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Understanding the Sorption of Thionine Dye

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Abstract

Silica and carbon as mesopores have been tested for their sorption ability of a cationic dye. The surface of carbon is activated by pretreatment with ammonium persulphate. The sorption efficiency of carbon after surface activation is higher than that of silica. Also the pH effect of the two sorbents is quite different. The study showed that the dye sorption did not reach saturation in the concentration range of 0-200 ppm. This indicates that probably the pores are also involved in the sorption.

***Keywords**: Thionine;* **Ammonium persulphate**

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Introduction

Sorption is an important process in the remediation of water body as it uses inexpensive and efficient sorbents which are effortlessly available. Though sorption is carried out from an application perspective and gives a scope for application based research, there is also a compass for basic research [1]. It is always of great interest to understand the possible changes that occur during sorption process [2]. There are large numbers of materials including nanomaterials which are explored for their sorption efficiencies. One such faction of materials are the mesoporous materials with pores of 0.2 to 2 nm and have regular geometries [3]. These mesoporous materials are model solid substrates as they are comprised of uniform and large pores with high pore volume as well as a large number of highly dispersed active sites on the mesopore walls and surface. Mesoporous silica and carbon have been extensively used for the removal of different types of dyes [4,5].

In the present study, an attempt has been made to study the sorption of thionine blue dye by mesoporous silica and carbon.

Experimental

The protocol for the synthesis of mesoporous silica and carbon are reported in literature. The mesoporous carbon was pre-treated with ammonium persulphate. The sorption was carried out in batch mode and different techniques were used to characterize these samples.

Results and Discussion

Thionine, also known as Lauth's violet, is the salt of a heterocyclic compound and is structurally related to methylene blue, which also features a phenothiazine core. The structural formula is given in **FIG. 1.**

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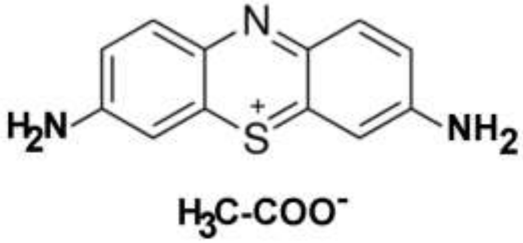
FIG.1. **Structure of thionine dye.**



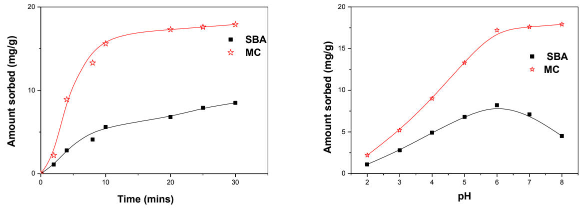
X-ray diffraction patterns of SBA-15 in the small-angle range shows an intensive peak at 2θ ≈ 0.8º and shows three reflections which can be indexed to the (100), (110) and (200) reflections of the two dimensional hexagonal space group p6mm, thus confirming that the SBA-15 prepared are hexagonally ordered meso structures [3]. XRD pattern of mesoporous carbon in the small-angle range shows an intensive peak at 2θ≈1º corresponding to the (211) plane and reflexes in the range 2θ≈1.8-2.3º, indicating highly ordered regular structure. The pre-treatment with ammonium persulphate results in the loss of intensity of all the peaks. These results are similar to those reported earlier [6]. BET studies revealed that the values of surface area, pore volume and pore size of SBA 15 are 600 m^2/g, 0.42 mL/g and 7.1 nm respectively [3]. For mesoporous carbons the values of surface area, pore volume and pore size obtained are 700 m^2/g, 0.34 mL/g and 5.1 nm respectively which upon pre-treatment decrease to 660 m^2/g, 0.26 mL/g and 4.6 nm respectively. This could be due to the partial blocking of the pores during oxidation process. It could be possible that the surface oxygen groups on the mesopore wall could be positioned at the entrance of the pores. Silica is well known to have surface active hydroxyl groups which contribute cation exchange property for silica. Mesoporous carbon upon pre-treatment with ammonium persulphate is found to have surface acidic groups. The pre-treated mesoporous carbon is then used for uptake studies and compared with mesoporous silica. The effect of different experimental parameters like contact time, pH, nature of sorbent and the amount on the uptake of dye were studied. The studies of effect of time of equilibration and pH on the sorption efficiency were carried out using 0.05g of sorbent with 10 mL of 20 ppm of dye solution. The results are shown in **FIG. 2**. It is seen from **FIG. 2a.** that the sorption kinetics is fast and also superior for carbon as compared to silica. A quantitative assessment the rate of change of amount sorbed in the initial stage of sorption before reaching saturation can be used to confirm this. The values of the slope of rate of change of amount sorbed with respect to time for carbon (1.56 mg/g*min) is nearly three times more than that of silica (0.59 mg/g*min). The change has been represented in **FIG 2a.**

This could be attributed to the presence of COOH groups created on the surface of mesoporous carbon due to the pre-treatment with ammonium persulfate. COOH groups are well known cation exchangers and have better uptake efficiency as compared to the hydroxyl groups on the surface of silica. Since the dye is cationic in nature and the surface groups also behave like ion exchanger, the pH of the external solution is bound to affect the sorption behaviour. The variation of sorption capacity with pH is shown in **FIG. 2b**. It is seen that increase in pH up to 6 results in increased sorption. This could be attributed to the fact that at lower pH, there is a competition between the H^+ and dye cations for the sorption sites and therefore sorption efficiency is poor. At pH greater than 6, the behaviour of mesoporous carbon is quite different to that of silica. For carbon, the sorption increases with increase in pH. This is because COOH gets completely ionized at higher values of pH and therefore show better efficiency. But for silica, the presence of excess of Na^+ ions at high pH results in the decrease in dye uptake.

The effect of amount of sorbent on the uptake was studied by varying the sorbent amount in the range of 0.02-0.1 g and it was observed that 0.05g of sorbent can be used for subsequent studies. The effect of initial solution concentration on the sorption capacity was evaluated by varying the concentration in the range of 0-200 ppm. The results given in **FIG. 3.** showed that the value keeps on increasing and does not reach saturation for the present range of concentration.

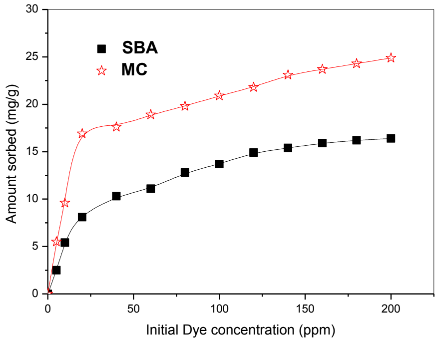
The enhanced sorption efficiency of carbon may not only arise from its high surface area (900 m2/g) as compared to that of silica (600 m2/g) but also from the presence of surface carboxyl groups which tend to behave like a cation exchanger. In the present concentration range, it is seen that the cation exchanger sites of carbon are not completely filled and therefore no saturation occurs

FIG.2. **Effect of different parameters (a) Equilibration time and (b) pH on sorption.**



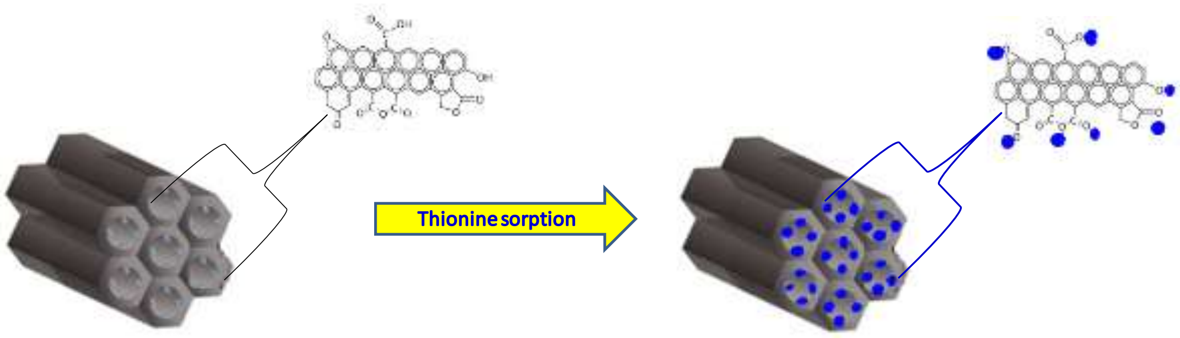
(a) (b)

FIG.3. **Effect of initial dye concentration on the sorption efficiency of silica (SBA 15) and mesoporous carbon (MC).**



A schematic representation of the formation of surface groups and the sorption of dye is given in **SCHEME 1.**

SCHEME.1. **Representation of the surface groups and sorption of dye on carbon.**



Conclusions

It is seen that the surface activity of carbon can be enhanced by pretreatment. The sorption behavior is dependent on various factors like pH, concentration etc. It is seen that the uptake is greater for carbon as compared to silica. The pH variation studies showed that though silica shows a decrease in sorption capacity at pH>6, the sorption ability of silica decreases while that of carbon keeps increasing. It is seen sorption isotherms do not saturate in the studied concentration range. This indicates the involvement of the pores in sorption.

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