Adsorption from Aqueous Solutions of Dyes on Activated Silica gel

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Adsorption behaviour of aqueous solutions of acid red-4, acid green-25 and sulphorhodamine-B on activated silica gel in relation to shaking time and solution pH has been studied. It is observed that the dyes are chemisorbed on the surface of silica gel. The effect of pH has been explained in terms of protonation of the dyes.

Introduction

Dyes are extensively used for obtaining dye laser [1-5]. The degradation of the dyes occurs with continuous laser irradiation. The laser irradiated solution, however, is not completely depleted of the original dye which if recovered can be utilised again. This demands the study of the adsorption behaviour of the dyes on suitable adsorbent. Rauf and Zaman [6] have studied the adsorption of sulphorhodamine-B on activated charcoal and have reported the conditions under which the dye can be recovered from the adsorbent.

This paper reports the results of adsorption from aqueous solutions of acid red-4, acid green-25 and sulphorhodamine-B (commonly known as kiton red) on activated silica gel. The adsorption behaviour of the dyes by changing solution pH and the time of adsorption was also studied.

Results and Discusion

The absorbance of each of the dye solutions was measured at various wave lengths and values of λ_{max} were obtained (Fig. 1). A test experiment was performed in order to find out the time of maximum adsorption. Distribution coefficient, K_D, was determined [7] by varying the time of contact between the adsorbent (1g) and 50 cm^3 of dye solution (1×10^{-5} mol. dm^{-3}) at a shaking rate of 120 strockes/m and at a temperature of 298K. Activated silica gel possessed excellent adsorption ability and 95% colour removal from the dye solution resulted after shaking for 50 minutes which decreased on further shaking. The results are depicted in Fig (2). This may be due to the desorption of dyes from the adsorbent surface because of increased agitation. An optimum time of
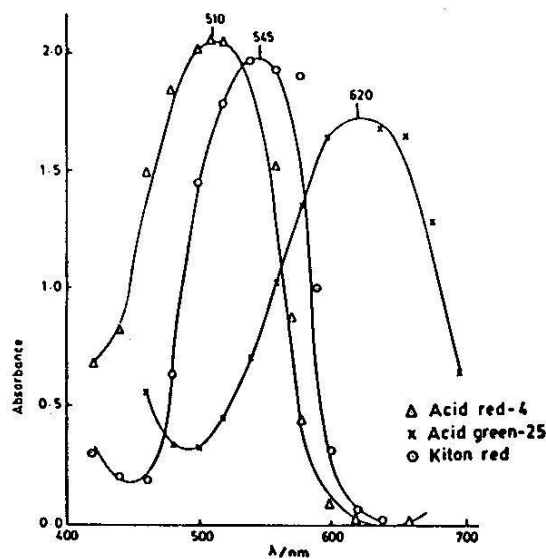

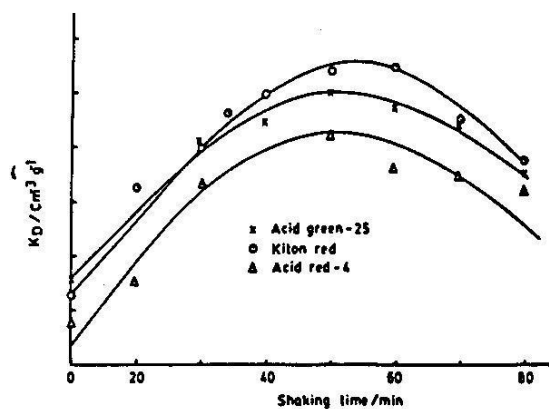Fig. 1: Plot of absorbance of dye solutions at various wave lenghts (λ).

Fig. 2: Plot of distribution coefficients, K_D, of dyes versus shaking time.

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50 minutes shaking was, therefore, chosen for all adsorption studies. The concentrations of both the adsorbent and the dye solutions were the same as mentioned above except otherwise stated.

Adsorption is often affected by pH changes of the solution [6,8]. The desorption of dyes takes place as the pH is increased; for kiton red the desorption is very fast by changing the pH on either side whereas for acid red and acid green the desorption takes place slowly. This is shown in Fig. 3. The adsorption behaviour of the dye solutions can be explained if we consider the surface of silica gel to have chemisorbed impurities in the form [9], and that the adsorbates whose structures are as follows; can be protonated by acceptance of H^+ from the solvent.
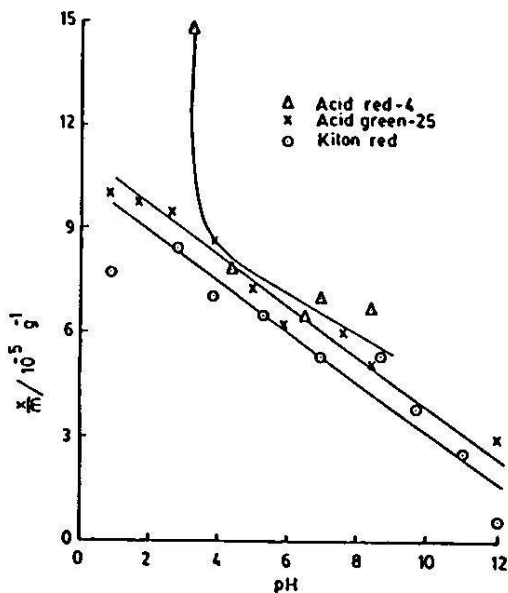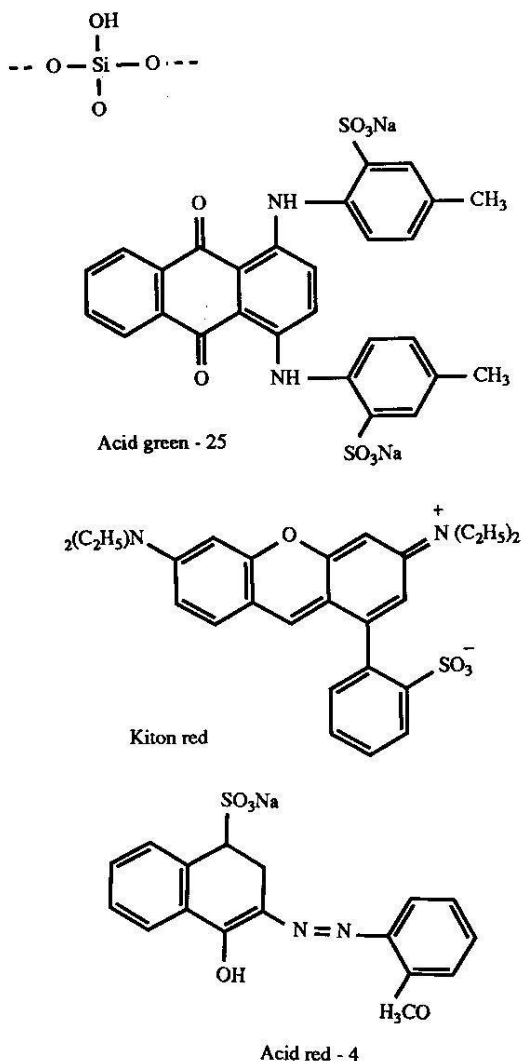

Fig. 3: Amounts of the dyes adsorbed at various pH of the solutions.

An equilibrium exists between the protonated and non-protonated dye in solution, e.g. Dye $+ H^+ \rightleftharpoons$ Dy......H^+ . At low pH, the equilibrium is expected to be shifted to the right (protonated form) because protons are to be found in excess in the solution. The protonated form is able to strongly interact with the hydroxyl groups at the surface of silica gel resulting into large adsorption.

At higher pH, however, the equilibrium is towards the left (non-protonated form) due to an excess of OH^- ions in the solution. Therefore, no cationic sites are available for bonding the polar groups of the adsorbent surface resulting in lower adsorption.

Adsorption isotherms were obtained at 293K for the dye solutions which are shown in Fig. 4. For acid green-25 and kiton red, the adsorption isotherms are of the 'L' type which indicated that these adsorbates have high affinity for silica gel. However, for acid red-4 the adsorption isotherm is of the 'S' type indicating weak adsorption of acid red on silica gel (physical adsorption).

Freundlich and Langmuir isotherms are obeyed by acid green-25 and kiton red whereas for acid red-4 these isotherms are obeyed only at low
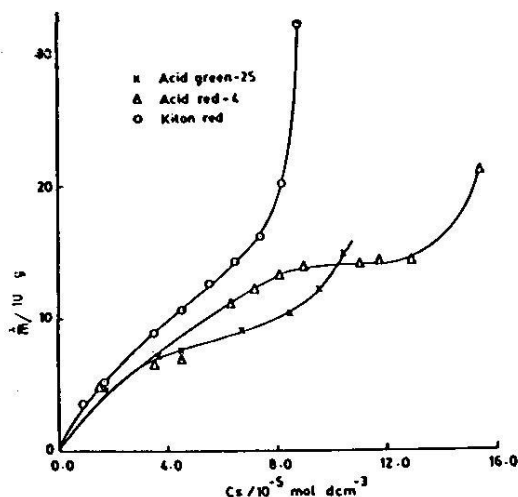
Fig. 4: Adsorption isotherms at 293K for dye solutions.

concentrations. Values of constants K and 1/n were calculated from Freundlich equation and of $1/K_1K$ and V_m (manolayer capacity) were computed from Langmuir equation. The values of these terms are given in Table (1).

Table 1: Adsorption parameters computed from Freundlich and Langmuir isotherm at 293K.

| Adsorbate | Langmuir | | Freundlich | |
	$1/K_1K/mol$ $dm^{-3}g^{-1}$	$V_m/$ cm^3g^{-1}	K	1/n
Kiton red	0.34	0.290	2.18×10^4	0.787
Acid Red-4	0.27	0.074	2.40×10^4	0.684
Acid Green -25	0.34	0.179	1.29×10^4	0.490

As discussed earlier, the dyes can be protonated resulting into cationic forms which can from stable bonding with the ⁻OH groups of the silica gel surface. For example.
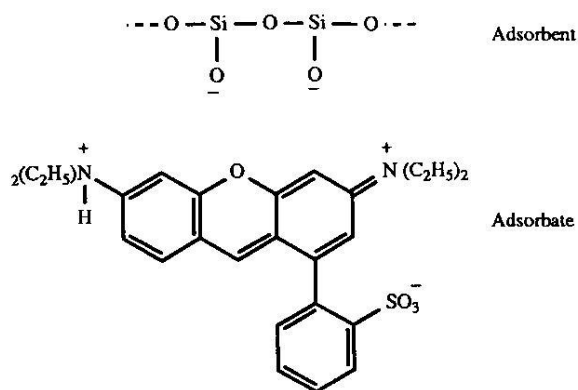
In acid green-25 and in kiton red, protonation results in two cationic centres. In acid red-4 one N can be protonated because repulsion between two adjascent positions -N = N- may result in a high energy configuration leading to unstability. Also, the hydroxyl group in the vicinity of -N = N____ group can also be involved in intramolecular hydrogen bonding and thus reduces the possibility of bonding of the dye with the silica gel surface [10]. For this reason, the V_m values of acid green-25 and of kiton red are higher and of acid red-4 the V_m value is small. Both the former adsorbates obey Langmuir isotherm showing that these dyes are chemisorbed on silica gel whereas acid red appear to be physically adsorbed.

Experimental

Sulphorhodamine-B, obtained from Exiton (USA) and acid red-4 and acid green-25, supplied by Janssen Chemica (Belgium), were high purity (laser grade) chemicals and were used as received. Silica gel (60-120 mesh) was supplied by BDH (Germany) and was activated before adsorption studies by heating at 473K for three hours. The total surface area of activated silica gel was determined, by Langmuir isotherm, to be 307 m^2g^{-1}

Stock solutions of dyes were prepared by dissolving weighed amounts in conductivity water and thereby necessary dilutions were made in the same solvent. Various pH solutions were obtained by addition of necessary amounts of either HCl or NH_4OH in dye solutions. The pH being monitored by a Horiba F-8 pH meter. Weighed amounts of activated silica gel in a test tube containing a dye solution was shaken in a Yamato BT-47 Water Bath Incubator at 298K. The solutions were filtered and the absorption spectra were recorded by a Shimadzu UV-120-01 spectrophotometer at the respective λ_{max} of each dye. The percentage adsorption and the distribution coefficients, K_D, were computed by the usual method [7].

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