Dyes and Pigments **15** (1991) 175–182

Adsorption of Anionic Dyes by Kaolinites

M. M. Kamel, B. M. Youssef & Magda M. Kamel

Textile Division, National Research Centre, Dokki, Cairo, Egypt

(Received 12 March 1990; accepted 8 May 1990)

ABSTRACT

This study outlines the kinetic rate of adsorption of three commercial anionic direct dyestuffs by two types of Egyptian kaolinite, i.e. Sinai and Kalabsha. The structure of the dyestuffs, as well as the structure of kaolinites, plays a great role in dye adsorption. The Sinai kaolinite shows a higher apparent ion-exchange capacity than the Kalabsha one. Some factors affecting dye adsorption are investigated, e.g. kaolinite and dye concentration, shaking time, temperature and addition of electrolytes.

1 INTRODUCTION

A number of low-cost materials such as clays, bentonites, coal, kaolinite and cotton wastes have been used as adsorbents for dyestuffs. Many investigations have been carried out on the adsorption of cationic dyes, particularly that of Methylene Blue by clay minerals.[1–7] Equilibrium isotherms for each dye–adsorbent system have been noted and adsorption capacities also obtained.[8–10]

Although it is well known that basic dyes are adsorbed to a greater extent than other dye classes on kaolinite, no single characteristic of the dye or adsorbent appears to be responsible for such dye–adsorbent interactions and adsorption capacities.[10–12] Little work has been reported on the adsorption of anionic dyes and the rate of adsorption by kaolinite.[4]

In this present investigation, a study of the kinetics of the adsorption of three direct dyes from aqueous solution by two types of Egyptian kaolinites has been undertaken.

Dyes and Pigments 0143-7208/91/$03·50

TABLE 1
Analysis of Kaolinites

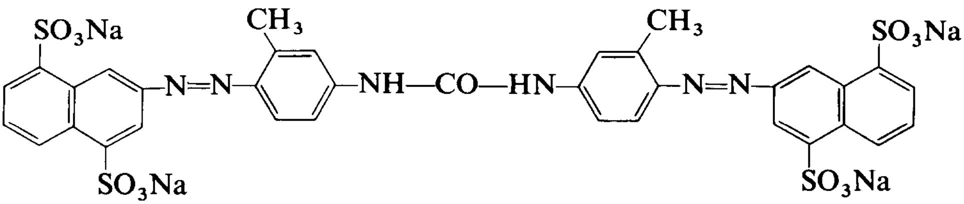
X-ray analysis			*Chemical analysis*			*Particle size of kaolinites*			
	Sinai (%)	*Kalabsha* (%)		*Sinai* (%)	*Kalabsha* (%)	*Sinai*		*Kalabsha*	
						(μm)	(%)	(μm)	(%)
Kaolinite	72·00	91·5	SO_3	—	0·57	100	13·34	63	1·02
Quartz	—	5·0	Cl	—	0·03	100–53	3·53	63–36	9·43
Mica	—	3·5	SiO_3	47·22	44·20	53–20	8·31	36–20	17·62
Muscovite	4·25	—	Al_2O_3	36·01	37·75	20–5	16·62	30–3·6	32·21
Paragonite or Na-felds	13·98	—	Fe_2O_3	0·77	0·93	5–2	8·31	3·6–1	21·86
Ca-felds	3·75	—	TiO_2	2·21	1·85	2–1	8·31	Less 1	17·86
Chlorite									
Mg	1·05	—	CaO	0·77	0·82	Less	41·56		
Al	1·08	—	MgO	0·10	0·52				
Fe_2O_3, TiO_2	2·78	—	Na_2O	0·11	1·15				
			K_2O	0·14	0·72				
			IL	12·39	13·01				

IL = ignition loss.
felds = feldspar.

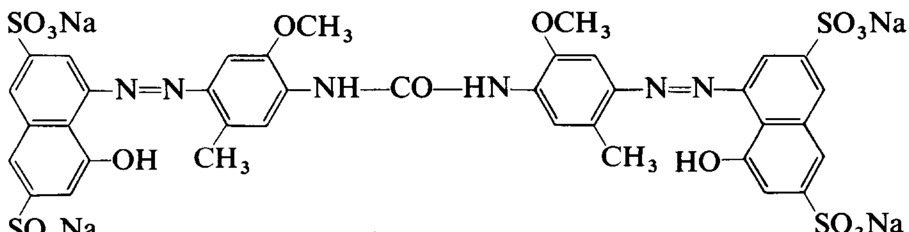
2 MATERIALS

Commercial Egyptian kaolinite samples from Sinai and Kalabsha deserts were used as adsorbents for the dyes; the clays were used without any pretreatment, so that natural conditions were simulated as far as possible. X-ray and chemical analyses of the kaolinites are listed in Table 1, together with the particle size of the kaolinites.

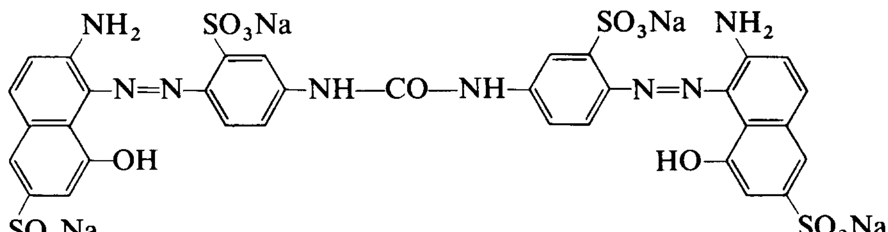
The three direct dyes used were Solophenyl Yellow GFL (**I**), Solophenyl Red 6BL (**II**) and Diphenyl Pink BF (BK) (**III**).



I Solophenyl Yellow GFL; CI Direct Yellow 50 (CI 29025)



II Solophenyl Red 6BL; CI Direct Red 79 (CI 29065)



III Diphenyl Pink BF (BK); CI Direct Red 75 (CI 25380)

3 EXPERIMENTAL

Different amounts (0·5–2 g) of the two types of kaolinite (Sinai and Kalabsha) were added to aqueous solutions of the direct dyes **I**, **II** and **III** (10–100 mg) in 100 ml of distilled water. The pH of the final suspension was 7·9. The suspension was shaken for varying times (2–30 min), temperatures (30–60°C) and additions of sodium chloride (0·5–2·5 g). At the end of a run, an aliquot was centrifuged at 3000 rpm for 10 min and the dye concentration in the clear supernatant liquor was determined colorimetrically using a Schimadzu UV 240 spectrophotometer, at 400 nm for Solophenyl Yellow GFL and at 510 nm for Solophenyl Red 6BL. Diphenyl Pink BF (BK) showed a sharp band at 340 nm and a broad band at 530 nm. The band at 340 nm was used for the measurements and the results obtained were checked using the band at 530 nm (giving identical results).

4 RESULTS AND DISCUSSION

4.1 Effect of concentration of kaolinite and shaking time

Figures 1 and 2 show the rate of adsorption of the dyestuffs **I–III** by Sinai and Kalabsha kaolinite respectively. It can be seen that rapid adsorption of the dyestuff was obtained with a shaking time of up to 5 min and that thereafter little or no change in adsorption occurs up to 30 min.

Generally the adsorption of the dyestuffs by both kaolinites follows the order **II** > **III** > **I**. This sequence may be related to the number and orientation of the sulphonic acid groups and their dissociation ability, and to the polar characteristics of substituents such as NH_2 and OH on the rate of the dissociation.

Although dyes **I**, **II** and **III** all contain four sulphonic acid groups, dye **II** may be expected to have a higher tendency to be adsorbed on the two kaolinites studied, due to the position of the sulphonic acid groups in dyes **I** and **III**. In the case of dyestuff **III**, the sulphonic acid group is *ortho* to the azo groups and is not as easily dissociated as that in dyestuff **II** (*meta* position) (higher dye adsorption, **II** > **III**).

On the other hand, it appears possible that the presence of the amino group in the naphthalene ring of dye **III** and of the hydroxy group in dyes **II** and **III** plays an indirect role, and influences the polar characteristics of the sulphonic acid groups in dyes **II** and **III**.

The results obtained show a higher adsorption of dye **II** than of dye **III** on both kaolinites. This may be related to possible hydrogen bonding of the hydroxyl group in dye **III** with the neighbouring azo group, and subsequent decrease in its dissociation. In dye **II**, the presence of the methyl group *ortho* to azo may be expected to inhibit hydrogen bonding, and its dissociation will thus be higher than that of dye **III**. Dye **I** contains no other electron-donor groups, and may thus be expected to show a lower dissociation ability, and consequent lower anion-exchange rate, on both kaolinites.

X-ray diffraction analysis (Table 1) shows a higher kaolinite percentage (91·5%) for Kalabsha compared to that of Sinai (72%). These values may be

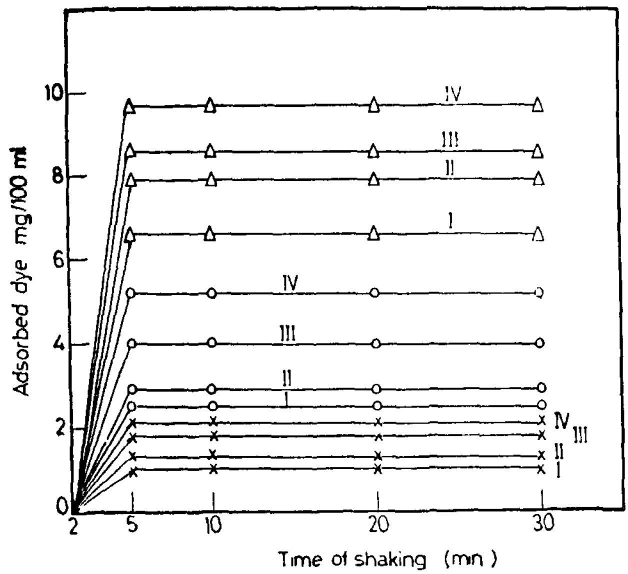


Fig. 1. Effect of time of shaking on the adsorbed dye: ×, dye **I**; ○, dye **II**; △, dye **III**. Weights of Sinai kaolinite: I, 0·5 g; II, 1·0 g; III, 1·5 g; IV, 2·0 g.

contrasted with high adsorption rates of the Sinai clay compared with the Kalabsha clay. This may be attributed to the particle size of both kaolinites; 41·46% of the Sinai kaolinite (Table 1) is less than 2–1 μm mesh, whereas in the Kalabsha kaolinite only 17·86% is less than 1 μm. This may be responsible for the higher adsorption rates for the Sinai material than for the Kalabsha material.

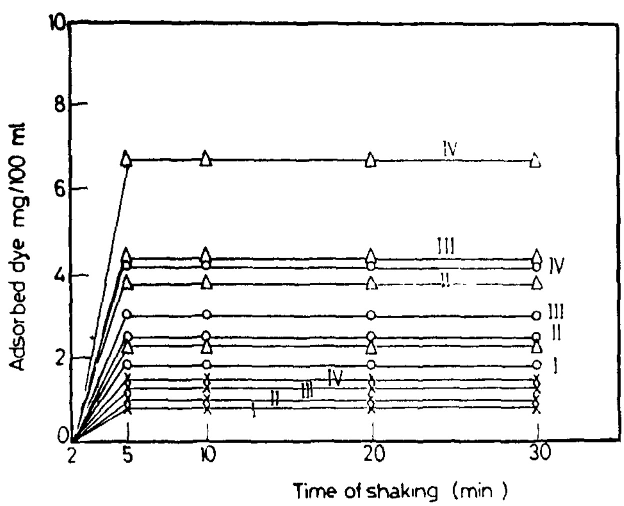


Fig. 2. Effect of time of shaking on the adsorbed dye: ×, dye **I**; △, dye **II**; ○, dye **III**. Weights of Kalabsha kaolinite: I, 0·5 g; II, 1·0 g; III, 1·5 g; IV, 2·0 g.

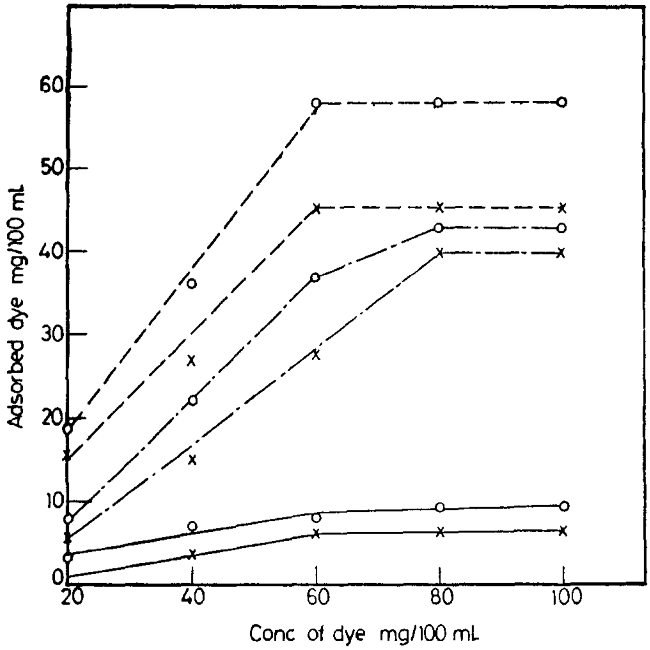


Fig. 3. Effect of concentration of dye on the adsorbed dye with Sinai (○) and Kalabsha (×) kaolinites: ——, dye **I**; – – –, dye **II**; — —, dye **III**.

4.2 Effect of dye concentration

Kaolinite (Sinai and/or Kalabsha) (1·5 g) was added to dyes **I**, **II** and/or **III** (20–100 mg) in 100 ml distilled water. The suspension was shaken for 30 min and separated as described in Section 3.

From Fig. 3, it is apparent that an increase in the dye concentration (20–100 mg) is accompanied by an increase in dye adsorption, until equilibrium occurs. It is also apparent that the adsorption efficiency of the Sinai kaolinite is higher than that of the Kalabsha kaolinite. It can be concluded that, from a dyebath containing 60 mg of dyestuff in 100 ml distilled water, 96·7% of dye **II**, 61·7% of dye **III** and 13·3% of dye **I** can be adsorbed on the Sinai kaolinite, whereas 75·8%, 45·8% and 10·83% respectively (for dyes **II**, **III** and **I**) can be adsorbed on the Kalabsha kaolinite (1·5 g). Any further increase in the concentration of dyebath cannot result in further adsorption, since there is no more anion-exchange capacity.

4.3 Effect of temperature

Raising the temperature from 30°C to 60°C for a suspension of 1·5 g of both kaolinites, 60 mg of dyes **I**, **II** and **III** in 100 ml distilled water (the clay then being separated as usual), results in a slight decrease in dye adsorption by

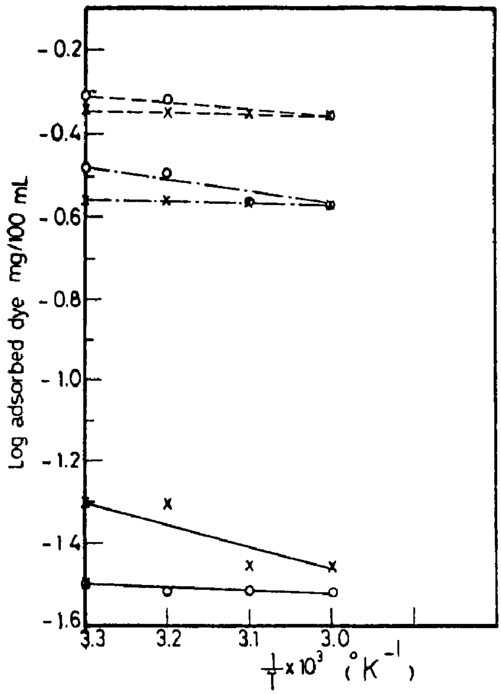


Fig. 4. Effect of temperature on log (adsorbed dye) for Sinai (○) and Kalabsha (×) kaolinites: ——, dye **I**; - - -, dye **II**; —·—, dye **III**.

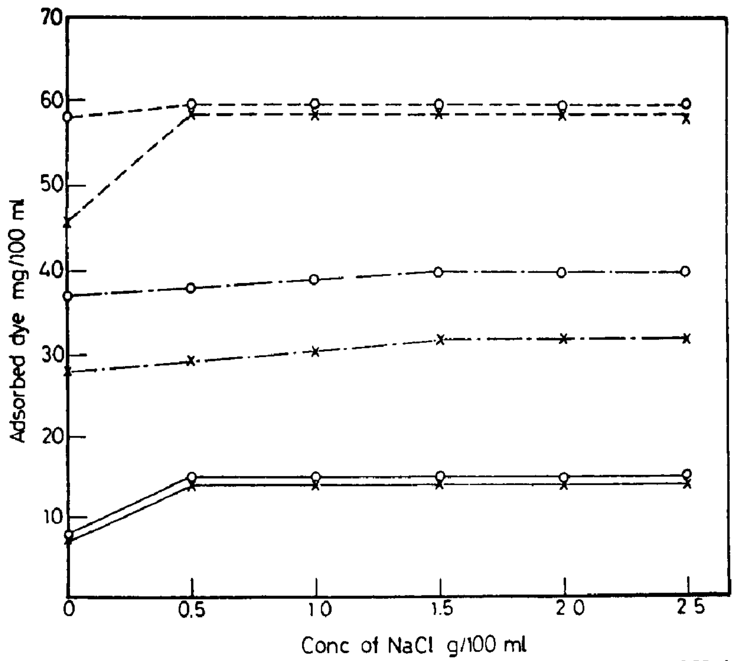


Fig. 5. Effect of concentration of NaCl on the adsorbed dye for Sinai (○) and Kalabsha (×) kaolinites (1·5 g/100 ml): ——, dye **I**; - - -, dye **II**; — —, dye **III**. Dye concentration 60 mg/100 ml distilled water. Shaking time 30 min.

both Sinai and Kalabsha kaolinites for the three dyes. This is expected, since the exchange process generally is exothermic. This is illustrated in Fig. 4, which shows the relation between log (adsorption) and $1/T$ in absolute values.

4.4 Effect of addition of NaCl

Figure 5 shows that 13·3%, 96·7% and 61·7% of dyes **I**, **II** and/or **III** is adsorbed on the Sinai kaolinite without addition of NaCl. An increase in dye adsorption takes place after addition of sodium chloride, to 25%, 99·2% and 66·7% respectively. This holds true also for the Kalabsha kaolinite, an enhancement in adsorption of dyes **I**, **II** and **III** occurring from 11·7% to 23·3% for **I**, 96·7% to 99·2% for **II** and 76·7% to 97·5% for **III**. This may be due to the addition of NaCl increasing the activity of the aqueous solutions of the dyes, with subsequent increase in the amount of the exchange ions. It is, however, also possible that the sodium chloride is acting by precipitating the dye onto the clays.

5 CONCLUSIONS

Natural kaolinite can be used for removal of dyes from wastes of dyeing baths, the uptake by the kaolinite being related to the structure of the dye. The adsorption of the dyes is slightly decreased with temperature, but the presence of an electrolyte, such as sodium chloride, enhances the adsorption of dyes on the kaolinite.

REFERENCES

1. Doroshenko, V. E., Tarasevich, Yu. I. & Sivalov, E. G., *Khim. Tekhnol. Vody*, **4**(2) (1982) 112 (in Russian).
2. Plesch, P. H. & Robertson, R. H. S., *Nature*, **161** (1948) 1020.
3. Ramachandran, V. S., Kacher, K. P. & Patwardhan, N. K., *Nature*, **191** (1961) 696.
4. Faruqi, F. A., Okuda, S. & Williamson, W. O., *Clay Miner.*, **7** (1967) 19.
5. Hang, P. T. & Brindley, G. W., *Clay Miner.*, **18** (1970) 203.
6. Brindley, G. W. & Thompson, T. D., *Isr. J. Chem.*, **8** (1970) 409.
7. Sethuraman, V. V. & Raymahashay, B. C., *Environ. Sci. Technol.*, **7**(13) (1975) 1139.
8. Fairbairn, P. E. & Robertson, R. H. S., *Clay Min. Bull.*, **3** (1957) 129.
9. De, D. K., Chakravarti, S. K. & Mukherjee, S. K., *Sci. Cult. (Calcutta)*, **32**(4) (1966) 182.
10. McKay, G. & Otterburn, M. S., *Anal. Proc.*, **17**(10) (1980) 406.
11. McKay, G., Ramprasad, G. & Mowli, P. P., *Water, Air, Soil Pollut.*, **29**(3) (1986) 273.
12. McKay, G., Otterburn, M. S. & Aga, J. A., *Water, Air, Soil Pollut.*, **24**(3) (1985) 307.