CHAPTER - 5

INFLUENCE OF PH

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INFLUENCE OF pH OF THE MEDIUM ON THE ADSORPTION OF DYES ONTO OXIDES AND GRAPHITE SURFACES

5.1 Introduction

The pH of the medium has been found to play an important role in deciding not only the extent but sometimes even the actual nature of adsorption of a given system. It is therefore necessary to make the proper adjustment in the pH of a system to obtain the desired results. Studies employing dyes or ionic species as the adsorbates and various adsorbents of common use (e.g , metals, their oxides and hydroxides, clay, minerals etc.) indicate that the choice of the pH range for favourable adsorption depends on the adsorbate-adsorbent pair. Both acidic and basic media of pH range were found to be suitable for different adsorbate-adsorbent system With some systems large adsorption was seen in acidic medium while with some other systems basic medium was found suitable. Thus acidic medium favoured [1-4] the adsorption of chloride, sulphate, phosphate and similar other ions onto soil, ionic surfactant (like sodium dodecyl sulphate) onto alumina, and a number of paraffin chain anions on cotton and wool. Similar results have also been observed using dyestuffs as the adsorbates. Thus large adsorption has been seen in acidic medium with the adsorption of Acid Green Anthraquinone onto the surface of organo silica [5], crystal violet onto polymer [6], chrome dye onto activated carbon [7] and fly ash [8]. An enhanced adsorption [9-11] has also been found at lower pH with the adsorption of thymol blue onto active carbon, congo red onto clay and kaolin and acidic dye from HCl solution onto silk fibre. On the otherhand, in many cases especially with cationic types of adsorbate, basic medium was found to be favourable for large adsorption. Examples of such results are the adsorption of bromcresol green and bromthymol blue onto polymer [5], synthetic basic dyes onto activated sludge [12], adsorption [13-15] of calcium, magnesium, strontium and barium ions onto alumina, ions of copper, cobalt and nickel onto antimony oxide and several heavy cations (dodecyltrimethylammonium and cetyltrimethylammonium ions) onto silica. An increase in adsorption with pH has been observed in the adsorption of Acid Red 114 and Reactive Blue 4 onto silica-magnesia mixed gel [16] as well as in the adsorption [17,18] of basic dyes (e.g., methylene blue, crystal violet, malachite green and rhodamine B) on iron oxide and silica.

In some cases the adsorption was found to be maximum at a certain pH value. Such results have been observed with the adsorption of congo red onto wollastonite [19], Acid Red 114 onto silica-magnesia and alumina-magnesia mixed oxide gel [20], adsorption [1, 21-23] of phosphate ions onto alumina and polyethelene, sulphate ions onto alumina and astrazone blue BG onto polyesters.

Results showing two maxima [1,24] as well as no marked variation in the amount adsorbed over an appreciable pH range are also known. It has been reported [25] that there is no such change in the amount adsorbed in the adsorption of acid dyes onto polymers as a result of variation in the pH of the solution. The amount adsorbed at a given pH is also affected by the presence of substances of ionic nature. Thus in the study with the phosphate ions, the addition of cations such as Ca^{2+}, La^{3+}, etc., was seen to increase the adsorption onto alumina and kaolinite at pH values greater than 4 whereas presence of anions such as succinate, poly-styrene sulphonate, decrease it in the pH range less than 6 [22].

It is evident from the above that the study of the pH variation has been restricted mostly to ascertain its influence on the total amount adsorbed and then to find out the optimum conditions for favourable adsorption. The corresponding influence on the rate of the adsorption process has however, been studied in a few limited cases. Thus Beckmann et al. [26] found that in dyeing of cotton with some reactive dyes, the rate of dyeing is higher at basic medium. In the present work, attention is made in order to understand the possible modification in the actual time of the uptake as a result of variation in the pH of the medium. In the present study results of the adsorption of cationic and anionic dyes used as adsorbates and oxides and graphite as adsorbents are reported with the variation of the pH of the medium.

5.2 Experimental

The procedure followed in the present study was the same as described earlier (Chapter 2) except for the use of dye solutions having different pH values. A known amount of the adsorbent was kept in contact with a fixed volume of dye solution of which the pH was pre-adjusted for a definite value. The necessary pH of the solution was obtained using hydrochloric acid and sodium hydroxide respectively for acidic and basic ranges of pH. The same method was adopted by Sasaki et al. [27] for the adjustment of pH of the solution of neucoccin anions. For the adjustment of pH of the solution, calculated volumes of the standard solutions of acid or alkali were used. These volumes were adjusted in such a way, which on addition to the measured quantity of the stock dye solution and subsequently diluting to a fixed volume, that were expected to give the required pH in the resulting dye solution. Before use in the adsorption experiments, the pH of the experimental solution was measured using a glass electrode with the help of an electronic digital pH meter. The sample solutions withdrawn at various intervals were used (in the same way as described in Chapter 2) for measuring the corresponding concentrations of the residual solutions ; values thus obtained were employed for the estimation of the amount adsorbed on the surface.

As the aim of the present experiments was to see the influence of pH on the time rate study of adsorption, the

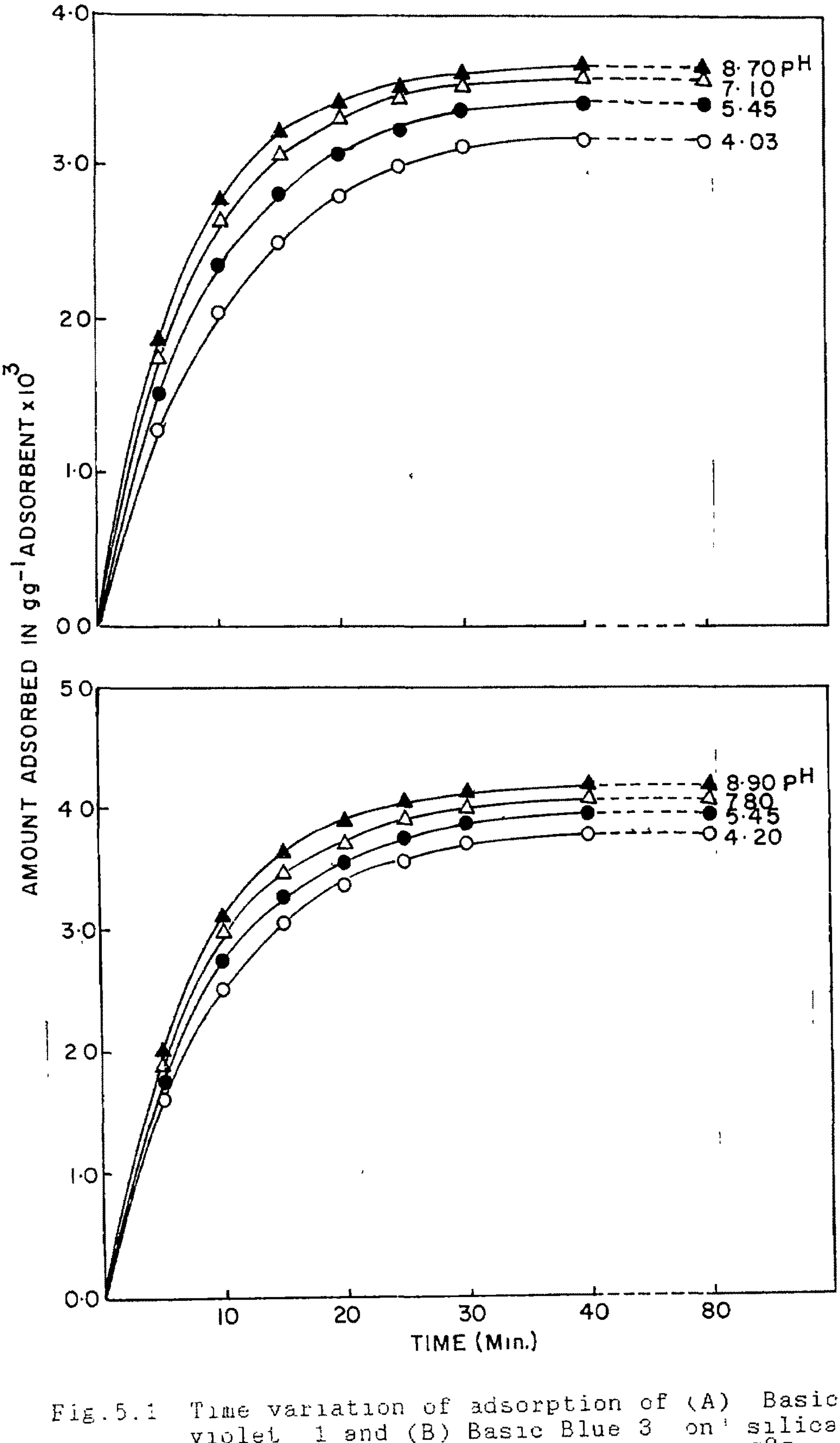

Fig.5.1 Time variation of adsorption of (A) Basic violet 1 and (B) Basic Blue 3 on silica gel with pH of the dye solution at 30°C.

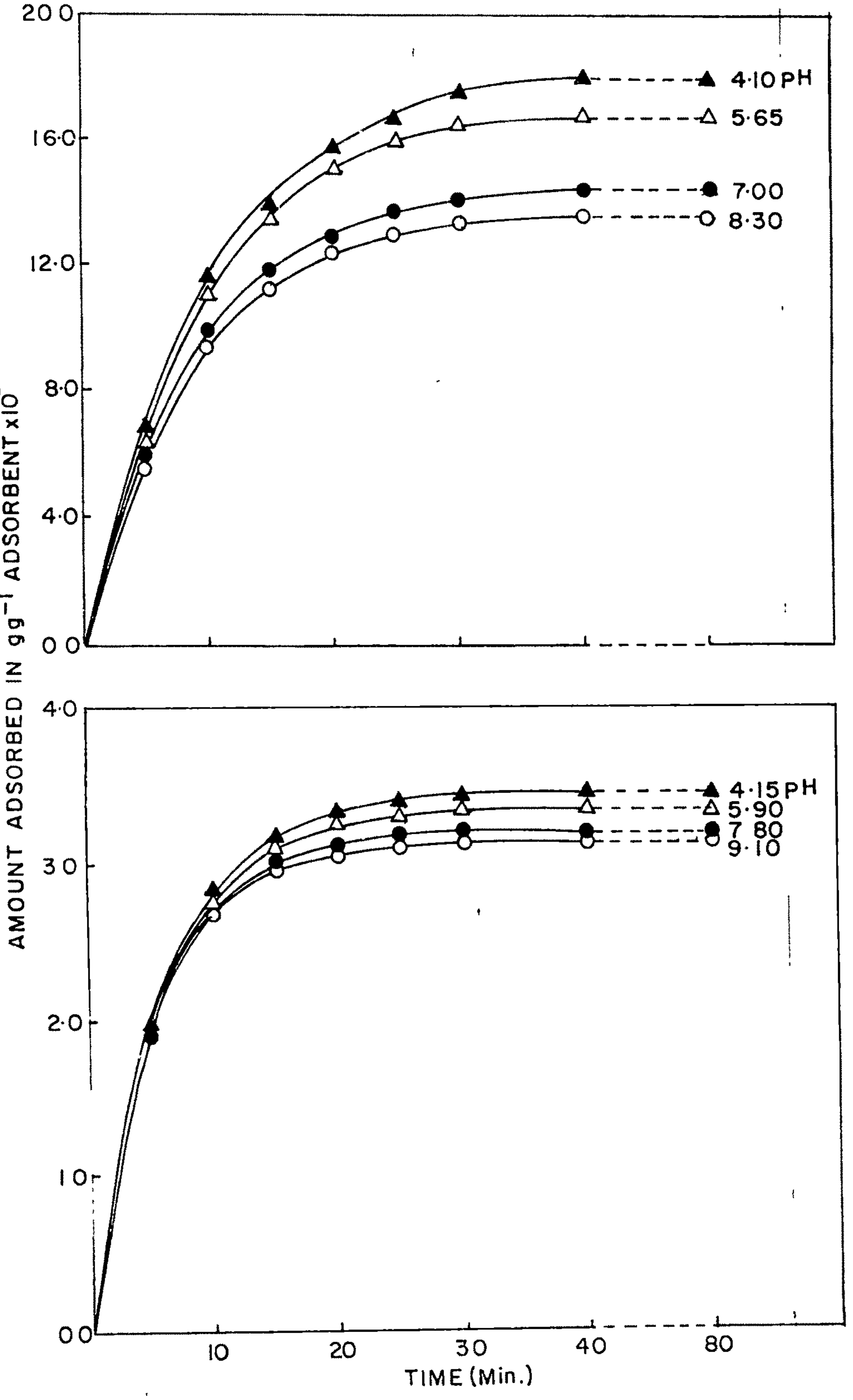

Fig 5 2 Time variation of adsorption of (A) Acid Black 1 and (B) Ketone Blue A on neutral alumina with pH of the dye solution at 30°C

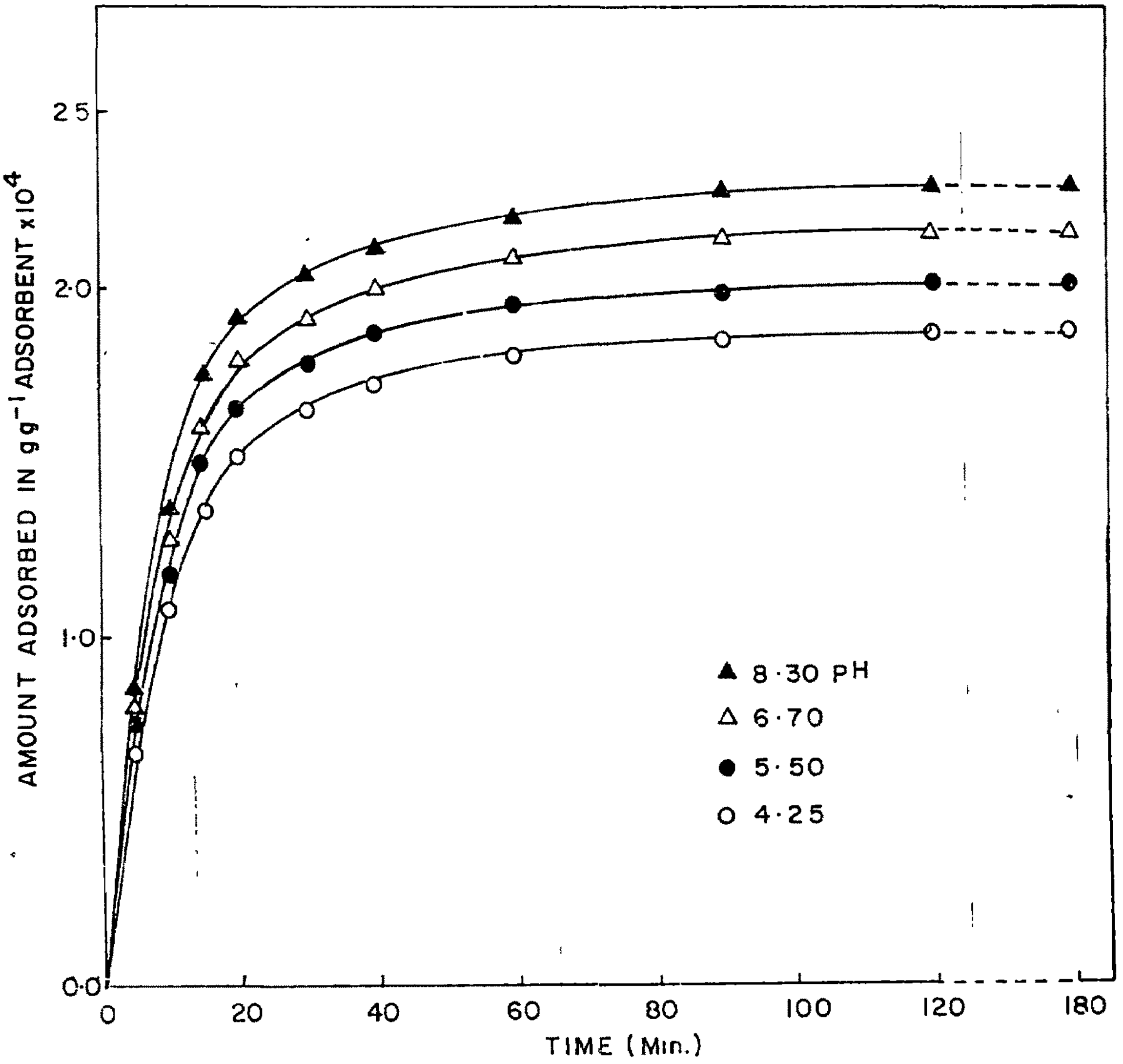

Fig 5 3 Time variation of adsorption of (A) Basic Blue 3 onto graphite with pH of the solution at 30°C.

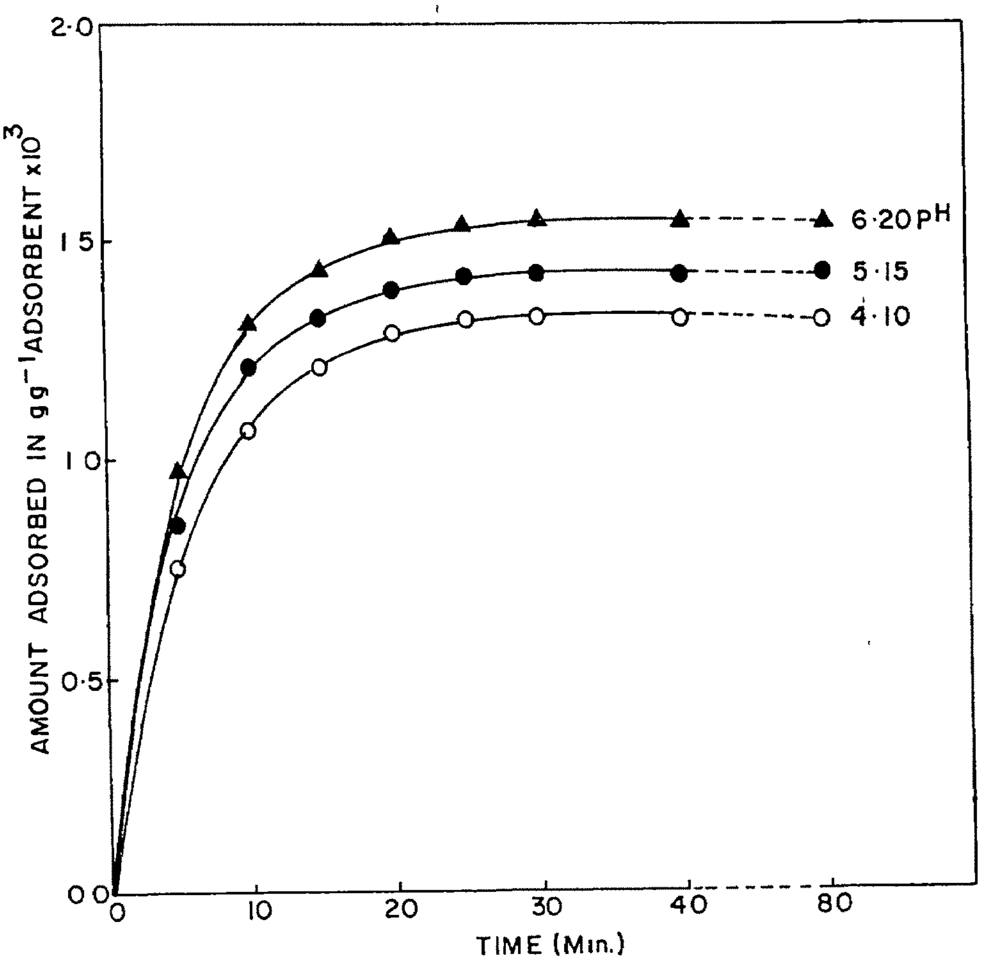

Fig.5 4 Time variation of adsorption of (A) Basic Brown 4 onto basic alumina with pH of the dye solution at 30°C.

entire series of experiments with a given system were carried out with the dye solution having the same concentration but of different pH values. Use of very high and very low pH values were avoided because of possible changes in the colour appearance of the dye under these extreme conditions [28-30]. Therefore for the present study the selection of pH values were restricted within a conveniently small range of 4 to 9. However, the selection of pH values was restricted within the range 4 to 6 for Basic Brown 4, Basic Violet 2, Basic Green 1 because these dyes were found to partially decolourise in the alkaline range.

The time variation curves for some systems are shown graphically for each of the pH values in Figures 5.1-5.4. The results for the total amount of dye adsorbed at equilibrium at different pH are given in Table 5.1 for the sake of brevity, the corresponding values for intermediate stages are not given. The values for the specific reaction rate, calculated from the plots of-log (1-f) Vs time are also given in Table 5.1 ; being similar in nature the plots are not given in this chapter.

5.3 Results and discussion

It is evident from the curves (Figures 5.1 to 5.4) that the general nature of the time variation of removal of dye from the aqueous solution does not show any alteration due to change in the pH of dye solution. The actual amount of dye

Table 5.1 ADSORPTION OF DYES ONTO OXIDES AND GRAPHITE SURFACES AT DIFFERENT pH OF THE SOLUTION AT 30^{o}C.

1 System	2 Initial dye concentration. $(M)\times10^{5}$	3 pH of the solution	4 Amount adsorbed in $g g^{-1}$ adsorbent at equilibrium	5 Specific reaction rate $k(min^{-1})$
Silica-Basic Blue 3	2.0	4.20	3.80×10^{-3}	0.109
		5.45	3.93	0.122
		7.80	4.08	0.131
		8.90	4.15	0.141
Silica-Basic Violet 1	1.0	4.03	3.18×10^{-3}	0.101
		5.45	3.42	0.114
		7.10	3.59	0.134
		8.70	3.65	0.141
Silica-Basic Brown 4	5.0	4.55	5.08×10^{-3}	0.160
		5.40	5.25	0.174
		6.30	5.40	0.187
Silica-Basic Green 1	1.0	4.10	3.87×10^{-3}	0.112
		5.60	4.37	0.123
		7.10	4.25	0.128
		8.50	4.22	0.133
Basic alumina-Basic Brown 4	5.0	4.10	1.31×10^{-3}	0.171
		5.15	1.42	0.186
		6.20	1.53	0.197
Basic alumina-Basic Violet 2	1.0	4.15	2.02×10^{-4}	0.061
		5.25	2.21	0.066

Table 5.1 continuation

1	2	3	4	5
Graphite Acid Green 25	0.5	4.15	2.12×10^{-4}	0.089
		5.55	1.87	0.099
		7.20	1.58	0.108
		8.25	1.47	0.115
Graphite-Ketone Blue A	1.0	4.04	2.29×10^{-4}	0.098
		5.95	1.98	0.103
		7.20	1.82	0.108
		8.60	1.62	0.113
Graphite-Basic Blue 3	1.0	4.25	1.88×10^{-4}	0.083
		5.50	2.02	0.086
		6.70	2.17	0.089
		8.30	2.30	0.093
Graphite-Basic Green 1	1.0	4.05	2.80×10^{-4}	0.089
		5.15	3.12	0.097
		6.25	3.43	0.105
		7.40	3.69	0.115
Neutral alumina-Acid Green 25	1.0	4.30	0.93×10^{-3}	0.495
		5.85	0.73	0.585
		7.30	0.43	0.672
		8.45	0.25	0.774
Neutral alumina-Acid Black 1	3.0	4.10	18.00×10^{-3}	0.098
		5.65	16.84	0.106
		7.00	14.45	0.115
		8.30	13.54	0.120
Neutral alumina-Ketone Blue A	2.0	4.15	3.46×10^{-3}	0.166
		5.90	3.36	0.174
		7.80	3.21	0.183
		9.10	3.15	0.190

adsorbed due to change in the pH of the solution is however seen to be affected both at intermediate as well as at the saturation stage of adsorption. The amount adsorbed as well as the rate was found to be dependent on the nature of both the adsorbent and the adsorbate. A medium of higher pH value is found to be favourable for large adsorption for cationic dyes. Thus the extent of adsorption of Basic Blue 3 adsorbed (from 2.0×10^{-5} M solution) by silica gel is found to increase from 3.80×10^{-3} to 4.15×10^{-3} gg^{-1} when the pH of the solution is raised from 4.2 to 8.9. Results with the other systems also indicate the similar nature of variation with pH. Thus the amount of Basic Green 1 adsorbed from 1.0×10^{-5} M solution onto graphite are 2.80×10^{-4} gg^{-1} and 3.69×10^{-4} gg^{-1} respectively at pH values of 4.05 and 7.40. Similar results have also been reported by several workers [16-18,31-33] with the adsorption of cationic dyes on solid adsorbents. On the otherhand, acidic medium is found suitable for a large adsorption for anionic dyes. Thus the adsorption of Acid Green 25 (from 1.0×10^{-5} M solution) by neutral alumina is found to increase from 0.25×10^{-3} to 0.93×10^{-3} gg^{-1} respectively as the pH of the dye solution decreased from 8.45 to 4.30. The other systems comprising of anionic dyes also show the similar pattern. The similar is the findings of Gupta et al.[34] with the adsorption of chrome dye onto mixed adsorbent (fly ash and coal). An enhanced adsorption of anionic dyes or other anionic species at lower pH has also been reported by various workers onto common solid adsorbents [16,27,35,36].

With all the systems employed in the present work, the rate of adsorption of uptake of dye is found to increase with pH of the medium. This is evident from the corresponding specific reaction rate, k values given in Table 5.1. Thus with the adsorption of Basic Brown 4 onto silica the rate increased from 0.109 to 0.141 $min.^{-1}$ when the pH of the solution is raised from 4.2 to 8.9. The increase is from 0.190 to 0.212 with the adsorption of Basic Brown 4 onto basic alumina. Similar is the result with the other systems. An enhancement in the rate of adsorption of methylene blue on silica has been observed by Ram and Prasad [18] and also by Singh et al.[31] with the adsorption of crystal violet onto alumina. On the otherhand Kwun [37] found, in the use of Korean and Japanese acid clays that the rate of adsorption of basic dyes increases as the acidity of the clay increases.

It is reported that the adsorption of inorganic ions on oxides is, in general, controlled by the electrical double layer at the oxide-water interface. In the case of oxides, it is well established that hydrogen and hydroxyl ions are responsible for the charge on the surface of the solid and that through adjustment of the pH, the magnitude and even the sign of the surface charge can be changed. The pH at which the surface charge is reversed is termed the point of zero charge [38]. The adsorption of dyes or ionic species on the solid surfaces is influenced markedly by the presence of electrical charges on or in the near vicinity of the surface. This may arise due to the dissociation of the surface product (if any) or due to the pre-adsorption of ionic substances. Any modification in this surface charges results in exhibiting marked variation in the actual adsorption. The phenomenon is considered in terms of the zeta potential and the corresponding alteration due to the variation in the pH of the medium. Most adsorbents are heterogeneous in the surface chemical sense in that they contain a wide range of high to low energy sites, both polar and non polar, as well as impurity atoms and adsorbed materials, e.g., moisture and organic contaminants arising from exposure to the environment. In the use of such adsorbents of which surface nature is prone to considerable changes when in contact with hydrogen or hydroxyl ions, the pH of the medium becomes the deciding factor. In the present work the adsorbents are inorganic oxides and graphite, and the adsorbates are the cationic as well as the anionic dyes. The possible modification of the surface nature and consequently the extent of adsorption due to variation in the pH of the medium are considered for each of the adsorbents employed in the present study separately.

Silica

It is evident from the IR study that the silica contains the surface hydroxyl groups [39-42]. Spectroscopic studies of amorphous silica show the presence of both free and hydrogen-bonded surface hydroxyl groups [43]. These surface hydroxyl groups are responsible for its important surface properties (Chapter-3). The consideration of the dissociation [14] of these groups yielding thereby SiO^- and H^+ is helpful in understanding the extent of availability of the surface charge and its dependence on the pH of the medium, a variation in the adsorption of ionic species is thus anticipated.

Silica being slightly soluble in water, forms silicic acid when in contact with water [44]. Results of various electrical measurements with quartz in contact with water have been interpreted in terms of the dissociation of the surface silicic acid [44,45]; a modification in the resulting surface charge due to additionally present H^+ or OH^- (arises from pH adjustment) ions is thus evident. At low values of pH (2-3.7) quartz surface remains positively charged whereas at high values it becomes negatively charged. This may well be understood from the explanation given by Onada and Fuerstenau [46].

$$\underset{\text{positive surface}}{SiOH_2^+} \rightleftharpoons \underset{\text{neutrol}}{SiOH} \rightleftharpoons \underset{\text{negative}}{SiO^- + H^+}$$

From the above discussion it is clear that in high acidic medium the surface should oppose the adsorption of cationic dyes whereas it represents a favourable situation in alkaline medium. It is evident from the Table 5.1 that the results are in agreement with the above views.

Graphite

It is observed from the results that both types of the dyes (i.e. cationic and anionic) get adsorbed on the surface of graphite. On the basis of the adsorption of both types of dyes on bone char Giles and coworkers [30] suggested the absence of any ionizable group on the surface of bone char and also possibly on graphite. It has also been reported that adsorption takes place due to dispersion forces rather than ion exchange [30]. Various other important results however, indicate the presence of negative charge on the surface of graphite or charcoal [47-49] when in contact with water. This negative charge arises either due to the adsorption of OH^- ions of water and/or due to the dissociation of the pre-existing oxygen surface complexes [50]. The presence of surface oxygen groups on the surface of charcoal/carbon is also reported by various workers [51,52].

In a medium of low pH, the surface is surrounded by excess of H^+ ions and it is expected that the negative charge present on the surface of graphite would be neutralized by the protonation at the lower pH. As a result this situation may favour the large adsorption of anionic dyes. Similar view is also expressed by several other workers [7,18,51]. On the otherhand, at higher pH, the surface experienced a negative surrounding due to the presence of excess OH^- ions and this situation is obviously favourable for large adsorption of cationic dyes. Similar results have also described by Abram [53] with the adsorption of methylene blue onto carbon where the maximum uptake was observed at the pH value of 10. From the present discussion it is evident that at low pH adsorption is favoured for anionic dyes whereas for cationic dyes a higher pH preferred the large adsorption. The results obtained with both cationic and anionic dyes by graphite (Table 5.1) are in accord with the above view.

Alumina

Alumina is an amphoteric oxide. Depending on the nature of the surrounding it exhibits acidic or basic character. In a medium containing excess hydrogen ions, the positive charge [49] on the surface will increase whereas reverse is true for the basic medium. Alumina normally contains varying amount of water molecules, especially all of which either exist as surface hydroxyl groups or adsorbed water [54]. In water these OH^- ions are released from the surface [55] and the cationic centres remaining on the surface would be source of attraction for anionic dyes. This type of positively charged surface would favour the adsorption of anionic dyes. The improved adsorption at lower pH may be explained on the assumption that as the surface comes in contact with water it is surrounded by hydroxyl groups. On increasing the concentration of the hydrogen ion in the dye solution, the surface OH^- ions would get neutralized by protonation which facilitates the diffusion of dye molecules in vicinity of the adsorbent. On the other hand, a diminished adsorption at higher pH may be due to the abundance of OH^- ions and consequently ionic repulsion between the negatively charged surface and the anionic dye molecules. Similar is the view expressed by Kapoor et al. [35] regarding the surface properties of guargum derivatives due to variation of pH of the medium. Thus the results (Table 5.1) obtained with the adsorption of anionic dyes onto neutral alumina are in agreement with the above view.

Again at higher pH the dissociation of OH^- ions will decrease, as a result the negative charge on the surface will increase due to presence of excess OH^- ions. Obviously this type of situation is suitable for large adsorption of cationic species. In actual experiment it is found that the adsorption of cationic dyes by basic alumina is favoured at higher pH of the dye solution.

5.4 References

1. H.Gebhardt and N.T.Coleman, Soil Sci. Soc. Am.Proc., 38 255 (1974).
2. H.C.Evans, J.Colloid Sci., 13, 537 (1958).
3. D.W.Fuerstenau, in "The Chemistry of Biosurfaces", (M.L.Hair ed.), vol.I, Marcel Dekker, New York, 143 (1971).
4. J.S.Stanley, J.Phys. Chem., 58, 533 (1954).

5. I.I. Denisova, S.I. Meleshevich and V.N. Mishchenko, Zh.Prikl.Khim (Leningrad), 57,2548 (1984); C.A., 102,33081e.

6. V.V.Podlesnyuk and T.M.Levchenko, Khim. Tekhnol. Vody, 7, 3 (1985);C.A.,103, 7721q.

7. G.S.Gupta, G.Prasad and V.N.Singh, Res. and Ind., 33, 132 (1988).

8. G.S.Gupta, G.Prasad, K.K.Panday and V.N.Singh, Water, Air, and Soil Pollution, 37, 13 (1988).

9. K.S.Han, Y.B.Kim and H.K.Park, Soul Taehakkyo Nonmunjip,Chayon Kwahak, Saengnongge, 22, 41 (1972); C.A., 77,66520r.

10. K.S.G. Doss and A.Singh, J.Sc. Ind. Res. (India), 12B, 79 (1953).

11. G.Aida and M. Mitsuishi, Nippon Sanshigaku Zasshi, 25, 454 (1956); C.A., 51,18615d.

12. M. Nakaoka, S. Tamura, Y. Maeda and T.Azumi, Sen'i Gakkaishi, 39, T69 (1983); C.A., 98, 113101a.

13. V.M.Balantseva, G.G.Zhuiko and R.K. Drachavskaya, Mendelecvsk S'ezd Obshch Prikl. Khim., 11th (1974); C.A., 85,131106s.

14. B.H.Bijsterbosch, J.Colloid Interface Sci., 47, 186 (1974).

15. C.P.Haung, W.Stumm, J.Colloid Interface Sci., 43, 409 (1973).

16. S.Kaneko, H.Saitoh, Y.Maejima and M.Nakamura, Analytical Letters, 22, 1631 (1989).

17. R.N.Ram and B.B.Prasad, Proc. Indian Natl.Sci. Acad., 48, 92 (1982).

18. R.N.Ram and B.B.Prasad, Indian J. Chem., 24A, 24 (1985).

19. V.N. Singh, G.Mishra and K.K.Panday, Indian J. Technol., 22, 70 (1984).

20. M.Nakamura, Y.Maejima, H.Saitoh, S.Yamagiwa and S.Kaneko, Mizu Shori Gijutsu, 31, 81 (1990); C.A., 112, 224095d.

21. P.S.M. Tripathi, R. Tripathi and B.B.Prasad, Proc. Indian Natl. Sci. Acad., 41A, 156 (1975).

22. Y.R.Chen, J.Butler and W.Stumm, J.Colloid Interface. Sci., 43, 421 (1973).

23. V.Rossbach, H.Mueller and D.Nessen, Textilveredlung, 9, 339 (1974); C.A.,83, 61344a.

24. P. G. Johansen and A. S. Buchanan, Aust. J. Chem., 10, 392 & 398 (1957).

25. K.M.Chen and P.Y.Wang, Hsin Hsien Wei, 24, 3 (1982); C.A., 98, 199700e.

26. W.Beckmann, D.Hilderbrand, J.Soc.Dyers Colourists, 81,11 (1965).

27. T.Sasaki, O.Asakawa, K.Kurosawa, M.Mizushima and T.Nakazono, Bull. Chem. Soc.Jpn., 53, 1867 (1980).

28. I.L.Finar, "Organic Chemistry vol.1, 6th Ed.", ELBS and Longman group Ltd., 888 (1973).

29. C.H.Giles, in "Adsorption from Solution at the Solid/Liquid Interface", (G.D.Parfitt and C.H.Rochester ed.), Academic Press Inc. (London), 360 (1983).

30. C.H.Giles and A.P.D'Silva, Trans. Faraday Soc., 65, 2516 (1969).

31. R.Singh, J.R.P.Gupta and B.B.Prasad, Proc. Indian Natl. Sci.Acad., 41A, 163 (1975).

32. C.K.Lee and K.S.Low, Pertanika,10, 327 (1987); C.A., 109, 11167e.

33. R.Y.Sid'ko, B.K.Kerzhner and V.V.Goncharuk, Khim. Tekhnol.Vody 11, 902 (1989); C.A., 113, 28702f.

34. G.S.Gupta, G.Prasad and V.N.Singh, Water Res.,24, 45 (1990).

35. R.C.Kapoor, A. Prakash and S.L.Kalani, J.Indian Chem. Soc., 61, 600 (1984).

36. G.S.Gupta, G.Prasad and V.N.Singh, J.Environ. Sci.Health, A23, 205 (1988).

37. O.C.Kwun, Daehan Kwahak Hwoejee, 9, 179 (1965); C.A., 65, 3041h.

38. D.W.Fuerstenau and K.Osseo-Asare,J.Colloid Interface Sci., 118, 524 (1987).

39. C.H.Rochester and D.A. Trebilco, J.Chem. Soc. Faraday Trans.1, 75, 2211 (1979).

40. C.H.Rochester, Adv. Colloid Interface Sci., 12, 43 (1980).

41. S.N.W.Cross and C.H.Rochester, J.Chem. Soc. Faraday Trans. 1, 74, 2130 (1978).

42. S.N.W.Cross and C.H.Rochester, J.Chem. Soc. Faraday Trans. 1, 75, 2865 (1979).

43. L.R.Snyder, "Principles of Adsorption Chromatography", Marcel Dekker Inc. New York, 158 (1968).

44. S.A.Greenberg, J.Phys. Chem., 60, 325 (1956).

45. B.J.Hathaway and C.E.Lewis, J. Chem. Soc. Sect A, 1176 (1969).

46. G.Y.Onada and D.W. Fuerstenau, Proc. of 7th International Mineral Processing Congress, New York, 301 (1964).

47. J.W.Galbraith, C.H.Giles, A.G.Halliday, A.S.A.Hassan, D.S.McAlliste, N.Macaulay and N.W.MacMillan, J. Appl. Chem., 8, 416 (1958).

48. W.J.Weber, Jr., Physicochemical Processes for Water Quality Control, Weley Interscience, New York, 61 (1972).

49. C.H.Giles, in "Adsorption from Solution at the Solid/Liquid Interface" (G.D.Parfitt and C.H.Rochester ed.), Academic Press Inc. (London), 359 (1983).

50. B.R.Puri, S.S.Bhardwaj and U.Gupta, J.Indian Chem. Soc., 53, 1095 (1976).

51. G.S.Gupta, G.Prasad and V.N.Singh, Env.Technol.Letters, 9,153 (1988).

52. L.R.Snyder, "Principles of Adsorption Chromatography", Marcel Dekker Inc. New York, 168 (1968).

53. J.C.Abram, Chem.Ind. (London), 43,1557 (1969).

54. L.R.Snyder, "Principles of Adsorption Chromatography", Marcel Dekker Inc. New York, 165 (1968).

55. C.H.Giles, In "Adsorption from Solution at the Solid/Liquid Interface", (G.D.Parfitt and C.H.Rochester ed.), Academic Press Inc. (London), 356 (1983).