

Binding of Basic Dyes by the Algae, *Chara aspera*

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ABSTRAK

Suatu algae, *Chara aspera*, yang bukan hidup boleh menambat dua pewarna berbes, metilena biru dan basik biru 3, dari larutan akueus. Faktor yang mempengaruhi pengerapan seperti kepekatan pewarna, masa tindakan, dos pengarap dan pH larutan telah dikaji. Isoterma Langmuir menunjukkan bahawa muatan erapan maksimum algae untuk metilena biru dan basik biru 3 adalah 139.4 dan 17.8 mg/g.

ABSTRACT

Non-living biomass of the algae *Chara aspera* is capable of binding two basic dyes, methylene blue and basic blue 3, from aqueous solution. Factors such as dye concentration, contact time, sorbent dosage and pH of solution were studied. Maximum sorption capacities of the algae for methylene blue and basic blue 3 are 139.4 and 17.8 mg/g, respectively, as determined from the Langmuir isotherms.

Keywords: sorption, cationic dyes, algae, *Chara aspera*

INTRODUCTION

The disposal of coloured substances poses one of industry's major problems in wastewater treatment. This is because the discharge of coloured wastes is not only damaging to the aesthetic nature of the receiving streams but also toxic to aquatic life. Dye is one such coloured substance. The treatment of dyes is fraught with numerous problems as they are generally stable to light and oxidation and hence cannot be treated by conventional methods of aerobic digestion.

An alternative method for the total or partial removal of dye is by sorption technique. Various such treatment systems have been developed using activated carbon as the sorbent (Davis *et al.* 1973; McKay 1982; McKay *et al.* 1986). While carbon has been used successfully to remove dyes from solution, it is, however, expensive. Alternative, cheaper sorbent materials such as bark (Asfour *et al.* 1985), rice husk (Nawar and Doma 1989), coal, bentonite clay, cotton waste (Poots *et al.* 1976a, 1976b), biogas slurry waste (Namasivayam and Yamuna 1992) moss (Lee and Low 1987), banana pith (Namasivayam and Kanchana 1993) and coconut husks (Low and Lee 1990) have been used with varying degrees of success. This paper reports the

preliminary findings of a study on the effectiveness of an algae, *Chara aspera*, in removing two cationic dyes from aqueous solutions and the parameters affecting the sorption process.

MATERIALS AND METHODS

The algae *Chara aspera* was collected from a mining pool in the vicinity of the university. It was cleaned thoroughly before drying at 40°C. Two basic dyes, methylene blue (C.I. 52015) and basic blue 3 (C.I. 51004) were used without further purification.

Contact Time Experiments

In these experiments the uptake of the dyes by the algae was conducted by shaking the samples in the dye solutions continuously on a gyratory shaker at 200 rpm. Aliquots of 1 ml-solution were withdrawn at regular intervals and analysed for dye content using a Shimadzu UV-160 UV-visible spectrophotometer at λ_{max} 's 665 and 654 nm for methylene blue and basic blue 3, respectively. All experiments were conducted in duplicate and variation in results was generally less than 5 %.

Effect of pH

The effect of pH was studied under equilibrium conditions. The pH of the solution was adjusted with either dilute HCl or NaOH before experimentation.

Effect of Initial Dye Concentration

The effect of initial concentration was studied by varying the concentrations of the dye solution from 25-500 p.p.m. Samples were shaken in 100 ml of dye solution and the uptake was monitored at regular intervals.

Effect of Sorbent Dosage

In the study of the effect of sorbent dosage on dye uptake, the weight of *Chara* was varied from 0.05-0.50 g for methylene blue and 0.25-1.00 g for basic blue 3 solutions. The dye concentration for both dyes was maintained at 100 p.p.m.

Sorption Isotherms

The adsorption isotherms for the uptake of different dyes by *Chara* were studied by shaking 0.1 g of *Chara* with methylene blue solution and 1.00 g *Chara* with basic blue 3 solution. Concentration was varied from 50 to 800 p.p.m.

RESULTS AND DISCUSSION

Effect of pH on Sorption

The effect of pH on the uptake of methylene blue and basic blue 3 by *Chara* is shown in Table 1. In the pH range of 4-10 the sorption was fairly

constant for both systems. However, the ability to sorb started to decrease when pH was lower than 4. The decrease could be attributed to the presence of excess H⁺, making sorption less favourable. Subsequent experiments were performed without adjusting the pH of the dye solutions (6.3 and 4.3 for methylene blue and basic blue 3, respectively).

TABLE 1
Effect of pH on the sorption of dyes

Methylene blue		Basic blue 3	
pH	Uptake (%)	pH	Uptake(%)
2.40	60.00	2.17	17.36
3.48	75.25	4.23	27.71
6.14	77.75	5.60	26.31
9.66	78.85	7.89	28.39
11.16	81.25	9.43	27.33

Conditions: 0.5 g of algae in 100 ml of 100 p.p.m. dye solution; equilibration time : 2 h

Effect of Initial Concentration on Sorption Isotherm

The effect of initial dye concentration on the rate of sorption is shown in Fig. 1 and Fig. 2. The initial concentration had very little effect on the contact time required to reach equilibrium. Poots *et al.* (1978), in their study on the removal of basic dye using wood as an adsorbent, reported the same observation. For both dyes the initial uptake was very rapid, but subsequently slowed down. Equilibrium was attained in about 1 hour.

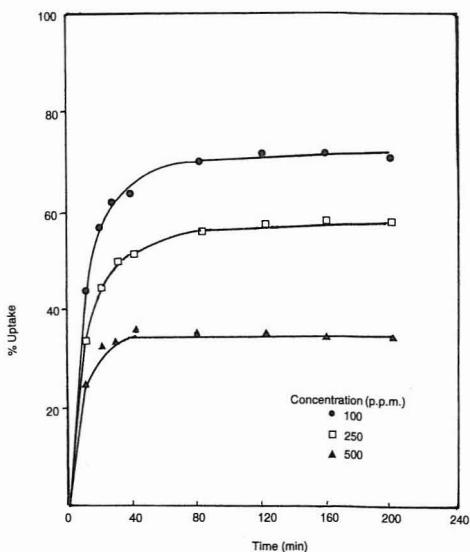


Fig. 1. Effect of initial concentration on the uptake of methylene blue by algae.
Condition: 0.1 g algae in 100 ml solution

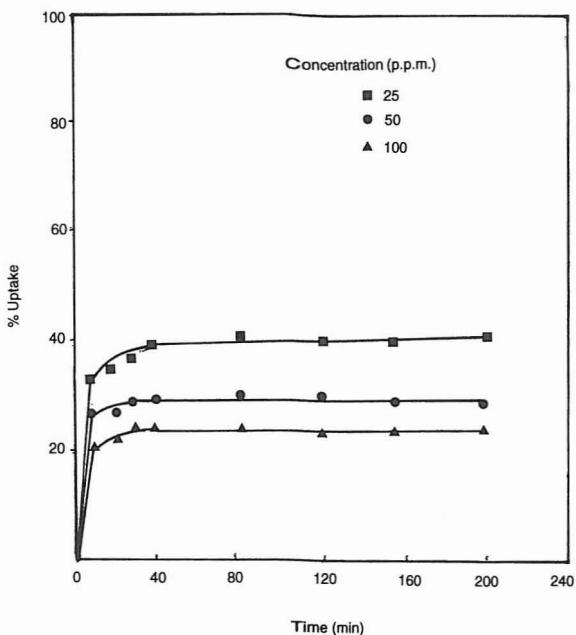


Fig. 2. Effect of initial concentration on the uptake of basic blue 3 by algae
Condition: 0.5 g algae in 100 ml solution

A long equilibrium time could indicate that the predominant mechanism is physical adsorption and that the process will be reversible. A relatively shorter equilibrium time would imply that chemisorption is probably important and that regeneration would be more difficult to achieve. From the sorption curves, it appears that the mode of dye sorption on *Chara* is essentially a chemisorption process. Under the same experimental conditions, *Chara* was able to remove a larger percentage of methylene blue (80%) than basic blue 3 (22%). This could be attributed to the different type and number of functional groups in the dyes.

Effect of Dosage on Sorption

The effect of sorbent dosage on the uptake of a fixed quantity of dye is shown in Fig. 3 and Fig. 4. As expected, the percentage sorption of the dye increased with increasing dosage. This is due to the greater number of sorption sites on the aquatic plant.

Sorption Isotherms

The results from contact time experiments can be used to determine the maximum amount of dye sorbed by *Chara* using a modified Langmuir isotherm

$$Ce/Ne = 1/N^*b + Ce/N^*$$

where N_e is the amount of dye sorbed (mg per gram) of *Chara* at C_e , the equilibrium concentration of the dye solution (p.p.m.). Plots of sorption isotherm

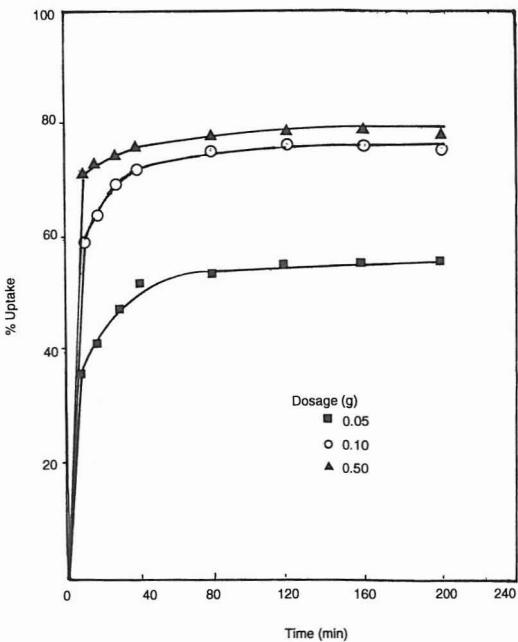


Fig. 3. Effect of sorbent dosage on the uptake of methylene blue by algae
Condition: 100 ml of 100 p.p.m. methylene blue; equilibrating time: 2h

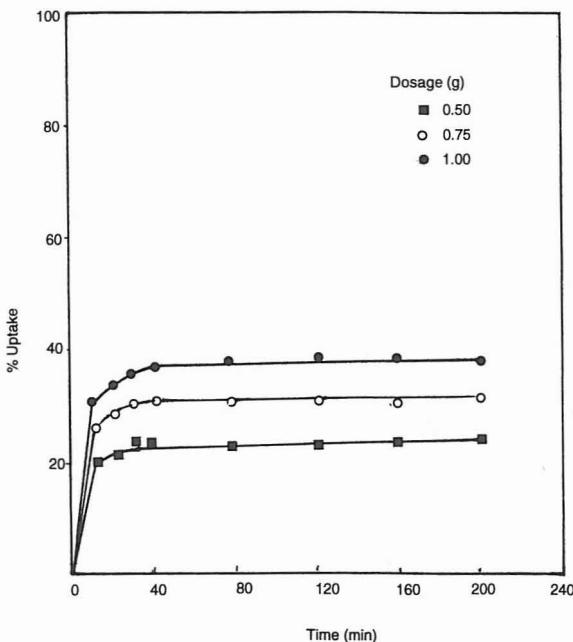


Fig. 4. Effect of sorbent dosage on the uptake of basic blue 3 by algae
Condition: 100 ml of 100 p.p.m. basic blue 3; equilibrating time: 2h

are shown in Fig. 5. The linearity of the plots indicates that Langmuir isotherm can be applied successfully to the dye-*Chara* system. The maximum sorption capacities (N^*) are 139.4 and 17.8 mg/g for methylene blue and basic blue 3, respectively. These values confirm the earlier observation in the contact-time experiment that *Chara* could sorb more methylene blue than basic blue 3 under similar conditions. The maximum sorption capacity of algae compares favourably with that of moss (185.0 mg/g) (Lee and Low 1987) and coconut husk (99.0 mg/g) (Low and Lee 1990).

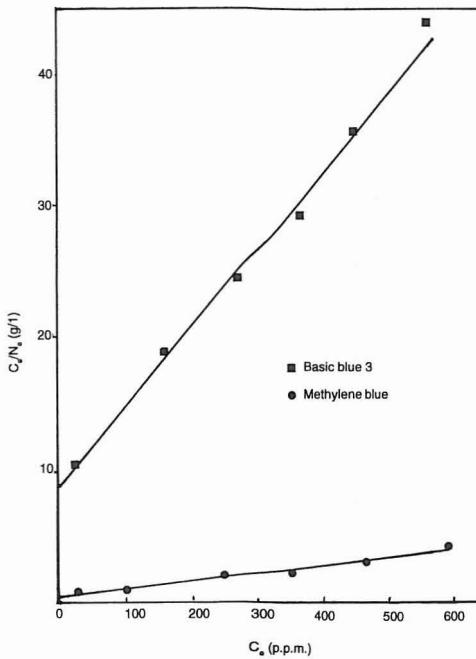


Fig. 5. Langmuir isotherms for methylene blue and basic blue 3 systems

Condition: methylene blue-0.1 g algae in 100 ml of dye solution;
basic blue 3-1.0 g algae in 100 ml of dye solution

Comparative Study on the Sorption of Acidic and Basic Dyes

In order to explore the potential of *Chara* to remove a broader spectrum of dyes, experiments were conducted using two acid dyes, reactive yellow 2 and reactive orange 16. The results are shown in Fig. 6. The acid dyes showed very little affinity for the algae. The difference could be attributed to the nature of the algae, whose structure is probably cellulose-based and negatively charged. The acid dyes dissociate in water to an anionic coloured component and a cationic species. The approach of an acidic dye anion will experience coulombic repulsion due to the presence of anionic groups in *Chara*. Geundi (1991) also reported that acidic dyes showed less affinity than basic dyes on maize cob. However, Poots *et al.* (1976a) reported that the sorption of acid dye on wood was quite successful although a longer time was required to reach equilibrium.

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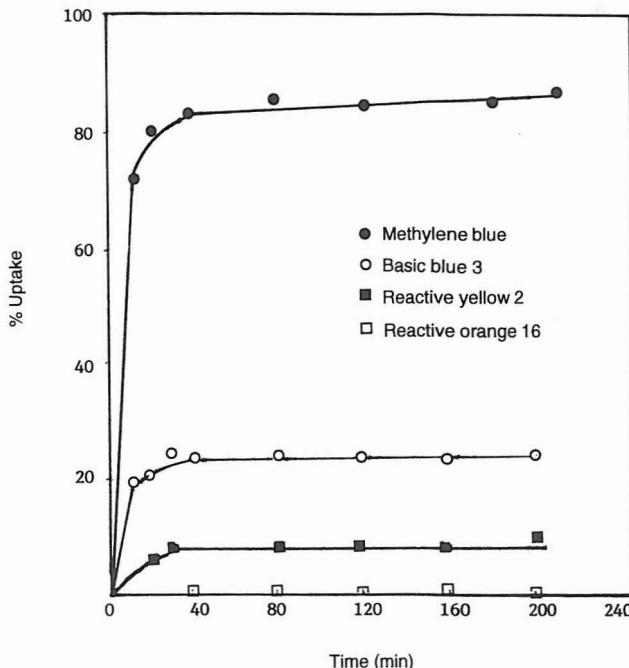


Fig. 6. Sorption of cationic and anionic dyes by algae
Condition: 0.5 g algae in 100 ml of 100 p.p.m. dye solution

CONCLUSION

This preliminary study shows that the algae *Chara aspera*, an easily available aquatic plant, has the potential to remove basic dyes from solution. Methylene blue showed greater adsorptivity than basic blue 3. *Chara aspera* is, however, ineffective in binding with acidic dyes.

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REFERENCES

- ASFOUR, H.M., O.A. FADAL, M.M. NASSAR and M.S. EL-GEUNDI. 1985. Equilibrium studies on adsorption of basic dyes on hardwood. *J. Chem. Tech. Biotechnol.* **35A**: 21-27.
- DAVIS, R.A., J.K. HARMUT and M.M. CLEMUS. 1973. Removal of organic material by adsorption on activated carbon. *Chem. and Ind.* **1**: 827.
- GEUNDI, M. 1991. Colour removal from textile effluent by adsorption techniques. *Water Res.* **25(3)**: 271-273.
- LEE, C.K. and K.S. Low. 1987. The removal of cationic dyes by a natural moss. I: Adsorption studies. *Pertanika* **10(3)**: 327-334.

Low, K.S. and C.K. Lee. 1990. The removal of cationic dyes using coconut husk as an adsorbent. *Pertanika* **13**(2): 221-228.

McKAY, G., G. RAMPRASAD and P.P. MOWLI. 1986. Equilibrium studies for the adsorption of dyestuffs from aqueous solutions from low-cost materials. *Water, Air, Soil Pollut.* **29**: 273-283.

McKAY, G. 1982. Adsorption of dyestuffs from aqueous solutions with activated carbon. I: Equilibrium and batch contact-time studies. *J. Chem. Tech. Biotechnol.* **32**: 759-772.

NAMASIVAYAM, C. and N. KANCHANA. 1993. Removal of Congo red from aqueous solution by waste banana pith. *Pertanika J. Sci. & Technol.* **1**: 33-42.

NAMASIVAYAM, C. and R.T. YAMUNA. 1992. Removal of Congo red from aqueous solutions by biogas waste slurry. *J. Chem. Tech. Biotechnol.* **53**: 153-157.

NAWAR, S.S. and H.S. DOMA. 1989. Removal of dyes from effluents using low-cost agricultural by-products. *Sci. Total Environ.* **79**: 271-279.

POOTS, V.J.P., G. Mc KAY and J.J. HEALY. 1976a. The removal of acid dye from effluent using natural adsorbents. I. Peat. *Water Res.* **10**: 1061-1066.

POOTS, V.J.P., G. Mc KAY and J.J. HEALY. 1976b. The removal of acid dye from effluent using natural adsorbents. II. Wood. *Water Res.* **10**: 1067-1070.

POOTS, V.J.P., G. Mc KAY and J.J. HEALY. 1978. Removal of basic dye from effluent using wood as an adsorbent. *J. Wat. Pollut. Cont. Fed.* **50**: 926-935.