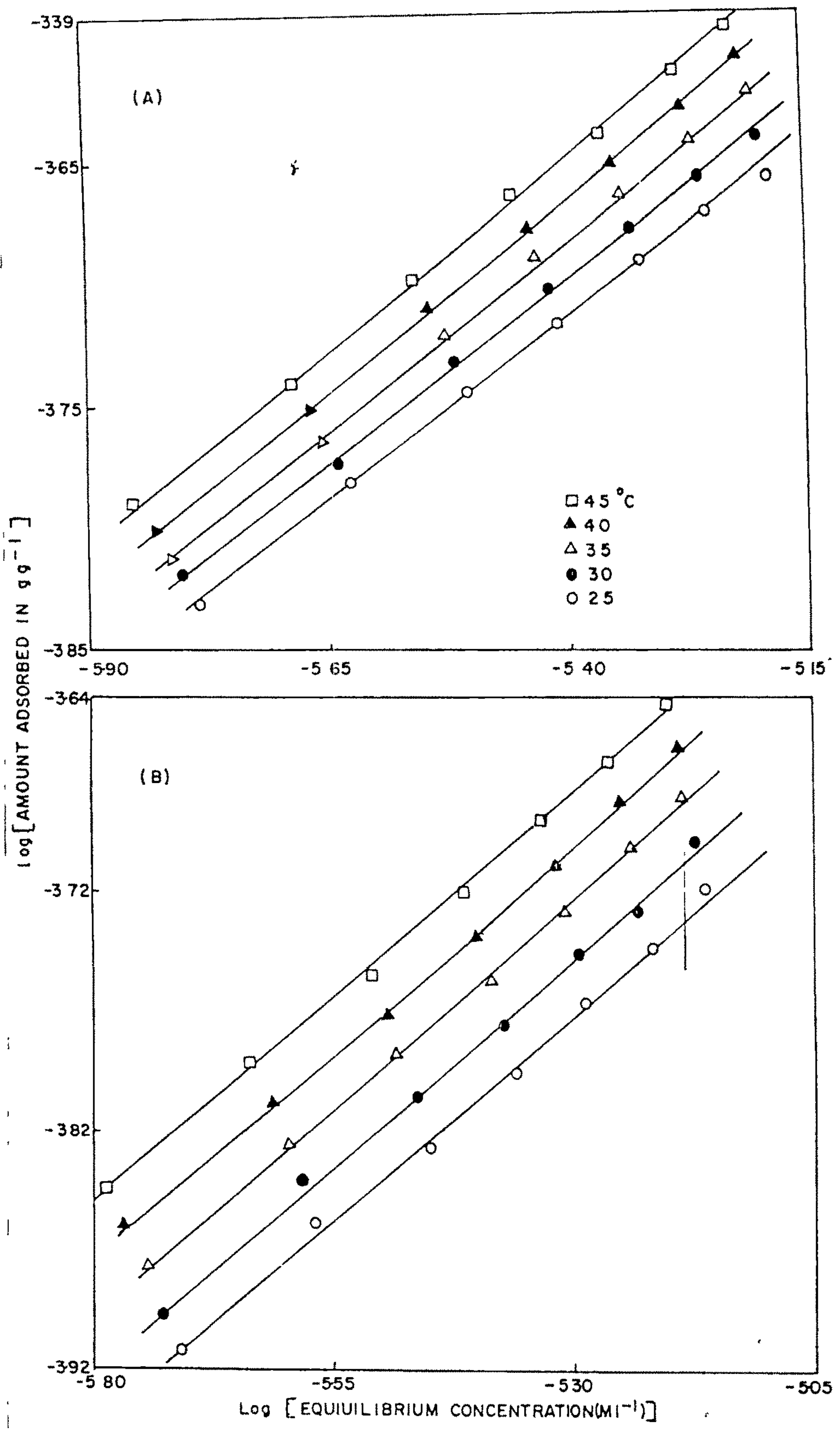

Fig 6 1 5 Plots of log x/m Vs log C_e with the adsorption of (A) Acid Green 25 on silica and (B) Ketone Blue A on graphite at different temperatures

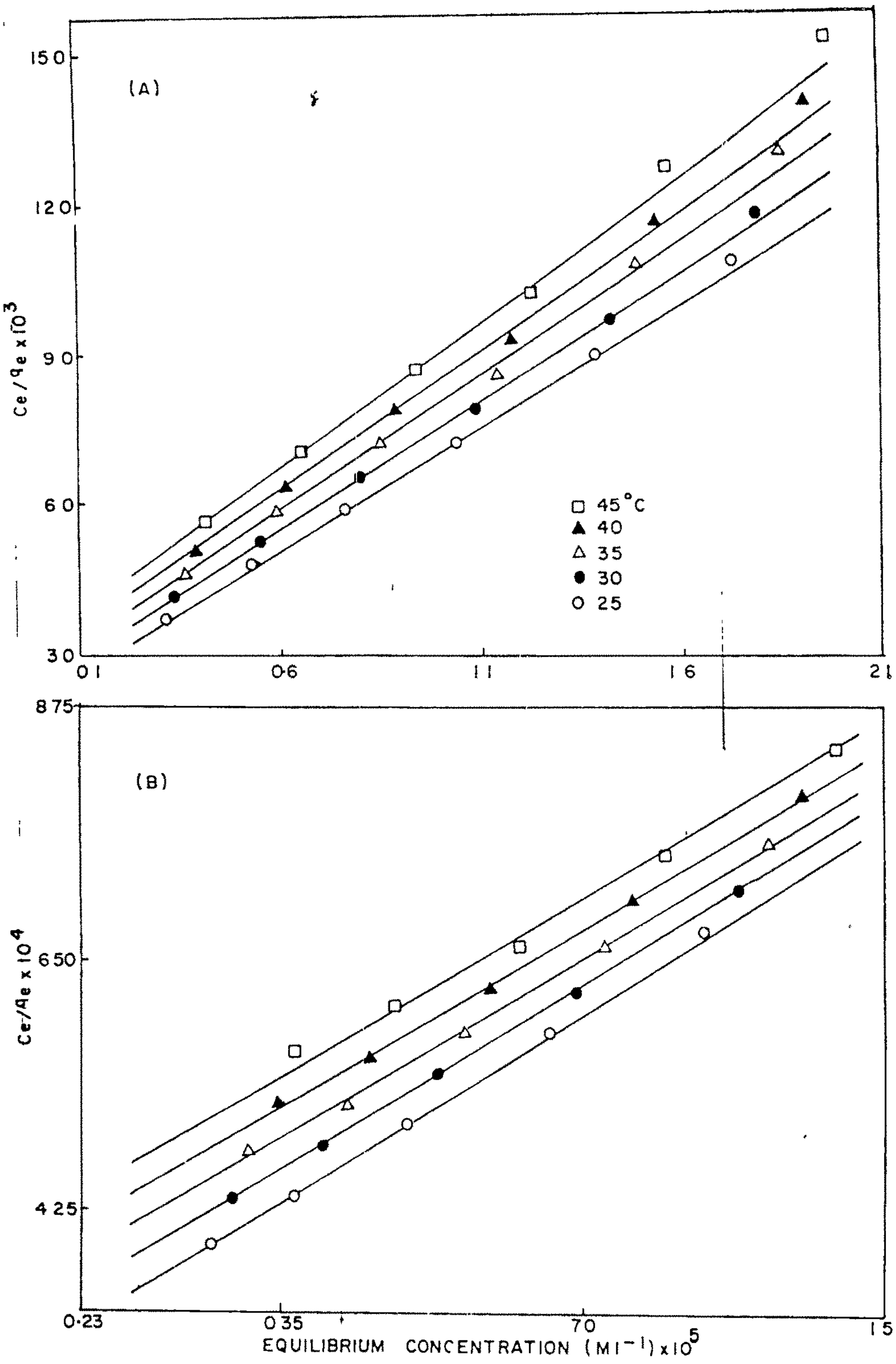

Fig 6 1 6 Plots of C_e/q_e Vs C_e with the adsorption of (A) Acid Green 25 on neutral alumina and (B) Basic Violet 1 on silica at different temperatures

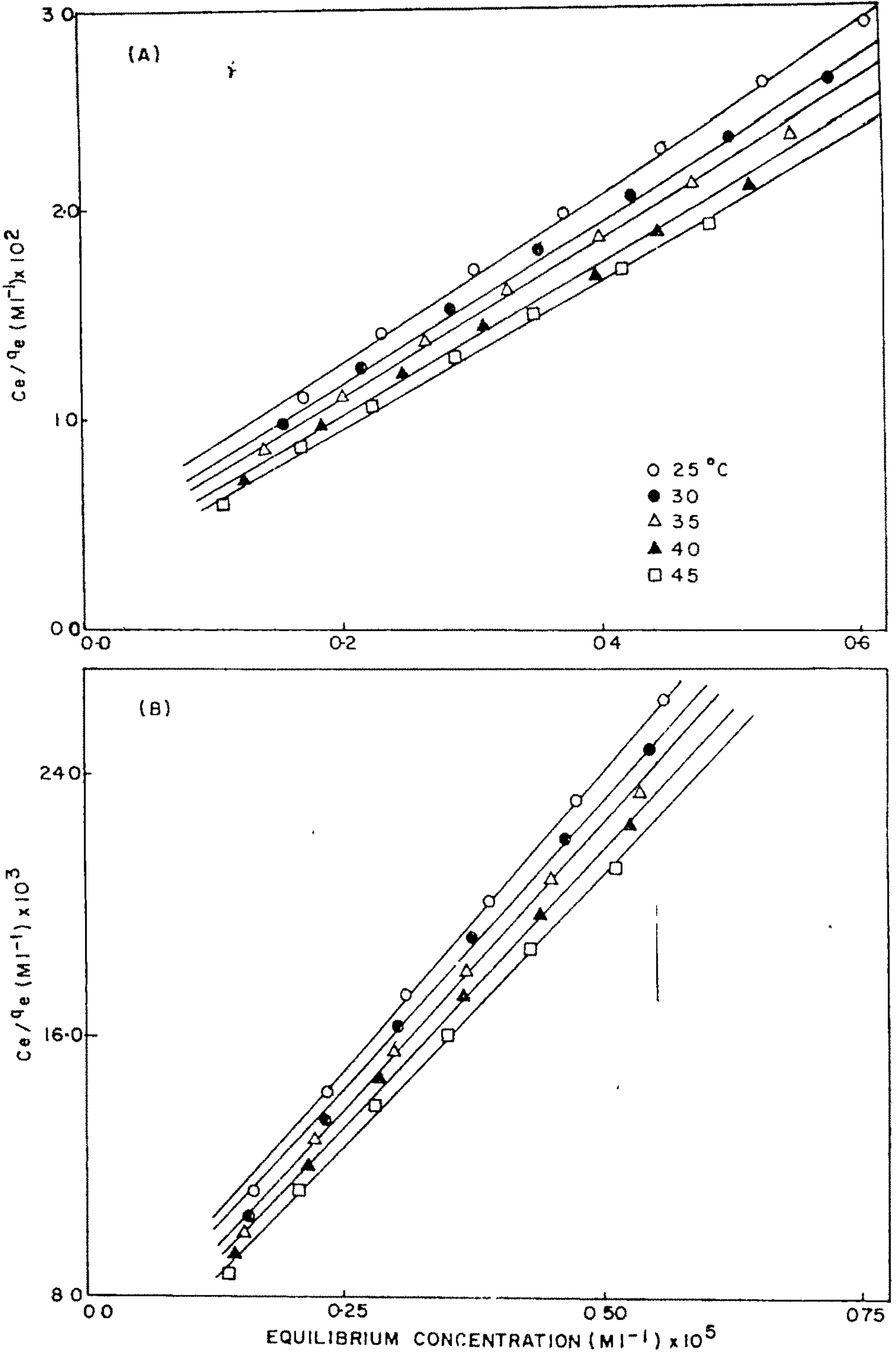

Fig 6 1 7 Plots of C_e/q_e Vs C_e with the adsorption of (A) Basic Blue 3 and (B) Acid Green 25 on graphite at different temperatures

6.1.5 VALUES OF FREUNDLICH ISOTHERM CONSTANTS AND AFFINITY OF DYES CALCULATED FROM THE RESPECTIVE PLOTS AT DIFFERENT TEMPERATURES.

System	Temperature (°C)	Freundlich constants		Affinity $-\Delta\mu$ kJ mole^{-1}
		K_F	1/n	
(1)	(2)	(3)	(4)	(5)
Silica-Basic Blue 3	25	1.262	0.419	0.58
	30	1.364	0.428	0.78
	35	1.432	0.434	0.92
	40	1.563	0.443	1.16
	45	1.726	0.454	1.44
Silica-Basic Violet 1	25	9.307	0.572	5.53
	30	15.736	0.611	6.94
	35	25.924	0.654	8.34
	40	46.257	0.703	9.98
	45	65.866	0.741	11.03
Silica-Basic Green 1	25	1.996	0.432	1.71
	30	2.685	0.460	2.48
	35	3.531	0.486	3.28
	40	4.623	0.513	3.98
	45	5.989	0.528	4.73
Basic alumina-Basic Brown 4	25	5.662	0.822	4.30
	30	6.759	0.832	4.81
	35	7.228	0.845	5.06
	40	8.069	0.865	5.43
	45	8.808	0.878	5.75
Neutral alumina-ketone Blue A	25	9.705	0.584	5.63
	30	11.482	0.602	6.15
	35	13.183	0.618	6.60
	40	15.488	0.637	7.13
	45	16.218	0.645	7.37
Graphite-Basic Blue 3	25	0.004	0.249	-13.53
	30	0.005	0.258	-13.32
	35	0.006	0.266	-13.13
	40	0.007	0.271	-13.04
	45	0.007	0.274	-12.99

Table 6.1.5

Graphite-Basic Green 1	25	0.675	0.613	-1.21
	30	0.569	0.593	-1.32
	35	0.472	0.573	-1.43
	40	0.395	0.554	-1.54
	45	0.319	0.530	-1.68
Graphite-Ketone Blue A	25	0.010	0.343	-11.41
	30	0.011	0.345	-11.36
	35	0.012	0.346	-11.30
	40	0.013	0.348	-11.28
	45	0.014	0.349	-11.21
Graphite-Acid Green 25	25	0.008	0.298	-12.02
	30	0.009	0.301	-12.01
	35	0.009	0.308	-12.00
	40	0.010	0.310	-11.96
	45	0.011	0.313	-11.94

from slopes and intercepts of the respective plots and are given in Table 6.1.6. The isotherm constant Q^{o} is a measure of the amount of dye adsorbed when the monolayer is completed. Theoretically the value of Q^{o} should remain constant over the temperature range studied. However, a small variation in Q^{o} values is seen with rise of temperature.

6.1.3.3 Determination of affinity of dyes

The affinity of dyes ($\Delta\mu$) can be calculated using the following expression :

$$\Delta\mu = - RT \ln K_F$$

Where K_F, is the Freundlich isotherm constant and is calculated from the intercepts of the plots of log x/m against log C_e. The values for $\Delta\mu$ are given in Table 6.1.5. It is observed that the values are negative and found to decrease with temperature with all the systems comprising of oxides. The decrease in $\Delta\mu$ value with temperature is indicative of the larger adsorption at lower temperatures. Similar results have also been reported by Bird and Manchester [44] with the adsorption of disperse dyes onto secondary cellulose acetate. On the other hand, in graphite-dye systems no significant variation in $\Delta\mu$ is found with change in temperature.

6.1.6 VALUES OF LANGMUIR ISOTHERM CONSTANTS CALCULATED FROM THE RESPECTIVE PLOTS AT DIFFERENT TEMPERATURES

System (1)	Temperature (^oC) (2)	Langmuir constants Q^o(mg g^{-1}) (3)	b(l mg^{-1}) (4)
Silica-Basic Blue 3	25	11.21	1.173
	30	11.16	1.102
	35	11.13	1.011
	40	11.12	0.952
	45	11.05	0.870
Silica-Basic Violet 1	25	20.92	0.465
	30	21.02	0.408
	35	21.48	0.360
	40	21.71	0.327
	45	21.82	0.300
Silica-Basic Green 1	25	17.69	0.079
	30	17.97	0.067
	35	18.48	0.057
	40	18.60	0.050
	45	19.12	0.043
Neutral alumina Ketone Blue A	25	24.84	0.146
	30	25.55	0.129
	35	26.17	0.115
	40	27.00	0.102
	45	27.60	0.093
Neutral alumina Acid Green 25	25	2.01	0.369
	30	1.95	0.345
	35	1.86	0.332
	40	1.81	0.305
	45	1.73	0.291
Neutral alumina Acid Black 1	25	33.36	0.322
	30	34.24	0.277
	35	34.20	0.242
	40	34.14	0.214
	45	33.80	0.192

Table 6.1.6 Continuation

Graphite-Basic Blue 3	25	0.25	2.373
	30	0.26	2.689
	35	0.27	2.900
	40	0.28	2.456
	45	0.28	2.987
Graphite-Basic Green 1	25	1.27	0.177
	30	1.25	0.201
	35	1.23	0.229
	40	1.22	0.261
	45	1.21	0.299
Graphite-ketone Blue A	25	2.36	0.855
	30	2.45	0.888
	35	2.56	0.921
	40	2.66	0.954
	45	2.81	0.977
Graphite-Acid Green 25	25	0.276	1.015
	30	0.282	1.052
	35	0.293	1.086
	40	0.297	1.145
	45	0.301	1.214

6.1.3.4 Determination of thermodynamic parameters

The effect of temperature on dye adsorption may be characterized in terms of change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS). The values of these parameters are calculated using various methods. The change in free energy is calculated using the following relationship [45]

$$\Delta G = - RT \ln K$$

where K is the equilibrium constant and is obtained by considering that the dye adsorption is a reversible process with an existence of equilibrium between two phases.

$$\underset{\text{(Solution)}}{A + \text{dye}} \rightleftharpoons \underset{\text{(Surface dye)}}{A - \text{dye}}$$

where A is the adsorbent.

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

The change in enthalpy is determined from the slope of the linear plot (Fig. 6.1.8) of logK Vs 1/T. The systems comprising of oxides have the negative values of ΔH whereas with that of graphite have positive values. The values (Table 6.1.7) are found to be low which is indicative of physical adsorption or weak chemisorption. The ΔS values are calculated using the following relationship.

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

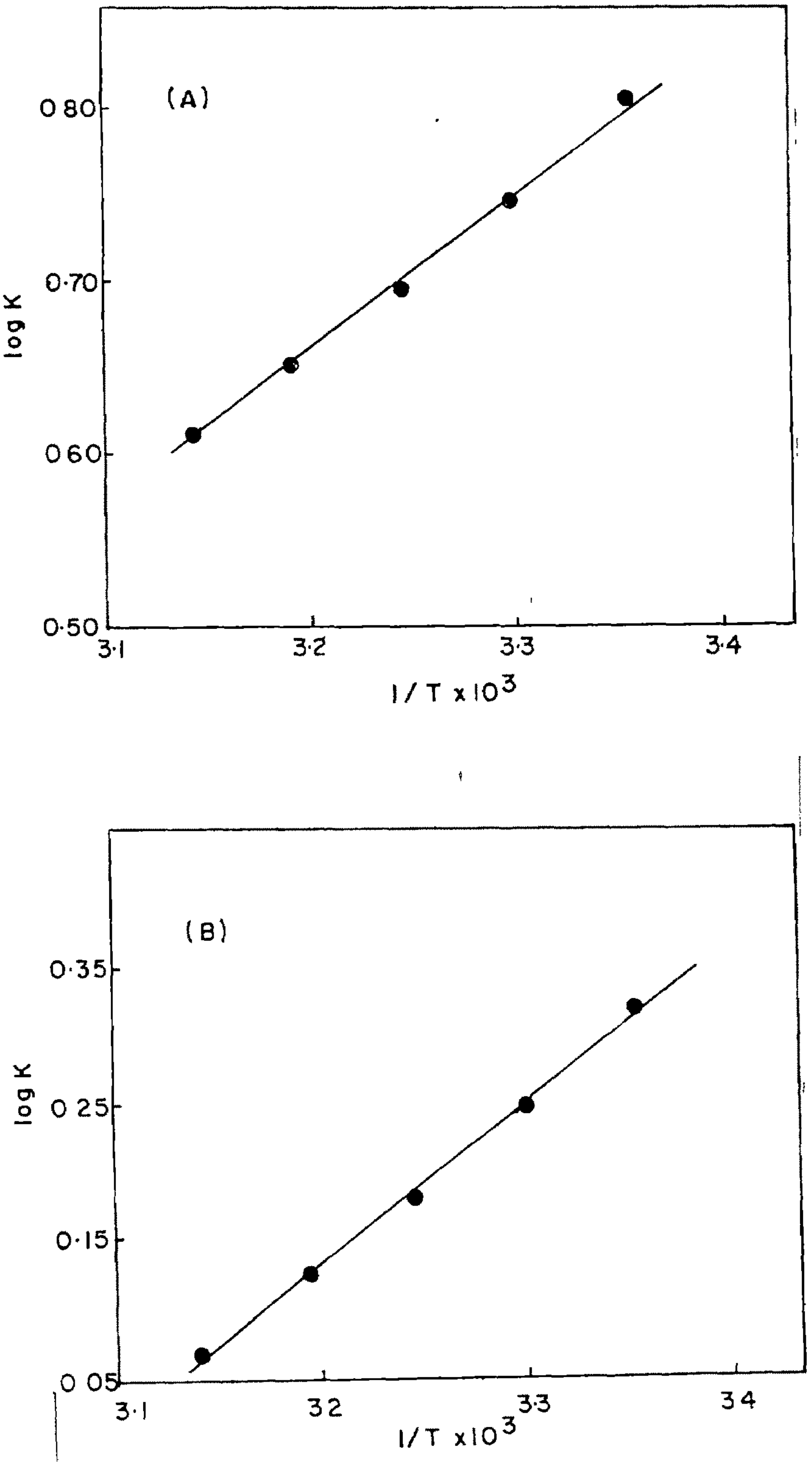

Fig . 6·18 Plote of log K Vs 1/T for the adsorption of (A) Ketone Blue A and (B) Acid Green 25 onto neutral alumina

Table 6.1.7 THRMODYNAMIC QUANTITIES CALCULATED FROM THE ADSORPTION ISOTHERM

System 1	Temperature (°C) 2	Equilibrium constant 3	Free energy change $-\Delta G$ (kJ mole^{-1}) 4	Entropy change $-\Delta S$ (J mole^{-1}.degree^{-1}) 5	Enthalpy change $-\Delta H$ (kJ mole^{-1}) 6
Silica-Basic Blue 3	25	24.60	7.95	26.36	15.81
	30	22.28	7.82	26.36	
	35	20.33	7.70	26.36	
	40	17.82	7.49	26.57	
	45	16.54	7.41	26.44	
Silica-Basic Violet 1	25	5.65	4.29	41.6	16.69
	30	5.08	4.09	41.5	
	35	4.61	3.91	41.5	
	40	4.26	3.77	41.3	
	45	3.58	3.37	41.8	
Silica-Basic Green 1	25	5.02	3.99	48.62	18.48
	30	4.50	3.79	48.48	
	35	4.04	3.57	48.40	
	40	3.63	3.35	48.34	
	45	3.25	3.12	48.30	
Silica-Basic Brown 4	25	14.05	6.55	138.36	47.78
	30	10.22	5.86	138.35	
	35	7.56	5.18	138.34	
	40	5.68	4.52	138.31	
	45	4.37	3.90	137.99	
Basic alumina-Basic Brown 4	25	7.80	5.09	173.72	56.86
	30	5.00	4.05	174.29	
	35	3.45	3.17	174.43	
	40	2.53	2.42	173.92	
	45	2.06	1.91	172.80	
Basic alumina-Basic Violet 2	25	1.40	0.83	33.15	10.71
	30	1.31	0.68	33.10	
	35	1.22	0.51	33.11	
	40	1.14	0.34	33.13	
	45	1.07	0.18	33.11	

Table 6.1.7 Continuation

Neutral alumina-Acid Green 25	25	2.10	1.84	69.73	
	30	1.75	1.41	70.00	
	35	1.52	1.07	69.97	22.62
	40	1.33	0.74	69.90	
	45	1.18	0.44	69.75	
Neutral alumina-Acid Black 1	25	5.30	4.13	52.98	
	30	4.69	3.89	52.90	21.73
	35	4.12	3.62	52.92	
	40	3.65	3.37	52.88	
	45	3.24	3.11	52.86	
Graphite-Basic Blue 3	25	1.64	-1.23	-128.99	
	30	2.05	-1.81	-128.77	-37.21
	35	2.51	-2.35	-128.44	
	40	3.21	-3.03	-128.56	
	45	4.25	-3.82	-129.02	
Graphite-Basic Green 1	25	8.96	-5.43	-86.67	
	30	7.45	-5.06	-86.87	-22.13
	35	6.41	-4.76	-87.30	
	40	5.72	-4.54	-88.02	
	45	5.08	-4.30	-88.69	
Graphite-ketone Blue A	25	0.70	-0.86	-86.24	
	30	0.84	-0.44	-86.20	-26.56
	35	0.98	-0.04	-86.10	
	40	1.16	0.38	-86.07	
	45	1.36	0.81	-86.06	
Graphite-Acid Green 25	25	0.74	-0.75	-59.47	
	30	0.83	-0.46	-59.44	-18.47
	35	0.93	-0.18	-59.38	
	40	1.04	0.10	-59.33	
	45	1.15	0.37	-59.25	

The values for ΔG, ΔH and ΔS are summarized in Table 6.1.7. The negative values of ΔG indicate that the process involved is spontaneous with a high affinity of dye for adsorbent. Further, the negative values of ΔH and ΔS suggest the exothermic and random nature of adsorbing molecules respectively. Similar is the findings of several workers with the adsorption of dyes onto commonly used adsorbents [4,46,47]. Again the negative entropy change (ΔS) found in many systems could be understood in terms of restriction of the movement of the molecules to two dimensions in the surface as against three dimensions in the bulk. Similar results have also been reported by Wright and Pratt in the adsorption of aromatic molecules by solid adsorbents such as carbon blacks, Speron 6 and Graphon etc. [48].

6.2 INFLUENCE OF ELECTROLYTE, SURFACTANTS AND ALCOHOL IN ADSORPTION STUDY AND METHODS FOR REGENERATION OF ADSORBENTS

6.2.1 Introduction

Study of reversibily of adsorption i.e., desorption of the species once adsorbed on the surface, is helpful in understanding the stability of the adsorbed phase and thus the nature of interaction involved in the process [49-51]. It is also helpful in the study of regeneration of adsorbent. The desorption from the gases as well as the liquid phase has been extensively studied. In the adsorption of dissolved substances from solution, results exhibiting desorption to varying degrees have been found. In some cases the removal of the adsorbed substances has been achieved simply by using the solvent and in others, the desorption was either difficult or not possible [52,53]. Thus, an easy desorption has been reported in the case of higher n-alkanes on Spheron 6, vinyl polymers and platinum foils, sulphate ions on oxides, clay and kaolin, and cationic dyes on alumina, quartz and several varieties of coal. On the otherhand, with dyes capable of forming hydrogen bonds with the surface, complete desorption was not seen. The removal of the adsorbed tracer ions (like iodide, sulphate, phosphate etc.) on a variety of of surfaces including metals and metal oxides [54] has been reported to be difficult.

In the case where strong interaction between the adsorbed phase and surface exists, various dissolving solvents and solutions of suitable electrolytes have been used for the detachment of the adsorbed species. For example, for the desorption of adsorbed polyvinyl acetate from the surface of iron powder and for cationic dyes from asbestos and bentonite surfaces various cations (like Na^+, K^+, Ba^{2+} etc.) have been used [50,55]. Resistance towards detachment has generally been interpreted as indicative of some sort of chemical bonding with the surface.

Textile wastewater usually contains sufficient amount of electrolytes (both weak and strong) and surfactants as they have been used as carrier in the dyeing process [56,57]. The aim of the present work is to find out appropriate methods and optimum conditions to remove dyes from aqueous solutions. It is, therefore, planned to investigate the adsorption of dyes in the presence of electrolyte as well as ionic and non ionic surfactants.

6.2.2. Experimental

The present study is broadly divided into two parts. The experimental procedure followed in the first series of the experiments is essentially the same as described in the case of adsorption isotherm (Section 6.1.2) except the dye solution containing various amounts of surfactants, electrolytes or alcohol. Thus an appropriate volume of dye solution from the stock was mixed with various amounts of the above mentioned materials and was diluted to a constant volume so that it could give desired concentration of dye as well as that of the materials. The amount of surfactants in the solution were chosen in such a way that the range of above and below the critical micelle concentration (c.m.c.) was covered. The normality of potasium chloride in the dye solution was chosen from 0.01 to 0.08 N and the percentage of ethanol was from 10 to 70% v/v. The results obtained in the presence of ethanol, potasium chloride and surfactants are summarized in Tables 6.2.1 to 6.2.3 respectively.

In the second series of experiments, the efforts were made for the regeneration of the adsorbents. For this purpose a weighed quantity of adsorbents was kept in contact with a fixed volume of dye solution of known concentration at 30^{o} C. After attainment of equilibrium the solution was filtered and the adsorbent sample was washed with distilled water till the complete removal of the excess dye adhering with the surface. The sample (dye adsorbed adsorbent) thus obtained was dried at $\sim$ 85 ^{o}C for 16 hours. The amount of dye adsorbed on the surface was determined from the difference in initial and equilibrium concentration of dye solution.

In order to study the regeneration of adsorbents, batch desorption and column elution experiments were carried out. In the first series, a known amount (0.5g) of silica gel pre adsorbed with Basic Blue 3 was kept in contact with different percentage of KCl solutions (1 - 10%) and was allowed to attain equilibrium for 24 hours. The amount of dye desorbed from the surface was calculated by the method described earlier and the results are summarised in Table 6.2.4. From trial experiment ethanol was not found to be suitable for desorption study from the surface of silica gel pre-adsorbed with Basic Blue 3.

In another series of experiments 1.0g of silica gel (pre adsorbed with Basic Blue 3) was placed in a column (1 cm diameter and 3 cm height) and 1% KCl solution was passed through it at a rate of 1ml per minute and the column eluent fractions (15 ml) have been collected. Elution was allowed to proceed and more than 500 ml solution of several fractions were analysed spectrophotometrically for dye present. The results are shown graphically in Figure 6.2.1. Using the same procedure neutral alumina (saturated with Ketone Blue A) sample was treated with KCl solution of

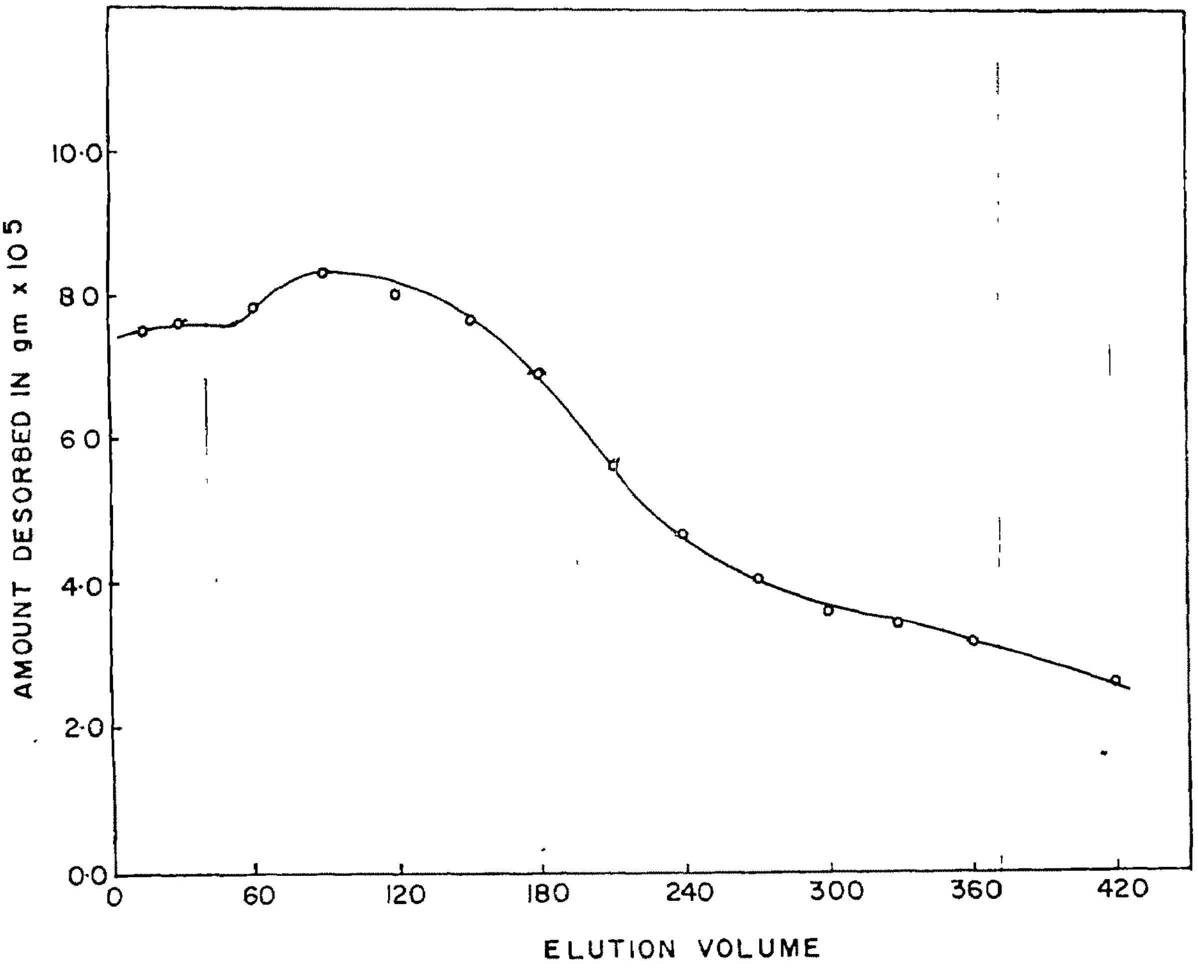

Fig 6 2 1 Plot of amount of dye desorbed against elution volume from the surface of silica gel using KCl solution as eluent

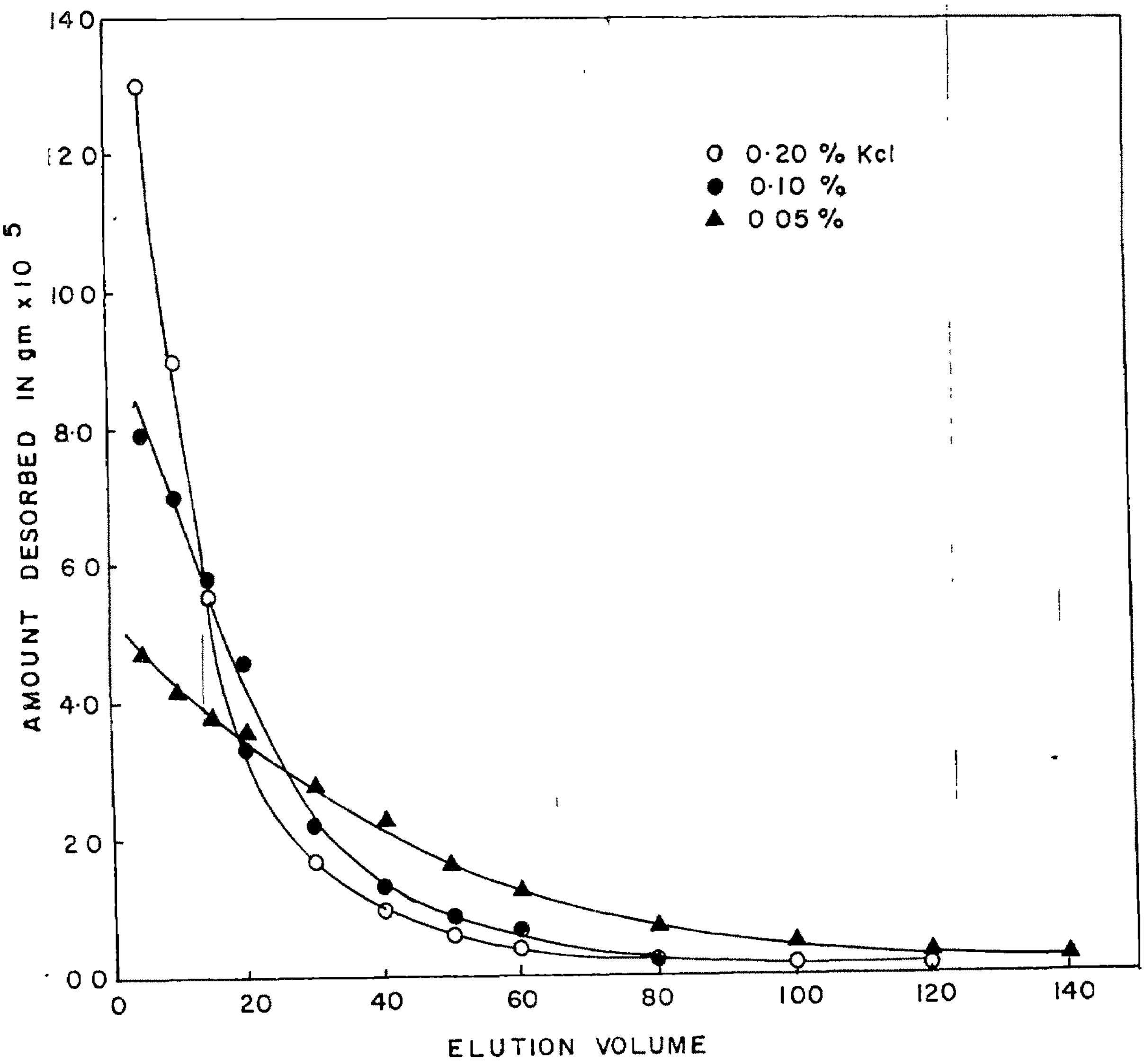

Fig.6 2.2 Plots of amount of dye desorbed against elution volume from the surface of neutral alumina using KCl solution as eluent different percentages (0.05 - 0.2%, range was selected by trial experiments). The results are shown graphically in Figure 6.2.2.

6.2.3 Results and discussion

It is seen from the Tables 6.2.1 to 6.2.3 that the adsorption of the dye in the presence of electrolyte, surfactants or ethanol decreases as the amount of these substances increases in the dye solution. Such a behaviour is due to the interaction between surface and added solutes which may block some of the sorption active sites, for the dye molecules. Thus, the amount adsorbed from 2.0×10^{-5} M solution of Basic Blue 3 onto silica gel decreases from 2.94×10^{-3} to 0.37×10^{-3} gg^{-1} when the percentage of ethanol increases from 10 to 70% v/v while in absence of ethanol the amount adsorbed is 3.44×10^{-3} gg^{-1}. Similar results are obtained with other systems in the presence of ethanol (Table 6.2.1). In presence of KCl the extent of decrease in adsorption is different with different systems. The adsorption is found mainly dependent on the nature of the adsorbent. In general, the decrease is more pronounced with oxides, than with graphite. Thus, the amount adsorbed from 2.0×10^{-5} M solution of Ketone Blue A on neutral alumina decreases from 0.83×10^{-3} to 0.21×10^{-3} gg^{-1} as the normality of KCl in the dye solution increases from 0.01 to 0.08 N whereas in absence of KCl the amount is 5.09×10^{-3} gg^{-1}. On the other hand, the decrease is from 1.97×10^{-4} to 1.85×10^{-4} gg^{-1} using the same dye solution (1.0×10^{-5} M) onto graphite; the

Table 6.2.1 ADSORPTION OF DYES ONTO OXIDES AND GRAPHITE SURFACES IN PRESENCE OF ALCOHOL AT 30°C

Adsorbent : Silica

% of ethyl alcohol in dye solution	Amount adsorbed in gg^{-1} at equilibrium			
	Basic Blue 3 (2.0×10^{-5}M)	Basic Brown 4 (5.0×10^{-5}M)	Basic Green 1 (1.0×10^{-5}M)	Basic Violet 1 (1.0×10^{-5}M)
0	3.44×10^{-3}	8.11×10^{-3}	4.34×10^{-3}	3.51×10^{-3}
10	2.94	6.64	3.40	2.65
20	2.33	5.42	2.41	2.14
30	1.42	4.02	1.37	1.50
40	0.93	2.45	0.80	0.94
50	0.73	1.05	0.70	0.74
60	0.59	0.70	0.59	0.67
70	0.37	0.61	0.54	0.62

Adsorbent : Graphite

	Basic Green 1 (1.0×10^{-5}M)	Basic Blue 3 (1.0×10^{-5}M)	Acid Green 25 (0.5×10^{-5}M)	Ketone Blue A (1.0×10^{-5}M)
0	3.18×10^{-4}	2.07×10^{-4}	1.69×10^{-4}	2.00×10^{-4}
10	2.53	1.60	1.12	1.53
20	1.86	1.00	0.27	0.58
30	0.94	0.55	nil	0.29
40	0.62	0.33	–	0.29
50	0.56	0.26	–	0.29
60	0.52	0.21	–	0.29
70	0.51	0.21	–	0.29

Adsorbent : Neutral alumina

% of ethyl alcohol in dye solution	Amount adsorbed in gg^{-1} at equilibrium		
	Ketone Blue A (2.0×10^{-5}M)	Acid Green 25 (1.0×10^{-5}M)	Acid Black 1 (3.0×10^{-5}M)
0	5.09×10^{-3}	0.82×10^{-3}	15.60×10^{-3}
10	3.86	0.56	15.03
20	3.05	0.48	14.37
30	2.24	0.45	13.79
40	1.20	0.43	12.86
50	0.65	0.41	12.48
60	0.21	0.41	12.10
70	0.21	0.41	12.10

Table 6.2.1 Continuation

Adsorbent : Basic alumina

	Basic Violet 2 (1.0×10^{-5} M)	Basic Brown 4 (5.0×10^{-5} M)
0	1.73×10^{-4}	1.05×10^{-3}
10	1.60	0.84
20	1.35	0.71
30	1.00	0.62
40	0.71	0.50
50	0.43	0.44
60	0.37	0.36
70	0.32	0.34

Table 6.2.2 ADSORPTION OF DYES IN PRESENCE OF ELECTROLITES AT 30°C

Adsorbent : Silica

KCl present in dye solution (N)	Amount adsorbed in gg^{-1} at equilibrium			
	Basic Blue 3 (2.0×10^{-5}M)	Basic Brown 4 (5.0×10^{-5}M)	Basic Green 1 (1.0×10^{-5}M)	Basic Violet 1 (1.0×10^{-5}M)
0.00	3.44×10^{-3}	4.34×10^{-3}	8.11×10^{-3}	3.51×10^{-3}
0.01	3.12	2.09	6.20	1.81
0.02	2.90	1.62	5.58	1.31
0.03	2.85	1.18	3.74	1.13
0.04	2.81	1.06	2.97	0.97
0.05	2.78	0.94	2.56	0.88
0.06	2.75	0.82	2.49	0.78
0.07	2.75	0.82	2.43	0.75
0.08	2.75	0.82	2.43	0.75

Adsorbent : Graphite

	(1.0×10^{-5}M)	(1.0×10^{-5}M)	(0.5×10^{-5}M)	(1.0×10^{-5}M)
0.00	2.07×10^{-4}	3.18×10^{-4}	1.69×10^{-4}	2.00×10^{-4}
0.01	1.99	3.06	1.58	1.97
0.02	1.99	2.90	1.53	1.93
0.03	1.99	2.85	1.49	1.85
0.04	1.99	2.81	1.44	1.85
0.05	1.99	2.75	1.44	1.85
0.06	1.99	2.75	1.44	1.85
0.07	1.99	2.75	1.44	1.85
0.08	1.99	2.75	1.44	1.85

Table 6.2.2 Continuation

Adsorbent : Neutral alumina

KCl present in dye solution (N)	Amount adsorbed in gg^{-1} at equilibrium		
	Ketone Blue A (2.0×10^{-5}M)	Acid Green 25 (1.0×10^{-5}M)	Acid Black 1 (3.0×10^{-5}M)
0.00	5.09×10^{-3}	0.82×10^{-3}	15.60×10^{-3}
0.01	0.83	0.56	14.31
0.02	0.42	0.48	13.35
0.03	0.21	0.45	12.38
0.04	0.21	0.43	11.82
0.05	0.21	0.41	11.10
0.06	0.21	0.41	10.13
0.07	0.21	0.41	10.13
0.08	0.21	0.41	10.13

Adsorbent : Basic alumina

	Basic Violet 2 (1.0×10^{-5}M)	Basic Brown 4 (5.0×10^{-5}M)
0.00	1.73×10^{-4}	1.05×10^{-3}
0.01	0.34	0.96
0.02	0.06	0.90
0.03	0.00	0.86
0.04	0.00	0.82
0.05	0.00	0.78
0.06	0.00	0.74
0.07	0.00	0.72
0.08	0.00	0.71

Table 6.2.3 ADSORPTION OF DYES IN PRESENCE OF SURFACTANTS AT 30°C

Adsorbent : Silica

% of Surfactants		Amount adsorbed in gg^{-1} at equilibrium X 10^{3}		
		Basic Blue 3 (2.0×10^{-5}M)	Basic Green 1 (1.0×10^{-5}M)	Basic Violet 1 (1.0×10^{-5}M)
(A)	0.00	3.44	4.34	3.51
CTAB	0.01	1.91	2.56	1.97
	0.02	1.41	1.71	1.49
	0.03	1.12	1.41	1.16
	0.04	0.93	1.27	0.98
	0.05	0.84	1.12	0.81
	0.06	0.81	1.06	0.70
	0.07	0.80	1.03	0.65
(B)	0.000	3.44	4.34	3.51
Birj35	0.001	3.39	4.15	3.44
	0.002	3.33	4.10	3.41
	0.003	3.30	4.06	3.35
	0.004	3.29	4.03	3.32
	0.005	3.28	4.01	3.28
	0.006	3.28	4.01	3.25
	0.007	3.28	4.01	3.22

Table 6.2.3 Continuation

Adsorbent : Graphite

% of Surfactants		Amount adsorbed in gg^{-1} at equilibrium $\times 10^4$			
		Basic Blue 3 (1.0×10^{-5}M)	Basic Green 1 (1.0×10^{-5}M)	Acid Green 25 (0.5×10^{-5}M)	Ketone Blue A (1.0×10^{-5}M)
(A)	0.00	2.07	3.18	1.69	2.00
	0.01	0.44	3.08	2.35	3.88
	0.02	0.15	2.86	2.39	3.90
	0.03	0.05	2.69	2.43	3.92
	0.04	0.00	2.45	2.48	3.96
	0.05	0.00	2.41	2.57	4.01
	0.06	0.00	2.38	2.66	4.06
	0.07	0.00	2.37	2.71	4.10
(B)	0.000	2.07	3.18	1.69	2.00
	0.001	0.45	2.75	0.00	0.00
	0.002	0.37	2.41	0.00	0.00
	0.003	0.30	2.19	0.00	0.00
	0.004	0.27	1.85	0.00	0.00
	0.005	0.27	1.80	0.00	0.00
	0.006	0.27	1.77	0.00	0.00
	0.007	0.27	1.77	0.00	0.00

Table 6.2.3 Continuation

Adsorbent : Neutral alumina

% of Surfactants		Amount adsorbed in gg^{-1} at equilibrium x 10^3		
		ketone Blue A (2.0×10^{-5}M)	Acid Green 25 (1.0×10^{-5}M)	Acid Black 1 (3.0×10^{-5}M)
(A)	0.00	5.09	0.82	15.60
	0.01	4.26	0.25	0.84
	0.02	3.91	0.22	0.67
	0.03	2.01	0.20	0.50
	0.04	1.00	0.17	0.33
	0.05	0.75	0.15	0.24
	0.06	0.60	0.15	0.17
	0.07	0.50	0.15	0.16
(B)	0.000	5.09	0.82	15.60
	0.001	5.36	0.20	15.96
	0.002	5.48	0.19	16.23
	0.003	5.56	0.18	16.68
	0.004	5.58	0.17	16.86
	0.005	5.61	0.16	17.04
	0.006	5.63	0.16	17.41
	0.007	5.65	0.16	17.41

Adsorbent : basic alumina

		Basic Violet 3 (1.0×10^{-5})
(A)	0.00	1.73×10^{-4}
	0.01	1.37
	0.02	1.18
	0.03	1.01
	0.04	0.88
	0.05	0.78
	0.06	0.72
	0.07	0.67

Table 6.2.4 STUDY OF REGENERATION OF SILICA GEL USING DIFFERENT CONCENTRATION OF POTASSIUM CHLORIDE SOLUTIONS

Sample	Concentration of KCl solution used % (w/v)	Percentage of dye removal
Silica gel saturated with Basic Blue 3	0	0.28
	1	4.39
	2	4.91
	3	5.08
	5	5.08
	10	5.08

amount adsorbed in the absence of KCl is 2.0×10^{-4} gg^{-1}.

Adsorption is found to be dependent on the nature of the surfactant as well as the adsorbate. A decrease in adsorption of Basic Blue 3 on silica gel is from 1.91×10^{-3} to 0.80×10^{-3} gg^{-1} as the percentage of cetyltrimethylammoniumbromide (CTAB) varies from 0.01 to 0.07% (without CTAB the amount adsorbed is 3.44×10^{-3} gg^{-1}) whereas in presence of Brij 35 (varying from 0.001 to 0.007%) a decrease is observed from 3.39×10^{-3} to 3.28×10^{-3} gg^{-1}. Anionic dyes in presence of CTAB favours the adsorption onto graphite whereas reverse is true for cationic dyes. The respective results are given in Table 6.2. However, the adsorption is almost negligible in most cases in presence of sodium dedocyl sulphate.

From batch desorption study where KCl is used as desorbing agent, the removal of Basic Blue 3 from the surface of dye adsorbed silica gel increases initially with an increase in the concentration of KCl solution and finally reaches towards the saturation. The results are given in Table 6.2.4. Thus, the removal of dye from the surface increases from 0.28 to 5.08% as the concentration of KCl solution varies from 0.0 to 3.0%. On the other hand, using column elution experiment the removal of same dye from same surface is about 50% using KCl solution as the eluent. It is seen that initially the removal (Figure 6.2.1) is more rapid and later on slows down and approaches towards a constant value. The initial rate of desorption of Ketone Blue A from the surface of neutral alumina is observed to be higher on increasing the concentration of KCl solution, however, the total amount desorbed is almost found to be constant. Thus the amount desorbed is from 55 to 57% as the concentration of KCl varies from 0.05 to 0.2% .

It is to be noted that by using column elution only, 50 - 60% dye can be removed from the surface with a reasonable times; this is indicative of appreciable stability of the adsorbed phase. It is thus concluded that the forces involved in the stabilization are sufficiently strong and therefore, the detachment are resisted greatly in these cases.

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