

## REMOVAL OF BASIC BLUE 3 AND REACTIVE ORANGE 16 BY ADSORPTION ONTO QUARTENIZED SUGAR CANE BAGASSE

(Penyingkiran Basik Biru 3 Dan Reaktif Oren 16 Dengan Penjerapan Ke Atas Sisa Tebu Yang Diquarternasi)

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### Abstract

The effectiveness of using sugar cane bagasse, an agricultural by-product, as a sorbent to remove basic and reactive dyes from aqueous solution was studied. The quartenized sugar cane bagasse (QSB) is capable in removing both Basic Blue 3 (BB3) and Reactive Orange 16 (RO16). The sorption of dye solutions was strongly affected by pH, where the optimum pH is 6-8. The kinetics of the dye sorption processes fitted a pseudo-second order kinetic model. Results indicated that the adsorption isotherms fitted well into both the Langmuir and Freundlich isotherms. The removal of BB3 was favourable at higher temperature, indicating that the sorption process was endothermic. On the other hand, sorption of RO16 on QSB was more favourable at low temperature.

**Keywords:** Sugar cane bagasse; quartenization; sorption; reactive dyes; basic dyes

### Abstrak

Keberkesanan menggunakan sisa tebu, produk sampingan pertanian, sebagai penjerap untuk menyingkirkan pewarna basik dan reaktif daripada larutan telah dikaji. Sisa tebu yang dikuarternasi (QSB) adalah berupaya untuk menyingkirkan kedua-dua pewarna Basik Biru 3 (BB3) dan Reaktif Oren 16 (RO16). Penjerapan pewarna adalah dipengaruhi oleh pH, di mana pH optimum ialah 6-8. Kinetik proses erapan pewarna didapati mengikut model kinetik tertib pseudo-kedua. Keputusan eksperimen menunjukkan bahawa isoterma penjerapan mematuhi kedua-dua isoterma Langmuir dan Freundlich. Penyingkiran BB3 adalah lebih baik pada suhu tinggi, menunjukkan proses erapan adalah endotermik. Manakala erapan RO16 ke atas QSB adalah lebih digemari pada suhu rendah.

**Kata kunci:** Sisa tebu, quartenisasi; erapan; pewarna reaktif; pewarna basik

### Introduction

Dyes or dyestuffs are essentially coloured substances capable of imparting their colour to other substances. Today, the vast majority of dyes produced synthetically. Due to ever-growing demands in textiles, synthetic organic dyes are widely used for dyeing textile fibers such as cotton and polyester [1]. Besides textile industry, synthetic dyes have been increasingly used in the leather, paper, rubber, plastics, cosmetics, pharmaceuticals and food industries. The dyes are used to colour their products and the residual are discharged into the environment, particularly aquatic environment. Synthetic dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade [2]. Thus, the removal of colour from wastewater becomes a challenging problem.

Removal of the contaminants from wastewater has been extensively studied using various physicochemical and biological techniques. Adsorption is one of the most effective methods and this process has aroused considerable interest during recent years. It is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the decolouration process [3]. Although activated carbon is the most effective adsorbent for adsorption of dye, its high operating costs with the need of regeneration after each sorption cycle hamper its large-scale application [4,5]. Hence there is an increasing need for equally effective but cheaper materials as alternative adsorbents in order to remove the pollutants from wastewaters. In this context, agricultural by-products have shown its potential as a low-cost sorbent and they are usually being modified chemically in order to enhance their sorption capacity towards dye [6-8]. Generally, these materials possess high sorption capacities for either positively or negatively charged dye molecules, but

not both. However, a mixture of different types of dyes is usually found in the industrial effluents. Hence there is a need to have sorbents capable of removing different types of dyes either singly or simultaneously [9].

Sugar cane bagasse appears as a biomass natural fibre. Sugar cane bagasse is referred to fibre remaining after the extraction of the sugar-bearing juice from sugar cane and appears as the end product of the sugar cane mill. The natural cellulosic fibre contains approximately 13.00 % of lignin content, 30.27 % of cellulose content, and 56.73 % of hemicellulose content [10]. Cellulose is a large, linear-chain polymer with a large number of hydroxyl groups. Functional groups may be attached to these hydroxyl groups through a variety of chemistries [11]. In this study, the feasibility of quartenized sugar cane bagasse as an adsorbent for removal of a cationic dye Basic Blue 3 (BB3) and an anionic dye Reactive Orange 16 (RO16) from single and binary dye solutions was investigated.

## Experimental

### Sorbents

Sugar cane bagasse was washed several times to remove dust and dirt. It was then boiled in boiling water for 1 hour to remove the sugar residue in the bagasse. The bagasse was washed again with tap water and subsequently rinsed several times with distilled water. The cleaned sugar cane bagasse was dried overnight, ground, and labeled as natural sugar cane bagasse (NSB). Quartenization of sugar cane bagasse was carried out according to the method reported by Laszlo (1996) [12] with minor modification. NSB was soaked in NaOH solution for 30 minutes at room temperature. The sorbent was then mixed with quartenary ammonium chloride solution ( $C_6H_{15}Cl_2NO$ , 65 % w/w in water) which was adjusted to pH 5.3. The mixture was subsequently heated at 60-70 °C for 4 hours in oven with intermittent stirrings. It was then rinsed with distilled water and suspended in dilute HCl with pH 2 for 30 minutes. After washing with distilled water until neutral, the modified sorbent was dried in oven overnight at 50 °C and labeled as quartenized sugar cane bagasse (QSB).

### Dye solution

For the study of dye sorption, synthetic dye solutions of BB3 (25 % dye content, Sigma Aldrich) and RO16 (50 % dye content, Sigma Aldrich) were used. The dye stock solutions of 2000 mg/L were prepared by dissolving accurately weighted dyes in distilled water by taking the dye content into consideration. The experimental solutions for subsequently study were obtained by diluting the dye stock solutions when necessary.

### Batch experiments

Sorption experiments were carried out by agitating 0.10 g of sorbent in 20 mL of 100 mg/L dye solution in centrifuge tube at 150 rpm on an orbital shaker for 8 hours at room temperature. All the batch experiments were conducted in duplicate and the results are the means with 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 after sorption were analyzed using a Shimadzu UV-1650 PC UV-visible Spectrophotometer. The absorbance were measured at maximum wavelengths of dyes; for BB3,  $\lambda_{max} = 654$  nm, and for RO16,  $\lambda_{max} = 494$  nm. The dyes solutions were diluted when measurements of absorbance exceeded the linearity of the calibration curve.

The effects of various parameters affecting the sorption were determined during batch experiments. For the study of the effect of pH, a series of 100 mg/L single and binary dye solutions of BB3 and RO16 were prepared by adjusting them to an initial pH range of 2-10 by adding dilute HCl on NaOH. The sorption experiments were carried out by shaking 0.10 g of sorbent in 20 mL of dye solutions for 4 hours. The study of the effect of contact time was performed by varying the dye concentrations ranging from 50 to 150 mg/L of BB3 and RO16 for both single and binary dye solutions. The samples were withdrawn at increasing contact time intervals ranging from 5 minutes to 8 hours. The kinetics of adsorption was determined subsequently. Sorption isotherms were obtained by varying the dye concentrations from 5 to 150 mg/L of single and binary dye solutions. The sorption studies were also carried out with increasing temperature from 26 to 80 °C. A water bath with shaking mechanism was used to keep the temperature constant.

## Results and Discussion

### Sorption study

A comparative study of sorption of BB3 and RO16 was carried out by using NSB and QSB as sorbents. The results of dye removal were shown in Table 1. The experiments were performed by agitating 0.10 g of each sorbent in 20 mL of 100 mg/L dye solution at 150 rpm for 4 hours. The NSB showed good adsorption behavior towards BB3 dye solution, where the % dye removal was 77.65 and 82.16 in single and binary systems,

respectively. The hydroxyl groups of the natural sorbent help in the binding of the cationic dye molecules. However, removal of RO16 dye solution was not favourable by NSB where less than 8 % of the dye was removed.

This was due to the coulombic repulsion between the negatively charged dye molecules and the negatively charged surface groups of NSB. The bagasse after modification showed its sorption capability for different charged dyes. The sorption of RO16 in both single and binary dye solutions were greater than 75 % whereas for BB3, the percentage of dye removal was 16.52 and 34.32 in single and binary systems, respectively. The hydroxyl and (Si-O-N<sup>+</sup>-C) groups on the surface of QSB contribute to the binding sites for the adsorption of positively and negatively charged dyes.

Table 1: 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

#### Effect of pH

The pH value of dye solution is an important influencing factor in the dye removal study. In order to find out the optimum pH value for the removal of both BB3 and RO16, the dye solutions were adjusted to pH 2-10. Figure 1 shows the results of dye removal in different pH value. Solution pH affects both aqueous chemistry and surface binding sites of the adsorbents. For single BB3 dye solution, the percentage removal of dye increased from 11.11 to 72.32 with increasing pH from 2-10. Similar trend was observed for BB3 binary system, with slightly higher removal of dye compared to the single dye system. It was verified that the sugar cane bagasse is mainly consisting of natural cellulosic fibres and these fibres are negatively charged due to the presence of hydroxyl groups of cellulose [10]. Depending on pH, these groups may change their charges. At low pH condition, most of the potential binding sites on QSB are protonated and the surface of sorbents is surrounded by hydronium ions, thus inhibiting the binding of cationic BB3 dye molecules. With increasing pH of dye solution, the surface groups will be deprotonated, resulting in an increase of negatively charged sites which favour the sorption of cationic dye (BB3) due to electrostatic attraction [9].

However, the acidic pH system showed good adsorption behavior for the RO16 dye solution. The removal of RO16 increased from 28.62 to 97.14 % with the decrease of pH from 10 to 2. Reactive dyes are known to ionize to a high degree in aqueous solutions to form coloured anions due to the sulfonate groups in their structures. Two sulfonate (-SO<sub>3</sub><sup>-</sup>) groups of RO16 dye are easily dissociated and have negative charges in the aquatic environment. As the pH of the system decreases, the protonated surface groups (Si-O-N<sup>+</sup>H<sub>2</sub>-C) facilitate the sorption of negatively charged dye. The number of positively charged sites increases resulting in an increase of binding sites for anionic dye molecules (RO16) [13]. The deprotonation of surface groups in high pH range results in the electrostatic repulsion between the anionic dye and negatively charged sites. This has contributed to the decreased uptake of RO16 [14] in alkaline condition. The binary system showed the similar trend for the dyes removal. Therefore, it is suggested that the optimum pH for the removal of both BB3 and RO16 is between pH 6-8.

#### Effect of initial concentration and contact time

The effect of initial dye concentration on removal of BB3 and RO16 by QSB in different contact time is shown in Figure 2. The dye solutions of 50, 100 and 150 mg/L were prepared for this study. From the results obtained, the percentage removal of both BB3 and RO16 increased with decreasing initial dye concentration, where the highest percentage removal was achieved in 50 mg/L. In both single and binary dye systems, the adsorption of dyes was rapid during the initial stages of sorption processes, followed by a gradual process. For BB3 dye solution, 120 minutes is required for the equilibrium adsorption. The initial rapid phase may be due to the large number of vacant sites available at the initial stage, consequently exist an increase in the driving force of the concentration gradient between adsorbate in solution and adsorbate in the adsorbent [15-16]. For single RO16

of 50 mg/L, the dye removal was up to above 85 % after 180 minutes, while for binary system, more than 90 % of dyes were removed.

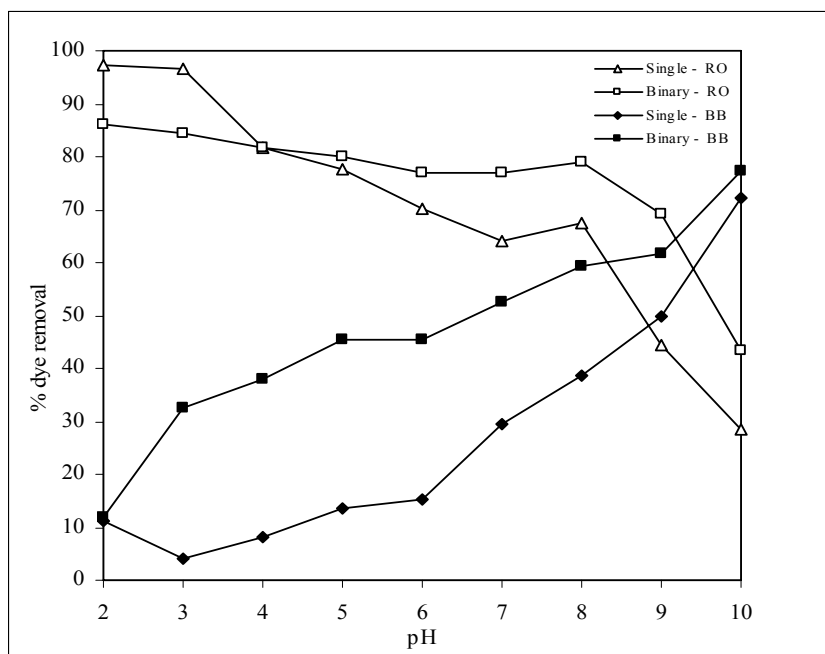


Figure 1: Effect of pH on dye sorption by QSB.

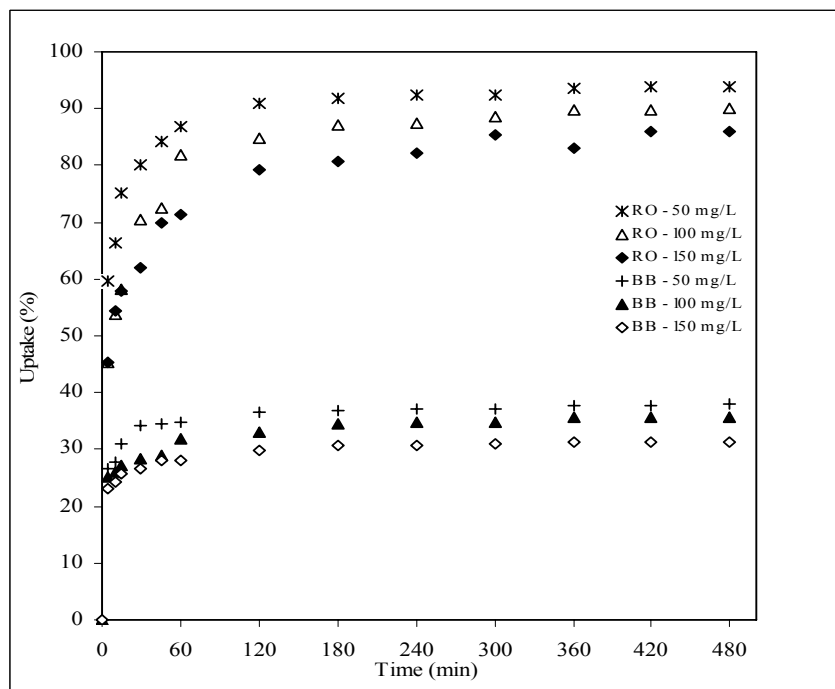


Figure 2: Effect of initial concentration and contact time on sorption of binary BB3 and RO16 by QSB.

**Adsorption kinetics**

To find out the potential rate-controlling steps involved in the adsorption of BB3 and RO16 onto QSB, both pseudo-first-order and pseudo-second-order kinetic models have been used to fit the experimental data at various dye concentration.

The pseudo-first-order equation was expressed as below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{1}$$

where  $q_e$  is the amount of dyes sorbed at equilibrium (mg/g),  $q_t$  is the amount of dyes sorbed at time,  $t$  (mg/g),  $k_1$  is the rate constant of pseudo-first-order sorption ( $\text{min}^{-1}$ ). The pseudo-first-order plots ( $\log (q_e - q_t)$  vs.  $t$ ) of BB3 and RO16 in both single and binary systems were not fitted where their correlation coefficient,  $R^2 \ll 1$  (Figure is not shown).

The pseudo-second-order equation was expressed as below:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{2}$$

where  $h$  ( $k_2 q_e^2$ ) is the initial sorption rate (mg/g min) and  $k_2$  is the rate constant of pseudo-second-order kinetics (g/mg min). The pseudo-second-order model plots ( $t/q_t$  vs.  $t$ ) of BB3 and RO16 in single system are shown in Figure 3. For all the systems studied, good correlation coefficients are obtained ( $R^2 \approx 1$ ) by fitting the experimental data to pseudo-second-order kinetics than that for the pseudo-first-order kinetic model. Therefore, the sorption is more favorably by 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 sharing or exchange of electron between sorbent and sorbate [17].

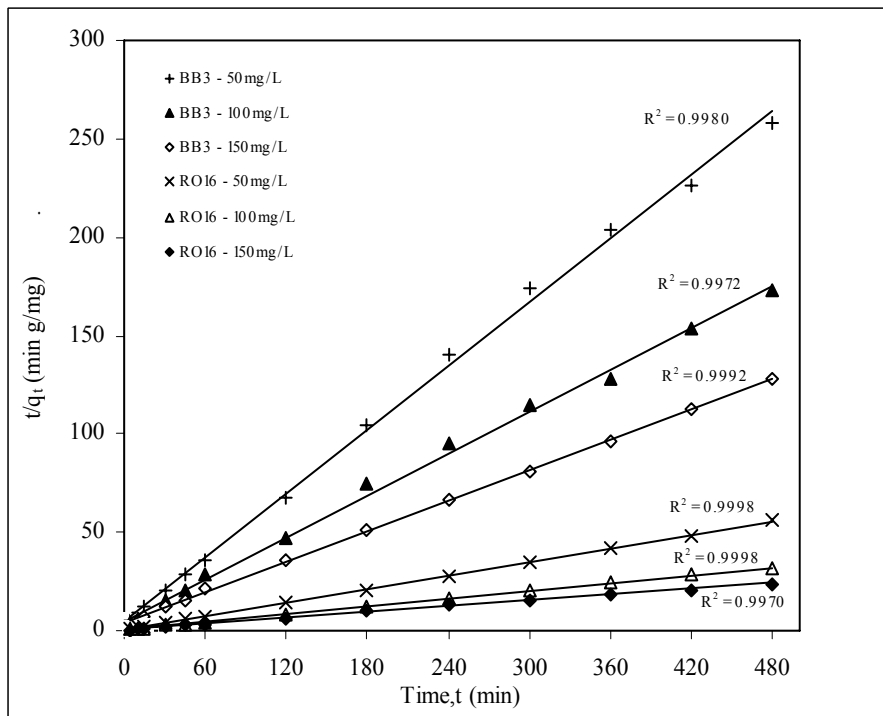


Figure 3: Pseudo-second-order kinetics of BB3 and RO16 in single dye solutions.

**Adsorption isotherm**

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Two isotherm models were used to determine the suitable one of describing the adsorption process of BB3 and RO16 onto QSB. The application of Langmuir isotherm suggests that every adsorption site is equivalent, and that the ability of a particle to bind there is independent of whether or not nearby sites are occupied and that the adsorbent is saturated after one layer of adsorbate molecules formed on the adsorbent surface [18].

The Langmuir equation is expressed as:

$$\frac{C_e}{N_e} = \frac{1}{N^*b} + \frac{C_e}{N^*} \tag{3}$$

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

$$\log N_e = \frac{\log C_e}{n} + \log K_f \tag{4}$$

where  $C_e$  is the equilibrium concentration of the dye (mg/L),  $N_e$  is the amount of dye sorbed at equilibrium (mg/g),  $N^*$  is the maximum sorption capacity (mg/g),  $b$  is the constant related to the energy of the sorbent (L/mg),  $n$  is the Freundlich constant for intensity and  $K_f$  is the Freundlich constant for sorption capacity. The linear plots of  $C_e/N_e$  versus  $C_e$  (Figure 4) suggests the applicability of Langmuir model, showing formation of monolayer coverage of the dye molecules at the outer surface of the adsorbent. The high correlation coefficients of  $\log N_e$  versus  $\log C_e$  plots in Figure 6 indicated that the sorption agreed with the Freundlich isotherm as well, with better fitting compared to Langmuir isotherms. This might be because the biosorbent's surface is non-homogeneous and there could be more than one type of sorption sites on the surface. The agreement of both isotherms have been reported previously [7,9].

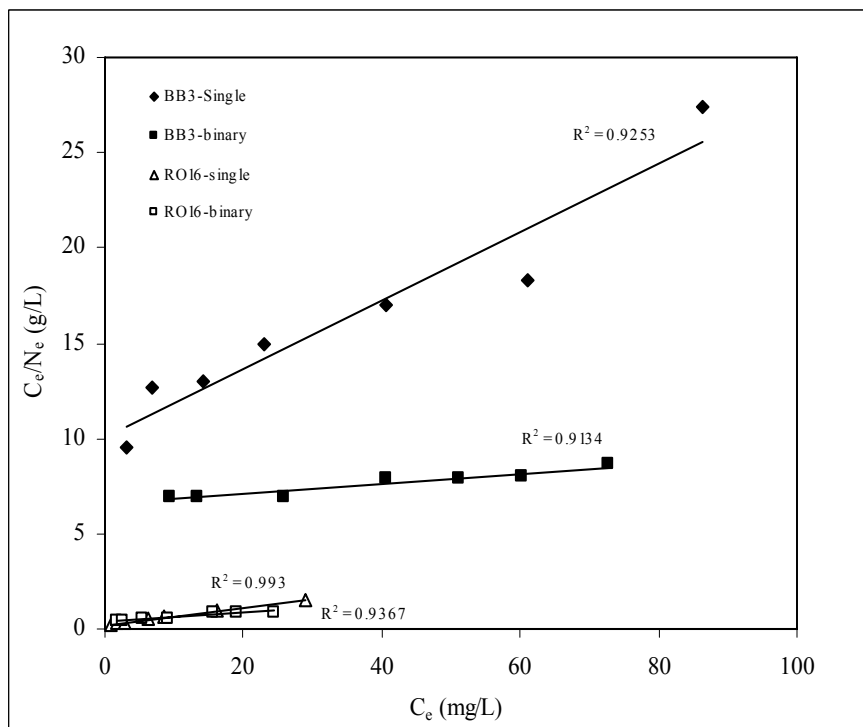


Figure 4: Langmuir isotherms for the sorption of BB3 and RO16 from single and binary dye solutions.

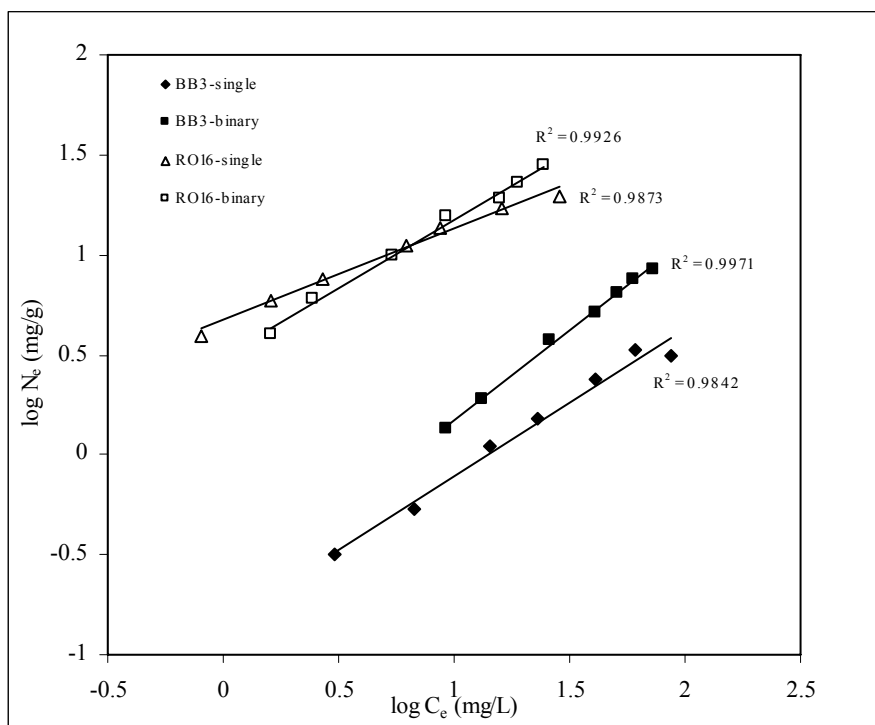


Figure 5: Freundlich isotherm for the sorption of BB3 and RO16 from single and binary dye solutions.

### Effect of temperature

Figure 6 shows the effect of temperature on sorption of BB3 and RO16 dyes in both single and binary systems. With temperature increased from 26 to 80 °C, the percentage removal of BB3 increased from 16.59 to 22.01, and 33.28 to 42.49 for single and binary systems, respectively. This indicated that the sorption of the dye involves an endothermic process. This suggested the adsorption process is controlled by the diffusion process (intra-particle transport-pore diffusion), where the sorption capacity will show an increase with an increase in temperature. This is basically due to the fact that the diffusion process is an endothermic process. With an increase in temperature, the mobility of the BB3 ions increases and the retarding forces acting on the diffusing ions decrease, thereby increasing the sorptive capacity of adsorbent [19].

However, the sorption of RO16 by QSB decreased with increasing temperature. The percentage of removal decreased from 77.52 to 70.48 and 83.33 to 77.87, for single and binary dyes, respectively. This indicated that it involved an exothermic process. 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 [20]. The elevated temperature may also weaken the adsorptive forces between the binding sites and anions, thus leading to a decrease in the sorption of RO16.

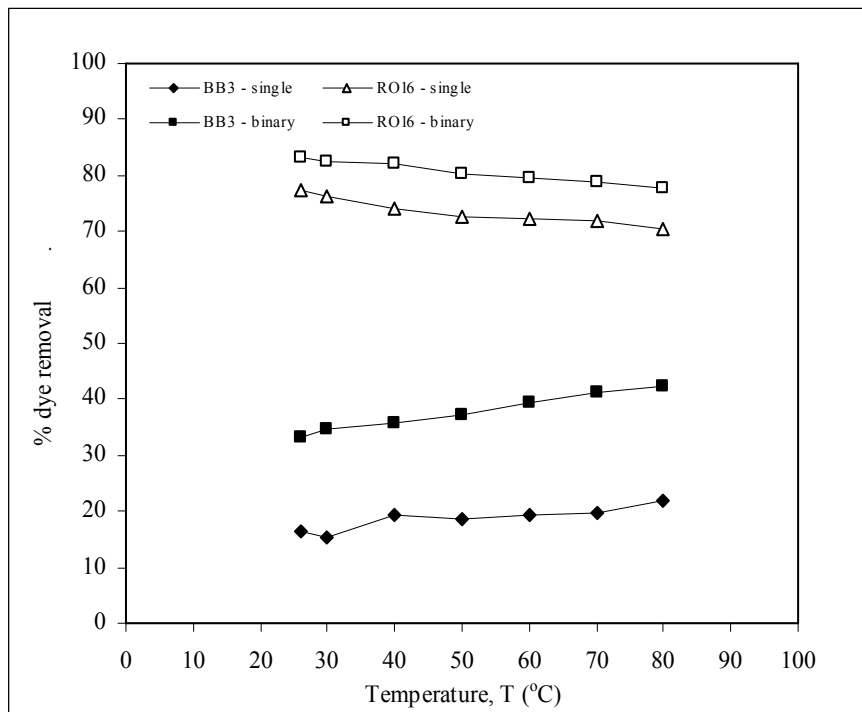


Figure 6: Effect of temperature on sorption of single and binary BB3 and RO16 dyes by QSB.

### Conclusion

This study shown that quartenized sugar cane bagasse has the potential to be a sorbent to remove both cationic dye BB3 and anionic dye RO16 from aqueous solution. The batch adsorption study indicated that the removal of both BB3 and RO16 is pH dependent. The optimum pH is suggested at 6-8. The percentage removal of dyes increased with decreasing concentration, and for BB3 dye solution, equilibrium was reached at 120 minutes. From the study of adsorption kinetics, it is found that the sorption of both BB3 and RO16 in single and binary solution fitted pseudo-second-order kinetic model, suggesting the involvement of chemisorption process. Both the Langmuir and Freundlich isotherms were fitted well, with a better agreement in the latter. The sorption of BB3 is an endothermic process; whereas the sorption of RO16 is an exothermic process.

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