Utilization of agricultural waste as a biosorbent for the removal of dyes from aqueous solution

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Abstract

The effectiveness of using sugarcane bagasses and modified rice hull as a low cost material for the removal of dyes from both single and binary dye solutions was investigated. Surface morphology analysis was carried out using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Batch and column studies were performed under various experimental conditions. Batch studies revealed that the removal of the studied dyes was both pH and concentration dependent. Maximum sorption capacities calculated from the Langmuir model were in the range of 14.68 - 67.11 mg g^{-1} in single dye solutions. In column studies, results revealed that breakthrough was influent concentration, flow rate and bed height dependent. The breakthrough curves exhibited the typical S shape of packed bed system.

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1 Introduction

Dyes are coloured substances that can be applied to various substrates (textile materials, leather, paper, hair) from a liquid in which they are completely, or at least partly, soluble. Man has made use of dyes since prehistoric times, and in fact, the demand and the usage of dyes have continuously increased. However, the presence of dyes even in trace quantities is very undesirable in aqueous environment as they are generally stable to light and oxidizing agents, and are resistant to aerobic digestion.

Some of the conventional methods of color removal from industrial effluents include ion exchange, activated carbon adsorption, membrane technology and coagulation. Amongst all, the sorption process by activated carbon has been shown to be one of the most efficient methods to remove dyes from effluents (Malik, 2002). Activated carbon is the most widely used adsorbent in the industries due to its capability to adsorbing many types of dyes with high adsorption capacity. However, it remains as an expensive adsorbent and has high regeneration cost while being exhausted (Han et al., 2008). There is thus a need to search for new and economical process that could remove dyes that are commonly used in the industry.

Generally, a low-cost sorbent can be defined as one which requires little processing and is abundant in nature. In this context, agricultural by-products and industrial waste can be seen as having a great potential to be developed as a low cost sorbent. The feasibility of using these materials could be beneficial not only to the environment in solving the solid waste disposal problem, but also the economy. Literature survey revealed that numerous biological materials have been utilized as adsorbents. These include durian peel (Ong et al., 2011), rice husk (Han et la., 2008; Han et al., 2007; Ong et al., 2010a; Ong et al., 2010b), orange peels (Ardejani et al., 2007; Arami et al., 2005), spent tea leaves (Hammed et al., 2009; Hameed 2009) and wheat straw (Gong et al., 2008). However, studies of dye removal in mixture dye

system were very limited for recent years. The present project aims to search for a low cost material that could remove dyes that present either singly or in a mixture.

2   Experimental

2.1   *Sugarcane bagasse*

Sugarcane bagasse was collected and cut into small pieces. Then the bagasse was boiled for 3 hours to remove the sugar residue within it. It was rinsed several time with tap water and dried overnight at 60 °C. The dried bagasse was ground and sieved through a 3 mm sieve and labeled as NSB.

2.2   *Modified rice hull (MRH)*

The modification on the potential low cost sorbent, rice hull was carried out by treating natural rice hull (NRH) with ethylenediamine (EDA) in a ratio of 1.00 g rice hull to 0.02 mole of EDA in a well-stirred water bath at 80 ^{o}C for 2 hours.

2.3   *Sorbates*

Synthetic dye solutions of Reactive Orange 16 (RO16), Basic Blue 3 (BB3), Methylene Blue (MB) and Basic Yellow 11 (BY11) were the sorbates used in this study and all the dye structures were showed in Figure 1. The dyes RO16 (C.I. = 17757, 50 % dye content), BB3 (C.I. = 378011, 25 % dye content), MB (C.I. = M9140, 82 % dye content) and BY11 (C.I. = B7133, 20 % dye content) were used without further purification. All synthetic dyes used in this study were purchased from Sigma-Aldrich Pte. Ltd. (United Stated of America). Standard dyes solutions of 1000 mg L^{-1} were prepared as stock solutions and subsequently diluted when necessary.

2.4   *Batch Experiments*

The batch experiments were carried out by mixing 0.1 g of NSB or MRH with 20.0 mL of dye solutions in a centrifuge tube and shaken on an orbital shaker at 150 revolutions per minute (rpm) for 4 hours unless otherwise stated at room temperature

(25 $\pm$ 2 $^{\circ}$C) The supernatant was analysed for its dye concentration using Perkin Elmer Lambda 35 UV-Vis spectrophotometer. Measurements were made at the wavelength corresponding to the maximum absorption; for RO16, λ_{max} = 494 nm, BB3, λ_{max} = 654 nm, MB, λ_{max} = 664 nm and for BY11, λ_{max} = 412 nm. Dilutions were made when measurements exceeded the linearity of the calibration curves. All the batch experiments were carried out in duplicates ant the results showed were the average.

For the study of the effect of pH, a series of dye solutions with the adjusted pH of 2-10 were prepared. The desired pH was obtained by adding HCl or NaOH (0.1 - 2.0 M). The study of sorption isotherms was carried out using initial dye concentrations from 50 to 300 mg L^{-1}. Samples were withdrawn and analysed for their dye concentrations at predetermined intervals.

2.5   Column Experiments

Column studies were performed using a glass column of 1.0 cm internal diameter. The flow rate of the eluant was controlled by using a peristaltic pump.

2.6   Surface Morphology

The surface morphology of NSB and MRH was studied using SEM which is equipped with energy dispersive X-ray Spectrometer (SEM-EDX)- JEOL JSM-6400.

3. Results and discussion

3.1   Effect of pH

Since the efficiency of sorption process is strongly dependent on pH, which affects the degree of ionization of the sorbate as well as the surface properties of the sorbent, comparative experiments were performed at different pH to show the effect of pH on the sorption process of dyes onto NSB and MRH. In general, the uptake of basic dyes by both NSB and MRH increased as the pH of the solution increased (Figure 2 as representative). It is suggested that at low pH, the carboxyl groups on the surface of the sorbents that were responsible for binding with cationic dyes were

predominantly protonated (-COOH), hence incapable of binding positively charged dyes. With increasing pH, this phenomenon favoured the sorption of cationic dyes due to electrostatic attraction.

3.2   Sorption Isotherm

For all the dyes-NSB systems under studied, Langmuir isotherm was found to provide reasonable fitting (Table 1). However, both Langmuir and Freundlich models appear to provide reasonable fittings for the sorption data of dyes-MRH, irrespective of whether the dye is present singly or in combination (Table 2).

3.3   Column studies

Column studies indicate that breakthrough was bed depth, flow rate and influent concentration dependent. Unusual breakthrough curves were obtained for RO16, with very rapid initial breakthrough followed by complete retention at low flow rate, influent concentration and high bed depth (Figure 3 as representative). The breakthrough curves of basic dyes followed the typical S shape of packed- bed systems (Figure 4 as representative).

3.4   Surface Morphology

From the SEM micrographs, it is observed that both NSB and MRH are non-porous materials, due to the absence of pores and cavities (Figure 5).

4. Conclusion

The results of this study showed that NSB and MRH have the potential to remove dyes in both single and binary dye solutions. The sorption of all dye systems was pH dependent.   Maximum sorption capacities calculated from the Langmuir model were in the range of 14.68 - 67.11 mg g^{-1} in single dye solutions. The breakthrough curves of basic dyes followed the typical S shape of packed- bed systems, however, unusual breakthrough curves were obtained for RO16. A decrease

in the maximum sorption capacity was observed for all the dyes in the binary dye solution and this might be attributed to the competition for the binding sites.

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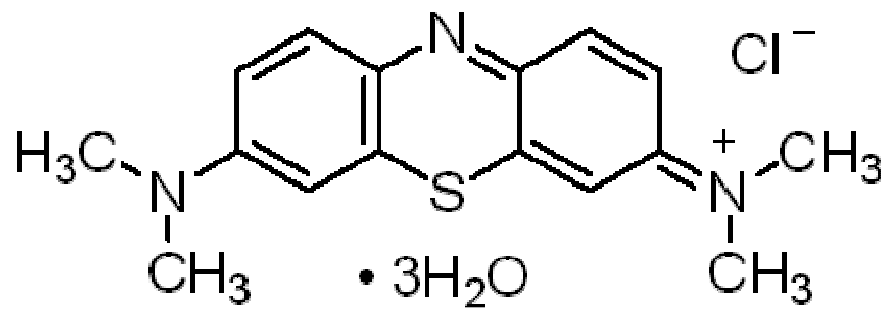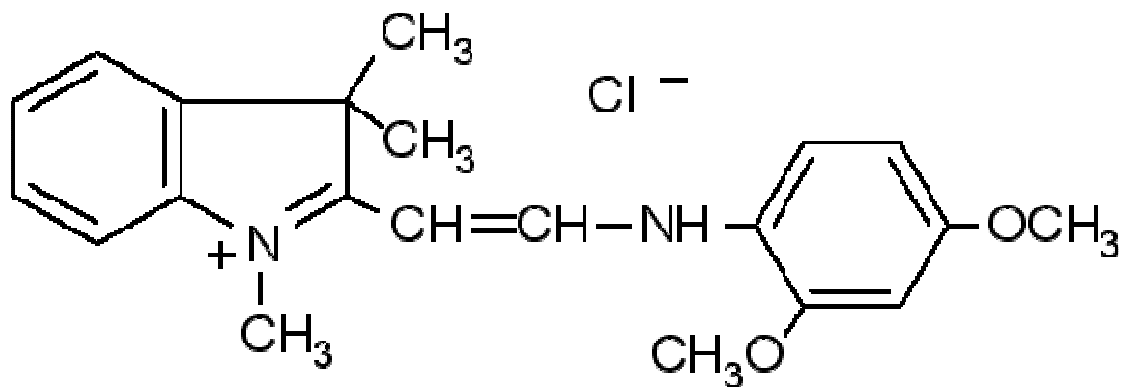**Figure 1: Chemical structure of dyes**
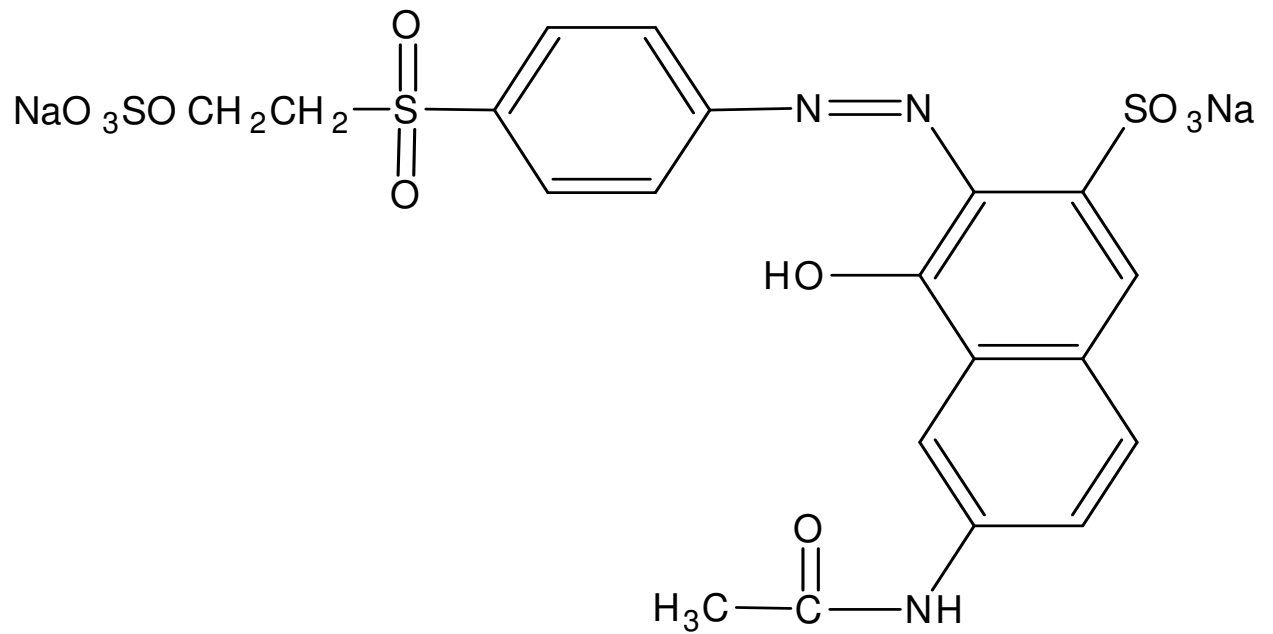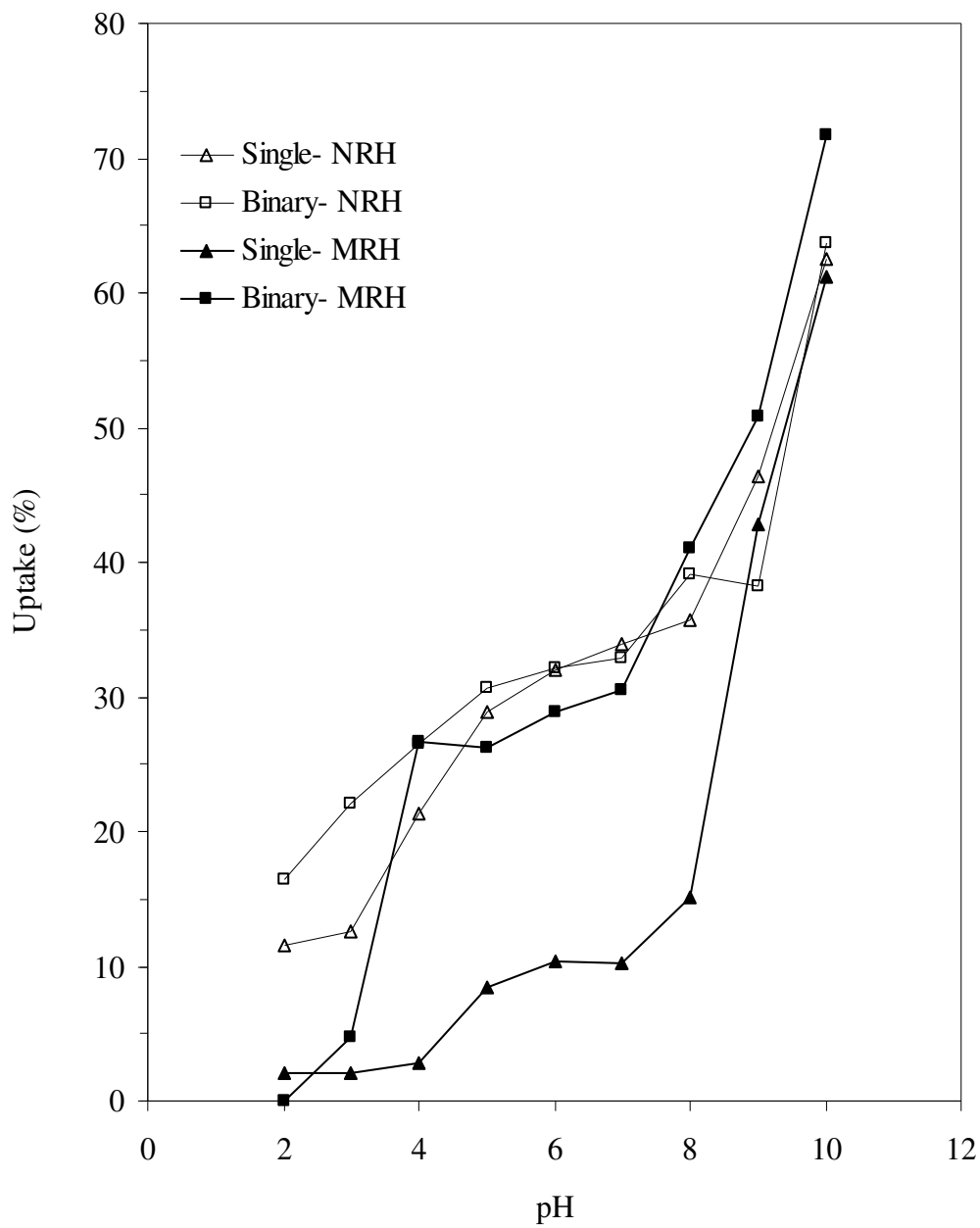

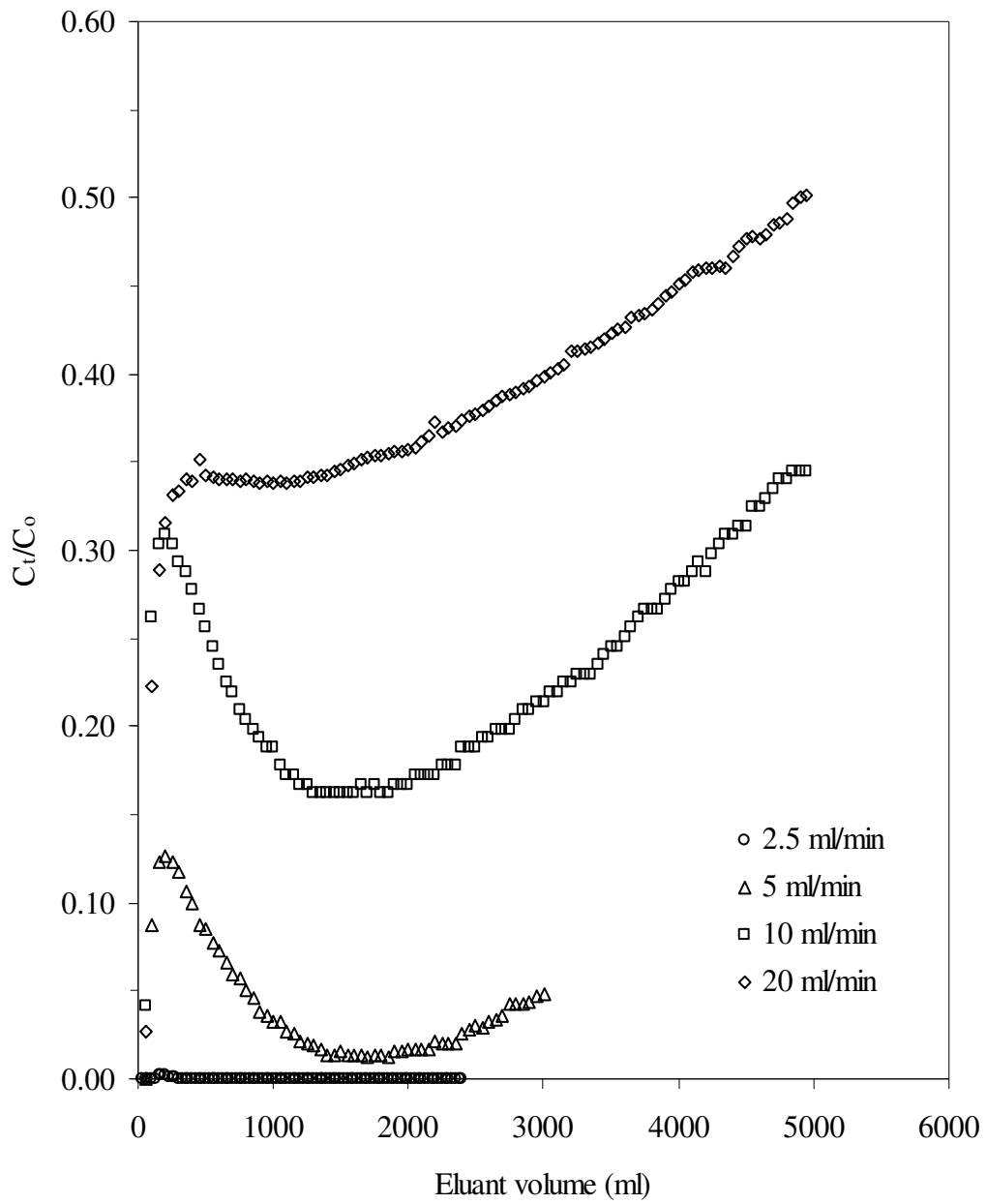Reactive Orange 16
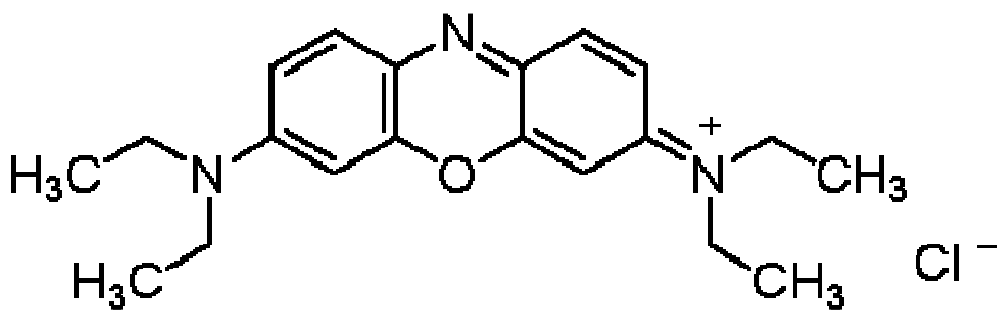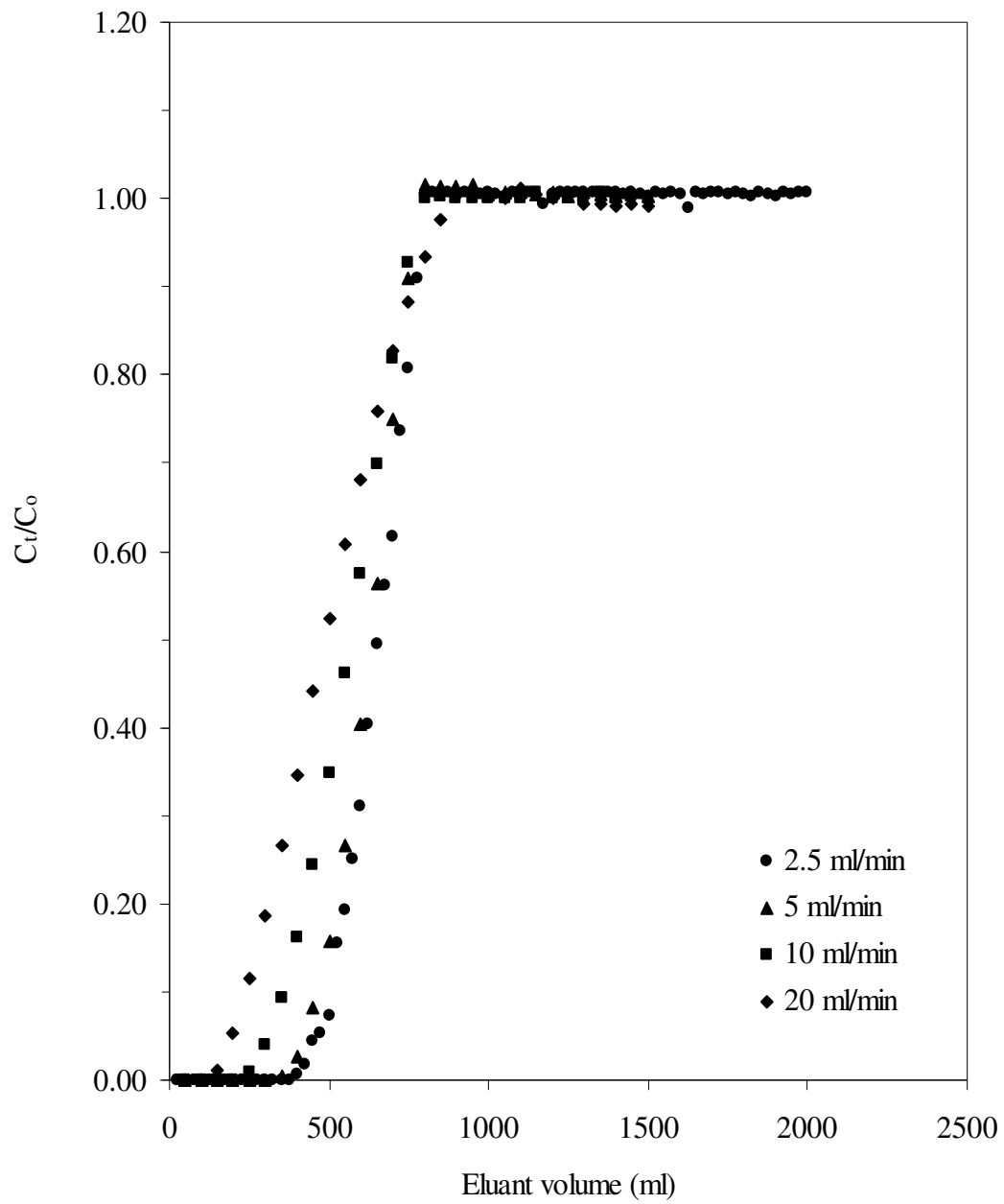

Basic Blue 3

Methylene Blue

Basic Yellow 11

**Figure 2: Effect of pH on the sorption of BB3 by NRH and
MRH from single and binary dye solutions**

Figure 3: Breakthrough curves of RO16 in single dye solutions at different flow rates at a bed depth of 11.5 cm

Figure 4: Breakthrough curves of BB3 in single dye solutions at different flow rates at a bed depth of 11.5 cm

Acc.V Spot Magn Det WD   200 µm
30.0 kV 3.0 100x SE 9.4
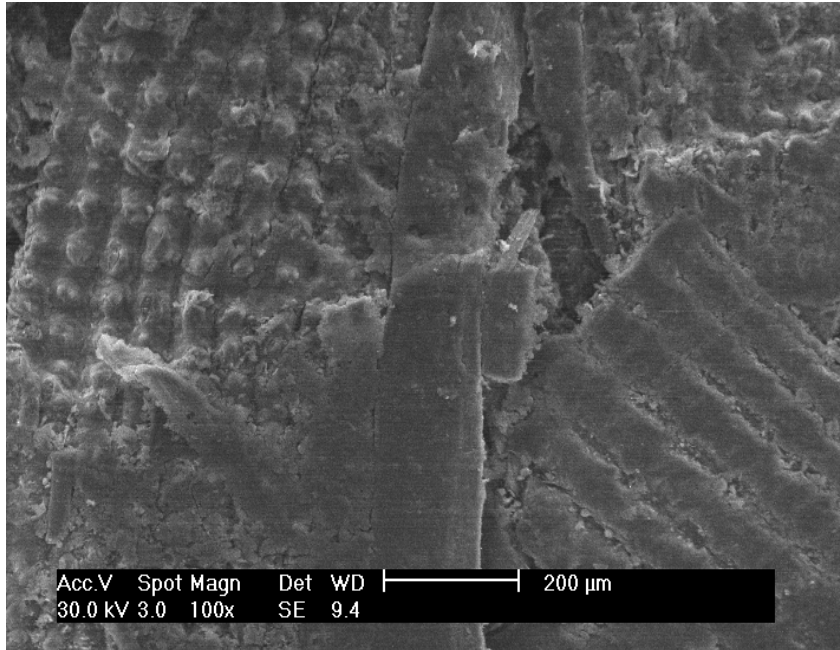
Figure 5: SEM micrograph of MRH

Table 1: Langmuir, Freundlich and BET constants for the sorption of dye-NSB systems

Dyes		q_m (mg g^{-1})	K_a (l mg^{-1})	R^2	K_f	n	R^2	B	R^2
		Langmuir			Freundlich			BET	
BB3 (Single)		23.641	0.077	0.975	7.268	4.554	0.953	-28.821	0.944
MB (Single)		28.249	0.106	0.997	7.231	3.663	0.961	-762.000	0.971
BY11 (Single)		67.110	0.060	0.984	6.276	1.791	0.933	-0.178	0.021
Binary BB3-BY11	BB3	21.834	0.059	0.976	6.077	4.303	0.953	-14.894	0.946
	BY11	18.416	0.039	0.959	4.535	4.120	0.949	-7.065	0.890
Binary MB-BY11	MB	26.178	0.097	0.988	7.065	3.851	0.923	-87.100	0.961
	BY11	21.142	0.028	0.927	5.664	4.760	0.757	5.762	0.781

Table 2: Langmuir and Freundlich constants for the sorption of dyes-MRH systems

Sorbent	Dye	Langmuir			Freundlich		
		N^*	b	R^2	K_f	n	R^2
		(mg/g)	(l/mg)				
NRH	BB3 (single)	13.41	0.41	0.998	3.72	0.35	0.959
	BB3 (binary)	14.12	0.25	0.975	3.80	0.35	0.932
MRH	BB3 (single)	3.29	0.10	0.956	0.73	3.02	0.939
	RO16 (single)	24.88	0.10	0.991	4.90	2.67	0.992
	BB3 (binary)	14.68	0.03	0.941	0.72	0.63	0.929
	RO16 (binary)	60.24	0.03	0.995	5.89	2.19	0.993