# Dye Removal from Aqueous Solution by using Adsorption on Treated Sugarcane Bagasse

<sup>1</sup>S. Saiful Azhar, <sup>2</sup>A. Ghaniey Liew, <sup>1</sup>D. Suhardy, <sup>1</sup>K. Farizul Hafiz, M.D Irfan Hatim <sup>1</sup>School of Materials Engineering, Northern Malaysia University College of Engineering (KUKUM) Jejawi 02600 Arau, Perlis, Malaysia

<sup>2</sup>Chemical and Environmental Engineering Department, Faculty of Engineering University Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia

Abstract: The use of cheap and ecofriendly adsorbents have been studied as an alternative substitution of activated carbon for the removal dyes from wastewater. Adsorbents prepared from sugarcane baggase-an agro industries waste were successfully used to remove the methyl red from an aqueous solution in a batch reactor. This study investigates the potential use of sugarcane baggase, pretreated with formaldehyde (PCSB) and sulphuric acid (PCSBC), for the removal of methyl red from simulated wastewater. Formaldehyde treated and sulphuric acid treated sugarcane bagasse were used to adsorb methyl red at varying dye concentration, adsorbent dosage, pH and contact time. Similar experiment was conducted with commercially available powdered activated carbon (PAC), in order to evaluate the performance of PCSB and PCSBC. The adsorption efficiency of different adsorbents was in the order PAC>PCSBC>PCSB. The initial pH of 6-10 flavours the adsorption of both PCSB and PCSBC. Adsorbents are very efficient in decolorized diluted solution. It is proposed that PCSB and PCSBC, in a batch or stirred tank reactors could be employed as a low cost alternative in wastewater treatment for the dyes removal.

Key words: Formaldehyde, sulphuric acid, dyes, adsorption

#### INTRODUCTION

Dyes production industries and many others industries which used dyes and pigments generated wastewater, characteristically high in colour and organic content. Presently, it was estimated about 10,000 of different commercial dyes and pigments exists and over 7 x 10<sup>5</sup> tones are produced annually world wide<sup>[1]</sup>.

Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic etc. Among these various industries, textile ranks first in usage of dyes for coloration of fiber.

The convectional wastewater treatment, which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes. Due to low biodegradation of dyes, a convectional biological treatment process is not very effective in treating a dyes wastewater. It is usually treated with either by physical or chemical processes. However, these processes are very expensive and cannot effectively be used to treat the wide range of dyes waste<sup>[2]</sup>.

The adsorption process is one of the effective methods for removal dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted

solution. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. But, commercially available activated carbon is very expensive. Furthermore, regeneration using solution produced small additional effluent while regeneration by refractory technique results in a 10-15% loss of adsorbents and its uptake capacity<sup>[3]</sup>.

This had lead to further studies for cheaper substitutions. Nowadays, there are numerous number of low cost, commercially available adsorbents which had been used for the dye removal (Table 1).

However, as the adsorption capacities of the above adsorbents are not very large, the new adsorbents which more economical, easily available and highly effective are still needed.

#### **MATERIALS AND METHODS**

**Preparation of adsorbents:** Powdered activated carbon was supplied by BDH Laboratory Supplies, Poles England. The adsorbents were used directly without any further grinding and sieving. Following specification are given by the manufacturer: pH value 5-8, loss on drying < 20%, methylene blue adsorption  $(0.15\% \text{ solution}) > 5 \text{ mL } 0.1 \text{ g}^{-1}$ .

Corresponding Author: S. Saiful Azhar, School of Materials Engineering, Northern Malaysia University
College of Engineering (KUKUM), Jejawi 02600 Arau, Perlis, Malaysia, Tel: +604-9798404,
Fax: +604-9798178

Table 1: Some low cost materials for dyes removal from aqueous solution

Adsorbent(s)	Dye(s)	References
Bamboo dust, coconut shell,	Methylene blue	[4]
groundnut shell, rice husk		
Silk cotton hull, coconut tree sawdust,	Rhodamine-B, Congo red, methylene blue, methyl violet, malachite green	[2, 5]
sago waste, maize cob		
Parthenium hysterophorus	Methylene blue, malachite green	[6]
Rice husk	Malachite green	[7]
Coir pith	Acid violet, acid brilliant blue, methylene blue, Rhodamine-B	[8, 9]
Orange peel	Acid violet 17	[10]
Indian Rosewood	Malachite green	[11]
Prosopic cineraria	Malachite green	[1]
Banana and orange peels	Methyl orange, methylene blue, Rhodamine-B, congo red, methyl violet, acid black 10B	[12]
Giant duckweed	Methylene blue	[13]
Banana pith	Congo red, Rhodamine-B, acid violet, acid brilliant blue	[14-17]
Orange peel	Congo red, Rhodamine-B, procion orange	[18]
Carbonized coir pith	Acid violet, Rhodamine-B	[19]
Hardwood	Astrozone blue	[20]
Chitosan	Acid blue 25, basic blue 69	[21]
Mahogany sawdust, rice husk	Acid yellow 36	[22]
Biogas residual slurry	Congo Red, Rhodmine-B, acis violet, acid brilliant blue	[23]
Plum kernels	Basic Red 22, acid blue 25	[24]
Rice husk	Safranine, methylene blue	[25]

Table 2: Characteristic of the meth	nyl red
CAS No.	493-52-7
C.I. No.	13020
Chemical Formula	C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>
Molecular weight	269.31
Melting Point	179-182 C
Dye Content	~ 95 %
Absorption Max (pH 4.5)	523-526 nm
Absorption Max (pH 6.2)	430-434 nm
Absorptivity (1%, 1 cm) pH 4.5	> 1330
Absorptivity (1%, 1 cm) pH 6.2	> 700
Transition Range	pH 4.2-6.2 (Red - Yellow)

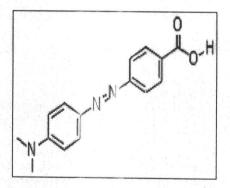


Fig. 1: The structural formula for methyl red

Formaldehyde treated bagasse: The bagasse obtained from the countryside was dried under the sunlight until all of the bagasse evaporated and was ground to a fine powder. The ground bagasse was sieved, so that the size of fiber used was between -80 to +230 mesh size.

In order to polymerize and immobilize the color and water soluble substances, the ground bagasse then was treated with 1% formaldehyde in the weight to volume ratio of 1:5 at 50 °C for 4 h. Then, this bagasse was filtered out by using Buchner funnel. It was washed with distilled water in order to removed free formaldehyde and it was activated at 80 °C in the air

oven for 24 h. The material was kept in an air tight container for further use.

Sulphuric acid treated bagasse: One part of the bagasse was mixed with one part of sulphuric acid and then heated in a muffle furnace for 24 h at 150 °C. The heated bagasse was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residue acid.

The material was dried in an oven at 150 C for 24 h. Then, the material was ground and sieved, until the size between -80 to +230 mesh size was obtained, which will be used for this study.

Dye solution preparation: For this study, methyl red was used and it was obtained from the local supplier. Following Table 2 shows characteristic of the methyl red.

An accurate weighed quantity of the dye was dissolved in double distilled water to prepared stock solution (500 mg  $L^{-1}$ ). Experimental solution of the desired concentration was obtained by successively dilutions.

Dye concentration was determined by using absorbance values measured before and after the treatment, at 617 nm with Shimadzu UV Visible Spectrometer (Model No.: UVmini 1240).

Experiment were carried out at initial pH values ranging from 2 to 9, initial pH was controlled by the addition of sodium hydroxide, NaOH or hydrochloric acid, HCl.

Adsorption experiment: In each adsorption experiment, 100~mL of dye solution of known concentration and pH was added to 400~mg of adsorbents in 250~mL round bottom flask at room temperature ( $26+1~^\circ\text{C}$ ) and the mixture was stirred on a rotary orbital shaker at 160~rpm.

Table 3: Effect of initial dyes concentration on dye removal (adsorbent dosage=0.4 g 100 mL<sup>-1</sup>; initial pH=7.0)

Initial Dye concentration (mg L <sup>-1</sup> )	Percentage of dye removal with time (min)						
	15	30	45	60	90	120	
Formaldehyde treated SB							
50	77.0	78.8	80.3	82.3	84.5	85.9	
100	66.8	68.0	69.9	70.5	71.8	72.3	
150	57.4	58.8	60.5	61.9	62.8	63.5	
200	44.6	48.5	50.1	52.8	54.4	60.8	
250	24.3	28.4	30.2	32.4	36.8	40.5	
Formaldehyde treated SB							
50	90.1	92.5	92.8	93.4	94.0	96.2	
	89.5	90.2	90.8	92.1	93.3	93.9	
	85.2	87.2	89.0	90.0	90.5	90.9	
200	78.0	80.9	84.0	87.7	88.5	88.4	
250	70.3	73.5	78.4	82.0	85.0	87.3	

Table 4: Effect of initial dyes concentration on dye removal (adsorbent dosage=0.4 g 100 mL<sup>-1</sup>; initial pH=7.0)

Adsorbent dose (g 100 mL <sup>-1</sup> )	Percentage of dye removal with time (min)						
	15	30	45	60	90	120	
Formaldehyde treated SB				The same of the same of			
0.2	7.8	9.3	11.5	12.2	15.4	17.5	
0.4	20.5	29.2	32.5	37.3	42.6	44.8	
0.6	38.2	44.4	49.5	52.3	58.5	62.7	
0.8	44.3	51.2	54.4	59.6	64.6	68.7	
1.0	58.4	62.5	64.7	68.3	73.4	74.5	
Formaldehyde treated SB							
0.2	38.4	42.5	48.7	52.5	55.7	59.4	
0.4	54.3	63.4	69.0	72.5	75.8	77.6	
0.6	74.5	78.9	81.2	83.6	84.5	88.0	
0.8	88.4	92.5	93.2	94.5	94.8	95.5	
1.0	92.5	93.1	93.7	94.2	95.1	96.3	

The sample was withdrawn from the shaker at the pre determined time intervals and absorbents were separated from the solution by centrifugation at 4500 rpm for 5 min. The absorbance of the supernatant solution was estimated to determine the residue of dye concentration.

The experiment was done by varying the amount of absorbents (0.2 to 1.0 mg  $100 \text{ mL}^{-1}$ ), concentration of dye solution (50-250 mg  $\text{L}^{-1}$ ) and pH (2-10) at different time intervals.

# RESULTS AND DISCUSSION

Effect of initial dye concentration: The study had shown that for the powdered activated carbon (PAC), the percentage of dye removal was very high, nearly 100% for all initial dye concentration and agitation time (Table 3). The lowest dyes removal was were measured for initial dye concentration of 250 mg L<sup>-1</sup> and 15 min contact time. The efficiency of dye removal was increased as the agitation time increased and lowers initial dye concentration.

For the treated sugarcane bagasse (undergo physical and chemical treatment), it had shown an increment in the percentage of dye removal. Also, it was found that an increasing in the dye concentration had caused the decreasing in the percentage of dye removal, even though the amount of dye being

adsorbed is increased. This will suit the finding which had been quotes by the other researchers<sup>[1-3]</sup>.

As a comparison, sugarcane bagasses which undergo the chemical treatment (sulphuric acid treatment) had shown better result in the dye adsorption compared to sugarcane bagasse treated with physical treatment (Table 3). The process was rapid initially and a large fraction of the total amount of dye was removed within a few minutes.

The effect of pH: For the powdered activated carbon, it was found that the percentage of dye removal was not affected by pH variation. The uptake of the dyes was nearly 100% for all pH values.

For the sulphuric acid treated bagasse (PCSB), the dyes adsorption was significantly change over the pH value of 4 to 7. The lowest percentage of dye removal was recorded at pH 2 (52.2%). At the pH range 7 to 10, the percentage of removal was almost remains constant. As the pH of the solution decrease (more acidic), the number of negatively charged adsorbents site increased. This will not flavor the adsorption of the positively charge dyes cation<sup>[8]</sup>. This, however didn't applied to PAC, as it was remained almost 100% for all pH values. There might be another mode of adsorption, such as ion exchange<sup>[1]</sup>. As the pH value increased from 9 to 13, the efficiency of the dyes removal is slightly become lessen.

The nearly same pattern was obtained for the formaldehyde treated sugarcane bagasse (PCSBC). The minimum percentages of removal was recorded at pH 2 (78.5) and the highest percentage recorded at pH 10 (98.7%). Figure 2 shows the variation of dyes removal for different adsorbents at various pH values.

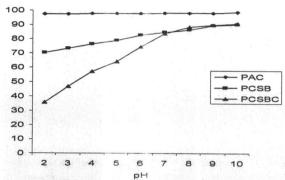


Fig. 2: Effect of pH on methyl red removal by PAC, PCSB and PCSBC (initial dye concentration 250 mg L<sup>-1</sup>, adsorbent dosage=0.4 g 100 mL<sup>-1</sup>, temperature 26°C, contact time=120 min

The effect of adsorbance dosage: For the powdered activated carbon (PAC), it was found that the percentage of dye removal was increased with the increament of adsorbance dosage. For the adsorbent dosage of 1.0 g 100 mL<sup>-1</sup>, it was found that after 45 min agitation time, the amount of dye being adsorbed was nearly 100% (Table 4).

As for sulphuric acid treated bagasse (PCSBC), the percentage of dye removal was increased from 54.9% to 96.5%, as the adsorbent dosage increased from 0.2 to 1.0 g 100 mL<sup>-1</sup> after the equilibrium time. Also, the increment from 17.5 to 74.5% was obtained for PCSB for the same increment of adsorbent dosage. This is due to increased in adsorbent dosage attributed to increase in surface area and availability of adsorption site.

# CONCLUSION

The removal of methyl red from simulated wastewater by using PAC, PCSB and PCSBC has been investigated for different variables viz contact time, adsorbent dosage pH and initial dye concentration.

From this study, it was found that PCSB and PCSBC has a lower adsorption efficiency compared to powdered activated carbon (PAC) at the any given initial dye concentration. The adsorption efficiency can be arranged in the following order GAC>PCSBC>PCSB.

This study had shown that PCSB and PCSBC had a lower adsorption efficiency compared to GAC at any given pH value. Initial dyes concentration over the range of 2 to 6, decreased the efficiency of the dyes removal. While, the pH range 7 to 10 is optimum for

the dyes removal for both adsorbents, PCSB and PCSBC.

As sugarcane bagasse is easily available in the countryside, it has potential to be used for the small scale industries which produced dyes as their effluent, after it was being pretreated with formaldehyde and sulphuric acid.

The data maybe useful for designing and fabrication of an economically cheap treatment process using batch or stirred tank flow reactors for the removal of methyl red from diluted industrial effluent.

### REFERENCES

- Grag, V.K., Raksh Kumar and Renuka Gupta, 2004. Removal of malachite green dye from aqueous solution by adsorption using agroindustries waste: A case study of *Phosopis* ceneraria. Dyes & Pigments, 62: 1-10
- Grag, V.K., Renuka Gupta, Anu Bala Vadar and Rakesh Kumar, 2003. Dye removal from aqueous solution by adsorption on treated sawdust. Bioresource Technol., 89: 121-124.
- Shaobin Wang, Y. Boyjoo, A. Choueib and Z.H. Zhu, 2005. Removal of dyes from aqueous solution using fly ash and red mud. Water Res., 39: 129-138.
- Kannan, N. and M.M. Sundram, 2001. Kinetic and mechanism of removal of methylene blue by adsorption on various carbons: A comparative study. Dyes & Pigments, 1: 25-40.
- Kadirvelu, K, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani and S. Pattabhi, 2003. Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metals ions from aqueous solutions. Bioresource Technol., 87: 129-132.
- Rajeshwarisivaraj, Subbaram V., 2002. Activated parthenium carbon as an adsorbent for the removal of dyes and heavy metal ions from aqueous solution. Bioresource Technol., 85: 205-206.
- Guo, Y., S. Yang, W. Fu, J. Qi, R. Li and Z. Wang, 2003. Adsorption of malachite green on micro and mesoporous rice husk based activated carbon. Dyes & Pigments, 3: 219-229.
- 8. Namasivayam, C., M. Dinesh Kumar, K. Selvi Begum, R. Ashruffunissa, T. Vanathi and R.T. Yamuna, 2001. Waste coir pith-a potential biomass for the treatment of dyeing wastewaters. Biomass Bioenergy, 21: 477-483.
- Namasivayam C, Kavitha D, 2002. Removal of Congo Red from water by adsorption on to activated carbon prepared from coir pith, an agricultural solid waste. Dyes Pigments 54: 47-58.

- Rajeshwarisivaraj, C. Namasivayam and K. Kadirvelu, 2003. Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. Waste Manage., 21: 105-110.
- Grag, V.K, M. Anita, R. Kumar and R. Gupta, 2004. Removal from simulated wastewater by adsorption using Indian Rosewood sawdust: A timber industry waste. Dyes & Pigments, 63: 243-250.
- Annadurai, G., R.S. Juang and D.J. Lee, 2002. Use of cellulose based wastes for adsorption of dyes from aqueous solutions. J. Hazard Mater., B92: 263-274.
- Waranusantigul, P, P. PokeThitiyook, M. Kruatrachue and E.S. Upatham, 2003. Kinetic of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza). Environ. Pollution, 125: 385-392.
- Namasivayam, C. and N. Kanchana, 1993. Removal of Congo red from aqueous solution by waste banana pith. J. Sci. Technol., 1: 33-42.
- Namasivayam, C., N. Kanchana and R.C. Yamuta, 1993. Waste banana pith as adsorbent for the removal of Rhodamine-B from aqueous solution. Waste Manage., 13: 89-95.
- Namasivayam, C. and N. Kanchana, 1992. Waste banana pith as adsorbent for color removal from waste waters. Chemosphere, 2: 1691-1705.
- Namasivayam, C., D. Prabha and M. Kumutha, 1998. Removal of dyes by adsorption onto agricultural solid waste. Bioresource Technol., 64: 77-79.

- Namasivayam, C., N. Muniasamy, K. Gayathri, M. Rani and K. Ranganathan, 1996. Removal of dyes from aqueous solutions by celulose waste orange peel. Bioresource Technol., 57: 37-43.
- Namasivayam, C., R. Radhika and S. Subha, 2001 Uptake of dyes by a promising locally available agricultural solid waste: coir pith. Waste Manage., 38: 381-387.
- Asfour, H.M., O.A. Fadali, M.M. Nassar and M.S. El-Geundi, 1985. Equilibrium studies on adsorption of basic dyes on hardwood. J. Chem. Technol. Biotechnol., 35A: 21-28.
- Juang, R.S., R.L. Tseng, F.C. Wu and S.J. Lin, 1996. Use of chitin and chitosan in lobster shell wastes for colour removal from aqueous solution. J. Environ. Sci. Health, A31: 325-338.
- Namasivayam, C. And R.T. Yamuna, 1992. Removal of Congo red from aqueous solution by biogass slurry. J. Chem. Technol. Biotechnol., 35A: 153-157.
- 23. Namasivayam, C. and R.C. Yamuta, 1992. Removal of Rhodamine-B by biogas slurry from aqueous solutions. Water Air Soil Pollutant, 65: 133-139.
- 24. Wu, F.C, R.L. Tseng and R.S. Juang, 1999. Pore structure and adsorption performance of the activated carbons prepared from palm kernels. J. Hazard. Mater., B69: 287-302.
- Singh, D.K. and N. Srivastava, 2001. Basic dyes removal from wastewater by adsorption on rice husk carbon. J. Chem. Technol., 8: 133-139.