Sorption of Congo Red on Cellulose

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Summary: The adsorption of Congo Red from aqueous solutions onto cellulose and cotton fibres has been carried out to investigate `Sorption'. Both substrates were given various treatments and the effect of such treatments was examined towards sorption. Two types of isotherms were observed namely, H- and S-type. A more specific form `HA' leading to `flatewise' adsorption on cotton was identified. The electrolytes strongly influence the sorption capacity of Congo Red on both fibres which is interpreted on the basis of Donnan Theory.

Introduction

The largest group of materials having similar dying properties consists of the textile fibres of vegetable origin. The most important class is cotton, but linen and the group of fibres comprising jute, hemp, straw and similar woody materials are also much used. The major chemical constituents of all vegetable fibres is cellulose. The purest form of cellulose is found in cotton. The cellulose is made up of very long chains of glucose residues linked together. A few studies on dying of cellulosic fibres with certain dyes have been carried out in the past. Ruggli [1] and Valko [2] have attempted a quantitative approach to describe adsorbability and desorbability of certain direct dyes on cellulose and cellulose derivatives. Hodgson [3] have studied adsorption of a series of direct dyes and have suggested that various benzene and naphthalene nuclei in a direct dye must be capable of laying in one plane. Robinson and Mills [4] have made quantitative studies on the adsorption of benzopurpurine B on cellulose. Crank [5] has shown adsorption of direct dyes on cellulose which follows the Langmuir type adsorption isotherm. Hanson, Neale and Stringfellow [6] have given theoretical approach of cellulose dying equilibria with direct dyes and have explained the effect of electrolyte on promoting adsorption. In our previous studies on dying process of a number of dyes on some inorganic materials, a series of articles have been published [7]. In the present investigations, Congo Red has been used for adsorption onto cellulose and cotton and the results have been interpreted in terms of mode of adsorption, monolayer capacity, maximum adsorption affinity and salt sensitivity on adsorption.

Results and Discussion

The adsorption behaviour of solute from solution have been recognized by Giles *et al.* [8]. According to their classification, four representative adsorption profiles, namely H-, L-, S- and C- type have been identified. The adsorption of Congo Red on cellulose follows H- and S-type adsorption behaviours. The H-type starts with a positive value on vertical axis followed by a plateau. The H-type is a representative of the monolayer adsorption isotherm where large ionic micelles of dye are formed on the surface. The S-type isotherm is initially convex to the solution concentration axis, then appears a plateau, followed by further increase in adsorption (in some cases another plateau may appear). The initial rise in adsorption depends upon the availability of active sites. The plateau in both isotherms indicates saturation of the surface. The H-type isotherm is the representative `flatewise' adsorption of the adsorbate. The specific HA-type (a typical H-type of isotherm with a very high affinity of solute for the solid) adsorption isotherm shows high affinity of solute towards the substrate, whereas S-type behaviour shows very slow adsorption. The plateau (Brunaur's point `B' or inflexion point) indicates completion of the monolayer and the adsorption at this point is of monolayer capacity. Further increase in adsorption reveals multilayer formation on top of the monolayer.

The S-type gives an 'edgewise' and 'end on' mode of adsorption, where at lower initial concentration of dye solution, the solvent is predominantly adsorbed and as the concentration of dye is increased, the adsorption of solute is significantly increased till monolayer is

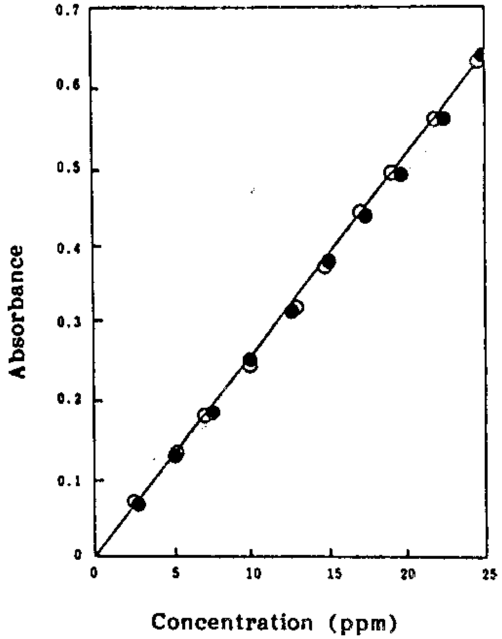

Fig. 1: Calibration curves for Congo Red from aqueous (●) and from caustic soda (⊙) solutions.

accomplished. It can be seen that S-type isotherms have been recognized over cellulose whereas H-type isotherms are the significant feature over cotton. The adsorption of Congo Red over cotton gives on H-type isotherm with a more specific 'HA' form indicating very rapid adsorption, where some of the dye may superfacially adsorb along with significant adsorption of dye into the bulk of the solid. The high uptake of dye may be attributed partially to the arrangement of the crystallites in the fibre where the dye molecules penetrate to the structure due to the greater pore size as compared with other cellulosic fibres [9].

The values of monolayer capacities, x/m (mono) and the maximum adsorption capacities, x/m (max) are shown in the Table-1. A few typical results are shown in Figures 2 and 3. It seems likely that electrolytes increase the adsorption affinity. However, addition of electrolyte in dye bath usually does not modify the mode of adsorption. The higher affinity of dye solution for fibres might be due to 'Sorption' (a combination of adsorption and absorption). The purest form of cellulose is found in cotton. Cellulose is made up of very long chain of glucose arranged parallel and the corresponding spacing of identical atoms along the chain is 10.3°A, and this spacing is probably an important factor for sorption of dye molecules. Furthermore, cotton gives a more diffuse pattern, which is attributed to the arrangement of crystallizes in a spiral manner along the fibre length. Figures 2 and 3 indicate increased adsorption produced by adding various salts to the dye bath. The earlier theory of Hanson *et al.* [6] made use of the Donnan Theory of membrane equilibrium to the differences in ionic concentration between the dye bath near the cellulose/water interface and the external solution. On the basis of this theory, the effect of electrolyte in promoting sorption could be threeflod. In the first place, it increases the activity of the dye in

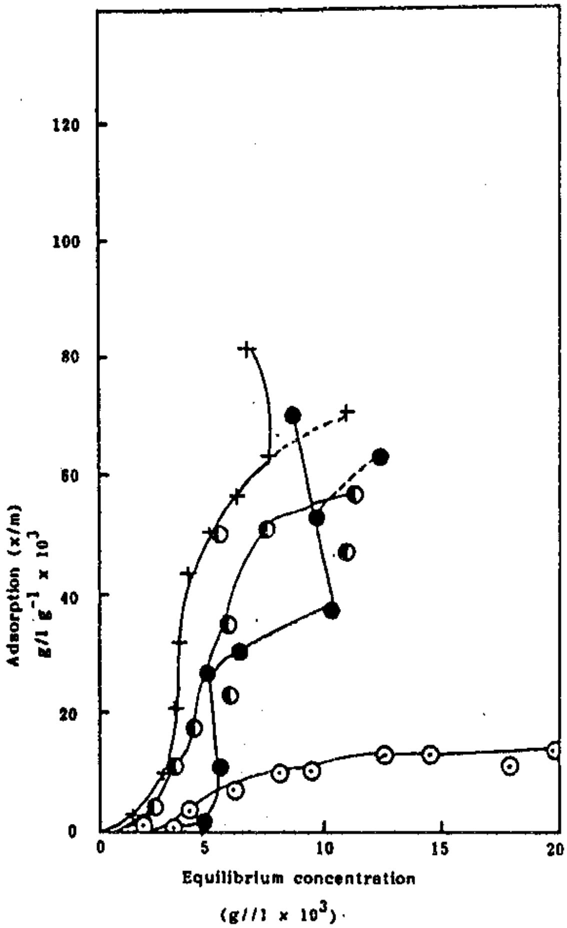

Fig. 2: Adsorption isotherms of Congo Red on cellulose from aqueous (⊖), sodium chloride (+), potassium chloride (●), and from ammonium chloride (◐) solution.

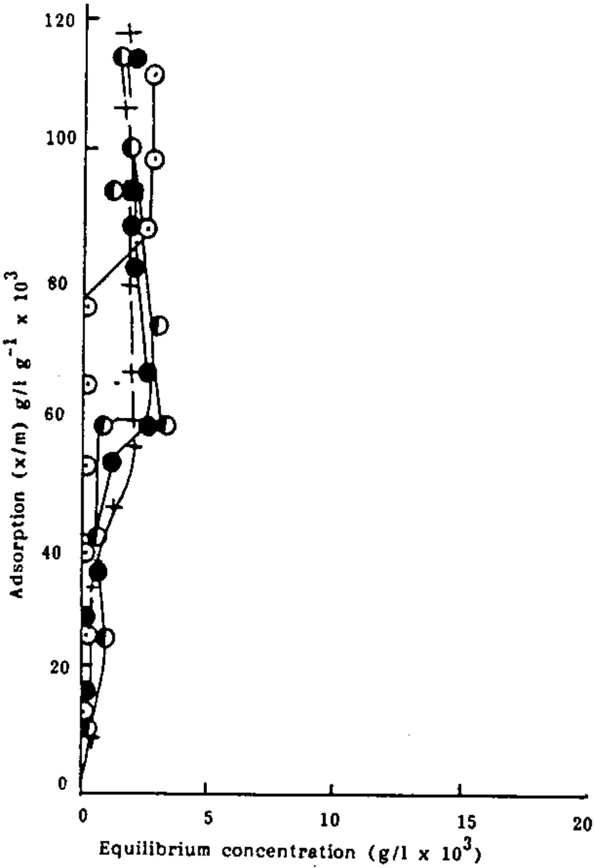

Fig. 3: Adsorption isotherms of congo red on cotton from aqueous sodium chloride (+), potassium chloride (-●-) and from ammonium chloride (○) solutions.

solution, secondly it increases the concentration of ions in solution and finally, the added electrolyte screens the electrical charge on the surface with the result that a dye ion can approach more closely to the surface. This causes reduction in activation energy of dye sorption. Furthermore, cellulose when swollen in an electrolyte (typically sodium chloride), it exposes large pore radius 20°A [10]. Nitrogen adsorption experiments on cellulose has also testified this theory [11]. This behaviour can be generalized that the expansion of pore size of cellulose/cotton is due to the added electrolytes which may cause increased adsorption (Table-1).

The greater increase in adsorption in the presence of electrolyte and the possibility of increasing adsorption by graded addition of salt are

Table-1: Mode of adsorption, monolayer capacities and maximum adsorption capacities of Congo Red from aqueous and from electrolytic solutions onto cellulose and cotton

Adsorbed	Mode of adsorption	x/m (mono) g/1g^{-1} x10^3	x/m (max) g/1g^{-1} x10^3
Cellulose	S	12.50	13.75
Cellulose + 5 ppm NaCl	S	42.50	44.00
Cellulose + 50 ppm NaCl	S	70.00	81.25
Cellulose + 5 ppm KCl	S	57.50	61.50
Cellulose + 50 ppm KCl	S	62.50	70.00
Cellulose + 5 ppm NH_4Cl	S	23.75	33.75
Cellulose + 50 ppm NH_4Cl	S	57.50	63.75
Cellulose + 5 ppm NaOH	S	28.75	61.25
Cellulose + 50 ppm NaOH	S	41.25	95.00
Cellulose + 5 ppm KOH	S	52.50	83.75
Cellulose + 50 ppm KOH	S	81.25	106.25
Cotton	H	75.00	111.25
Cotton + 5 ppm NaCl	H	77.00	110.00
Cotton + 50 ppm NaCl	H	98.75	116.25
Cotton + 5 ppm KCl	H	42.50	112.50
Cotton + 50 ppm KCl	H	62.50	118.50
Cotton + 5 ppm NH_4Cl	H	-	111.00
Cotton + 50 ppm NH_4Cl	H	57.50	117.50
Cotton + 5 ppm NaOH	H	86.25	115.75
Cotton + 50 ppm NaOH	H	90.00	120.00
Cotton + 5 ppm KOH	H	86.00	106.25
Cotton + 50 ppm KOH	H	86.25	108.75

of prime importance in practical dying. The effect of electrolytes other than sodium chloride has also been studied, although for economic reasons, there is little likehood of sodium chloride being replaced by other salts. The order of adsorption in the presence of different cations is sodium chloride > potassium chloride > ammonium chloride (Table-1).This is in accordance with the work of Neale and Patel [12] who examined the effect of several cations on the rate and equilibrium adsorption of Benzopurpurine 4B and Sky Blue FF on cellulose.

The effect of pyridine (a conventional poison) was observed when 24 ml dye solution (25 ppm with 0.5 ml pyridine) on cotton/cellulose was shaken for a period of 1/2 h. From the total dye adsorbed, portions of around 30% (from cotton) and 21% (from cellulose) were released. Further extraction of dye upto 37% and 26% respectively were possible by shaking the systems for 1 h. It can be anticipated that most of the adsorbed dye can be desorbed, if it is shaken for a prolonged period of time. The extraction of certain direct dyes from cellulosic fibres has successfully been made using aqueous pyridine by Relelade and Tschetvergov [13]. On the other hand addition of caustic soda in the dye bath have pronounced effect (but less than that of sodium chloride) towards dye adsorption (Table-1).The added caustic soda greatly enhances adsorption on both of the substances. These observations are in accordance with the observations made by Neale [14] that such treatment produced stronger effect on swelling of the fibre, causing increase in the micellar surface of the fibre resulting with increased dye adsorption.

Experimental

Chemically pure grade Congo Red (C.I. 22120) from Merck was used without purification. The glassware was washed with doubly distilled water. The stock solution (100 ppm) was prepared by dissolving an appropriate amount of dye in a doubly distilled water. Further test solutions ranging from 2.5-25 ppm were prepared by dilution of the stock solution. Analytically pure grade cellulose (E. Merck) was taken as substrate. The adsorption procedure was similar to as described in earlier communications [7]. The plots of absorbance against concentration of dye solution followed the Beer Lambert law (λ_{max} = 497 nm). The weighed quantity of the adsorbent (0.2 g) was taken in a series of 100 ml flasks. Then to each flask was added 50 ml test solution with varying concentration (2.5-25 ppm). The flasks were tumbled for 1 h in thermostating conditions at 25°C. The amount of dye adsorbed (x/m) per gram of solid was calculated by the difference between the initial concentration and the final dye bath equilibrium. The plot between the dye adsorbed against the equilibrium concentration gives a typical isotherm. The effect of electrolyte on sorption of Congo Red was monitored by determining the amount of dye adsorbed in the presence of electrolyte (5 and 50 ppm) in the dye bath.

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