The Removal of Basic and Reactive Dyes Using Quartenised Sugar Cane Bagasse

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Abstract: *Sugar cane bagasse, an agricultural by-product, acts as an effective sorbent for the removal of both basic and reactive dyes from aqueous solution after modification by the quartenisation method. Batch adsorption studies were investigated for the removal of Basic Blue 3 (BB3) and Reactive Orange 16 (RO16). The sorption of dye solutions was strongly affected by the pH and the optimum pH is in the range of 6–8. The kinetics of dye sorption processes fit a pseudo-second order kinetic model. The adsorption isotherms fitted well into both the Langmuir and Freundlich equations. Results indicated that according to the Langmuir isotherm, the maximum sorption capacities are 37.59 and 34.48 mg g^{-1} for BB3 and RO16, respectively. The effects of agitation rate, temperature, and sorbent dosage on the dye sorptions were investigated.*

Keywords: sugar cane bagasse, quartenisation, sorption, reactive dyes, basic dyes

1. INTRODUCTION

Dyes are a type of organic compounds that can provide bright and lasting colour to other substances.[1] There are more than 100,000 dyes available commercially, which are specifically designed to resist fading upon exposure to sweat, light, water, and oxidizing agents and, as such, are very stable and difficult to degrade.[2] Synthetic dyes have been increasingly used in the textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals, and food industries. These usually have complex aromatic molecular structures that make them more stable and less biodegradable.[1,3] The coloured wastewater discharged into environmental bodies of water is not only aesthetically unpleasant but also interferes with light penetration and reduces photosynthetic action. Many dyes or their metabolites have toxic as well as carcinogenic, mutagenic, and teratogenic effects on aquatic life and humans.[4] Hence, the removal of dyes from wastewater is essential to prevent continuous environmental pollution.

Some biological and physical/chemical methods have been employed for removing dye from industrial effluents, such as coagulation, membrane separation, electrochemical oxidation, ion exchange, and adsorption. Among these, adsorption currently appears to offer the best potential for overall treatment and it is found to be an efficient and economically cheap process for removing dyes using various adsorbents.[5] Activated carbon is known to be a highly effective adsorbent; however, its high operating costs with the need of regeneration after each sorption cycle hamper its large-scale application.[6,7] Therefore, in recent years, considerable attention has been devoted to the study of different types of low-cost materials as alternative adsorbents in order to remove aqueous phase pollutants, where examples are zeolite, coconut husk, wheat straw, corncobs, and barley husks. Agricultural by-products are considered to be low-value products, which are arbitrarily discarded or burned, resulting in resource loss and environmental pollution. Generally, sorption capacity of crude agricultural by-products is low.[8] These materials are chemically modified in order to enhance their sorption capacities and, by extension, their usefulness in the treatment of wastewater. These materials, in general, possess high sorption capacities towards either positively or negatively charged dye molecules, but not both. However, a mixture of different types of dyes is usually found in the industrial effluent. Hence there is a need to have sorbents capable of removing different types of dyes either singly or simultaneously.[9]

In this study, the feasibility of quartenised sugar cane bagasse as an adsorbent for the removal of a cationic dye, BB3, and an anionic dye, RO16, from single and binary dye solutions was investigated. Batch adsorption studies were performed under various parameters such as the pH, initial concentration and contact time, agitation rate, temperature, and sorbent dosage.

2.   EXPERIMENTAL

2.1   Preparation of the Sorbent

The collected sugar cane bagasse was washed several times to remove dust. It was then boiled in water for one hour to remove the sugar residue in the bagasse. It was washed again with tap water and subsequently rinsed several times with distilled water. The cleaned sugar cane bagasse was dried overnight in an oven at $50^{o}C$. The dried bagasse was ground, sieved through a 1 mm sieve, and labelled as natural sugar cane bagasse (NSB).

Quartenisation was carried out according to the method reported by Laszlo[10], with a minor modification. The NSB was soaked in 5 M NaOH for 30 min. The sorbent was then mixed with quartenary ammonium chloride

($C_6H_{15}Cl_2NO$, 65% w/w in water), which was adjusted to a pH of 5.3. The mixture was then heated at $60^{\circ}C$–$70^{\circ}C$ for 4 h in an oven with intermittent stirring. It was then rinsed with distilled water and suspended in dilute HCl with a pH of 2 for 30 min. After washing with distilled water until neutral, the modified sorbent was dried in an oven overnight at $50^{\circ}C$. The quartenised sugar cane bagasse (QSB) was used as a sorbent for subsequent dye removal studies.

2.2   Preparation of the Sorbates

For the study of dye sorptions of QSB, synthetic dye solutions of BB3 and RO16 were used. Figure 1 shows the structures of the dyes. The cationic dye, BB3 (25% dye content, Sigma Aldrich), and the anionic dye, RO16 (50% dye content, Sigma Aldrich), were used without further purification. Dye stock solutions of 2000 mg l^{-1} were prepared by dissolving accurately the dye powder in distilled water and taking the percentage by weight of the dye content into consideration. The experimental solutions were obtained by diluting the dye stock solutions when necessary.

2.3   Comparative Study of Dye Sorptions by NSB and QSB

In this study, the dye sorption capacities of NSB and QSB for BB3 and RO16 were compared in both single and binary dye solutions. 0.10 g of each sorbent was agitated in 20 ml of 100 mg l^{-1} single and binary dye solutions at 150 rpm for 4 h.
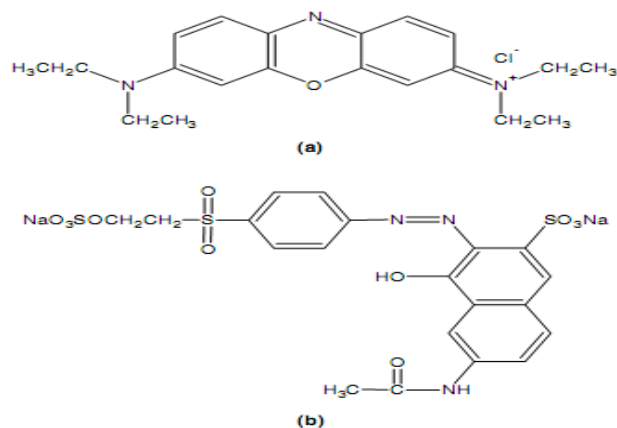

Figure 1: The structures of (a) BB3 and (b) RO16.

2.4   Batch Experiment Study

Sorption experiments were carried out by agitating 0.10 g of sorbent in 20 ml of 100 mg l^{-1} dye solution in a centrifuge tube at 150 rpm on an orbital shaker for 8 h at room temperature. The sorbent-sorbate mixture was subsequently centrifuged at 3.0×10^3 rpm for phase separation and then withdrawn. All of the batch experiments were conducted in duplicate and the results are the means with a relative standard deviation of less than 5%. A control without sorbent was simultaneously used to ensure that sorption in the duplicate samples was by the sorbent and not by the wall of the container. Dye concentrations in the supernatant solutions were analysed using a Shimadzu UV-1650 PC UV-visible Spectrophotometer. The absorbance was measured at the maximum wavelengths of the dyes: λ_{max} = 654 nm for BB3 and λ_{max} = 494 nm for RO16. The dye solutions were diluted when measurements of the absorbance exceeded the linearity of the calibration curve.

The effects of various parameters affecting the sorption were determined during batch experiments. The effect of the pH on dye sorption was studied by shaking 0.10 g of the sorbent in 20 ml of dye solutions for 4 h. A series of 100 mg l^{-1} single and binary dye solutions of BB3 and RO16 were adjusted to an initial pH range of 2–10 by adding dilute HCl or NaOH.

The study of the effect of contact time was carried out by varying the dye concentrations ranging from 50 to 150 mg l^{-1} of BB3 and RO16 for both single and binary dye solutions. The samples were withdrawn at increasing contact time intervals ranging from 5 min to 8 h. From this study, the kinetics of adsorption was determined. Sorption isotherms were obtained by varying the dye concentrations from 5 to 150 mg l^{-1} of single and binary dye solutions. The effect of the agitation rate was studied by varying the rate from 50 to 250 rpm using 100 mg l^{-1} dye solutions.

The effect of the sorbent dosage was investigated by varying the amount of QSB from 0.05 to 0.15 g. The sorption studies were also carried out at different temperatures, i.e., $26^{o}C$, $30^{o}C$, $40^{o}C$, $50^{o}C$, $60^{o}C$, $70^{o}C$, and $80^{o}C$, to determine the effect of temperature and to evaluate the sorption thermodynamic parameters. A water bath with a shaking mechanism was used to keep the temperature constant.

3.   RESULTS AND DISCUSSION

3.1   Comparative Study of Dye Sorption by NSB and QSB

Table 1 shows the comparative removal of BB3 and RO16 by NSB and QSB in both single and binary dye solutions. From the observation, the cationic BB3 dye was adsorbed by NSB effectively, with 77.65% and 82.16% in single and binary dye solutions, respectively. The composition of NSB that includes cellulose, hemicelluloses, and lignin contains a large number of hydroxyl groups.[11,12] The BB3 dye molecules dissociate into positively charged components and adsorb on the binding sites of NSB such as hydroxyl groups. However, the removal of RO16 by NSB was only 3.11% and 7.27% in single and binary systems, respectively. The low sorption capacity of RO16 by NSB was due to the coulombic repulsion between the anionic dye molecules and the negatively charged surface of the sugar cane bagasse.[9]

The QSB showed sorption capability towards both basic (BB3) and reactive (RO16) dyes. The percentage of dye removal of BB3 and RO16 in single dye solution by QSB was 16.52 and 76.80, respectively. The hydroxyl and (Si–O–N$^+$–C) groups on the surface of QSB contribute to the binding sites for the adsorption of differently charged dyes.[13] The binary dye systems showed a higher sorption process with 34.32% of BB3 and 83.33% of RO16 removed by QSB. The sorption of binary dye molecules by QSB is based on the electrostatic attraction as postulated below:

$$Si - O - N^+ - C \ + \ SO_3^- - Re - SO_3^- \ + \ BB^+ \longrightarrow$$
$$Si - O - N^+C - SO_3^- - Re - SO_3^- - BB^+ \tag{1}$$
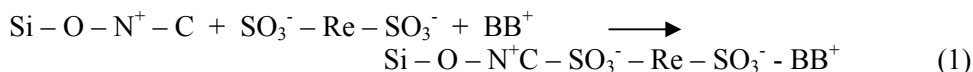
where $SO_3^- - Re - SO_3^-$ represents the structure of RO16 and BB^+ represents the BB3 molecule. According to the conversion scheme above, one surface group of QSB will bind with one binary dye molecule of RO16 and BB3. This resulted in an enhancement of the removal of binary dye molecules.

Table 1: The comparative study of dye sorption by NSB and QSB.

Sorbent	% Dye Removal			
	BB3 (single)	RO16 (single)	BB3 (binary)	RO16 (binary)
NSB	77.65	3.11	82.16	7.27
QSB	16.52	76.8	34.32	83.33

3.2   Effect of the pH

Figure 2 shows the effect of the initial pH of the dye solutions towards the adsorption of BB3 and RO16 by QSB in both single and binary dye solutions. The pH value of the solution is an important process-controlling parameter in the adsorption of dye. The initial pH values of the dye solutions affect the surface charge of the adsorbent and thus the adsorption of the charged dye groups on it.[14] For a single BB3 dye solution, the percentage removal of dye increased from 11.11 to 72.32 with an increase in the pH from 2–10. A similar trend was observed for the BB3 binary system with a slightly higher removal of dye compared to the single dye system. At an acidic pH condition, the hydroxyl and carboxyl groups on the surface of the sugar cane bagasse are protonated and they inhibit the binding of the BB3 dye cation. The excess H^+ ions compete with the dye cations for the adsorption sites. With an increasing pH of the dye solution, the surface groups will be deprotonated resulting in an increase of negatively charged sites that favour the sorption of the cationic dye (BB3) due to electrostatic attraction.[9] However, the acidic pH system showed good adsorption behaviour for the RO16 dye solution. The removal of RO16 increased from 28.62% to 97.14% with a decrease of the pH from 10 to 2. As the pH of the system decreases, the protonated surface groups ($Si-O-N^+H_2-C$) facilitate the sorption of the negatively charged dye. The number of positively charged sites increases resulting in an increase of binding sites for anionic dye molecules (RO16).[15] A lower percentage of the removal of RO16 in alkaline pH may be due to the presence of excess OH^- ions competing with the dye anions for the
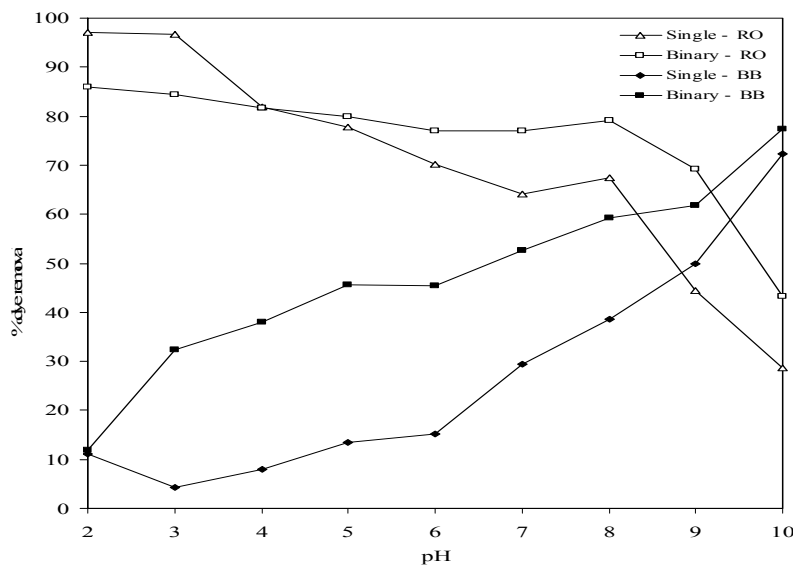

Figure 2: The effect of pH on dye sorption by QSB.

adsorption sites. The electrostatic repulsion between the anionic dye and the negatively charged sites contribute to the decreased uptake of RO16.[16,17] The binary system showed a similar trend for dye removal. Therefore, it is suggested that the optimum pH for the removal of both BB3 and RO16 is between 6 and 8.

3.3 Effect of Initial Concentration and Contact Time

Figure 3 shows the influence of the initial concentration of the dye solutions on the adsorption by QSB in a single system. The percentage of dye removal decreased with increasing initial dye concentration, although the actual amount of dye adsorbed per unit mass of adsorbent increased. In both single and binary dye systems, the adsorption of dyes was rapid during the initial stages of the sorption processes, followed by a gradual process. In the process of dye adsorption, the dye molecules have to first encounter the boundary layer effect, then adsorb from the surface and, finally, they have to diffuse into the porous structure of the adsorbent. This phenomenon will take a relatively longer contact time.[16] For BB3 dye sorption, equilibrium was attained at 120 min, independent of the initial dye concentration. The initial rapid phase may also be due to the increased number of vacant sites available at the initial stage. Consequently there exists an increased concentration gradient between the adsorbate in solution and the adsorbate in the adsorbent.[5] For a single RO16 of 50 mg l^{-1}, the dye removal was up to above 85% after 180 min, while for the binary system more than 90% of the dyes were removed.
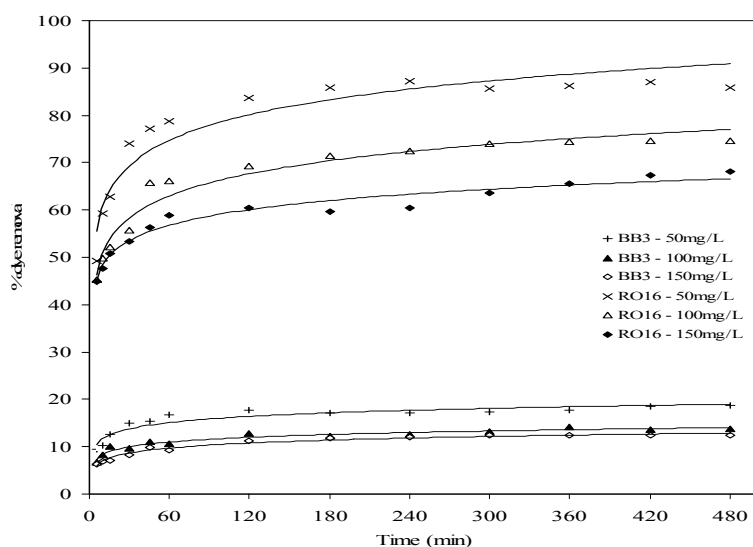

Figure 3: The effect of initial concentration and contact time on single BB3 and RO16 by QSB.

In order to investigate the adsorption processes of BB3 and RO16 by QSB pseudo-first-order and pseudo-second-order kinetic models were used with equations as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{(pseudo-first-order)} \tag{2}$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad \text{(pseudo-second-order)} \tag{3}$$

where q_e is the amount of dye sorbed at equilibrium (mg g^{-1}), q_t is the amount of dye sorbed at time t (mg g^{-1}), k_1 is the rate constant of the pseudo-first-order sorption (min^{-1}), h ($k_2 q_e^2$) is the initial sorption rate (mg g^{-1} min^{-1}), and k_2 is the rate constant of the pseudo-second-order kinetics (g mg^{-1} min^{-1}).

The values of k_1 and k_2, along with the correlation coefficients for the pseudo-first-order and pseudo-second-order models, are shown in Table 2. Furthermore, the pseudo-second-order model plots (t/q_t versus t) of BB3 and RO16 in a single system are shown in Figure. 4. The correlation coefficients are closer to unity for the pseudo-second-order kinetics than for the pseudo-first-order kinetic model. Therefore, the sorption is more favourable in the pseudo-second-order kinetic model, which is based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through the sharing or exchange of electrons between the sorbent and the sorbate.[18]

3.4   Sorption Isotherms

The sorption isotherms of BB3 and RO16 were analysed using the Langmuir and Freundlich equations. The Langmuir equation is based on the assumption that maximum sorption corresponds to a saturated monolayer of sorbate molecules on the sorbent surface. The energy of sorption is constant and there is no transmigration of the sorbate in the plane of the surface.[4]

The Langmuir equation is expressed as:

$$\frac{C_e}{N_e} = \frac{1}{N^* b} + \frac{C_e}{N^*} . \tag{4}$$

Table 2: The values of k_1, k_2, and the correlation coefficients of the pseudo-first-order and pseudo-second-order models for the sorption of dyes in single and binary solutions.

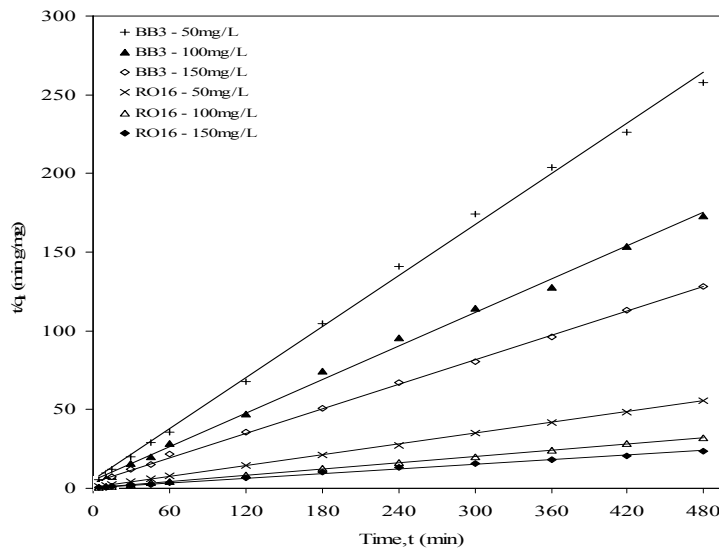| C_0 (mg l^{-1})	Pseudo-first-order model		Pseudo-second-order model	
	R^2	k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min^{-1})
BB3 (single)				
50	0.6324	5.07 x 10^{-3}	0.9980	5.80 x 10^{-2}
100	0.7317	6.68 x 10^{-3}	0.9972	2.78 x 10^{-2}
150	0.9752	19.80 x 10^{-3}	0.9992	2.00 x 10^{-2}
RO16 (single)				
50	0.9607	21.88 x 10^{-3}	0.9998	2.41 x 10^{-2}
100	0.8573	14.51 x 10^{-3}	0.9998	0.88 x 10^{-2}
150	0.6739	3.68 x 10^{-3}	0.9970	0.47 x 10^{-2}
BB3 (binary)				
50	0.9356	9.90 x 10^{-3}	0.9999	6.10 x 10^{-2}
100	0.9563	9.67 x 10^{-3}	0.9997	1.91 x 10^{-2}
150	0.9757	12.44 x 10^{-3}	0.9999	2.20 x 10^{-2}
RO16 (binary)				
50	0.9445	11.05 x 10^{-3}	0.9999	2.20 x 10^{-2}
100	0.9607	12.44 x 10^{-3}	0.9999	0.68 x 10^{-2}
150	0.8214	9.44 x 10^{-3}	0.9994	0.39 x 10^{-2}

Figure 4: Pseudo-second-order kinetics of BB3 and RO16 in single dye solutions.

The Freundlich isotherm is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces, and it is represented by the equation below:

$$\log N_e = \frac{\log C_e}{n} + \log K_f \; ; \tag{5}$$

where C_e is the equilibrium concentration of the dye (mg l^{-1}), N_e is the amount of dye sorbed at equilibrium (mg g^{-1}), N^* is the maximum sorption capacity (mg g^{-1}), b is the constant related to the energy of the sorbent (l mg^{-1}), n is the Freundlich constant for intensity, and K_f is the Freundlich constant for sorption capacity. The coefficients of the isotherm models for the sorption of dyes are shown in Table 3.

The linear plots of C_e/N_e versus C_e (Fig. 5) suggest the applicability of the Langmuir model showing the formation of monolayer coverage of the dye molecules at the outer surface of the adsorbent. Figure 6 shows that the sorption fitted the Freundlich isotherm well with higher coefficients compared to Langmuir isotherms. The agreement of both isotherms has been reported previously.[9,19]

Table 3: The Langmuir and Freundlich constants for the sorption of dyes in single and binary solutions.

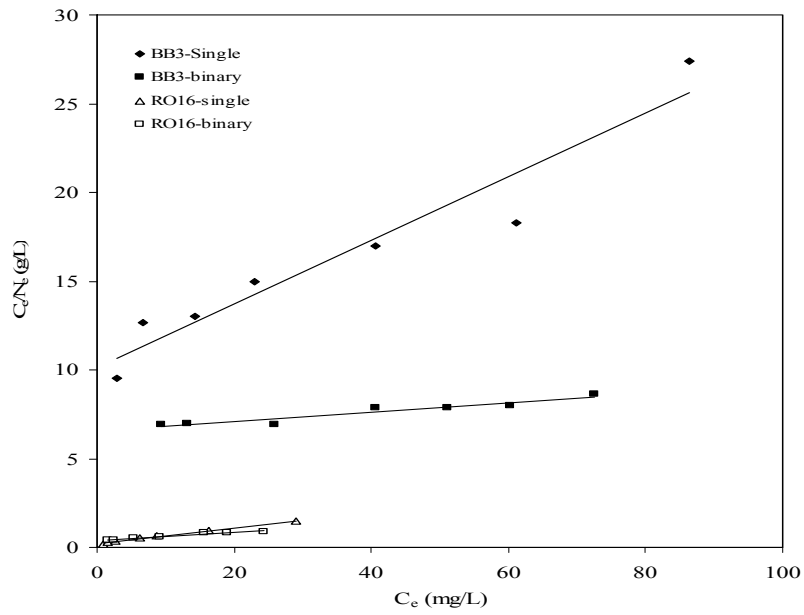| Dye	Langmuir			Freundlich		
	N^* (mg g^{-1})	b (l mg^{-1})	R^2	K_f	n	R^2
BB3 (single)	5.58	0.02	0.925	0.14	0.74	0.984
RO16 (single)	22.73	0.19	0.993	4.68	0.46	0.987
BB3 (binary)	37.59	0.01	0.913	0.06	0.90	0.997
RO16 (binary)	34.48	0.07	0.937	3.03	0.64	0.993

Figure 5: Langmuir isotherms for the sorption of BB3 and RO16 from single and binary
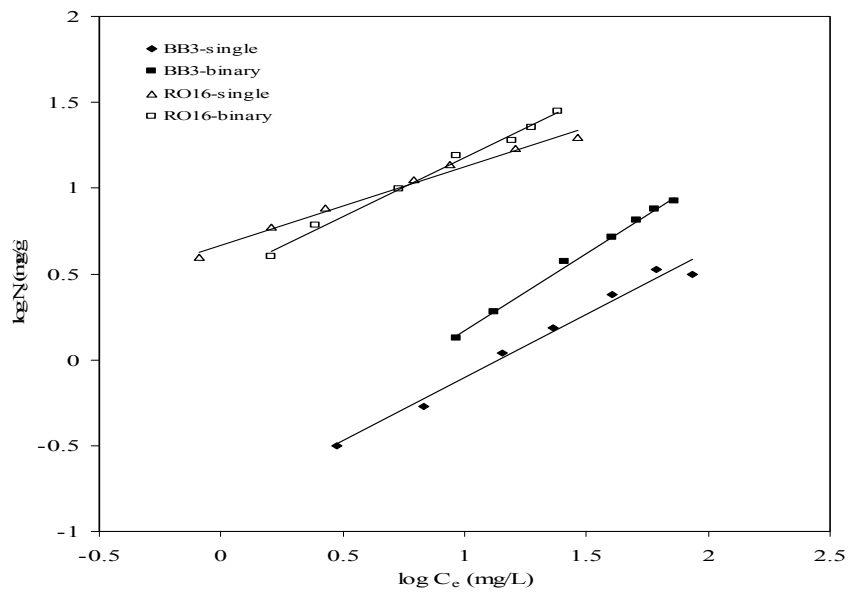dye solutions.

Figure 6: The Freundlich isotherm for the sorption of BB3 and RO16 from single and
binary dye solutions.

3.5   Effect of Agitation Rate

Figure 7 shows the influence of the agitation rate on the sorptions of BB3 and RO16 by QSB. The experiments were carried out at agitation rates of 50, 150, and 250 rpm by varying the contact time from 5 min to 8 h. From the results, the percentage removal of RO16 was found to increase with increasing agitation rate. Increasing agitation rate decreases the film resistance to the mass transfer surrounding the sorbent particles, thus increasing the sorption of dye molecules onto the sorbent.[9] However, the sorption of BB3 was not affected significantly by the agitation rate. For binary dye systems a similar trend as that seen in the single dye system was obtained.

3.6   Effect of Temperature

Figure 8 shows the effect of temperature on the sorptions of BB3 and RO16 in single and binary dye systems. Adsorption of BB3 by QSB increased with increasing temperature from $26^{o}C$ to $80^{o}C$, indicating an endothermic process. The increment of adsorption may be due to the increased rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles. An increased number of molecules may acquire sufficient energy to undergo an interaction with active sites at the surface.[20] However, the adsorption of RO16 decreased from 77.52% to 70.48% for a single dye solution, indicating that the sorption of RO16 was favourable at lower temperatures. Similar observations were obtained for binary systems. This may due to the enhancement of the relative escaping tendency of RO16 molecules from the solid phase to the bulk phase as the temperature increased.[21]
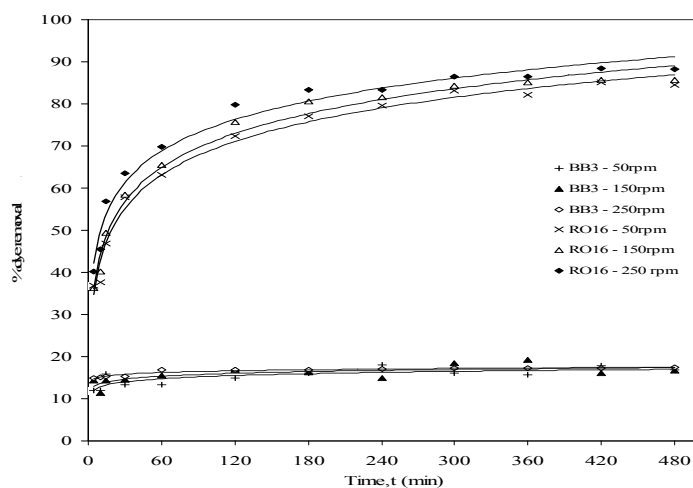

Figure 7: The effect of the agitation rate on the sorption of single BB3 and RO16 dye solutions by QSB.

3.7   Effect of Sorbent Dosage

The effect of sorbent dosage on the removal of dyes is shown in Table 4. Along with the increase of sorbent dosage from 0.05 to 0.15 g, the percentage of dye removal increased. This is due to the increase of active sites for adsorption of dye molecules with increasing sorbent dosage. The sorption equilibria of the dyes were reached at 0.10 g and the removal of dyes remained almost invariable above this dosage. Therefore, 0.10 g appears to be the optimum sorbent dosage.
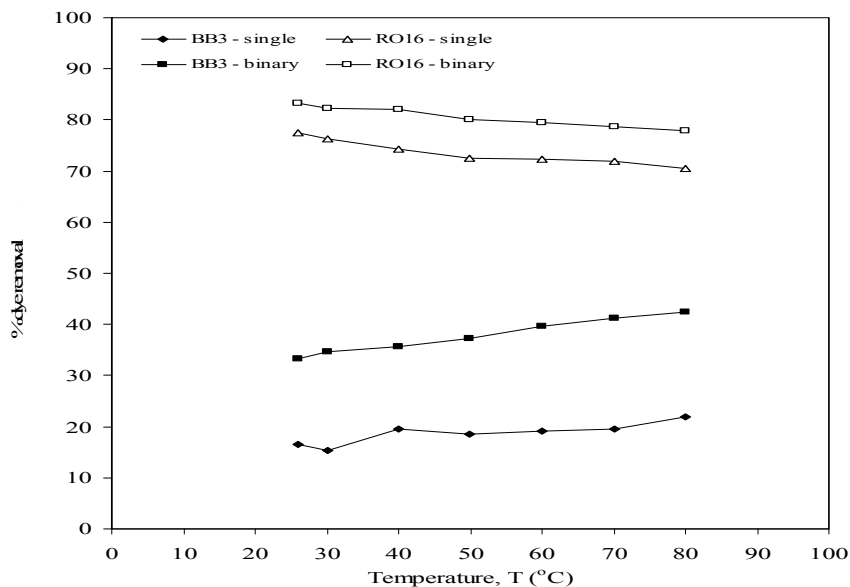

Figure 8: The effect of temperature on the sorption of single and binary BB3 and RO16 dyes by QSB.

Table 4: The effect of sorbent dosage on the removal of dyes.

Sorbent dosage (g)	% Dye Removal			
	BB3 (single)	RO16 (single)	BB3 (binary)	RO16 (binary)
	(Co = 100 mg l^{-1})			
0.05	9.14	57.80	34.09	74.14
0.08	8.63	76.62	36.37	82.19
0.10	11.68	84.14	40.91	87.32
0.12	16.83	86.39	43.43	89.07
0.15	19.30	92.67	45.71	90.93

4. CONCLUSION

This study has shown that the QSB is an effective sorbent for the removal of BB3, a basic dye, and RO16, a reactive dye, from aqueous solution either in single or binary dye systems. The optimum pH for removal of both BB3 and RO16 is between 6–8. The study showed that the adsorption of the dyes by the sorbent fitted the pseudo-second-order model better than the pseudo-first-order model. Furthermore, the sorption isotherm indicates that the sorption of dyes is applicable for both the Langmuir and Freundlich isotherms. The sorption of RO16 increased with increasing agitation rate, while the sorption of BB3 has a minimal effect. The sorption of BB3 was favourable with increasing temperature, while the sorption of RO16 was favourable at lower temperatures. The optimum sorbent dosage for the dye sorption was 0.10 g.

5. ACKNOWLEDGEMENTS

6. REFERENCES

1. Gong, R., Sun, Y., Chen, J., Liu, H. & Yang, C. (2005). Effect of chemical modification on dye adsorption capacity of peanut hull. *Dyes Pigments*, 67, 175–181.
2. Nigam, P., Armour, G., Banat, I.M., Singh, D. & Marchant, R. (2000). Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues. *Bioresource Technol.*, 72, 219–226.
3. Mane, V.S., Mall, I.D. & Srivastava, V.C. (2007). Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution. *Dyes Pigments*, 73, 269–278.
4. Gong, R., Jin, Y., Chen, J., Hu, Y. & Sun, J. (2007). Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw. *Dyes Pigments*, 73, 332–337.
5. Kavitha, D. & Namasivayam, C. (2007). Recycling coir pith, an agricultural solid waste, for the removal of procion orange from wastewater. *Dyes Pigments*, 74, 237–248.

6.   Figueiredo, S.A., Loureiro, J.M. & Boaventura, R.A. (2005). Natural waste materials containing chitin as adsorbents for textile dyestuffs: Batch and continuous studies. *Water Res*., 39, 4142–4152.

7.   Robinson, T., Chandran, B. & Nigam, P. (2002). Effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption. *Bioresource Technol*., 85, 119–124.

8.   Gong, R., Jin, Y., Sun, J. & Zhong, K. (2008). Preparation and utilization of rice straw bearing carboxyl groups for removal basic dyes from aqueous solution. *Dyes Pigments*, 76, 519–524.

9.   Ong, S.T., Lee, C.K. & Zainal, Z. (2007). Removal of basic and reactive dyes using ethylenediamine modified rice hull. *Bioresource Technol*., 98, 2792–2799.

10.   Laszlo, J.A. (1996). Preparing an ion exchange resin from sugar cane bagasse to remove reactive dye from wastewater. *Text. Chem. Color*, 28, 13–17.

11.   O'Connell, D.W., Birkinshaw, C. & O'Dwyer, T.F. (2008). Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technol.*, 99, 6709–6724.

12.   Jústiz-Smith, N.G., Virgo, G.J. & Buchanan, V.E. (2008). Potential of Jamaican banana, coconut coir and bagasse fibres as composite materials. *Mater. Charact*., 59, 1273–1278.

13.   Banerjee, S.S., Joshi, M.V. & Jayaram, R.V. (2006). Effect of quartenary ammonium cations on dye sorption to fly ash from aqueous media. *J. Colloid Interf. Sci*., 303, 477–483.

14.   Özacar, M. & Şengil, İ.A. (2003). Adsorption of reactive dyes on calcined alunite from aqueous solutions. *J. Hazardous Mater*., B98, 211–224.

15.   Chiou, M.S. & Li, H.Y. (2003). Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere,* 50, 1095–1105.

16.   Malik, P.K. (2003). Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of Acid Yellow 36. *Dyes Pigments*, 56, 239–249.

17.   Tor, A. & Cengeloglu, Y. (2006). Removal of congo red from aqueous solution by adsorption onto acid activated red mud. *J. Hazardous Mater*., B 138, 409–415.

18.   Ho, Y.S. & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochem*., 34, 451–465.

19.   Lata, H., Garg, V.K. & Gupta, R.K. (2007). Removal of a basic dye from aqueous solution by adsorption using *Parthenium hysterophorus* : An agricultural waste. *Dyes Pigments*, 74, 653–658.

20. Özdemir, Y., Doğan, M. & Alkan, M. (2006). Adsorption of cationic dyes from aqueous solutions by sepiolite. *Micropor Mesopor Mat.*, 96, 419–427.
21. Ho, Y.S. & McKay, G. (2003). Sorption of dyes and copper ions onto biosorbents. *Process Biochem.*, 38, 1047–1061.