CHAPTER - 3

NFLUENC OF CONCENTRATION AND AMOUNT OF ADSORBENT

C H A P T E R - 3

ADSORPTION OF DYES ONTO SOLID SURFACES. INFLUENCE OF INITIAL DYE CONCENTRATION AND AMOUNT OF MASS ON ADSORPTION.

Contents Page

3.1 Introduction

Adsorption of various substances has been studied on oxides and various other similar substances [1-5]. These include the gases and the vapours as well as the dissolved substances from the liquid phase. This phenomenon is important for biological, industrial as well as environmental studies. Besides its large application as in the heterogeneous catalysis, purification of the liquids and separation of substances, some other important techniques and parameters are there which are based on the adsorption process. Some such examples are the measurement of the surface area [6], the pore size and coverage factor of adsorbents [7], the determination of ion exchange capacities of adsorbents [8-10] and removal of dyes and toxic materials from wastewater [11-17]. The study has also been made in order to reduce pollutant level to an accepted lower level or to recover the desired materials from the wastewater using several adsorbents [18-26].

The study of adsorption of dyes has been made with several substances. The adsorbents usually employed for such purposes are the activated carbon [27-30], textile fibres [31-33], polymers [34,35] bentonite [36-39], montmorillonite [40-42], graphite [7,43], and other varieties of charcoals [44,45]; the oxides usually used are silica [7,46,47], alumina [47], titania [8], zirconia [48], mixed oxides [49-51] and oxides of iron, chromium, zinc etc. [52,53]. These

studies have been made useful in the measurement of adsorption capacity [54], the interpretation of the adsorption as simple monolayer or as multilayer type [47,55] and in some cases, the suggestion of possible orientation of the adsorbed molecules [1,56]. Adsorption of dyes is usually a fast process and is completed within a short interval of time. Perhaps because of this, attempts to measure the rate have been carried out only in isolated occasions, although a lot of adsorption isotherm studies have been done by various workers [57-59]. In order to understand the actual nature of the time-growth of adsorption, starting from beginning upto the saturation, it is necessary to measure the progress of adsorption at various intervals of time. For this purpose, appropriate adjustments in the experimental conditions are necessary so that a convenient measurement of adsorption could be made. These were determined in the present series of experiments by trial runs for each system separately and consisted mainly of the use of a large volume of the dye solution of an appropriate concentration and sufficient amount of adsorbent required for convenient measurement (Chapter-2).

The present study includes the actual time growth measurement of the adsorption of dyes onto silica gel, alumina (neutral and basic) and graphite. The selection of these adsorbents were made with a view to cover a wide range of adsorption capacity, their ability to adsorb different types of dyes

from aqueous solution as an alternative for eliminating dyes from industrial wastewaters. The corresponding adsorbates were the anionic dyes (Acid Green 25, Acid Black 1 and Ketone Blue A) and the cationic dyes (Basic Blue 3, Basic Violet 1 and 2, Basic Brown 4 and Basic Green 1).

3.2 Experimental

The time rate study of adsorption of dyes from aqueous solution consisted essentially of keeping a known amount of adsorbent in contact with a measured volume of the dye solution of appropriate concentration at constant temperature and measuring the residual concentration of the dye solution at various intervals of time. The actual amount of the adsorbent and volume of the adsorbate solution suitable for time-rate study were predetermined by trial experiments. The adsorbents, prior to their use in each experiment were activated for overnight at about 85 ^{o}C and then allowed to cool in a desiccator at room temperature for at least 4 hours. The experimental dye solutions of the desired concentrations were obtained by dilution from the stock solution (1.0×10^{-3} M). The dye concentrations chosen for the present investigation are in the range that are generally present in the textile effluent. The amount of the adsorbents suitable for this study was selected by trial runs. Thus 2.0g of graphite as well as basic alumina was found suitable for 200 ml of dye solution whereas 0.3 or 0.5g

Silica gel and 0.3 to 1.0g alumina were used for 300ml dye solution.

The system was kept in a thermostat at a constant temperature and was shaken continuously using an electrical device. The sample solutions (3ml) were withdrawn at various intervals of time. For this purpose, shaking was stopped momentarily to allow the adsorbent particles to settle ; the sample solution then was pipetted out from the supernatant liquid. These were later used for the determination of the remaining concentration present in the solution by using spectrophotometer (Spectronic-20, Bausch & Lomb, USA) at a particular wave length corresponding to the maximum absorbance. The amount adsorbed onto the surface was calculated from the drop in the concentration of dye solution (i.e., the difference in the initial and remaining concentration).

It was found that the saturation stage in the dye adsorption was obtained within a short interval of time. Once this stage was reached no sensible addition to the amount adsorbed was noticed though measurements were made for sufficiently prolonged time interval (at least 3 hours in each experiments). Additional confirmation of this conclusion was obtained by keeping the system (consisting of the adsorbate solution and adsorbent) for overnight. In order to avoid repetition of data and at the same time to illustrate the actual nature of the time-growth of adsorption, the results

upto saturation stage are given in Tables 3.1 to 3.5 and shown graphically in Figures 3.1 to 3.4. Because of the essential similarity in the time variation, the results of only one system (silica-Basic Green 1) with the residual concentrations of the dye solution at various stages of the adsorption (along with amount adsorbed) are given in Table 3.1. The results for the adsorption of other dyes on the adsorbents used in the present study are summarised in Tables 3.2 to 3.5. For shake of comparison, the consolidated results obtained at equilibrium for each system are given in Table 3.10.

In another series of experiments, different amount of adsorbent was kept in contact with fixed volume of dye solution of appropriate concentration. The experimental procedure adopted here was the same as described above. Thus 200 ml of dye solutions (except otherwise stated) of desired concentrations were found suitable with graphite and basic alumina which were taken in the range of 1.5 to 4.0 gm whereas 300 ml of Basic Brown 4 was used with above mentioned amount of basic alumina. Because of their high adsorption capacity comparatively lesser amounts of silica and neutral alumina were used (ranging from 0.3 to 1.0g) with 300ml of dye solution. The actual amount adsorbed at the equilibrium with saturation time are given in Tables 3.6 to 3.9; the corresponding consolidated results are summarised in Table 3.11 and graphical representation of some systems are shown in Figures 3.5-3.7.

Table 3.1 KINETICS OF ADSORPTION OF BASIC GREEN 1 ONTO SILICA GEL WITH CONCENTRATION OF DYE SOLUTION AT 30°.

Dye solution : 300ml

Amount of silica : 0.5g

Initial dye concentration	0.8×10^{-5}M		1.0×10^{-5}M		1.2×10^{-5}M		1.4×10^{-5}M	
Time (Mins.)	Residual concentration (M) $\times 10^{6}$	Amount adsorbed in gg^{-1} adsorbent $\times 10^{3}$	Residual concentration (M) $\times 10^{6}$	Amount adsorbed in gg^{-1} adsorbent $\times 10^{3}$	Residual concentration (M) $\times 10^{6}$	Amount adsorbed in gg^{-1} adsorbent $\times 10^{3}$	Residual concentration (M) $\times 10^{6}$	Amount adsorbed in gg^{-1} adsorbent $\times 10^{3}$
1	7.045	0.46	8.756	0.60	10.460	0.74	12.190	0.87
2	6.507	0.72	8.049	0.94	9.664	1.13	11.238	1.33
3	6.030	0.95	7.402	1.25	8.843	1.52	10.248	1.81
5	5.170	1.37	6.183	1.84	7.428	2.21	8.546	2.63
7	4.239	1.81	5.061	2.38	6.127	2.83	7.022	3.37
10	3.140	2.35	3.788	3.00	4.611	3.57	5.244	4.22
15	1.970	2.91	2.439	3.65	3.057	4.32	3.467	5.08
20	1.313	3.23	1.744	3.98	2.274	4.69	2.667	5.47
25	0.955	3.40	1.341	4.18	1.832	4.91	2.222	5.68
30	0.752	3.50	1.159	4.27	1.642	5.00	2.057	5.76
40	0.657	3.54	1.037	4.33	1.579	5.03	1.968	5.81
80	0.657	3.54	1.037	4.33	1.579	5.03	1.968	5.81

3.3 Results and discussion

The adsorption of dyes onto oxides and graphite surfaces is rapid in the beginning, slows down later on and finally reaches towards the equilibrium. A large fraction of the total amount of dye is found to be adsorbed within a few minutes. Thus 50% of the total amount of the dye is observed to be removed from solution within ten minutes. The total time required to attain the equilibrium depends on the nature of the adsorbent as well as the adsorbate. Thus the time required to attain the equilibrium in the adsorption of Basic Green 1 onto silica is found to be in the range of 30 to 40 minutes while with graphite it is in the range of 90 to 120 minutes. In case of adsorption of Acid Green 25 and Ketone Blue A onto neutral alumina, the saturation time is observed to be 10 and 40 minutes respectively. The saturation time is also found to be dependent on the amount of the adsorbent. Thus on increasing the amount of silica gel from 0.1 to 0.5g with the adsorption of Basic Green 1 the time required to reach to saturation varies from 90 to 30 minutes. However, a variation in the concentration of dye solution does not show any measureable change in the equilibrium time though the variation in uptake is observed at intermediate stages as well as at equilibrium.

The time growth of uptake increases with concentration of dye solution. Thus on varying the concentration of Basic Blue 3 from 1.4×10^{-5} M to 2.0×10^{-5} M, the amount adsorbed increases

from 2.86×10^{-3} to 3.99×10^{-3} gg^{-1} onto silica keeping the temperature constant at 30 ^{o}C. Similar are the results with other dyes and the adsorbents (Tables 3.2 to 3.5). A comparison of the amounts adsorbed onto one gram of adsorbent shows that the adsorption decreases in the following order :

Silica gel
Basic Green 1>Basic Violet 1>Basic Blue 3>Basic Brown 4

Graphite
Basic Green 1>Basic Blue 3>Acid Green 25>Ketone Blue A

Basic alumina
Basic Brown 4>Basic Violet 2

Neutral alumina
Acid Black 1>Ketone Blue A>Acid Green 25

Amongst the adsorbents used in the study, silica has comparatively higher adsorption capacity while graphite has lower adsorption capacity for dye adsorption. Thus the adsorption of Basic Green 1 onto silica gel is found to be 4.33×10^{-3} gg^{-1} while on graphite it is 3.21×10^{-4} gg^{-1} from 1.0×10^{-5} M solution at 30 ^{o}C. Neutral alumina has, however, shown an appreciable adsorption capacity for all the dyes used, except for Acid Black 1 where a large amount of dye is found to be adsorbed. The amount adsorbed from Acid Black 1 (from 2.0×10^{-5} M solution) is 11.4×10^{-3} gg^{-1} whereas from Ketone Blue A it is 3.24×10^{-3} gg^{-1} on the surface of neutral alumina. This excess adsorption of Acid Black 1 onto neutral alumina may be due to micelle formation and/or the aggregation of dye molecules in the concentration range studies. Similar results have also been reported by several

Table 3.2 TIME RATE STUDY OF ADSORPTION OF DYES ONTO SILICA GEL WITH CONCENTRATION.

Temperature : 30± 0.1°C
Dye solution : 300ml
Amount of silica : 1.0g

Adsorbate	Initial dye concentration / Time (Mins.)	Amount adsorbed in gg^{-1} adsorbent x 10^{3}			
		5.0×10^{-5}M	6.0×10^{-5}M	7.0×10^{-5}M	8.0×10^{-5}M
1	2	3	4	5	6
Basic Brown 4	1	0.98	1.31	1.58	2.05
	2	1.75	2.38	2.91	3.48
	3	2.34	3.15	3.91	4.72
	5	3.27	4.34	5.30	6.28
	7	3.88	5.10	6.20	7.25
	10	4.43	5.82	6.98	8.05
	15	4.74	6.16	7.35	8.41
	20	4.91	6.33	7.51	8.56
	25	5.02	6.46	7.64	8.68
	30	5.08	6.54	7.73	8.77
	80	5.08	6.54	7.73	8.77

Amount of silica : 0.3g

		0.8×10^{-5}M	1.0×10^{-5}M	1.2×10^{-5}M	1.4×10^{-5}M
Basic Violet 1	1	0.43	0.53	0.62	0.70
	3	0.93	1.16	1.38	1.64
	5	1.35	1.70	2.00	2.33
	7	1.65	2.13	2.46	2.89
	10	2.04	2.61	3.02	3.48
	15	2.46	3.06	3.54	4.00
	20	2.73	3.28	3.71	4.20
	25	2.91	3.41	3.85	4.33
	30	2.97	3.50	3.97	4.43
	40	2.97	3.56	4.04	4.50
	80	2.97	3.56	4.04	4.50

able 3.2 continuation

		Amount of silica : 0.5g			
1	2	3	4	5	6
		1.4×10^{-5}M	1.6×10^{-5}M	1.8×10^{-5}M	2.0×10^{-5}M
asic Blue 3	1	0.39	0.49	0.63	0.74
	2	0.57	0.76	0.90	1.06
	3	0.77	0.97	1.15	1.38
	5	1.24	1.43	1.64	1.89
	7	1.62	1.90	2.12	2.40
	10	2.00	2.32	2.64	2.97
	15	2.42	2.78	3.08	3.44
	20	2.75	3.09	3.43	3.59
	25	2.83	3.19	3.55	3.75
	30	2.86	3.26	3.58	3.88
	40	2.86	3.26	3.60	3.99
	80	2.86	3.26	3.60	3.99

		Amount of silica : 0.3g			
		0.8×10^{-5}M	1.0×10^{-5}M	1.2×10^{-5}M	1.4×10^{-5}M
Basic Green 1	1	0.46	0.60	0.74	0.87
	2	0.72	0.94	1.13	1.33
	3	0.95	1.25	1.52	1.81
	5	1.37	1.84	2.21	2.63
	7	1.81	2.38	2.83	3.37
	10	2.35	3.00	3.57	4.22
	15	2.91	3.65	4.32	5.08
	20	3.23	3.98	4.69	5.47
	25	3.40	4.18	4.91	5.68
	30	3.50	4.27	5.00	5.76
	40	3.54	4.33	5.03	5.81
	80	3.54	4.33	5.03	5.81

Table 3.3 TIME RATE STUDY OF ADSORPTION OF DYES ONTO GRAPHITE WITH CONCENTRATION.

Temperature : 30± 0.1°C
Dye solution : 200ml
Amount of graphite : 2.0g

Adsorbate	Initial dye concentration / Time (Mins.)	Amount adsorbed in gg^{-1} adsorbent x 10^4			
		0.6×10^{-5}M	0.8×10^{-5}M	1.0×10^{-5}M	1.2×10^{-5}M
1	2	3	4	5	6
Basic Green 1	1	0.25	0.30	0.37	0.45
	3	0.55	0.67	0.81	0.94
	5	0.83	1.02	1.25	1.46
	10	1.34	1.63	1.94	2.21
	15	1.70	2.05	2.41	2.75
	20	1.91	2.34	2.73	3.12
	30	2.10	2.51	2.89	3.30
	40	2.21	2.62	3.00	3.40
	60	2.30	2.72	3.10	3.48
	90	3.36	2.77	3.17	3.54
	120	2.40	2.81	3.21	3.58
	180	2.40	2.81	3.21	3.58
Ketone Blue A	1	0.20	0.23	0.26	0.30
	3	0.41	0.47	0.54	0.62
	5	0.61	0.71	0.81	0.92
	10	0.96	1.13	1.30	1.46
	15	1.20	1.39	1.59	1.77
	20	1.35	1.54	1.73	1.91
	30	1.47	1.66	1.85	2.02
	40	1.55	1.76	1.93	2.11
	60	1.58	1.80	1.98	2.17
	90	1.58	1.80	2.01	2.21
	180	1.58	1.80	2.01	2.21

Table 3.3 Continuation

1	2	3	4	5	6
Basic Blue 3	1	0.19	0.24	0.28	0.32
	3	0.35	0.45	0.51	0.60
	5	0.53	0.64	0.75	0.86
	10	0.88	1.05	1.21	1.36
	15	1.13	1.34	1.52	1.72
	20	1.29	1.51	1.70	1.93
	30	1.41	1.61	1.83	2.05
	40	1.51	1.70	1.93	2.14
	60	1.57	1.77	2.00	2.21
	90	1.60	1.82	2.04	2.26
	120	1.60	1.82	2.07	2.29
	180	1.60	1.82	2.07	2.29

		0.4×10^{-5}M	0.5×10^{-5}M	0.6×10^{-5}M	0.7×10^{-5}M
Acid Green 25	1	0.15	0.18	0.21	0.24
	3	0.31	0.37	0.42	0.46
	5	0.44	0.50	0.56	0.63
	10	0.72	0.83	0.91	1.00
	15	0.99	1.08	1.20	1.33
	20	1.18	1.28	1.40	1.54
	30	1.30	1.42	1.53	1.68
	40	1.40	1.52	1.64	1.79
	60	1.48	1.60	1.72	1.86
	90	1.52	1.64	1.77	1.91
	120	1.55	1.67	1.80	1.95
	180	1.55	1.67	1.80	1.95

Table 3.4 TIME RATE STUDY OF ADSORPTION OF DYES ONTO NEUTRAL ALUMINA WITH CONCENTRATION.

Temperature : 30± 0.1°C
Dye solution : 200ml
Amount of alumina : 1.0g

Adsorbate	Initial dye concentration / Time (Mins.)	Amount adsorbed in gg^{-1} adsorbent $\times 10^3$			
		0.8×10^{-5}M	1.0×10^{-5}M	1.2×10^{-5}M	1.4×10^{-5}M
1	2	3	4	5	6
Acid Green 25	1	0.26	0.32	0.37	0.41
	2	0.41	0.52	0.59	0.66
	3	0.52	0.65	0.75	0.83
	4	0.58	0.72	0.82	0.90
	6	0.65	0.80	0.90	0.97
	8	0.68	0.82	0.92	0.99
	10	0.69	0.83	0.93	1.00
	60	0.69	0.83	0.93	1.00

Dye solution : 300ml
Amount of alumina : 1.0g

		1.4×10^{-5}M	1.6×10^{-5}M	1.8×10^{-5}M	2.0×10^{-5}M
Ketone Blue A	1	0.34	0.42	0.49	0.57
	3	0.87	1.04	1.23	1.39
	5	1.28	1.49	1.72	1.93
	7	1.54	1.83	2.09	2.33
	10	1.82	2.14	2.44	2.72
	15	2.09	2.41	2.72	3.03
	20	2.18	2.52	2.82	3.13
	25	2.24	2.57	2.87	3.19
	30	2.28	2.61	2.91	3.22
	40	2.31	2.63	2.93	3.24
	60	2.31	2.63	[illegible]	[illegible]

Table 3.4 Continuation

Dye solution : 200ml

Amount of alumina : 0.2g

1	2	3 2.0×10^{-5}M	4 2.5×10^{-5}M	5 3.0×10^{-5}M	6 3.5×10^{-5}M
Acid Black 1	1	1.41	1.71	2.10	2.55
	3	2.80	3.42	4.10	4.95
	5	4.11	5.13	6.11	7.27
	7	5.55	6.72	8.04	9.59
	10	7.32	8.80	10.37	12.39
	15	9.02	10.70	12.78	15.26
	20	10.20	12.10	14.23	16.62
	25	11.10	12.70	14.88	17.34
	30	11.40	13.10	15.27	17.74
	40	11.40	13.40	15.60	18.06
	80	11.40	13.40	15.60	18.06

Table 3.5 TIME RATE STUDY OF ADSORPTION OF DYES ONTO BASIC ALUMINA WITH CONCENTRATION.

Temperature : 30± 0.1°C
Dye solution : 300ml
Amount of alumina : 2.0g

Adsorbate	Time (Mins.) \ Initial dye concentration	Amount adsorbed in gg^{-1} adsorbent			
		4.0×10^{-5}M	5.0×10^{-5}M	6.0×10^{-5}M	7.0×10^{-5}M
Basic Brown 4	1	0.20×10^{-3}	0.25×10^{-3}	0.31×10^{-3}	0.39×10^{-3}
	2	0.37	0.43	0.55	0.70
	3	0.53	0.59	0.75	0.93
	5	0.66	0.83	1.04	1.27
	7	0.79	1.00	1.23	1.50
	10	0.93	1.16	1.40	1.69
	15	1.04	1.27	1.51	1.80
	20	1.09	1.32	1.56	1.86
	25	1.12	1.35	1.59	1.89
	60	1.12	1.35	1.59	1.89

Dye solution : 200ml

		0.8×10^{-5}M	1.0×10^{-5}M	1.2×10^{-5}M	1.4×10^{-5}M
Basic Violet 2	1	0.19×10^{-4}	0.25×10^{-4}	0.31×10^{-4}	0.37×10^{-4}
	3	0.36	0.46	0.58	0.70
	5	0.51	0.67	0.82	0.99
	7	0.65	0.85	1.04	1.26
	10	0.83	1.10	1.31	1.57
	15	1.07	1.35	1.63	1.93
	20	1.20	1.50	1.78	2.08
	25	1.30	1.60	1.90	2.20
	30	1.38	1.68	1.99	2.29
	40	1.43	1.76	2.06	2.35
	60	1.43	1.76	2.06	2.35

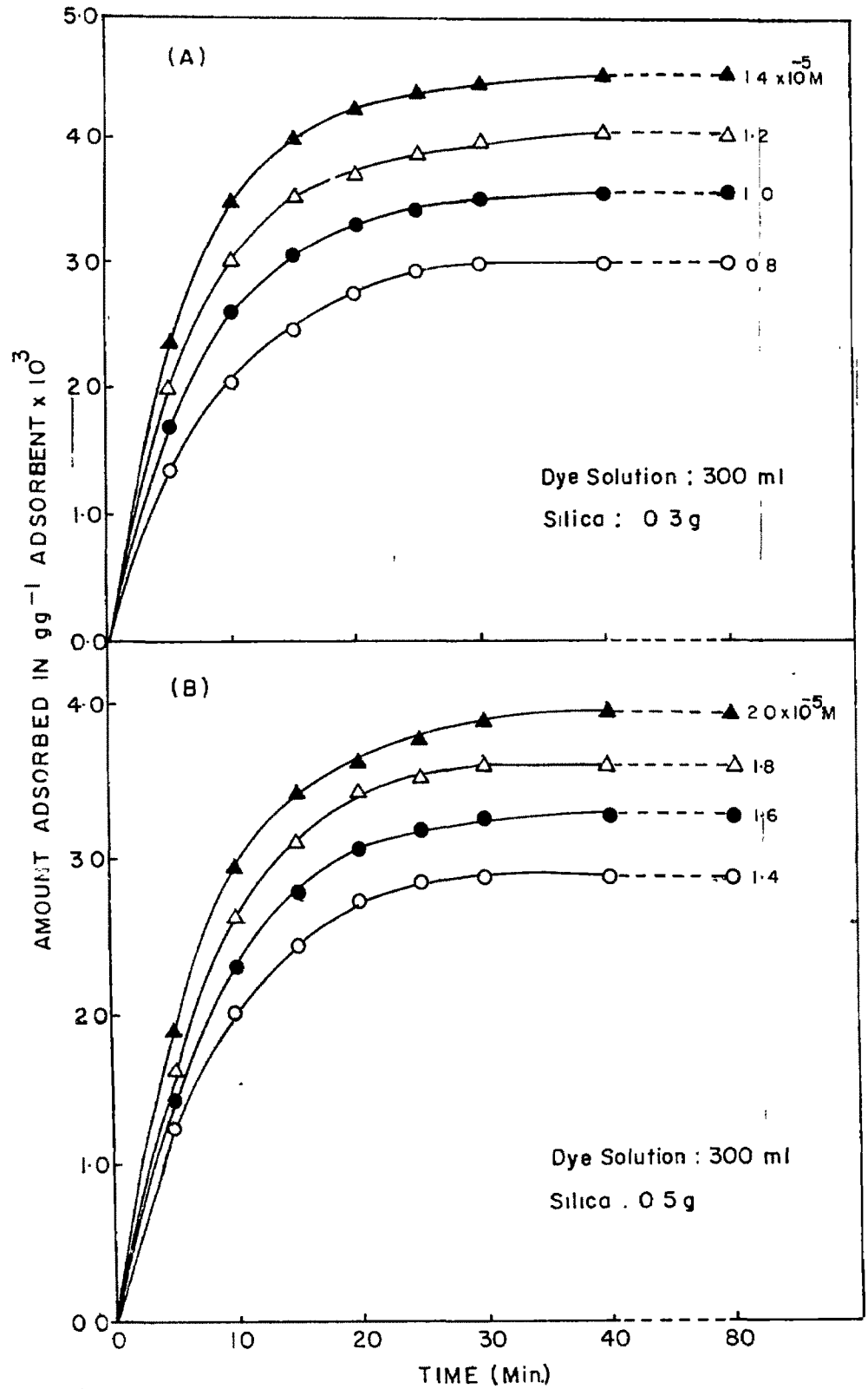
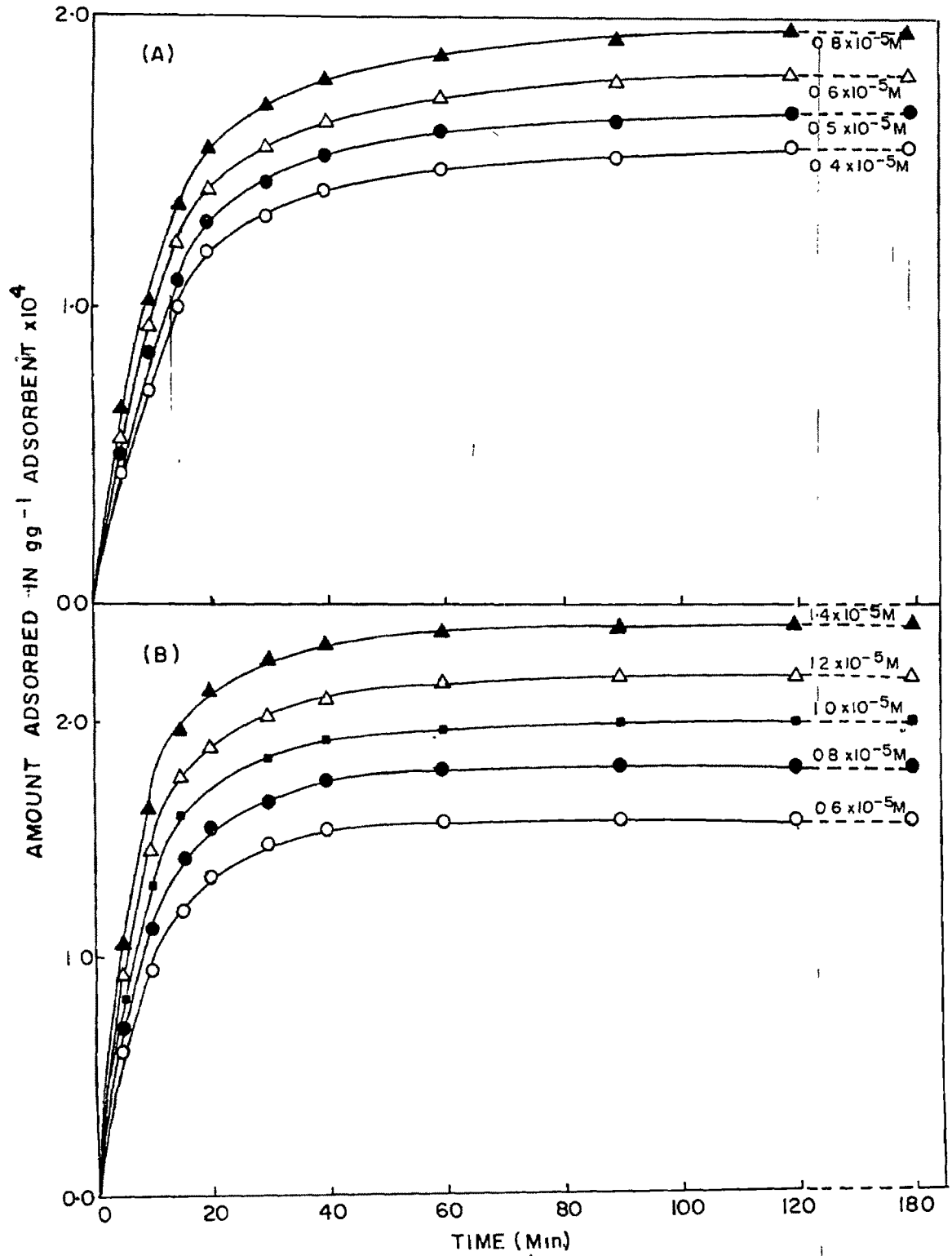


Fig 3·1 Time variation of adsorption of (A) Basic Violet 1 and (B) Basic Blue 3 onto silica gel with concentration at 30°C.

Fig.3.2 Time variation of adsorption of (A) Acid Green 25 and (B) Ketone Blue A onto graphite with concentration at 30°C (dye solution : 200 ml and graphite :2.0g)



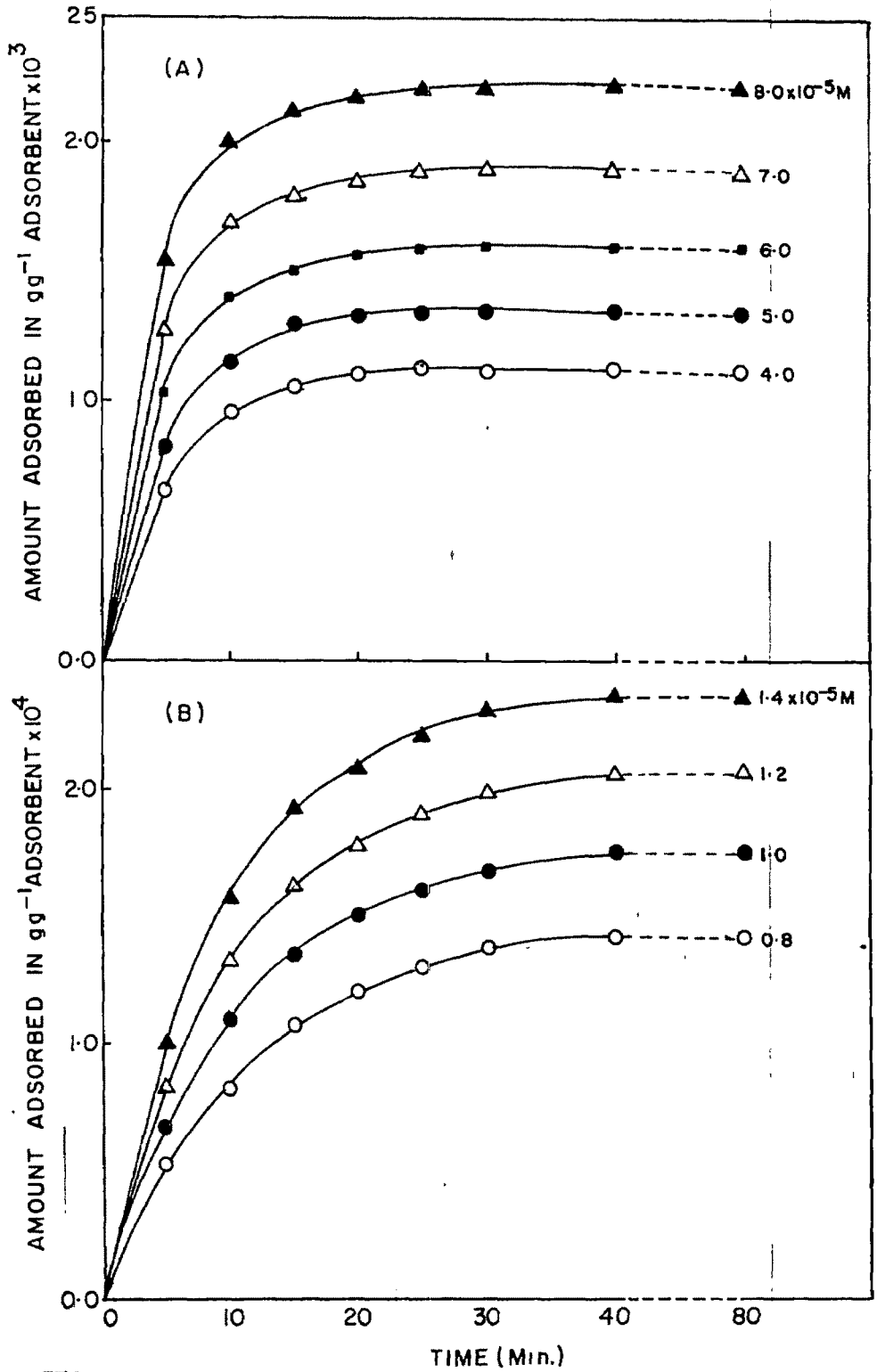


Fig 3.3 Time variation of adsorption of (A) Basic Brown 4 and (B) Basic Violet 2 onto basic alumina with concentration at 30°C (dye solution : 300ml and alumina : 2.0g)

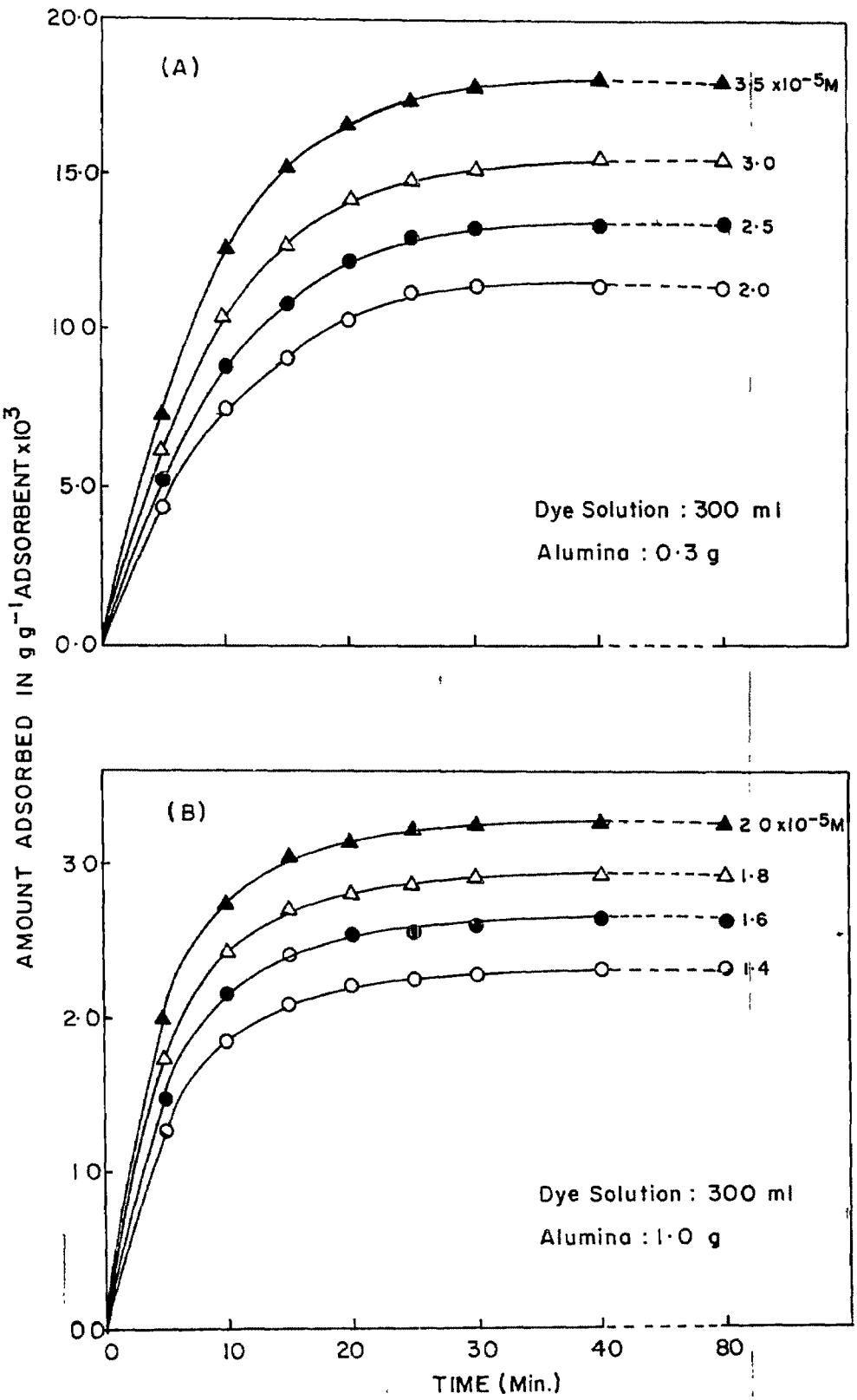


Fig 3 4 Time variation of adsorption of (A) Acid Black 1 and (B) Ketone Blue A onto neutral alumina with concentration at 30°C

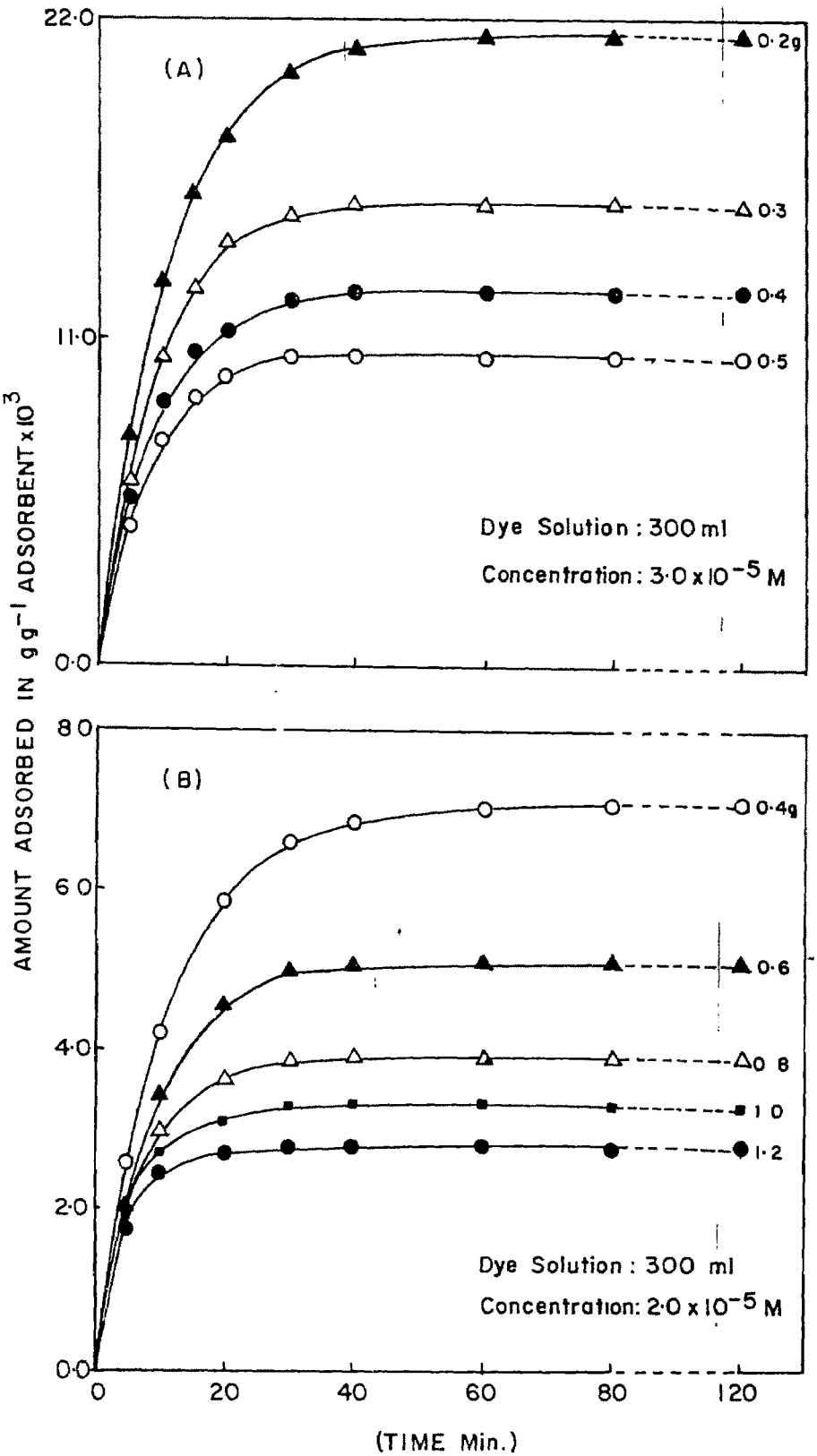


Fig 3.5 Time variation of adsorption of (A) Acid Black 1 and (B) Ketone Blue A onto neutral alumina with amount of adsorbent at 30°C

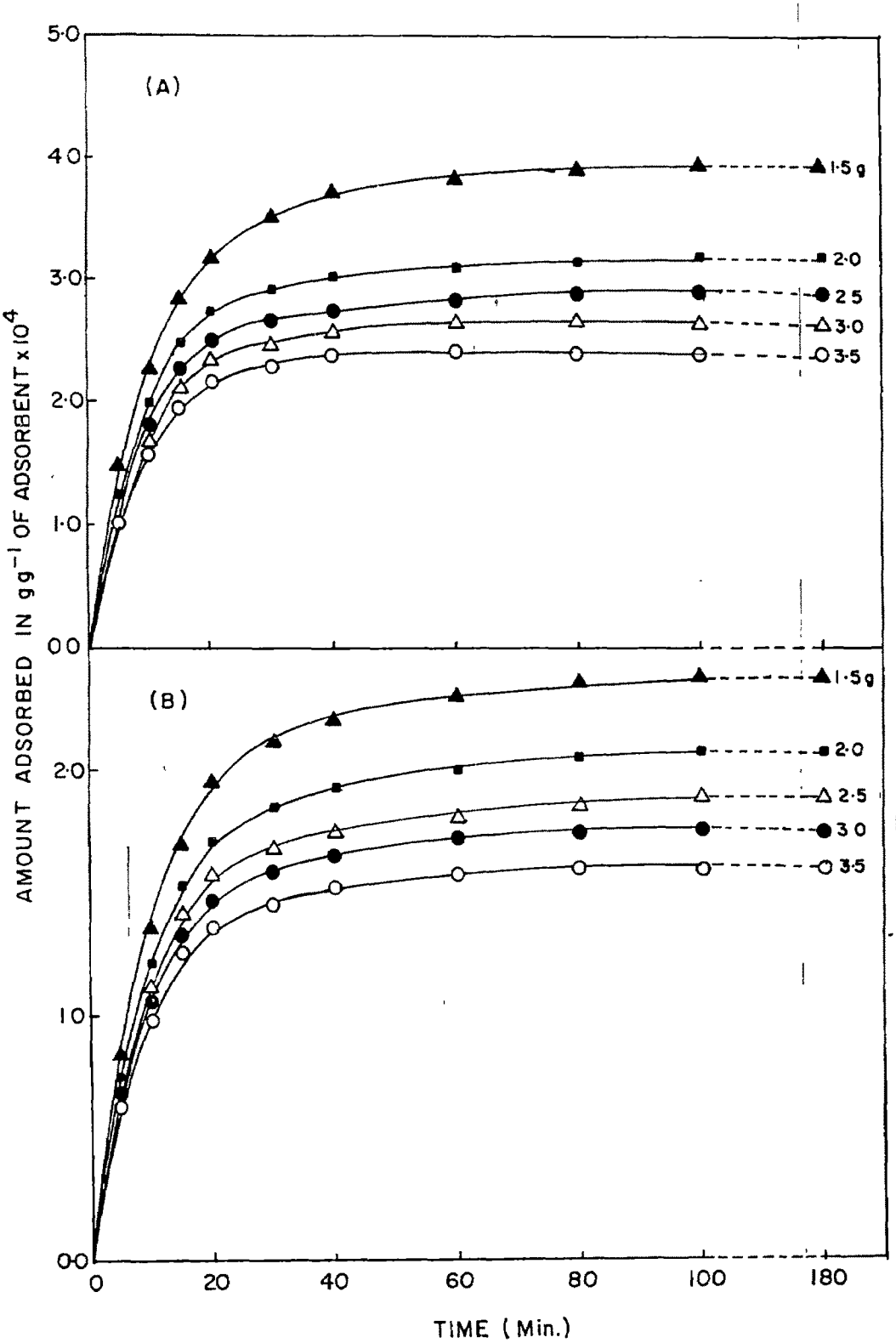


Fig 3 6 Time variation of adsorption of (A) Basic Green 1 and (B) Basic Blue 3 onto graphite with amount of adsorbent at 30°C (dye solution · 200 ml, concentration 1.0 x

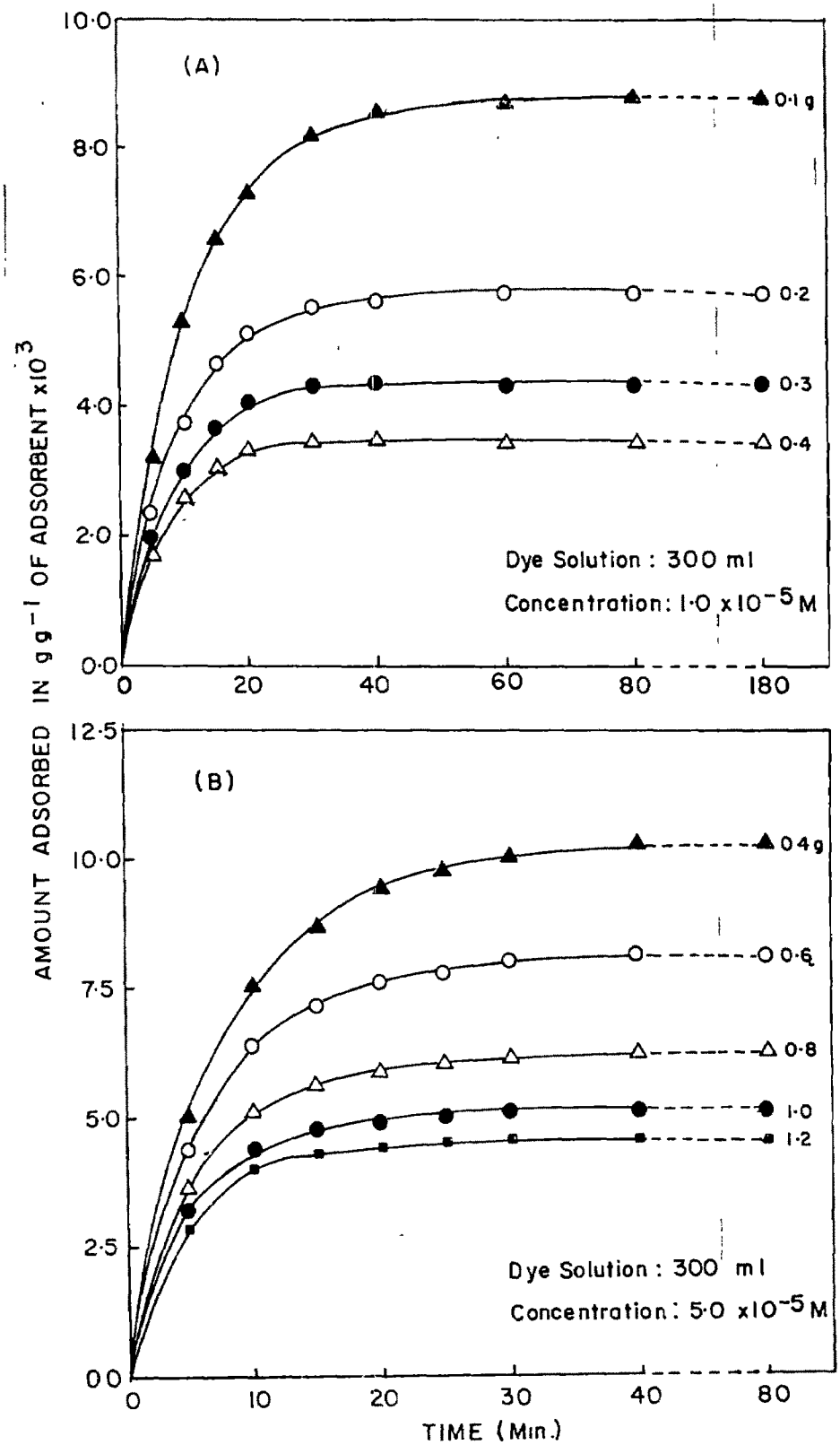


Fig 3.7 Time variation of adsorption of (A) Basic Green 1 and (B) Basic Brown 4 onto silica gel with amount of adsorbent at 30°C

Table 3.6 TIME RATE STUDY OF ADSORPTION OF DYES ONTO SILICA GEL WITH AMOUNT OF ADSORBENT.

Temperature : 30± 0.1°C
Dye solution : 300ml
Concentration : 1.0×10^{-5}M

Adsorbate	Initial dye concentration / Time (Mins.)	Amount adsorbed in gg^{-1} adsorbent x 10^{3}			
		0.1 g	0.2 g	0.3 g	0.4 g
1	2	3	4	5	6
Basic Violet 1	1	1.10	0.68	0.53	0.45
	3	1.94	1.40	1.16	0.99
	5	2.86	2.02	1.70	1.45
	10	4.71	3.19	2.61	2.11
	15	5.91	3.94	3.06	2.46
	20	6.65	4.41	3.28	2.63
	25	7.10	4.69	3.41	2.74
	30	7.48	4.83	3.50	2.79
	40	8.12	4.97	3.56	
	60	8.40	5.06		
	90	8.49			
	180	8.49	5.06	3.56	2.79

Dye solution : 300ml

		0.3 g	0.4 g	0.5 g	0.6 g
Basic Blue 3	1	0.90	0.86	0.74	0.70
	2	1.24	1.18	1.06	0.96
	3	1.57	1.46	1.38	1.22
	5	2.14	2.00	1.89	1.66
	7	2.76	2.53	2.40	2.10
	10	3.59	3.14	2.97	2.62
	15	4.41	3.88	3.44	3.06
	20	4.95	4.30	3.65	3.25
	25	5.43	4.60	3.78	3.37
	30	5.71	4.75	3.90	3.43
	40	6.05	4.92	3.99	3.45
	60	6.24	5.02		
	90	6.27			
	180	6.27	5.02	3.99	3.45

Continuation Table 3.6

Concentration : 5.0×10^{-5} M

1	2	3 0.4 g	4 0.6 g	5 0.8 g	6 1.0 g
Basic Brown 4	1	1.45	1.21	1.09	0.98
	2	2.45	2.14	1.88	1.75
	3	3.40	2.98	2.55	2.34
	5	5.02	4.31	3.63	3.27
	7	6.22	5.30	4.43	3.88
	10	7.53	6.33	5.16	4.43
	15	8.65	7.16	5.55	4.74
	20	9.35	7.57	5.82	4.91
	25	9.77	7.81	6.00	5.02
	30	10.05	8.00	6.14	5.08
	40	10.19	8.09	6.21	
	80	10.19	8.09	6.21	5.08

Concentration : 5.0×10^{-5} M

		0.1 g	0.2 g	0.3 g	0.4 g
Basic Green 1	1	1.06	0.75	0.60	0.48
	2	1.71	1.12	0.94	0.75
	3	2.30	1.59	1.25	1.10
	5	3.27	2.30	1.84	1.65
	7	4.15	2.96	2.38	2.05
	10	5.30	3.68	3.00	2.49
	15	6.62	4.55	3.65	2.98
	20	7.33	5.12	3.98	3.27
	25	7.86	5.34	4.18	3.36
	30	8.21	5.52	4.27	3.40
	40	8.48	5.62	4.33	
	60	8.71	5.69		
	90	8.83			
	180	8.83	5.69	4.33	3.40

workers [7,47,60] with the dye adsorption. On the basis of the adsorption capacity, the adsorbents used in the present study may be arranged in the following manner.

Silica gel > neutral alumina > basic alumina > graphite.

It has been found that the adsorption of cationic dyes is favoured by silica while neutral alumina favours adsorption of anionic dyes; graphite is found suitable for both cationic as well as anionic dyes. A higher adsorption has been noted with cationic dyes as compared to the anionic dyes on graphite. Thus the amount of Basic Green 1 adsorbed is found to be 3.21×10^{-4} gg^{-1} while of Ketone Blue A it is 2.01×10^{-4} gg^{-1} from 1.0×10^{-5} M solution. Similar results have aslo been reported by Giles and D'Silva [45] in the adsorption of dyes (both cationic and anionic) on the surface of charcoal.

The time variation curves of adsorption, are found to be smooth and continuous (Figure 3.1 - 3.7) which indicate the formation of monolayer coverage on the surface of the adsorbents. This general nature is observed with all dyes and the adsorbents employed in the present study. This also indicates that a single and uniform process is operative throghout and is free of any appreciable induction period for the initiation of adsorption. The interaction leading to the final surface is thus simple and unaccompanied by any complicating secondary process.

Table 3.7 TIME RATE STUDY OF ADSORPTION OF DYES ONTO GRAPHITE WITH AMOUNT OF ADSORBENT.

Temperature : 30± 0.1°C
Dye solution : 200ml
Concentration : 1.0×10^{-5} M

Adsorbate	Amount of absorbent / Time (Mins.)	Amount adsorbed in gg^{-1} adsorbent x 10^4			
		1.5 g	2.0 g	2.5 g	3.0 g
1	2	3	4	5	6
Basic Blue 3	1	0.32	0.28	0.25	0.23
	3	0.57	0.51	0.47	0.44
	5	0.82	0.75	0.70	0.66
	10	1.34	1.21	1.12	1.05
	15	1.68	1.52	1.40	1.31
	20	1.95	1.70	1.57	1.47
	30	2.11	1.83	1.68	1.57
	40	2.21	1.93	1.75	1.66
	60	2.28	2.00	1.81	1.72
	90	2.35	2.04	1.86	1.75
	120	2.38	2.07	1.89	
	180	2.38	2.07	1.89	1.75
Ketone Blue A	1	0.30	0.26	0.24	0.22
	3	0.62	0.54	0.51	0.48
	5	0.93	0.81	0.77	0.74
	10	1.47	1.30	1.22	1.17
	15	1.80	1.59	1.48	1.42
	20	1.98	1.73	1.62	1.53
	30	2.12	1.85	1.72	1.62
	40	2.23	1.93	1.81	1.70
	60	2.31	2.01	1.85	1.74
	90	2.35	2.01		
	180	2.35	2.01	1.85	1.74

Table 3.7 Continuation

1	2	3 1.5 g	4 2.0g	5 2.5 g	6 3.0 g
Basic Green 1	1	0.43	0.37	0.34	0.30
	3	0.93	0.81	0.75	0.69
	5	1.43	1.25	1.15	1.08
	10	2.27	1.94	1.79	1.66
	15	2.83	2.41	2.44	2.08
	20	3.22	2.73	2.52	2.30
	30	3.50	2.89	2.66	2.45
	40	3.68	3.00	2.75	2.55
	60	3.80	3.10	2.82	2.64
	90	3.90	3.17	2.88	2.67
	120	3.95	3.21	2.91	
	180	3.95	3.21	2.91	2.67
Acid Green 25	1	0.21	0.18	0.16	0.14
	3	0.44	0.37	0.34	0.32
	5	0.57	0.50	0.47	0.44
	10	0.90	0.83	0.73	0.68
	15	1.23	1.08	0.96	0.89
	20	1.44	1.28	1.12	1.00
	30	1.62	1.42	1.25	1.13
	40	1.74	1.52	1.35	1.22
	60	1.84	1.60	1.42	1.30
	90	1.92	1.64	1.46	1.34
	120	1.96	1.67	1.49	1.36
	180	1.96	1.67	1.49	1.36

Table 3.8 TIME RATE STUDY OF ADSORPTION OF DYES ONTO NEUTRAL ALUMINA WITH AMOUNT OF ADSORBENT.

Temperature : 30± 0.1°C
Dye solution : 300ml
Concentration : 3.0×10^{-5} M

Adsorbate	Amount of absorbent / Time (Mins.)	Amount adsorbed in gg^{-1} adsorbent x 10^{5}			
		0.2 g	0.3 g	0.4 g	0.5 g
1	2	3	4	5	6
Acid Black 1	1	2.65	2.10	1.81	1.60
	3	5.18	4.10	3.62	3.18
	5	7.60	6.11	5.43	4.68
	7	9.89	8.04	6.93	5.98
	10	12.90	10.37	8.80	7.53
	15	15.92	12.78	10.50	8.97
	20	17.85	14.23	11.15	9.75
	25	19.30	14.88	11.70	10.20
	30	20.14	15.27	12.30	10.74
	40	21.00	15.60	12.54	
	60	21.47			
	120	21.47	15.60	12.54	10.74

Concentration : 2.0×10^{-5} M

		0.4 g	0.6 g	0.8 g	1.0 g
Ketone Blue A	1	0.87	0.71	0.59	0.47
	3	1.82	1.48	1.40	1.32
	5	2.51	2.15	1.99	1.93
	7	3.24	2.70	2.43	2.33
	10	4.17	3.38	2.96	2.72
	15	5.17	4.19	3.46	3.05
	20	5.85	4.57	3.67	3.13
	25	6.29	4.77	3.80	3.19
	30	6.60	4.96	3.89	3.22
	40	6.91	5.07	3.95	3.24
	60	7.04	5.11		
	90	7.11			
	180	7.11	5.11	3.95	3.24

Table 3.8 Continuation

Dye solution : 200ml
Concentration : 2.0×10^{-5} M

1	2	3 1.0 g	4 1.5 g	5 2.0 g	6 2.5 g
Acid Green 25	1	0.72	0.27	0.24	0.21
	2	0.52	0.43	0.37	0.31
	3	0.65	0.52	0.43	0.37
	4	0.72	0.58	0.47	0.39
	6	0.80	0.61	0.49	0.40
	8	0.82	0.63	0.50	0.40
	10	0.83	0.63	0.50	0.40
	60	0.83	0.63	0.50	0.40

Table 3.9 TIME RATE STUDY OF ADSORPTION OF DYES ONTO BASIC ALUMINA WITH AMOUNT OF ADSORBENT.

Temperature : 30± 0.1°C
Dye solution : 300ml
Concentration : 5.0×10^{-5}M

Adsorbate	Amount of absorbent / Time (Mins.)	Amount adsorbed in gg^{-1} adsorbent			
		2.0 g	2.5 g	3.0 g	4.0 g
Basic Brown 4	1	0.25×10^{-3}	0.23×10^{-3}	0.20×10^{-3}	0.16×10^{-3}
	2	0.43	0.40	0.37	0.32
	3	0.59	0.54	0.49	0.43
	5	0.83	0.74	0.69	0.60
	7	1.00	0.90	0.83	0.70
	10	1.16	1.05	0.94	0.77
	15	1.27	1.12	1.00	0.82
	20	1.32	1.18	1.04	0.85
	25	1.35	1.21	1.06	0.85
	80	1.35	1.21	1.06	0.85

Dye solution : 200ml
Concentration : 1.0×10^{-5}M

	1.0 g	1.5 g	2.0 g	2.5 g
1	0.36×10^{-4}	0.30×10^{-4}	0.25×10^{-4}	0.20×10^{-4}
3	0.65	0.54	0.46	0.42
5	0.94	0.78	0.67	0.60
7	1.24	1.02	0.85	0.77
10	1.54	1.30	1.10	1.01
15	1.96	1.63	1.35	1.23
20	2.29	1.79	1.50	1.36
25	2.51	1.95	1.60	1.44
30	2.68	2.13	1.68	1.50
40	2.74	2.18	1.76	1.54
80	2.74	2.18	1.76	1.54

In order to confirm the nature of adsorption, the reflectance spectra (Fig. 3.8a) of the adsorbents (saturated with dye by the use of adsorption process) is taken with the help of spectrophotometer (Shimadzu UV - 240, Japan). It is evident from these spectra that the adsorption of dyes takes place on the outer surface of the adsorbent. Again the analysis of the reflectance spectra and the absorbance spectra (Fig. 3.8a & Fig.3.8b) corresponding to maximum absorbance, it is found that there is no change in the wave length corresponding to maximum absorbance. This indicates that the dye adsorbs as such on the surface of the adsorbents.

The straight line plots of -log (1-f) Vs time (Figures3.9a to 3.9d) is indicative of the first order process according to the equation

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

where 'f' is the fraction of the total amount of dye adsorbed at any time 't' and 'k' is the specific reaction rate. The values of, k calculated from the slopes of the corresponding straight line plots are seen to depend on the nature of the dye and the adsorbent. Thus the values of k for the adsorption of Basic Green 1 onto silica and graphite are 0.122 and 0.094 $min.^{-1}$ respectively at 30 ^{o}C for 1.0 x 10^{-5} M solution. The k values for the adsorption of Acid Green 25 on graphite and alumina are 0.073 and 0.46 $min.^{-1}$ respectively from 0.8 x 10^{-5} M solution at 30 ^{o}C. The k values for other systems are given in Tables 3.10 & 3.11. It is thus evident

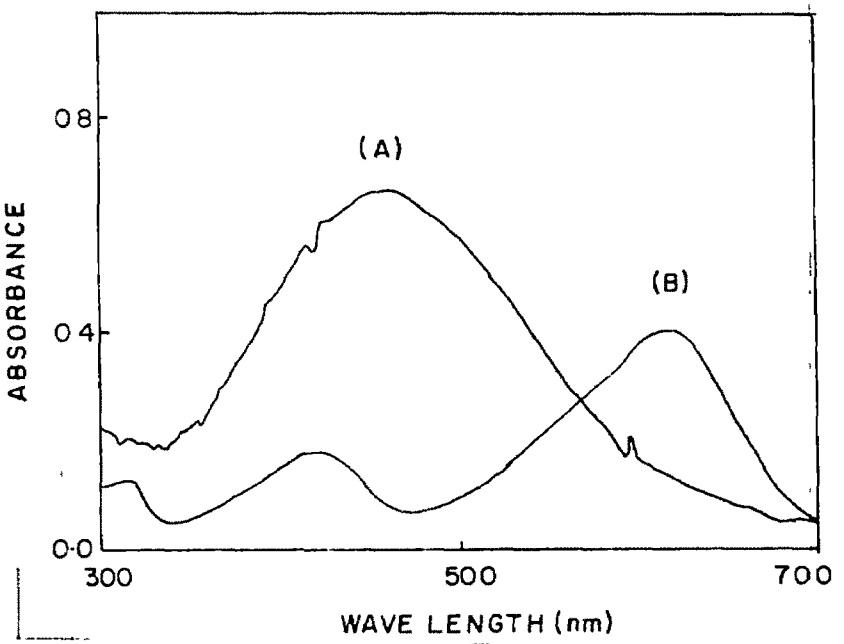


Fig 3 8a UV-Vis reflectance spectra of (A) Basic Brown 4 and (B) Basic Green 1 from the surface of silica gel

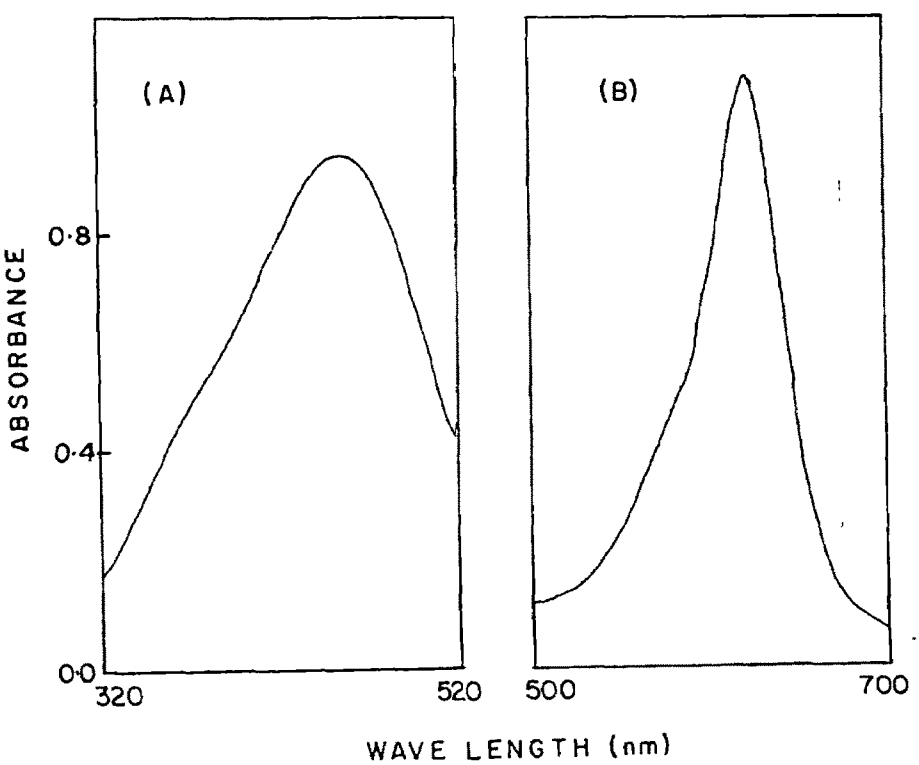


Fig 3.8b Adsorbance spectra of (A) Basic Brown 4 and (B) Basic Green 1 from aqueous solution

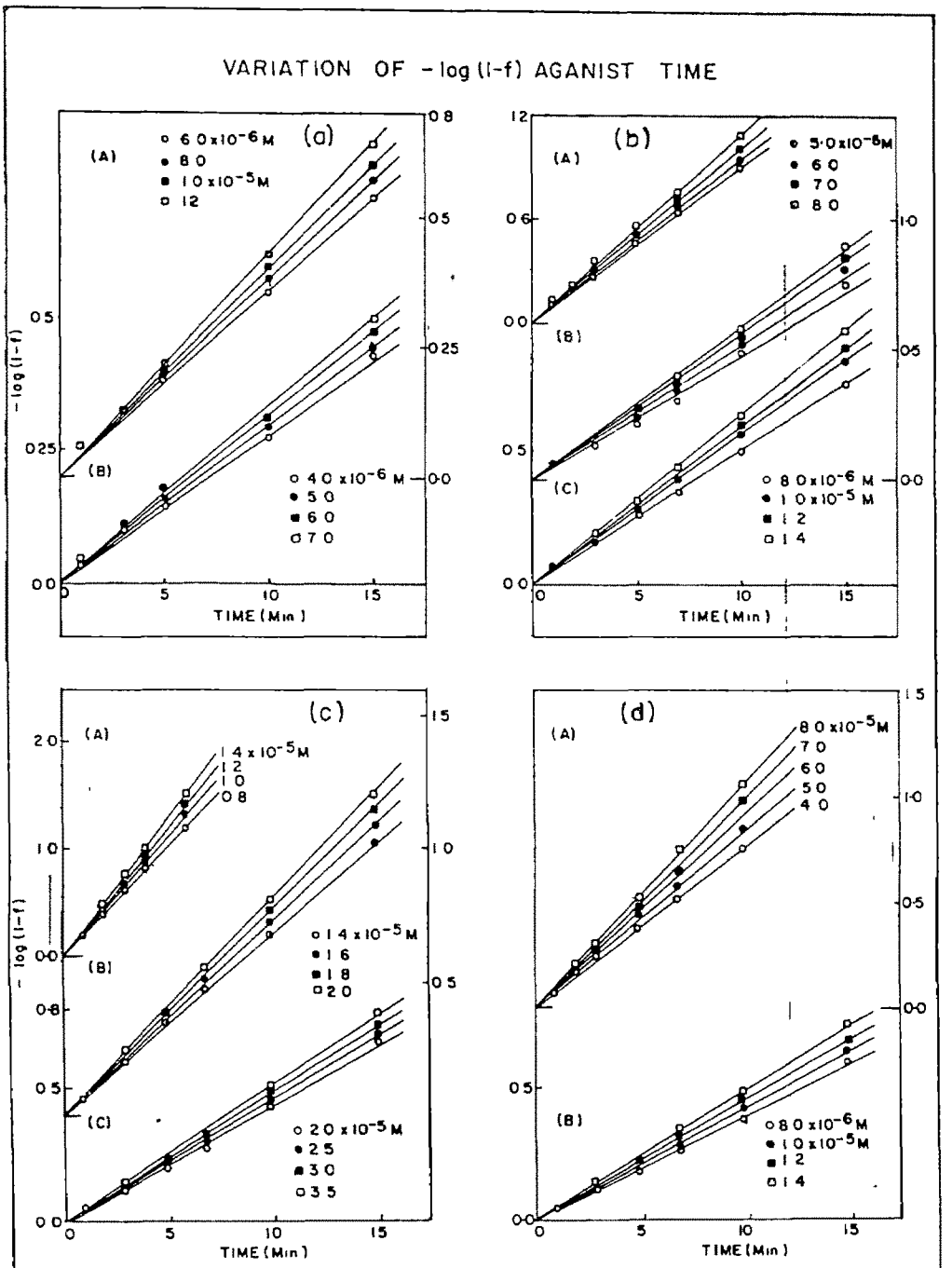


Fig 3.9a Adsorption of (A) Basic Green 1 and (B) Acid Green 25 on graphite with concentration.

Fig 3.9b Adsorption of (A) Basic Brown 4, (B) Basic Green 1 and (C) Basic Violet 1 on silica gel with concentration

Fig 3.9c Adsorption of (A) Acid Green 25, (B) Ketone Blue A and (C) Acid Black 1 on neutral alumina with concentration

Fig 3.9d Adsorption of (A) Basic Brown 4 and (B) Basic Violet 2 on basic alumina with concentration

from the consolidated results (Table 3.10) that the rate of adsorption of Acid Green 25 with neutral alumina is highest as compared to that of other systems.

The values of specific reaction rate k are also observed to be dependent on the amount of adsorbent (Table 3.11). An increase in the rate of adsorption is found with an increase in the quantity of the adsorbent, though a decrease is observed in gg^{-1} of the adsorption. Thus the values of k for the adsorption of Basic Violet 1 onto silica increases from 0.077 to 0.152 $min.^{-1}$ with an increase in the amount of the adsorbent from 0.1g to 0.5g (initial dye concentration is 1.0×10^{-5} M) although amount of dye adsorbed per gram of silica decreases from 8.49×10^{-3} to 2.25×10^{-3} g. This may be due to the fact that as the quantity of the adsorbent increases, there is an increase in the adsorption site though the number of dye molecules present in the solution remains constant. As a result, a decrease in adsorption in (gg^{-1}) is observed. On the other hand, the dye molecules may get adsorbed easily as the number of sites increases with the amount of adsorbent. This will cause a rapid decrease in the dye concentration, therefore the rate will increase with the amount of adsorbent. Similar to this result is the finding of Allen et al. for the adsorption of basic dye onto peat as well as of other workers with the adsorption of dyes on various solid surfaces [61,62]. The information obtained from the rate study will be helpful to establish the effluent treatment plant based on adsorption process.

Table 3.10 CONSOLIDATED RESULTS OF ADSORPTION OF DYES ONTO VARIOUS ADSORBENTS WITH CONCENTRATION.

Adsorbent	Adsorbate	Initial dye concentration (M)$\times 10^{5}$	Time (min.) to attain saturation	Amount adsorbed in gg^{-1} adsorbent	Specific reaction rate k (min^{-1})
(1)	(2)	(3)	(4)	(5)	(6)
Silica (0.5g)	Basic Blue 3 (300 ml)	1.4	30	2.86×10^{-3}	0.124
		1.6	30	3.26	0.128
		1.8	40	3.60	0.132
		2.0	40	3.99	0.135
Silica (0.3)	Basic Violet 1	0.8	30	2.97	0.115
		1.0	40	3.56	0.131
		1.2	40	4.04	0.138
		1.4	40	4.50	0.147
Silica (0.3g)	Basic Green 1	0.8	40	3.54	0.110
		1.0	40	4.33	0.120
		1.2	40	5.03	0.128
		1.4	40	5.81	0.137
Silica (1.0g)	Basic Brown 4	5.0	30	5.08	0.205
		6.0	30	6.54	0.215
		7.0	30	7.73	0.232
		8.0	30	8.77	0.248
Graphite (2.0g)	Basic Green 1 (200 ml)	0.6	120	2.40×10^{-4}	0.081
		0.8	120	2.81	0.087
		1.0	120	3.21	0.093
		1.2	120	3.58	0.100
Graphite (2.0g)	Ketone Blue A	0.6	60	1.58	0.093
		0.8	60	1.80	0.097
		1.0	90	2.01	0.103
		1.2	90	2.21	0.108

Table 3.10 Continuation

(1)	(2)	(3)	(4)	(5)	(6)
Graphite (2.0g)	Basic Blue 3	0.6	90	1.60×10^{-4}	0.079
		0.8	120	1.85	0.083
		1.0	120	2.07	0.087
		1.2	120	2.29	0.091
Graphite (2.0g)	Acid Green 25	0.4	120	1.55	0.062
		0.5	120	1.67	0.065
		0.6	120	1.80	0.069
		0.7	120	1.95	0.074
Basic alumina (2.0g)	Basic Brown 4 (300 ml)	4.0	25	1.12×10^{-3}	0.173
		5.0	25	1.35	0.196
		6.0	25	1.59	0.210
		7.0	25	1.89	0.225
		8.0	25	2.21	0.243
Basic alumina (2.0g)	Basic Violet 2 (200 ml)	0.8	40	1.43×10^{-4}	0.089
		1.0	40	1.76	0.098
		1.2	40	2.06	0.104
		1.4	40	2.35	0.112
Neutral alumina (1.0 g)	Acid Green 25 (200 ml)	0.8	10	0.69×10^{-3}	0.465
		1.0	10	0.83	0.507
		1.2	10	0.93	0.545
		1.4	10	1.00	0.605
Neutral alumina (0.1 g)	Ketone Blue A (300 ml)	1.4	40	2.31	0.158
		1.6	40	2.63	0.168
		1.8	40	2.93	0.175
		2.0	40	3.24	0.183
Neutral alumina (0.1 g)	Acid Black 1 (300 ml)	2.0	30	11.40	0.101
		2.5	30	13.40	0.106
		3.0	40	15.60	0.112
		3.5	40	18.06	0.120

Table 3.11 CONSOLIDATED RESULTS OF ADSORPTION OF DYES ONTO VARIOUS ADSORBENTS WITH DIFFERENT MASS OF ADSORBENT.

Adsorbent	Adsorbate	Amount of adsorbent (gm)	Time (min) to attain saturation	Amount adsorbed in gg^{-1} adsorbent	Specific reaction rate k (min^{-1})
(1)	(2)	(3)	(4)	(5)	(6)
Silica	Basic Blue 3 ($2.0x10^{-5}$M) (300 ml)	0.3	120	6.27x10-3	0.086
		0.4	90	5.02	0.102
		0.5	40	3.99	0.132
		0.6	40	3.45	0.143
Silica	Basic Brown 4 ($5.0x10^{-5}$M)	0.4	40	10.19	0.133
		0.6	40	8.09	0.152
		0.8	40	6.21	0.177
		1.0	30	5.08	0.205
		1.2	25	4.46	0.222
Silica	Basic Violet 1 ($1.0x10^{-5}$M)	0.1	90	8.49	0.077
		0.2	60	5.06	0.098
		0.3	40	3.56	0.130
		0.4	30	2.79	0.140
		0.5	30	2.25	0.152
Silica	Basic Green 1 ($1.0x10^{-5}$M)	0.1	90	8.83	0.090
		0.2	60	5.69	0.105
		0.3	40	4.33	0.123
		0.4	30	3.40	0.138
Graphite	Basic Blue 3 ($1.0x10^{-5}$M) (200 ml)	1.5	120	2.38x10-4	0.078
		2.0	120	2.07	0.086
		2.5	120	1.89	0.090
		3.0	90	1.75	0.093
		3.5	90	1.61	0.096

Table 3.11 Continuation

(1)	(2)	(3)	(4)	(5)	(6)
Graphite	Ketone Blue A (1.0×10^{-5}M)	1.5	90	2.35×10^{-4}	0.085
		2.0	90	2.01	0.103
		2.5	60	1.85	0.106
		3.0	60	1.74	0.110
		3.5	60	1.65	0.115
Graphite	Basic Green 1 (1.0×10^{-5}M)	1.5	120	3.95	0.083
		2.0	120	3.21	0.094
		2.5	120	2.91	0.097
		3.0	90	2.67	0.100
		3.5	90	2.45	0.103
Graphite	Acid Green 25 (0.5×10^{-5}M)	1.5	120	1.96	0.062
		2.0	120	1.67	0.065
		2.5	120	1.49	0.068
		3.0	120	1.36	0.071
Basic alumina	Basic Violet 2 (1.0×10^{-5}M) (200ml)	1.0	40	2.74×10^{-4}	0.081
		1.5	40	2.18	0.089
		2.0	40	1.76	0.096
		2.5	40	1.54	0.106
		3.0	40	1.36	0.113
Basic alumina	Basic Brown 4 (5.0×10^{-5}M) (200ml)	1.0	25	1.35×10^{-3}	0.195
		2.5	25	1.21	0.200
		3.0	25	1.06	0.215
		4.0	25	0.85	0.240
Neutral alumina	Acid Green 25 (1.0×10^{-5}M) (200ml)	1.0	10	0.80×10^{-3}	0.511
		1.5	8	0.63	0.600
		2.0	8	0.50	0.695
		2.5	6	0.40	0.803
		3.0	6	0.34	0.888

Table 3.11 Continuation

(1)	(2)	(3)	(4)	(5)	(6)
Neutral alumina	Acid Black 1 (3.0×10^{-5}M) (300ml)	0.2	60	21.47	0.089
		0.3	40	15.60	0.114
		0.4	40	12.54	0.122
		0.5	30	10.34	0.137
Neutral alumina	Ketone Blue A (2.0×10^{-5}M) (300ml)	0.4	90	7.11	0.0865
		0.6	60	5.11	0.110
		0.8	40	3.95	0.138
		1.0	40	3.24	0.183
		1.2	30	2.89	0.211

As expected, the amount of dye removal in gg^{-1} decreases exponentially with increasing amounts of adsorbent as shown in Figure 3.10; being similar in nature the plots (x/m Vs m) for other systems are not given.

The extent of adsorption in a system is determined by a number of factors of which the availability of the active adsorption sites and concentration of the dye solution are the most important. The adsorbents employed in the present study are in the powdered form and have been activated appropriately at suitable temperature and thus capable of providing excessive opportunity for large adsorption. According to the percentage of dye removal from the solution, silica gel has the highest capacity ranging from 80 -95% and neutral alumina has 60 -90% over the concentration range studied. Basic alumina and graphite have shown less removal capacity (Table 3.12). It is evident from the above that the dye concentration and the active sites available in the surface should play an important role in the kinetics of the adsorption process. Keeping active sites constant (i.e., using a fixed amount of adsorbent), however, the adsorption is dependent on the concentration of the dye solution and is expected to be a first order process with respect to dye concentration which is actually observed.

It has been stated earlier (Chapter 1) that most of the oxide surfaces in contact with water exhibit a surface charge which is dependent on the pH of the solution. In case the adsorbent

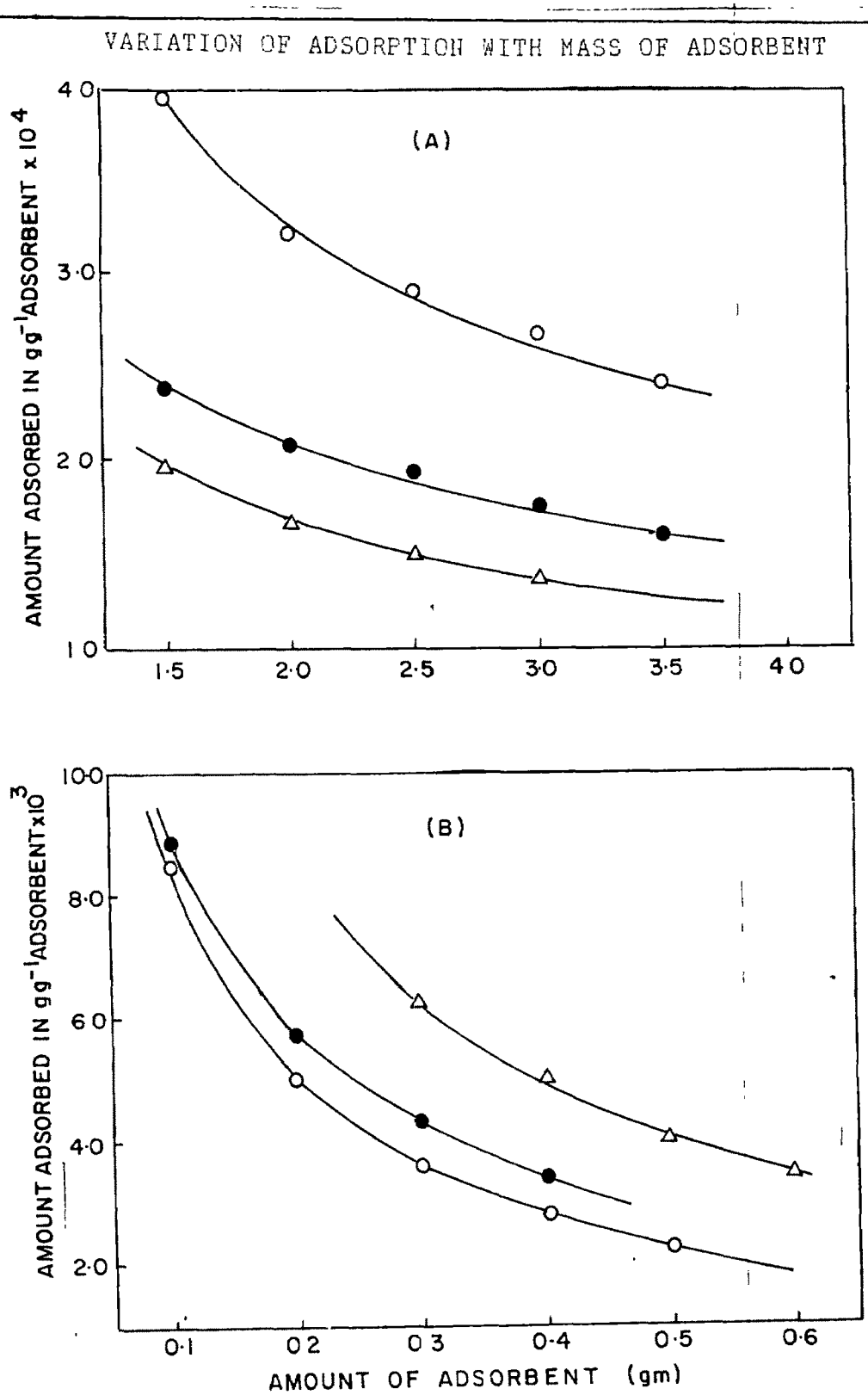


Fig 3.10 Adsorption of (A) Basic Green 1(O), Basic Blue 3 (●) & Acid Green 25 (Δ) on graphite and (B) Basic Violet 1 (O) Basic Green 1 (●) & Basic Blue 3 (Δ) on silica gel.

3.12 DYE REMOVAL CAPACITIES OF THE ADSORBENTS

Temperature : 30± 0.1°C

SYSTEM	Initial dye concentration (M)×10^{5}	Total dye available in the solution (g)×10^{-4}	Amount of dye adsorbed at the equilibrium g×10^{-4}	Removal capacity in percentage
(1)	(2)	(3)	(4)	(5)
Silica-Basic Green 1	0.8	1.16	1.06	91.37
	1.0	1.45	1.30	89.65
	1.2	1.73	1.51	87.28
	1.4			
Silica-Basic Violet 1	0.8	0.95	0.89	94.28
	1.0	1.18	1.07	90.5
	1.2	1.42	1.21	85.35
	1.4	1.65	1.35	81.82
Silica-Basic Brown 4	5.0	6.92	5.08	73.41
	6.0	8.30	6.54	78.80
	7.0	9.69	7.73	79.77
	8.0	11.07	8.77	79.22
Silica-Basic Blue 3	1.4	1.51	1.43	94.70
	1.6	1.73	1.63	94.22
	1.8	1.94	1.80	92.78
	2.0	2.16	1.92	88.88
Neutral alumina Acid Green 25	0.8	1.00	0.69	69.00
	1.0	1.25	0.83	66.40
	1.2	1.49	0.93	62.42
	1.4	1.74	1.00	57.47
Neutral alumina Acid Black 1	2.0	3.70	3.42	92.43
	2.5	4.62	4.02	87.01
	3.0	5.55	4.68	84.32
	3.5	6.47	5.42	83.77

Table 3.12 Continuation

(1)	(2)	(3)	(4)	(5)
Basic alumina Basic Brown 4	4.0	5.54	2.24	40.43
	5.0	6.92	2.70	39.02
	6.0	8.30	3.18	38.31
	7.0	9.69	3.68	37.97
Basic alumina Basic Violet 2	0.8	0.58	0.28	48.28
	1.0	0.73	0.35	47.95
	1.2	0.88	0.41	46.59
	1.4	1.02	0.47	46.08
Graphite-Acid Green 25	0.4	0.50	0.31	62.00
	0.5	0.62	0.33	53.22
	0.6	0.75	0.36	48.00
	0.7	1.00	0.39	39.00
Graphite-Ketone Blue A	0.6	0.72	0.32	44.44
	0.8	0.96	0.36	37.50
	1.0	1.20	0.40	33.33
	1.2	1.44	0.44	30.55
Graphite Basic Green 1	0.6	0.58	0.48	82.75
	0.8	0.77	0.56	72.73
	1.0	0.96	0.64	66.66
	1.2	1.16	0.72	62.07
Graphite-Basic Blue 3	0.6	0.43	0.32	74.42
	0.8	0.58	0.37	63.79
	1.0	0.72	0.41	56.94
	1.2	0.86	0.46	53.49

possesses a charged surface, it leads to an appreciable alteration not only in the amount and the rate of adsorption but sometimes in the actual nature of the adsorption behaviour.

The charge on the surface arises mainly due to (1) the presence of adsorbed ions either existing inherently or taken up at the moment and (2) the interaction with the solvent. The former may be excluded in the present case because in the preparation of the adsorbent samples, pure materials are used and the adsorbate solutions contained no additionally added ions. Consequently the latter, i.e., the interaction with the solvent is important. The influence due to this factor becomes very important when the solid consists of metal oxides and the adsorbate of aqueous solutions. The interaction thus of the adsorbent with water and the subsequent dissociation of the resulting product causes the development of a charged surface.

Silica, occurs in a variety of forms, both porous and non porous, and the type and number of surface hydroxyl groups (known as silanol group) depend on the method of preparation and the treatment given before the adsorption experiments [63]. The surface of silica heated at temperatures below 750 ^{o}K, contains not only isolated surface silanol groups but also adjacent interacting silanol groups [64]. The chemisorption of calcium hydroxide onto silica has been interpreted by Greenburg [65], considering the dissociation of Si - OH as represented below :

$$Si - OH \rightleftharpoons Si - O^{-} + H^{+}$$

Similar type of dissociation has also been considered by other workers [66,67]. According to this, the surface should become negatively charged and the aqueous layer should indicate a lowering in pH value. According to Greenburg [65], silica is slightly soluble in water and forms silicic acid in water which on dissociation develops a surface charge. From the measurement of streaming potential by O'Connor and Buchanan [68 - 70], and also from various other studies it is concluded that silica in contact with water possesses a negatively charged surface. Such a surface is thus expected to be favourable for adsorption of cationic dyes. In view of this, the observation of the increase in dissociation of the silanol group with increase in pH is important. In addition, the contribution due to gel forming nature and comparatively large surface area of the adsorbent is also significant. The other reasons for the excessive adsorption of dyes onto silica may be due to the formation of micelles and /or the aggregates of the dye molecules. Similar results have also been described by several workers [7,47,71] in the adsorption of dyes.

Alumina is a good multi purpose adsorbent and is commonly available in a variety of useful forms. The structure of different aluminas and of their respective surfaces has been studied intensively. Alumina normally contains varying amount of water, either in the adsorbed state or as surface

hydroxyl groups [72]. Heating alumina to 300 ^{o}C or higher drives off most of the adsorbed water, with simultaneous reaction of water molecules with the surface to form hydroxyl groups. Initially hydrated aluminas which have been heated to 400 ^{o}C in vacuum retain about six hydroxyl groups per 100 $\AA^{2}$ of surface. On further heating at 800 ^{o}C or above essentially all the surface hydroxyl groups are removed [72]. The experimental conditions employed in the present study are, however, far from the extreme case cited above and is more favourable for the presence of appreciable surface hydroxyl groups.

It has been reported that in water OH^{-} ions are released from the alumina surface and the cationic centres remaining are the source of the attraction of anionic dyes [73]. O'Connor et al. [74] have suggested the ionization of alumina in two ways depending on the nature of the bond holding the hydroxyl group to the surface :

$$Al(OH)_3 \rightleftharpoons Al(OH)_2^{+} + H^{-}$$

$$AlO.OH \rightleftharpoons AlO.O^{-} + H^{+}$$

Normally alumina in contact with water possesses a positively charged surface. Such a surface is thus expected to be favourable for the adsorption of anionic dyes. However, adsorption of cationic dyes is also possible when alkali treated alumina is used for the purpose. In actual experiment basic alumina is found suitable for an easy adsorption of cationic dyes.

Graphitized carbons are essentially pure carbon, and their surfaces are non polar [75]. Giles et al. [45] found that the carbon from acid extracted bone char adsorbed both anionic and cationic dyes and showed zero streaming potential. This indicates the absence of significant amount of ionizable groups on the surface and the process is mainly due to the dispersion forces. It has also been suggested that there could be a possibility of hydrogen bonding of the adsorbate molecules with the surface. This fact, when combined with the result that saturation stage for adsorption of dyes is obtained quickly, is indicative of a stronger force of attraction.

In an individual experiment a known amount of adsorbent was kept in contact with certain volume of deionized water for 24 hours. A decrease in the pH of the slurry is indicative of the acidic nature of silica. However, no measurable change in pH is observed in the case of alumina and graphite. This result is in accordance with the above discussion.

Surface area measurement of adsorbents was carried out using Carlo Ebra Strumentazione. Surface area of silica gel, neutral alumina and basic alumina are 510, 129 and 136 m^2/g respectively.

From the above discussion it appears that the entire attention of the present work is oriented towards determining conditions favourable for adsorption on oxides

and graphite surfaces and the understanding of the actual nature of the time growth of uptake in such cases and also the influence of the chief determining factors on it. The procedure to achieve this has been discussed in various chapters.

3.4 References

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