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Foreword

It is quite a commendable feat that within a short span of time since its last issue, the University Publication Centre (UPENA) of UiTM Pulau Pinang has produced its sixth volume of the Esteem Academic Journal UiTM Pulau Pinang. Of course, this issue would not come into fruition if not for the firm commitment and close cooperation of all the relevant parties involved.

First and foremost, I would like to extend my thanks to Associate Professor Mohd Zaki Abdullah, Director of UiTM Pulau Pinang, Associate Professor Dr Mohamad Abdullah Hemdi, Deputy Director of Academic Affairs and Associate Professor Ir. Damanhuri Jamalludin, Deputy Director of Research, Industry Linkages, Development & Maintenance for offering their continuous and untiring support. They were the driving force behind the successful publication of this journal. Time and again they rendered invaluable advice on how to address the problems that UPENA encountered in the publication of this academic journal.

UPENA highly appreciates the comments and expertise proffered by the panel of external reviewers when articles in this journal were sent to them for blind reviews. Likewise, UPENA also salutes the dedicated panel of language editors for their time in editing the authors' manuscripts.

However, all the assistance tendered would have been a futile effort if there were no authors willing to submit their articles for publication. This journal comprises articles on the social sciences and technology disciplines. I am proud to state that there is no shortage of writers from Penang and the response from them in these two disciplines has been overwhelming.

Lastly, I would like to urge more lecturers to submit their articles to UPENA. Authors' contributions of articles in this refereed journal help to disseminate and share knowledge with readers. It also helps to elevate the status of UiTM Pulau Pinang in research writing. In return, the authors gain recognition from the wider audience and also consideration for promotion in their career. It is a win-win situation for both parties. So lecturers, what are you waiting for? Put on your thinking caps and start contributing your research articles to UPENA.

Liaw Shun Chone
Chief Editor
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(Social Sciences and Technology)

Removal of Congo Red Dye from Aqueous Solution by Bagasse

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ABSTRACT

The present study deals with the utilisation of unmodified bagasse (UMB) as an adsorbent for the removal of congo red (CR) from aqueous solutions. The effect of adsorbent dosage, contact time and initial CR concentration on the adsorption are investigated. Then, the optimum conditions are applied to acid-modified bagasse (AMB) and base-modified bagasse (BMB) for comparative study. The maximum CR removal capacity by UMB, BMB and AMB are 6.813, 7.664 and 5.295 mg g^{-1} respectively. It is found that sufficient time for adsorption equilibrium of CR is 60 min. Equilibrium isotherms for the adsorption of CR on UMB is analysed by the Langmuir and Freudlich isotherm equations. These results can be helpful in designing a batch mode system for the removal of CR from wastewater.

Keywords: *Adsorption, congo red, bagasse, isotherms*

Introduction

Color is the first contaminant to be recognized in wastewater. Dyes are used in different industries such as paper and plastics, leather, pharmaceutical, food, cosmetics, dyestuffs, textiles, etc. to color the

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products. As a result, considerable amount of colored wastewater is generated. The presence of these dyes in water even at very low concentration is highly visible and undesirable (Jain and Sikarwar, 2006). Dyes can be classified as anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) (Mishra and Tripathy, 1993). Congo red (CR) (1-naphthalenesulfonic acid, 3,30-(4,40-biphenylenebis (azo)) bis (4-amino-) disodium salt) is a benzidine-based anionic disazo dye. This dye is known to metabolize to benzidine, a known human carcinogen. (Mall et al., 2005).

In general, the methods for the treatment of wastewater containing dyes can be divided into two main groups (Gupta and Suhas, 2009; Sohrabnezhad and Pourahmad, 2010): (I) chemical or physical methods of dye removal, which refers to the process called decoloration and (II) dye removal by means of biodegradation. Physical methods of decoloration include different precipitation methods, adsorption, filtration, reverse osmosis, etc. Among the chemical methods of dye removal, there are processes such as reduction, oxidation, complexime tric methods, ion exchange and neutralization. Biological treatment can be conducted in the presence or absence of oxygen (Slokar and Majcen, 1998; Sohrabnezhad and Pourahmad, 2010). These processes have their disadvantages and limitations, such as high cost, generation of secondary pollutants, and poor removal efficiency. Thus adsorption has been found to be the most effective economic alternative with high potential for the removal and recovery of dyes from wastewater (Gupta et al., 2006; Han, Wang and Zou, 2007; Sohrabnezhad and Pourahmad, 2010).

Sugarcane bagasse from the family of *Saccarhum officinarum* which is an abundant agricultural by-products in Malaysia. Bagasse is the solid residue left after the extraction of juice from sugarcane. In the current research, the potentials for the use of bagasse as a biosorbent for CR removal from aqueous solution are investigated. The aim of the present work is to explore the possibility of utilizing bagasse for the adsorptive removal of CR from aqueous solution. The effects of such factors including adsorbent dosage, contact time, initial concentration and pretreatment are investigated. Experimental equilibrium data are fitted to the Freundlich and Langmuir isotherm equations to determine the best-fit isotherm.

Materials and Methods

Congo Red

Congo red (CR) dye [C.I. = 22120, chemical formula = $C_{32}H_{22}N_6Na_2O_6S_2$, FW = 696.7, kmax = 500 nm] was supplied by the Fisher Scientific. The structure of CR is illustrated in Figure 1 (Fu and Viraraghavan, 2002; Mall et al., 2005).

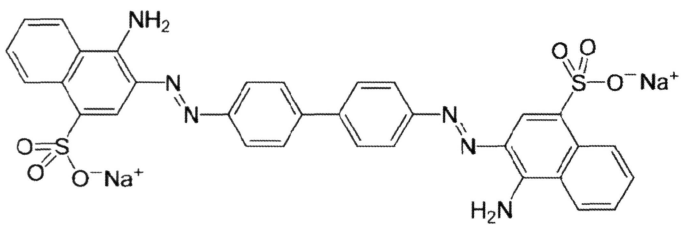

Figure 1: Molecular Structure of Congo Red Dye

Preparation of Raw Material

The adsorbent was prepared from bagasse, which is collected from Permatang Pauh, Pulau Pinang. The material is sieved to obtain the desired size fraction (150-212 μm), boiled and washed thoroughly with distilled water. Then, the adsorbent is dried in 90 °C to 110 °C in hot air oven for overnight.

Acid-treatment of Bagasse

For acid-pretreatment, 4.0 g of bagasse is immersed in 1000 mL 20% v/v H_2SO_4 in 2000 mL beaker on hot plate stirrer machine for 15 hours at 60 °C temperature. The acid-modified bagasse (AMB) is extensively washed with deionized water and filtered thoroughly until a pH 7 is attained. Finally the resulting AMB is oven dried for 48 hours at 60 °C to constant weight.

Base-treatment of Bagasse

For base-pretreatment, 4.0 g bagasse is immersed in 300 mL NaOH solution with very dilute concentration (0.15 M or 0.6% w/v) in 500 mL conical flask on plate stirrer machine for 3 hours at room temperature.

The fibres are then washed with deionised water until the pH value is 7. The base-modified bagasse (BMB) is then dried at 60 °C in an oven for 48 hours before using as adsorbents.

Spectroscopic Studies

Fourier Transform Infrared (FTIR) is used to identify the characteristic functional groups in the fibers. UMB sample is powdered and then dispersed in dry potassium bromide (KBr) respectively. The mixture is thoroughly mixed in a mortar and pressed with the pressure of 6 bars to form a KBr thin disc. Then the disc is placed in a sample cup of a diffuse reflectance accessory. The IR spectrum is obtained using Perkin Elmer 2000 infrared spectrometer. A FT-IR spectrum of each sample is obtained in the range of 4000 – 400 cm^{-1}. Spectral outputs are recorded in the transmittance mode as a function of wave number.

Adsorption Studies

The adsorption experiments are carried out with a batch method. A stock CR solution (1000 mg L^{-1}) is used in adsorption experiments. The concentration of CR is determined by Perkin Elmer UV-VIS RS Spectrometer 3000. A known amount of adsorbent and CR solution are taken in a 250 mL stoppered conical flask. The final volume is adjusted to 250 mL with distilled water and agitated at constant speed (150 rpm) on the orbital shaker GFL 3005 in room temperature over a period of time and then filtered. The initial pHs of all CR solutions are kept to pH 6-7. The concentration of CR in filtrate is determined and the amount of CR removal is calculated from the ratio of CR taken and that remaining in the solution. Adsorbed CR is calculated from mass balance. The experimental parameters studied are: contact time (10-210 min), initial CR concentration (10-100 mg L^{-1}), and the effects of dosage (0.2-2.0 g).

Equilibrium Adsorption Studies

The adsorption of CR from aqueous solutions by bagasse is carried out at room temperature, 27 ± 1 °C. In the experiments, 0.5 g bagasse is mixed with 250 ml solutions of various CR concentrations between 10 to 100 mg L^{-1}. After adsorption, the concentrations of CR remaining unabsorbed are determined.

Results and Discussion

Spectroscopic Study

Agricultural biomasses mainly consist of cellulose, hemi-cellulose, lignin and some proteins which make them effective adsorbent for dye. Bagasse mainly contains cellulose (45%), hemi-cellulose (28%) and lignin (18%) (Garg et al., 2008). Bagasse contains carboxylic and hydroxyl groups, hence its efficiency towards the removal of dye over wide range of pH. Figure 2 shows the FTIR spectra for UMB in the form of KBr pallet. Identification of the most important peaks is based on previous studies of sugar cane bagasse (Garg et al., 2008; Gurgel et al., 2008;), coconut husk (Shukla et al., 2005) and jute (Min et al., 2003).

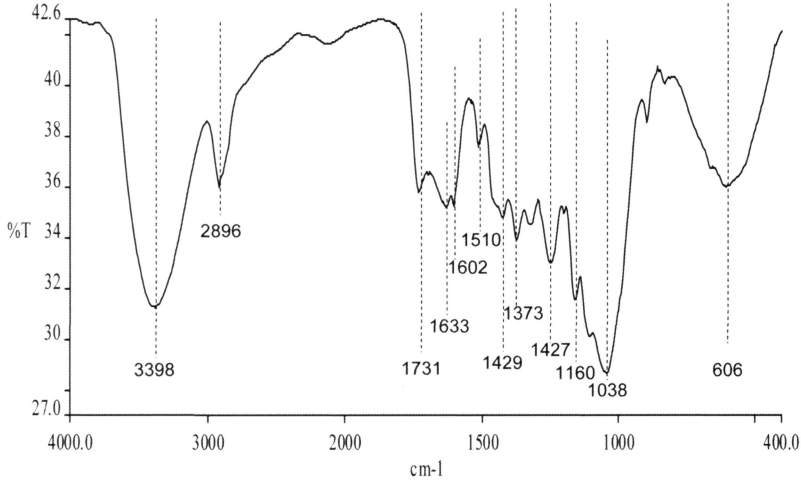

Figure 2: Infrared Spectra of UMB

For UMB, the broad adsorption at 3398 cm^{-1} was due to the stretching of hydroxyl groups and bonded O-H present in cellulose, hemicellulose and lignin. The peaks observed at 2896 cm^{-1} can be assigned to stretching vibration of the C–H. The peak around 1731 cm^{-1} corresponds to the C=O stretching of methyl ester and carboxylic acid in pectin or acetyl group in hemicelulose (Silverstein and Webster, 1998). The band at 1602 cm^{-1} was related to the bending mode of the absorbed water. The peaks around 1633 cm^{-1} corresponded to the C=C stretching and that may be attributed to the lignin aromatic groups. The small band at 1429, 1373

and 1323 cm^{-1} represent CH_2 bending, O-H bending, C-C and C-O stretching respectively. The absorbance at 1247 cm^{-1} is corresponded to C-O stretching in hemicellulose and lignin. The additional peak at 606 cm^{-1} and 830 cm^{-1} can be assigned to bending modes of aromatic compounds. The typical functional groups for the possible compounds are listed in Table 1.

Table 1: Infrared Spectra Band UMB

Wave number (cm^{-1})	Functional groups	Compounds	UMB Fequency, cm^{-1}
3600-3000	OH streaching	Acid, methanol	3398
2860-2970	C-H stretching	alkyl, aliphatic	2896
1700-1730	C=O stretching	aromatic	1731
1650-1600	Absorbed water	-	1602
1632	C=C	Benzene stretching ring	1633
1440-1400	OH bending	Acid	1373
1402	CH bending	alkyl, aliphatic	1429
1250	C-O stretching	Phenol	1247
1200-1100	C-O antisymmetric stretching	-	1160
1170, 1082	C-O-C stretching vibration	Pyranose ring skeletal	1038
700-400	bending vibration	-	606

Effect of Contact Time on Adsorption Equilibrium

The effect of contact time on the amount of CR adsorbed on the UMB was investigated at initial concentration of 50 mg L^{-1} and the pH of CR solution was kept in the range of 6 to 7. The system was subjected to an agitation speed 150 rpm for 210 min. Figure 3 shows a rapid adsorption of CR at the initial stages of the adsorption and equilibrium was attained within 60 minutes. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption was found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases (Mall, Srivastava and Agarwal, 2006).

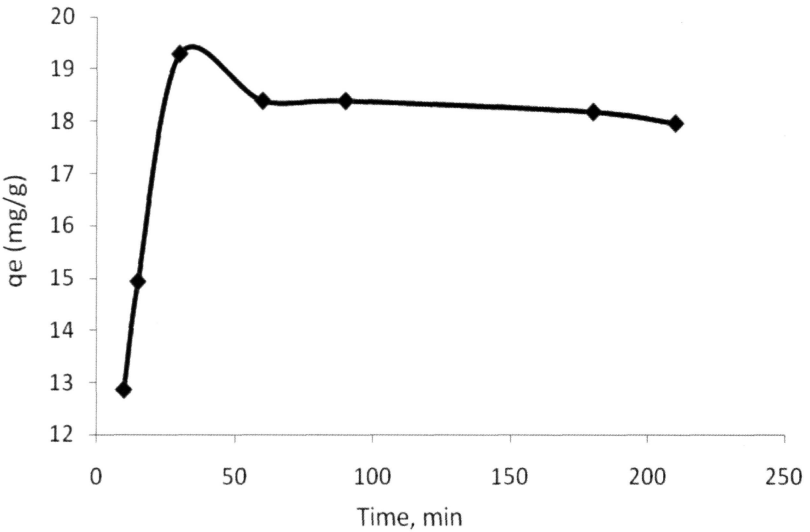

Figure 3: Effect of Contact Time on CR Removal Using UMB
(pH = 6 - 7, temp = 27 °C ± 1, particle size:150 - 212 μm,
CR concentration 50 mg L^{-1} and adsorbent dosage: 2 g L^{-1})

Effect of Initial CR Concentration on Adsorption Equilibrium

The effect of initial CR concentration, C_0 on the removal of CR by UMB is shown in Figure 4. From the figure, it is evident that the CR removal decreased with the increase in C_0, although the actual amount of dye adsorbed per unit mass of adsorbent increased with the increase in C_0. The CR removal increased with the increase in the adsorbate concentration as the resistance to the uptake of CR from the solution decreases with the increase in CR concentration. The rate of adsorption also increased with the increase in C_0 due to increase in the driving force. At lower concentrations, all CR present in the adsorption medium could interact with the binding sites so higher adsorption yields were obtained. At higher concentrations, lower adsorption yields were observed because of the saturation of the adsorption sites.

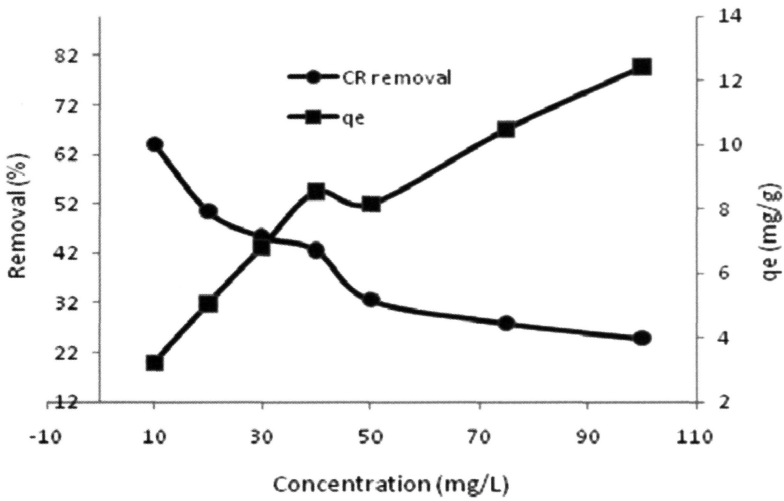

Figure 4: Effect of Initial CR Concentration Using UMB (pH = 6 - 7, temp = 27 °C ± 1, particle size: 150 - 212 μm, contact time: 60 min and adsorbent dosage: 2 g L^{-1})

Effect of Adsorbent Dosage, m on Adsorption Equilibrium

The effect of adsorbent dosage, m on the removal of CR by UMB at 50 mg L^{-1} is shown in Figure 5. It can be seen that the CR removal increases up to a certain limit and then it remained almost constant. An increase in the adsorption with the adsorbent dosage can be attributed to greater surface area and the availability of more adsorption sites (Mas and Sathasivam, 2009).

Effect of Pre-treatment on Adsorption Equilibrium

To evaluate the effect of pretreatments on bagasse, 50 mg L^{-1} CR solution was shaken at 150 rpm with 6.4 g L^{-1} (1.6 g adsorbent in 250 mL CR) of UMB, AMB and BMB having size 150 - 212 ìm at pH 6 - 7 for 60 min. Uptake capacity of adsorbent was significantly increased to 12% after acid-treatment and decreased to around 22% after base-treatment (Figure 6a.). The graph based on percentages of removal is shown in Figure 6b. From the results, we can conclude that, UMB was able to remove CR but with limited capability. This is because CR is relatively large molecule and negatively charges (Mall et al., 2005). A negatively charged surface site on the UMB and BMB does not favour the adsorption of CR dye

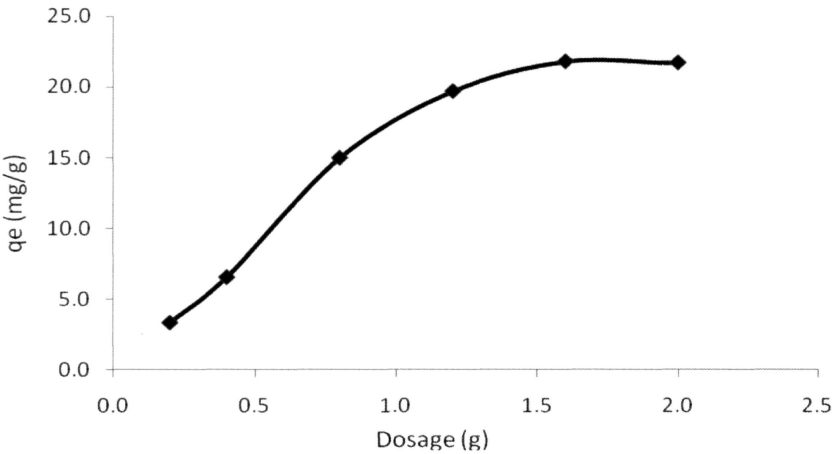

Figure 5: Effect of Adsorbent Dose on Adsorption of CR by UMB
(pH = 6 - 7, temp = 27 °C ± 1, particle size: 150 - 212 μm,
contact time: 60 min and MB concentration = 50 mg L^{-1})

due to the electrostatic repulsion. AMB had the highest uptake capacity for CR because acid treatments can enhance uptake capacity of adsorbent by increasing the surface area and porosity of original sample (Bhatti, et al. 2007). Besides that, the acid modification with H_2SO_4 altered the surface of bagasse an enhanced the adsorption of CR.

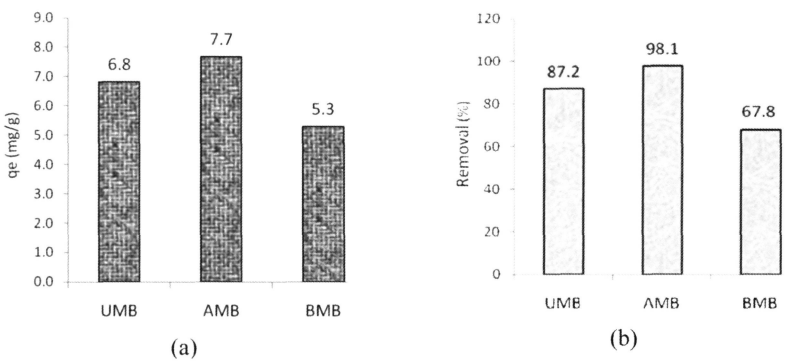

Figure 6: Effect of Pre-treatment (a) Adsorption Capacity, q_e (mg g^{-1}) of MB by UMB, AMB and BMB and (b) Percent Removal (%) of MB by UMB, AMB and BMB
(pH = 6 - 7, temp = 27 °C ± 1, particle size: 150 - 212 μm, contact time: 60 min, MB concentration: 50 mg L^{-1} and adsorbent dosage: 2 g L^{-1})

Adsorption Isotherms

Langmuir Isotherm Model

Langmuir isotherm model assumed the uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Langmuir sorption is a model based on the physical hypothesis that there are no interaction between adsorbed molecules and the adsorption energy over the entire coverage surface. Also there is no transmigration of the adsorbate in the plane of the surface of the adsorbent (Langmuir, 1918; Mas and Sathasivam, 2009). On the other hand in the Langmuir model, it is assumed that intermolecular forces decrease rapidly with distance and this lead to the prediction that coverage of the UMB is of monolayer type. Once a particular site of the adsorbent is occupied by an adsorbate molecule, no further adsorption takes place at that site. The linear form of Langmuir isotherm equation is given as

$$\frac{Ce}{qe} = \frac{1}{Q_O b} + \frac{Ce}{Q_O} \qquad (1)$$

Where:

C_e = The equilibrium concentration of the adsorbate (mg L^{-1})
q_e = The amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1})
Q_o and b = Langmuir constants related to adsorption capacity and rate of adsorption, respectively

When C_e/q_e was plotted against C_e, a straight line with slope of $1/Q_o$ was obtained, as shown in Figure 7. The value of Q_o was determined from the Langmuir plot at the concentration range 10-100 mg L^{-1} as 14.556 and then the b value was calculated to be 0.055. The correlation coefficient of Langmuir isotherm, R^2 is 0.9656. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given as

$$R_L = \frac{1}{1 + bCo} \qquad (2)$$

The value of R_L indicated the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The value of R_L was found to be 0.667 suggesting the isotherm to be favorable at the concentrations studied. Conformation of the experimental data into Langmuir isotherm model indicated the

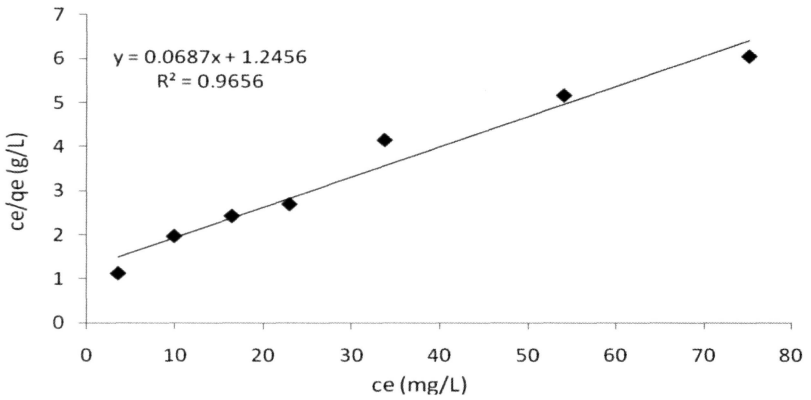

Figure 7: Langmuir Isotherms for the Removal of CR by UMB

homogeneous nature of UMB surface, i.e., each CR dye/UMB adsorption had equal adsorption activation energy; the results also demonstrated the formation of monolayer coverage of dye molecule at the outer surface of UMB.

Freudlich Isotherm Model

This model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption (Ahmad, Sumathi and Hameed, 2005). The Freundlich isotherm equation is written as

$$\log qe = \log kf + \frac{1}{n} \log ce \qquad (3)$$

Where:

C_e = The equilibrium concentration of the adsorbate (mg L^{-1})
q_e = The amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1})
K_f (mg g^{-1}) and n = Freudlich constants with n giving an indication of how favorable the adsorption process
K_f = The adsorption capacity of the adsorbent

K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the fibers for a unit equilibrium concentration. The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Ajmal et al., 1998). When

log q_e was plotted against log C_e, a straight line with slope of 1/n was obtained, as shown in Figure 8. The Freundlich constants were derived from the slopes and intercepts of log C_e versus log qe and were shown in Table 2. By analyzing the Freundlich isotherm, it described the heterogeneous system and reversible adsorption.

Table 2: The Langmuir and Freundlich Parameters of Adsorption Isotherms

Isotherms	Constants			
Langmuir	Q_o	B	R_L	R^2
UMB	14.556	0.055	0.667	0.9656
Freundlich		k_f	n	R^2
UMB		0.279	2.291	0.9761

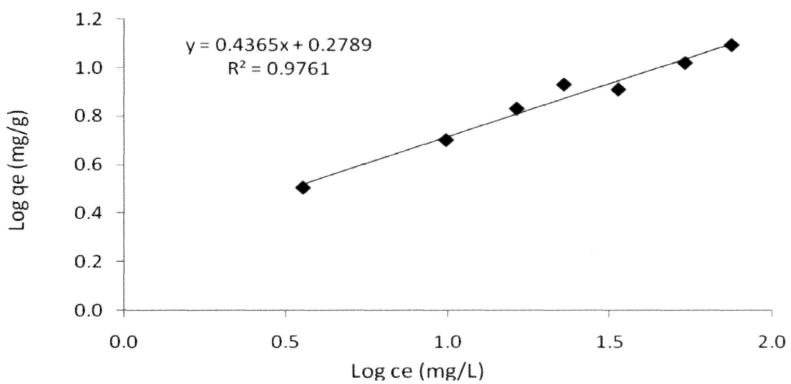

Figure 8: Freundlich Isotherms for the Removal of MB by UMB

As seen from Table 2, a high regression correlation coefficient, R^2 (0.9761) was shown by the Freundlich model. This indicates that the Freundlich model was suitable for describing the sorption equilibrium of CR by the UMB. From the plot shown in Figure 8, the K_f value and n value was recorded at 0.279 and 2.291, respectively. When the linearity of the plots of the Freundlich ($R^2 = 0.9761$) and Langmuir ($R^2 = 0.9656$) models was compared, it was found that the Freudlich adsorption model had a better fit. Thus it is reasonable to conclude that the adsorption of CR on the fibers that consist of heterogeneous adsorption sites, are similar to each other in respect of adsorption phenomenon.

Conclusions

The present study shows that bagasse is considerably efficient for removal of CR dye from aqueous solution. The adsorption is highly dependent on contact time, adsorbent dose and initial CR concentration. The optimum condition for UMB was applied to AMB and BMB. The results suggested that AMB has the highest % of removal. This can be interpreted as so because after the acid treatment, the active sites of the bagasse were increased. This provides valuable information on the ways to provide better removal of CR from aqueous solutions. The equilibrium data for UMB fit well in the Freudlich model of adsorption, which suggests a heterogeneous coverage of the CR molecules at the outer surface of UMB. This result is quite similar to the study carried by Mall (2005). He states that Freundlich isotherm shows very good fit with the experimental equilibrium for the CR on bagasse. The data showed that bagasse has considerable potential for the removal CR from aqueous solution. This result would be useful for fabrication and designing of textile dyeing wastewater for the removal of dyes. Since the raw material bagasse is freely available, the treatment method seems to be economical.

Acknowledgements

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