

TIME-RATE STUDY OF ADSORPTION OF DYES ON IRON OXIDE

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This paper discusses the adsorption of dyes on iron oxide in respect of time rate. Some important dyes as adsorbates and iron oxide as adsorbent have been used to measure the time progress of adsorption. The study is also extended to measure the influence of the chief determinants of adsorption and the desorption of the surface adsorbed phase.

Keywords: Time-Rate; Adsorption; Dyes; Iron Oxide; Desorption; Adsorption Isotherm; Irradiation of the Adsorbent

INTRODUCTION

STUDY of dye adsorption, initiated quite recently with oxides and insoluble salts as the adsorbent, has been restricted mostly to the determination of adsorption isotherm, surface area of powders and other related properties (Allingham *et al.*, 1958; and Giles *et al.*, 1969*a, b*). Investigation into its time-growth has in general, been neglected probably because the adsorption in these cases is usually very fast and the entire process is completed within a short interval of time. In view of its importance especially from the standpoint of understanding the process, present work was planned to measure the time-progress of adsorption using some of the important dyes as the adsorbate and iron oxide as the adsorbent. The corresponding influence on it of the chief determinants of adsorption has also been studied. This study of time-rate has further been made for the desorption process of the surface adsorbed phase.

MATERIALS AND METHOD

The adsorbent was prepared from the precipitated ferric hydroxide (starting material being ferrous ammonium sulphate). The washed and dried hydroxide was heated at 800 °C for 14 hours; the resulting oxide was sieved for particles of 72-100 (BSS) mesh size. Prior to use in any experiment, the sample was activated at 300 °C for 4 hours and was then allowed a rest period of 24 hours.

The dyes employed were methylene blue, crystal violet and malachite green; stock solutions (1.0×10^{-3} M) of these were prepared in double distilled water; experimental solutions of the desired concentration were obtained by successive dilutions.

The procedure consisted essentially of keeping a weighed quantity of the adsorbent in contact with a measured volume of the dye solution. For a convenient

time-rate measurement, an amount of 4.0g of iron oxide was found suitable with 200ml of dilute dye solution (5.0×10^{-6} – 2.0×10^{-5} M). The adsorbent-adsorbate system was kept in a thermostated bath at 30 ± 0.1 °C and was shaken continuously using an electric device. At suitable time-intervals, shaking was arrested so that necessary withdrawals of the sample solution (~ 3 ml) could be made; these were used later for the determination of dye concentration remaining as residuals. For this, measurement of light-absorbance was made at the characteristic frequency using a Beckman spectrophotometer. Experiments were repeated with different dye concentrations also. The results are summarised in Table I; curves in Fig. 1 show the actual nature of the time-development of adsorption.

TABLE I
Adsorption of dyes on iron oxide (Temperature 30 ± 0.1 °C)

System	Initial concentration of the adsorbate solution (M)	Amount adsorbed in g/g adsorbent at equilibrium	$k(\text{min}^{-1})$
Iron oxidemethylene blue	7.5×10^{-6}	6.070×10^{-5}	0.145
	1.0×10^{-5}	7.300	0.140
Iron oxidecrystal violet	5.0×10^{-6}	4.365×10^{-5}	0.148
	1.0×10^{-5}	6.510	0.148
Iron oxidemelachite green	1.5×10^{-5}	2.755×10^{-5}	0.191
	2.0×10^{-5}	3.980	0.193

Influence of temperature and pH of the medium, on the rate of adsorption was studied in the next two series of experiments; the results obtained using temperatures, varied in the range 25–40 °C, are given in Table II and those obtained at different

TABLE II
Adsorption of dyes on iron oxide at different temperatures

System	Temperature (°C)	Amount adsorbed in g/g adsorbent	$k(\text{min}^{-1})$	Energy of activation (kcal mole ⁻¹)
Iron oxide-methylene blue	25	6.275×10^{-5}	0.142	1.8
	30	6.072	0.147	
	35	5.800	0.155	
	40	5.540	0.166	
Iron oxide-crystal violet	30	6.510×10^{-5}	0.145	3.8
	35	6.042	0.164	
	40	5.877	0.175	
Iron oxide-malachite green	30	2.755×10^{-5}	0.193	2.8
	35	2.508	0.208	
	40	2.295	0.228	

pH values (4.3–9.7) are given in Table III. The corresponding plots are shown in Figs. 2 and 3 respectively.

TABLE III

Adsorption of dyes on iron oxide: variation with pH of the medium (Temperature 30 ± 1 °C)

System	Initial concentration of the adsorbate solution (M)	pH	Amount adsorbed in g/g adsorbent	$k(\text{min}^{-1})$
Iron oxide-methylene blue	1.0×10^{-5}	4.3	6.690×10^{-5}	0.118
		5.3	6.690	0.118
		7.2	7.310	0.140
		8.6	8.630	0.168
		9.7	11.100	—
Iron oxide-crystal violet	1.0×10^{-5}	4.8	3.120×10^{-5}	0.094
		6.4	5.517	0.134
		7.1	6.550	0.148
Iron oxide-malachite green	1.5×10^{-5}	4.4	0.125×10^{-5}	—
		6.0	1.530	0.184
		7.1	2.701	0.190

In independent experiments, adsorption isotherms were determined at various temperatures and the results were utilised to calculate the isosteric heat of adsorption Table IV. In these experiments, 1.0g of iron oxide was used with 50ml of dye solution having different concentrations.

TABLE IV

Adsorption of dyes on iron oxide: isosteric heat of adsorption and coverage

Adsorbate	Amount adsorbed in g/g adsorbent	Isosteric heat of adsorption ΔH , (kcal mole ⁻¹)
Methylene blue	5.8×10^{-5}	5.1
	6.2	6.8
Crystal violet	2.0×10^{-5}	7.1
	2.4	7.5
Malachite green	1.8×10^{-5}	9.2
	2.0	8.8

The rate of desorption, i.e., removal of the surface adsorbed dye, was measured in a similar manner as that adopted for the direct process. For this experiment, use was made of specifically prepared dye-adsorbed sample containing enough of adsorbed material on its surface. A weighed amount (15.0g) of this was kept in contact

with 100ml of distilled water and the dye released was measured using test samples withdrawn at various time-intervals. The results for the rate of desorption at various temperatures (30 to 40 °C) are given in Table V.

TABLE V
Specific reaction rate and energy of activation for desorption

Temperature (°C)	Amount desorbed from adsorbed sample in g/g	$k(\text{min}^{-1})$	Energy of activation (kcal mole ⁻¹)
30	4.06×10^{-5}	0.097	7.3
35	4.183	0.121	
40	4.382	0.144	

The variation in the rate and the amount of adsorption, due to prior exposure of the adsorbent to a mixed flux of neutron and γ -rays, was also studied. The results for such irradiation for durations of 24–168 hours are given in Table VI and shown graphically in Fig. 5.

TABLE VI
Adsorption of dyes on iron oxide : influence of irradiation of the adsorbent (Temperature 30 ± 1 °C)

Adsorbate (Initial concentration)	Time of irradiation (hours)	Amount adsorbed in g/g adsorbent	$k(\text{min}^{-1})$
Methylene blue (1.0×10^{-5} M)	0	7.420×10^{-5}	0.159
	24	7.130	0.147
	48	6.882	0.112
	72	6.880	0.112
	96	6.880	0.112
	∴	∴	∴
	168	6.880	0.112
Crystal violet (1.0×10^{-5} M)	0	6.650×10^{-5}	0.148
	24	3.592	0.112
	48	3.395	0.105
	72	2.800	0.087
	96	2.280	0.090
	120	1.920	0.088
	∴	∴	∴
	168	1.920	0.088

RESULTS AND DISCUSSION

Adsorption of dyes is found to be rapid in the beginning and a large fraction of the total adsorption is completed within a few minutes. Further, the amount adsorbed on the attainment of equilibrium depends on the choice of dye and its concentration.

Thus the amount of methylene blue adsorbed on one gram of iron oxide at 30 °C from 1.0×10^{-5} M solution is 7.300×10^{-5} g; the corresponding amount of crystal violet is 6.510×10^{-5} g. In the use of larger concentration, these amounts are found to be more both at equilibrium as well as at any of the intermediate stages (Fig. 1). Thus, e.g., the amount of malachite green adsorbed, increases from 2.755×10^{-5} to 3.980×10^{-5} g when the initial concentration of the adsorbate is increased from 1.5×10^{-5} to 2.0×10^{-5} M (Table I).

The time-variation curves (Fig. 1) are smooth throughout indicating thereby that the process is uniform and unattended by any secondary complication. Further, the process is found to be of first order as is evident from the straight line plots of $-\log(1-f)$ against time (where f represents the fraction of total dye adsorbed). The specific reaction rate ' k ' values obtained from these plots have been used in the present work to compare the influence of various factors on the rate of adsorption.

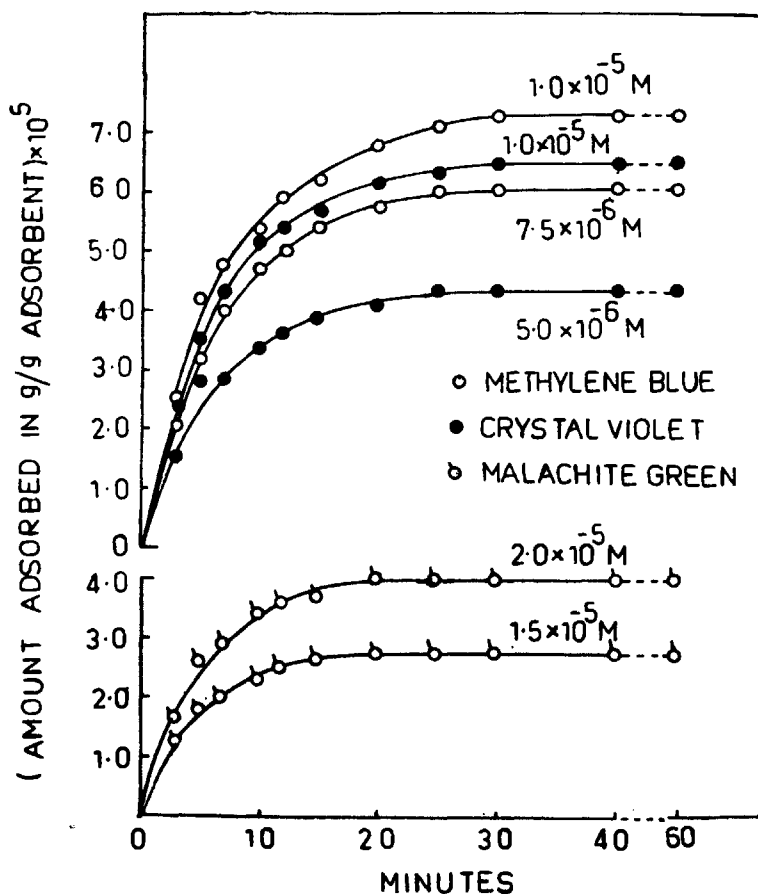


FIG. 1. Time-variation of adsorption of dyes on iron oxide.

Influence of Temperature and pH of the Medium

The general nature of time-variation of adsorption is found to remain sensibly unaltered due to changes in temperature and pH (Figs. 2 and 3). The amount actually adsorbed, however, shows marked variations; lower values of temperature and higher ones of pH are favourable for enhanced adsorption. Thus the amount of methylene blue adsorbed at 25 °C is 6.275×10^{-5} g and at 40 °C it is only 5.540×10^{-5} g. In a similar way, the values obtained at 30 °C with solutions of pH 4.3 and 8.6 are 6.690×10^{-5} g and 8.630×10^{-5} g respectively. The magnitude of the rate of adsorption increases uniformly with both the above variants. Thus k values at the above temperatures, are 0.142 and 0.166 min^{-1} and at the above pH values, are 0.118 and 0.168 min^{-1} respectively.

Energy of activation is low (1.8–3.8 kcal mole^{-1}) which is in agreement with the expectation for such fast processes. Entropy of activation (Laidler, 1965) is found to be negative and high (-63.15 to $-66.72 \text{ cal deg}^{-1} \text{ mole}^{-1}$) which suggests that the steric factor in the present process of adsorption is small suggestive (Griffin & Jurinak, 1974) of absence of any high specificity for adsorption of these dyes.

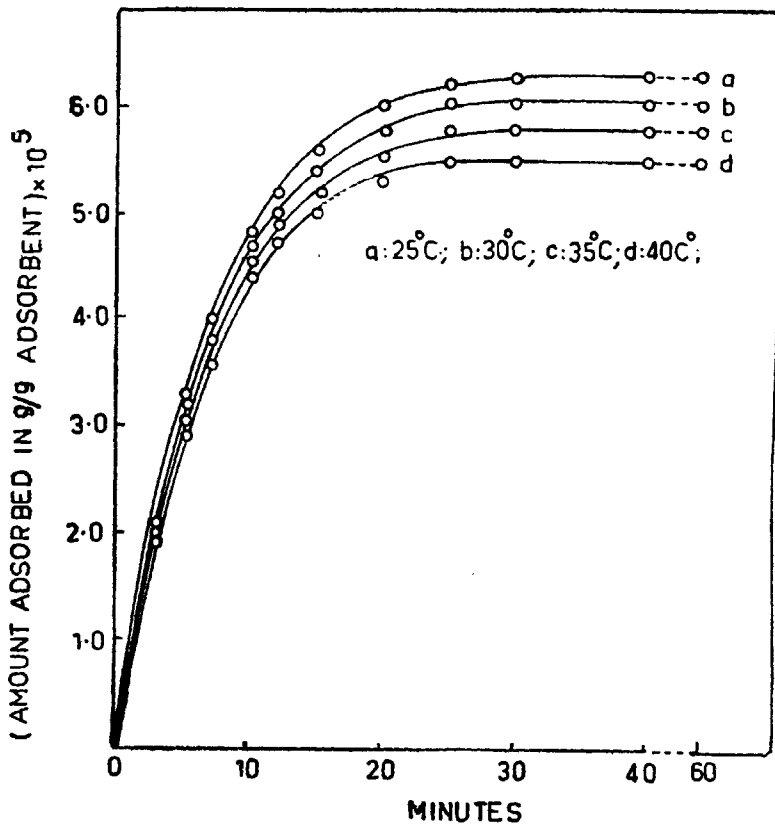


FIG. 2. Time-variation of adsorption of methylene blue on iron oxide at various temperatures.

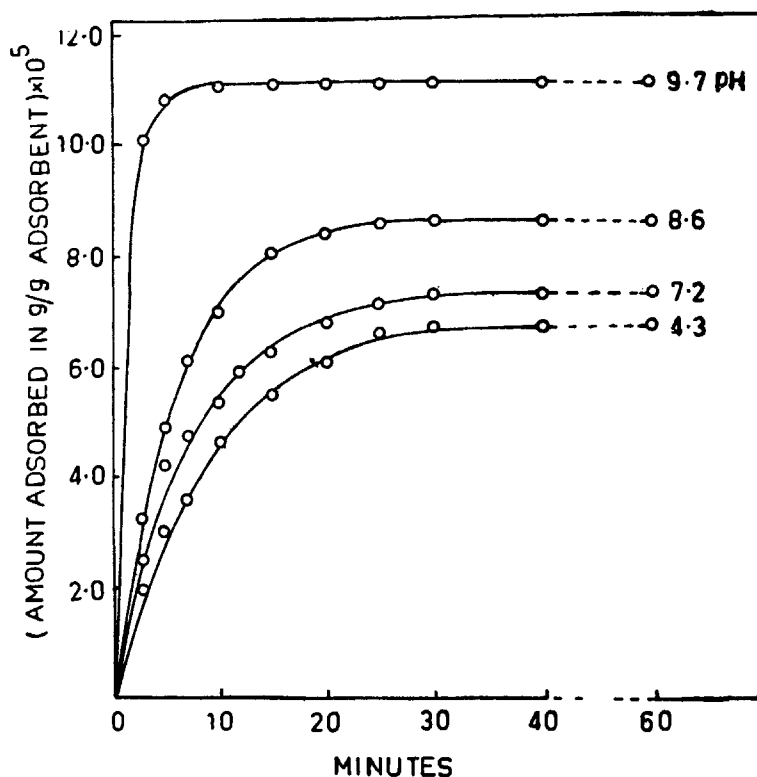


FIG. 3. Time-variation of adsorption of methylene blue on iron oxide: influence of pH.

Influence of Dye Concentration (Adsorption Isotherm)

Study with different concentrations of dye shows that adsorption increases rapidly with concentration in the beginning which slows down later indicating finally a tendency to approach saturation. The corresponding plots of logarithms of the amount adsorbed per gram against the logarithms of equilibrium concentrations are straight lines illustrative of the applicability of the Freundlich isotherm. The slopes are small varying between limits of 0 and 1 as is expected for such low concentration ranges as employed here. The isosteric heat of adsorption, determined (Koral *et al.*, 1958) for different amounts of dye adsorbed, shows its dependence on the extent of coverage (Table IV).

Desorption of Adsorbed Dye

The time-variation of release of the adsorbed dye is seen to be of a similar nature as that of the direct process of adsorption. A rise in temperature is helpful in removing more of the dye from the surface. Thus the amounts desorbed from the surface (containing initially a total of 1.929×10^{-4} g methylene blue per gram) are 4.063 , 4.183 and 4.382×10^{-5} g respectively at 30, 35 and 40 °C (Fig. 4). The rate of desorption 'k' also increases with temperature; corresponding value for the energy

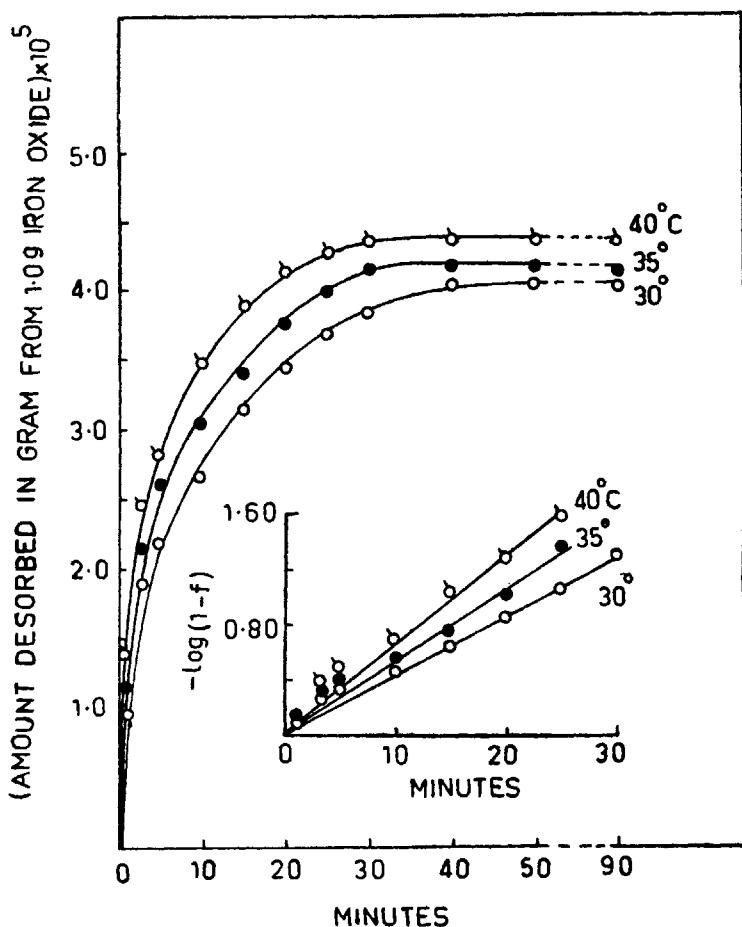


FIG. 4. Time-variation of desorption of methylene blue adsorbed on iron oxide.

of activation is $7.3 \text{ kcal mole}^{-1}$ (Table V). On comparison with that of the direct process ($1.8 \text{ kcal mole}^{-1}$) heat of adsorption is found to be $5.5 \text{ kcal mole}^{-1}$. Heat of adsorption thus obtained independently, from kinetic considerations, is of the same order as that of the isosteric heat value for average coverages (Table IV).

Influence of Irradiation of the Adsorbent with Mixed Flux of Neutron and γ -Rays

The general nature of the variation of time-uptake with the use of irradiated adsorbent samples is similar to that as observed with unirradiated ones. However, the amount actually adsorbed is found to decrease significantly; the rate is also seen to be affected similarly. The extent of this decrease depends on the duration of exposure to $n - \gamma$ source (Fig. 5). This result is contrary to the general expectation of enhancement in adsorption due to creation of newer active centres as a result of radiation effects. However, the factors like (i) decrease in surface area possibly due to the sintering of the adsorbent under irradiation (Gilmore & Newton, 1967) and

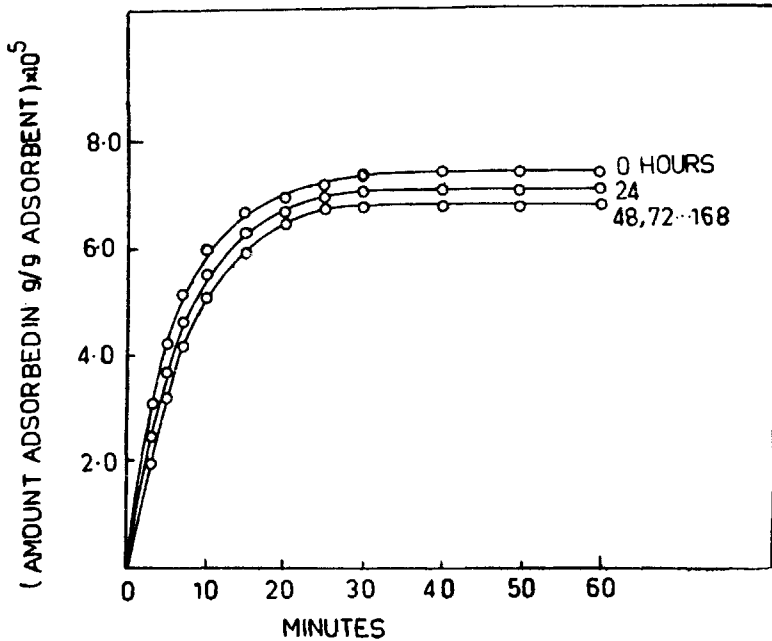
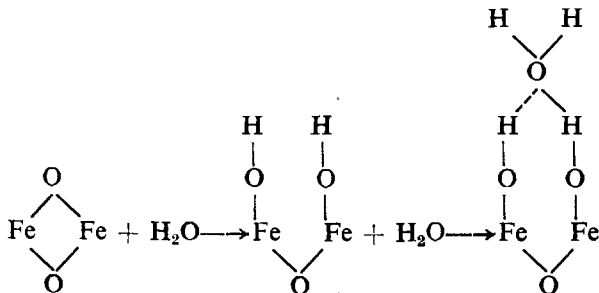


FIG. 5. Time-variation of adsorption of methylene blue on iron oxide: influence of n, γ irradiation.

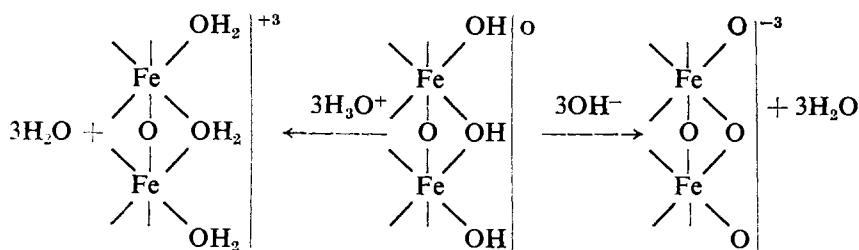
(ii) radiation annealing of the existing active sites (created during preparation and processing of the adsorbent) are also important. It appears that these factors are responsible for the observed decrease in adsorption.

In the adsorption of ionic species, nature of the electrical charge (actually available at the moment on the adsorbent surface) plays an important role in deciding not only the extent of adsorption but also its rate. The surface of iron oxide has been examined from the study of water adsorption, heat of immersion and I. R. spectroscopy (Blyholder & Richardson, 1962; and Ishikawa & Inouye, 1973). Breeuwsma (1973) (following the general lines of Morimoto *et al.*, 1969) considers the adsorption of water on hematite to proceed in the following way; a molecule of water first gets adsorbed on the surface and gives rise to two surface hydroxyl groups; subsequent adsorption takes place through hydrogen bonding as shown below:



The ferric ions remain thus buried under the surface and influence only indirectly. From I. R. studies, it has been concluded (Blyholder & Richardson, 1962) that these surface OH groups interact with the adsorbate molecules in various ways depending on the circumstance.

Such an interaction also with H⁺ or OH⁻ ions (as available additionally at low and high pH values) gives rise to a surface possessing positive or negative charge. Parks and Bruyn (1962) have discussed about the nature of the charge available at the surface due to adsorption of these ions or by dissociation of the surface sites. According to these workers, the scheme may be represented in the following way:



Breeuwsma and Lyklema (1973) have also concluded that the surface groups, possibly available on hematite surface, are —OH₂⁺, —OH and O⁻; the relative abundance is decided by the pH of the medium. At low pH values, preponderance of H⁺ ions makes the surface thus positively charged; this situation is unfavourable for the adsorption of substances which are cationic in nature (as the present dyes). Diminution of the acid concentration makes the availability of OH₂⁺ group gradually low and ultimately at and beyond a particular value, the surface proceeds towards a situation having only —OH and —O⁻ groups. The fact that iron oxide in contact with water, even under ordinary conditions, exhibits negatively charged surface, has been confirmed by Johansen and Buchanan (1957) from streaming potential measurements. Such a surface should, therefore, present an attractive atmosphere for faster and larger adsorption of cationic dyes. Increase in the rate and the amount of adsorption of the above dyes on raising the pH of the medium, as observed, is thus anticipated.

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