KINETICS STUDY OF METHYLENE BLUE DYE BIOADSORPTION ON BAGGASE

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Abstract. The adsorption potential of agricultural (sugarcane) by-product, the baggase was investigated in batch experiments with two different forms i.e., raw and chemically activated forms, for the removal of Methylene Blue dye, with different parameters like dye concentration, contact time, temperature and adsorbent dose. The removal is better and more effective with chemically activated baggase in comparison to the raw baggase. An average percent removal difference between the two adsorbents of around 18% was achieved under the different conditions in the experiment. The data fit well in the Freundlich isotherm.
Key words: *Adsorbent, Adsorption, Methylene Blue dye, Raw Baggase, Chemically Activated Baggase.*

Introduction

Of various pollutants contained in industrial wastewaters, colour is considered to be very important from the aesthetic point of view and is stated as 'visible pollutant'. Almost every industry uses colouring matter to colour their products. Unspent colouring materials are usually discharged, with/without treatment into the aquatic environment. Dyes are highly coloured polymers and low biodegradable. Color/dye being one of the important recalcitrant, persist for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen and also decrease the recreation value of stream.

India produces more than 400 million tonnes (MT) of agricultural waste annually which include a very large percentage of the total world production of rice husk, baggase, jute, stalk and coconut fiber. India became the largest producer of sugar cane/sugar in the world, producing 285.4 MT of cane representing about a little more than 20% of cane sugar production. Presently, there are over 450 mills with installed capacity of 20.2 MT with average size of 2150 TPD with some units of 10000 TPD and few of 5000 TPD. Sugarcane production has increased in last decade and has reached to a maximum production of 300.1 MT in 2001-02 [www.indiaonestep.com] [1]. It have been analysed that after sugar extraction, one third of the waste product generated is baggase. Thus baggase production in India has reached a little above 100MT in 2001-02. Per capita consumption of sweetner in India, (prepared form sugarcane) is 24.4 kg, which is higher compared to world average of 20.4 kg.

Burning of baggase also releases large quantities of smoke, soot, ash and carbon dioxide into the air with detrimental environmental effects. Most efficient as well as balanced mills should be able to save baggase to the extent of 10% of its production, which can be used as captive fuel in the mill as power. Total production of baggase if used for power generation can generate 4000 MW surplus eco-friendly energy. Power generation

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from baggase comes under clean power and is very much eligible to get carbon emission benefits. But still in India, use of baggase for power generation is considered as the secondary option.

Literature Review

There is an ever-increasing demand of fabrics and food in the country for the rapid expanding population, which is growing at a rate of 11.04 %. Nearly 10-15% of the synthetic textile dyes, used yearly are lost to waste streams and about 20% of these losses enter the environment through effluent from wastewater treatment plant. The wastewaters discharged from dying processes exhibit high BOD, high COD are highly coloured, hot, alkaline and contain high amounts of dissolved solids [2]. The disposal of coloured wastes such as dyes and pigments into receiving waters damages the environment, as they are carcinogenic and toxic to humans and aquatic life [3, 4]. Besides the problem of colour, some dye impart non-visibility and can be modified biologically to toxic or carcinogenic compounds. Nowadays concern has increased about the long-term toxic effect of water containing these dissolved pollutants.

Basic dyes are the brightest class of dyes [5] and are applied widely in small scale industries like textile, carpets and wool industries whose discharge bearing dyes throught effluents are added into natural streams [6]. In dying industry above 30-60 litres of water is consumed per kg of cloth dyed and large quantities of effluents are released during process [7]. Its amount is to be about 16% of the total water consumed in the mill [8].

Various treatment methods for removal of dyes from industrial effluents like coagulation using alum, lime, ferric chloride, ferric sulphate, chemical oxidation methods using chlorine and ozone; and membrane separation methods are in vogue [8]. Many of them do not operate at low concentration of coloured compounds in the effluent. Special measures therefore are necessary to be taken to remove them from the effluents.

Adsorption has received considerable attention for colour removal from wastewaters as it offers the most economical and effective treatment method. Low cost adsorbents like flyash, coal, peat, sawdust [9], sawdust [10] lignite and wood have received considerable interest because of their local availability and their practically low cost [6]. Use of bio-adsorbent like rice husk [11], coconut coir, banana pith [12] wheat straw, baggase, saw dust [9,11,13], used tea leaves, cow dung [14] have been found to be highly effective, cheap and eco-friendly

Objective of present study was to explore equilibrium as well as the rate of adsorption of basic dye (Methylene Blue) in aqueous solution and efficiency of cellulose based adsorbents prepared from Baggase with its different states i.e., Raw and Chemically Activated form.

Materials and Methods

Preparation of Adsorbents

Baggase was obtained from a nearby sugarcane mill. Two parts, of the total cellulosic material by weight, were made and one part of the baggase was processed to obtain chemically treated baggase carbon. Four parts of raw baggase were treated with three parts by weight of concentrated Sulphuric acid and kept in air tight oven, maintained at

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150°-160°C for a period of 36 hours. The carbonized material was washed well with distilled water to remove the free acid and dried at 110-115°C for 24 hours. This material was grounded and sieved to obtain carbon particle size £ 0.33 mm and was used as chemically activated baggase adsorbent.

Another part of cellulosic baggase was soaked in distilled water for forty-eight hours with repeated change of distilled water, every 12 hours. It was then treated with alkali for 12 hours to make it lignin free, thoroughly washed with distilled water and then was treated with formaldehyde to prevent any further colour interference during treatment (adsorption) process. The material was now dried in an oven at 50-60°C for 24 hours and this dried material was pulverized to convert it into fine powder and was used as raw baggase adsorbent. Table 1 gives the physical properties of prepared treated adsorbent.

Table 1. Physical properties of chemically Treated Sawdust Adsorbent

Parameters	Characteristic Value
pH 6.5	
Moisture (%)	12.1
Bulk density (g/ml)	0.33
Matter soluble in water (%)	Nil
Matter soluble in acid (%)	Nil
Surface area,m2/g	1.713
Pore volume (ml/g)	0.11
Ash content (%)	36.62
Iodine Number	75
Ion exchange capacity (meq/g)	1.06

Dye and Chemicals

Methylene Blue [3,9-bis dimethyl- aminophenazo thionium chloride], a cationic dye (figure 1), is a G.R. Product of Merck, Germany and was used as received. All chemicals used were of analytical reagent grade and supplied by Merck Germany.

Adsorption Studies

To evaluate the efficiency of adsorbents, laboratory batch mode studies were conducted. 0.1 to 1 gm of adsorbents, taken separately, were shaken in 100ml aqueous solution of dye of varying concentration for different time periods and temperatures at natural pH. At the end of pre-determined time intervals, adsorbent was removed by centrifu-

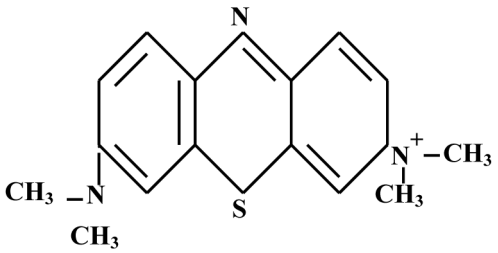

Figure 1. Methylene Blue [3,9-bis dimethylaminophenazo thionium chloride]

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gation at 2000 rpm for 10 minutes and supernatant was analyzed for the residual concentration of Methylene Blue, spectro-photometerically at 665 nm wavelength. All experiments were carried out in triplicate with respect to each condition and mean values are presented. The maximum deviation was 4%.

Results and discussion

Effect of Initial Dye Concentration and Time

Effect of initial dye concentration on the rate of adsorption by baggase (raw and chemically activated) was achieved as presented in Table 2. The data table of amount of dye adsorbed at various intervals of time indicates that the removal of dye (adsorbate) initially increases with time but attains an equilibrium within 45-60 minutes. The adsorption process was found to be very rapid initially, and a large fraction of the total concentration of dye was removed in the first 30 minutes. Though it was observed that adsorption of dye increased with an increase in dye concentration in the solution, which shows that removal of dye is dependent upon the concentration of the dye solution. But as a whole the percent removal decreases with the increase in dye concentration as observed in the plot.

Table 2. *Effect of Initial dye concentration on MB removal by Raw and Chemically Activated Baggase*

Conc.→	50ppm		100 ppm		150 ppm		200 ppm		250 ppm		300 ppm	
Time ↓ (mins)	RB	CAB	RB	CAB	RB	CAB	RB	CAB	RB	CAB	RB	CAB
15	61.3	71.54	56.4	66.32	44.48	61.64	38.72	55.49	28.51	42.96	20.58	31.85
30	79.8	80.26	69.81	77.91	58.84	67.52	48.03	60.32	35.48	48.93	33.71	36.55
45	83.96	89.54	77.52	82.95	66.22	72.58	54.67	64.91	41.24	54.79	37.98	39.23
60	86.28	92.46	83.90	85.67	70.28	78.92	56.62	67.95	47.36	57.29	39.93	42.67
90	88.72	94.84	86.28	87.03	74.29	82.99	61.26	69.67	49.25	59.28	42.39	44.59
120	90.11	96.12	88.90	90.11	78.26	84.91	66.19	72.03	51.76	61.54	44.35	46.32

For a particular experiment, the rate of adsorption decreased with time, it gradually approached a maximum adsorption, owing to continuous decrease in the concentration driving force and it also indicate that the adsorbent is saturated at this level. In addition it is observed that initial rate of adsorption was greater for higher initial dye concentration because as the resistance to the dye uptake decreased, the mass transfer driving force increased. The time variation adsorption increases continuously and seems to be smooth which, is indicative of the formation of monolayer coverage on the surface of adsorbent [15].

Raw (RB) and Chemically Activated baggase (CAB) could remove a maximum of 83.93% and 85.67% respectively, of Methylene Blue at initial dye concentration of 100 ppm, while for dye concentrations of 50 ppm, the adsorption of the dye was well above 90% and 96% in two hours. Both cases were studied at natural pH, temperature 250°C and adsorbent dose of 4 gm/l.

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Effect of adsorbent dose and time

The effect of varying the RB and CAB mass on aqueous dye solution are presented in Table 3. Data show a decreasing trend in dye concentration at a faster rate as the adsorbent mass is increased. Of the two adsorbents, CAB gave the greater removal at all levels of the adsorbent dose. An equilibrium percentage removal rate of 77.91% and 69.81% was achieved with 4 gm/l in 30 minutes by CAB and RB respectively of adsorbate concentration of 100 ppm. Initially the rate of increase in the percent dye removal has been found to be rapid which slowed down as the dose increased. This phenomenon can be explained, based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher.

Table 3. *Effect of adsorbent dose on MB removal by RB and CAB*

Dose →	0.1 gm		0.2 gm		0.4 gm		0.6 gm		0.8 gm		1.0gm	
Time ↓ (Mins)	RB	CAB	RB	CAB	RB	CAB	RB	CAB	RB	CAB	RB	CAB
15	20.56	38.98	31.56	54.28	56.4	66.32	70.64	78.62	84.98	87.28	96.01	95.09
30	25.77	45.78	41.98	62.82	69.81	77.91	82.52	84.28	92.44	92.91	98.68	97.52
45	27.24	50.75	48.35	69.59	77.52	82.95	88.85	88.35	94.70	94.79	99.23	98.73
60	29.36	54.17	51.49	75.48	83.93	85.67	90.58	91.47	96.46	93.71	99.47	98.61
90	31.17	57.67	53.61	79.55	86.28	87.03	92.08	93.25	97.16	97.68	99.52	99.54
120	33.11	60.45	54.72	80.62	88.90	89.46	93.98	95.34	97.80	98.06	96.56	99.63

The initial rise in adsorption with adsorbent dose is probably due to bigger driving force and lesser surface area. Larger surface area of the adsorbent and smaller size of adsorbate favour adsorption. The rate of adsorption is higher in the beginning as sites are available and unimolecular layer increases. Adsorption and desorption occur together and rate become equal at a stage called adsorption equilibrium, when isotherms are applied. The subsequent slow rise is observed in percent removal, which states that adsorption and intra-particle diffusion taking place simultaneously with dominance of adsorption. With rise in adsorbent dose, there is less commensurate increase in adsorption, resulting from lower adsorptive capacity utilization of adsorbent. [16].

Thus, the results obtained from this section of experiment indicate that chemically activated baggase has a large potential as an adsorbent for dye removal than raw baggase.

Effect of temperature

Temperature dependence of adsorption process is a complex phenomenon. Thermodynamic parameters, like heat of adsorption and energy of activation play an important role in predicting the adsorption behavior and both are strongly dependent on temperature. Temperature rise affects the solubility and chemical potential of the adsorbate, the latter being a controlling factor for adsorption. It have been reported that if solubility of the adsorbate increases with increase in temperature, then chemical potential decreases and both of these effects work in the same direction, causing a decrease in adsorption [17]. On the other hand if temperature has the reverse effects on the solubility than both the said effects will act in the opposite direction and adsorption may increase or decrease depending upon the predominant factor.

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In the present experiments the adsorption rate at three different temperatures (30°, 40°, 50°C) have been analysed as presented in data Table 4. In case of raw baggase, the rate of dye uptake decreases with an increase in temperature from 74.26% to 55.92% at 30°C to 50°C with 4 gm/l dose in 30 minutes for 100 ppm dye solution, indicating that the process is exothermic in nature [18]. This may be due to a tendency of dye molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution [19]. Whereas in the case of Chemically activated baggase rate of dye uptake increases rapidly from 78.09% to 86.35% with rising temperature at 30°C to 50°C with 4 gm/l dose in 30 minutes from 100 ppm dye solution, since the adsorption rate increase as the diffusion coefficient rises with temperature. [5].

Table 4. *Effect of Temperature on MB removal by Raw and Chemically Activated Baggase*

Temp.	30°C		40°C		50°C	
Time	RB	CAB	RB	CAB	RB	CAB
5 Minutes	64.38	61.04	57.39	65.25	46.48	71.22
10 Minutes	67.21	68.84	60.72	72.85	50.16	76.28
15 Minutes	70.56	74.54	64.09	78.06	53.63	81.5
30 Minutes	74.26	78.09	67.28	83.54	55.92	86.35
45 Minutes	76.59	80.21	69.52	86.19	56.85	90.16
60 Minutes	77.72	81.55	70.25	88.94	57.73	92.42

For adsorption of dye using baggase (raw and chemically activated) adsorbent there is the possibility of intra-particle diffusion. This was also investigated and is presented in Fig 2 and 3. The graph is plotted with log (% adsorption) vs. log (time), for adsorption at three (30°, 40°and 50°C) temperatures resulting in straight lines, which indicate the occurrence of intra-particle diffusion. The adsorption at higher temperature becomes more dependent on intra-particle diffusion, which would be the rate-determining step [20].

Adsorption isotherm

The analysis of equilibrium data for the adsorption of the Methylene blue on adsorbents baggase (RB and CAB) have been done in the light of the Freundlich isotherm model [21].

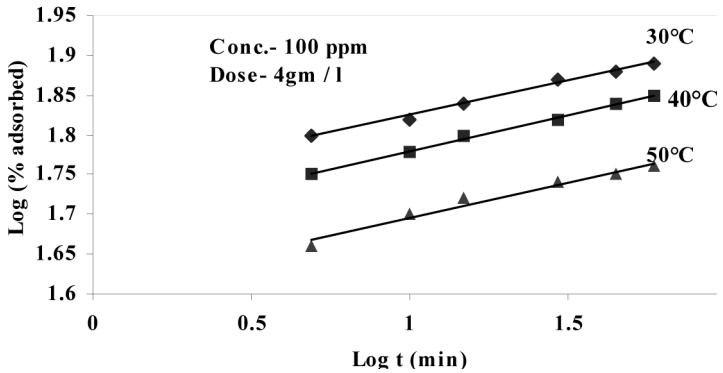

Figure 2. *Kinetics of Adsorption of MB Dye on Raw Baggase at Different Temperatures*

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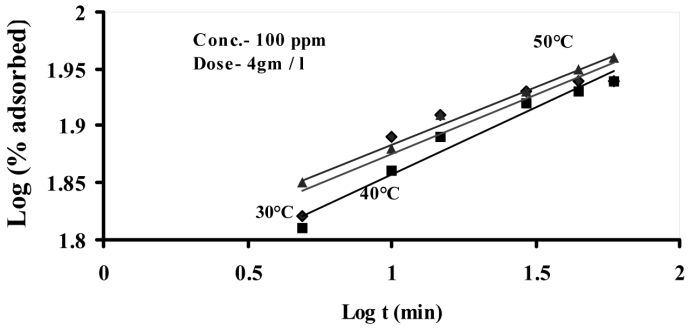

Figure 3. *Kinetics of Adsorption of Dye by Chemically activited Baggase at Different Temperatures*

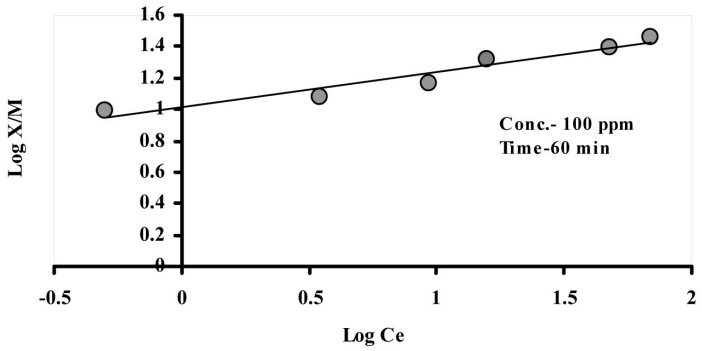

Figure 4. *Freundlich Isotherm for Adsorption rate of MB Dye on Raw Baggase*

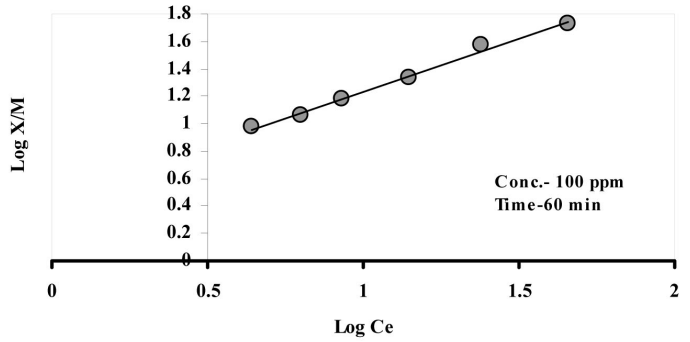

Figure 4. *Freundlich Isotherm for Adsorption rate of MB Dye on CA Baggase*

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$$\log_{10}\frac{x}{m} = \log_{10} K_f + \frac{1}{n}\log_{10} C_e \qquad \text{(Eq. 1)}$$

Where, Ce is the equilibrium concentration (mg/l), x is the amount of dye adsorbed (mg), m is the adsorbent dose used (g) and Kf and n are constants, incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. Linear plots of log10 (x/m) vs. log Ce shows that adsorption follows Freundlich isotherm model. Fig. 4 and 5.

These preliminary studies state that adsorbents prepared from baggase can be used effectively for the adsorption of dyes. Cost analysis for the preparation of activated carbon of baggase has not been done since Baggase is available abundantly and can be obtained for nominal price as agricultural by-product in the country. The present method has been adopted for further analytical kinetics study of other agricultural by-products for the removal of dyes and heavy metals from aqueous solutions and industrial effluents.

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