AZO DYE REMOVAL BY ADSORPTION USING WASTE BIOMASS: SUGARCANE BAGASSE

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ABSTRACT

Dyes are usually present in trace quantities in the treated effluents of many industries. The effectiveness of adsorption for dye removal from wastewaters has made it an ideal alternative to other expensive treatment methods. This study investigates the potential use of sugarcane bagasse, pretreated with formaldehyde and sulphuric acid, for the removal of methyl red, an azo dye from simulated wastewater. The effects of condition such as adsorbent dosage, initial dye concentration, pH and contact time were studied. The results showed that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of methyl red. Sulphuric acid treated sugarcane baggase showed a better performance compared to formaldehyde treated sugarcane baggase, thus making it an interesting option for dye removal from dilute industrial effluents.

Keywords: *azo dye, methyl red, adsorption, sugarcane bagasse*

INTRODUCTION

Colored compounds are the most easily recognizable pollutants in the environment because of their appearance. Most of the industries such as textile, paper, carpet, and printing use dyes and pigments to color their products. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. However, the discharge of dye-bearing wastewater into natural streams and rivers possess a severe problem, as dyes impart toxicity to aquatic life and are damaging the aesthetic nature of the environment. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents due to their structure and molecular size [1,2]. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [3,4]

If the adsorption system is designed correctly it will produce a high-quality treated effluent. Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Adsorption techniques have gained favor in recent years because of their proven efficiency in the removal of pollutants from effluents too stable for conventional treatment methods. Apart from the high-quality product obtained, the processes have proved economically feasible [5,6]. The successful removal of acid dyes by fixed beds of activated carbon has been demonstrated by Walker and Weatherley [7].

Activated carbon (powdered or granular) is the most widely used adsorbent because it has excellent adsorption efficiency for organic compounds, but its use is usually limited due to its high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. Consequently, a number of low cost and easily available materials, such as waste biomass, are being studied for the removal of different dyes from aqueous solutions at different operating conditions.

Forest and agricultural production byproducts have been long considered as potential dye adsorbents. Unfortunately, without prior chemical modification these materials uniformly have very low adsorption capacities for acidic dyes [8]. The binding of Acid Blue 25 to sugarcane bagasse is slow (greater than 3 h for equilibrium to be reached) and the capacity only 0.05 mol/kg [9,10]. Table 1 shows comparison for adsorption of some dyes on various adsorbents.

The aim of the present study was to determine the optimum conditions for the removal of an azo dye, *i.e.* methyl red, from simulated wastewater by adsorption technique using formaldehyde treated sugarcane bagasse and sulphuric acid treated sugarcane bagasse. Methyl Red, also called C.I. Acid Red 2, is an indicator dye that turns red in acidic solutions. Its formula is $C_{15}H_{15}N_3O_2$ (Figure 1). It is an azo dye, and is a dark red crystalline powder with melting point between 179-182 °C. It has 95% dye content, molecular weight of 269.31; and its transition range is pH 4.2 – pH 6.2 (red-yellow) with maximum adsorption of 430 nm – 434 nm for pH 6.2 and 523 nm – 526 nm for pH 4.5. Figure 1 shows the molecular structure of methyl red [21].

Table 1: Comparison for adsorption of some dyes on various adsorbents.

Adsorbent(s)	Dye(s)	References
Duckweed	Methylene blue	[11]
Sewage Sludge	Basic red 46	[12]
Waste newspaper	Basic blue 9	[13]
Rice husk	Malachite green	[14]
	Acid yellow 36	[15]
	Acid blue	[16]
Sugarcane bagasse	Acid orange 10	[17]
Coir pith	Congo red	[18]
Straw	Basic blue 10	[19]
Treated Sawdust	Methylene blue	[20]

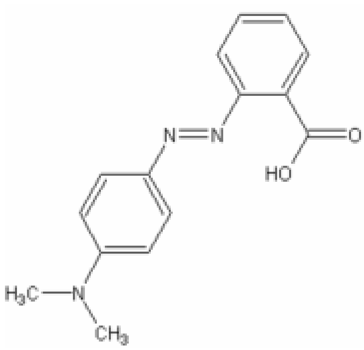

Figure 1: Molecular structure of methylene red [21].

MATERIALS AND METHODS

Adsorbents

Formaldehyde treated sugarcane bagasse

Sugarcane bagasse was collected from a local market in Kajang. It was dried under sunlight until all the moisture has evaporated. The material was ground to fine powder. The resulting material was sieved in the size range of 80-230 mesh ASTM. To immobilize the colour and watersoluble substances, the ground powder was treated with 1% formaldehyde in the ratio of 1:5 (bagasse:formaldehyde, w/v) at 50^{o}C for 4 h. The sugarcane bagasse was filtered out, washed with distilled water to remove free formaldehyde and activated at 80^{o}C in hot air oven for 24 h. The material was placed in an airtight container for further use.

Sulphuric acid treated sugarcane bagasse

One part of dried sugarcane bagasse was mixed with one part of concentrated sulphuric acid and heated in a muffle furnace (Naber, Germany, Model: L51/S) for 24 h at 150^{o}C. The heated material was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid. The material was dried in an oven at 105^{o}C for 24 h and sieved in the size range of 80-230 mesh ASTM and used for the further study. All adsorbents were dried at 110^{o}C overnight before the adsorption experiments.

Sorbate

Methylene red (Sigma-Aldrich Chemie GmbH, Germany) was used to prepare the simulated wastewater. An accurately weighed quantity of methylene red (0.5635 g) was dissolved in distilled water to prepare the stock solution (500 mg/L). The stock solution was then properly wrapped with aluminium foil and stored in a dark place to prevent direct sunlight, which may cause decolourisation. Experimental solutions of the desired concentration were obtained by successive dilutions.

Experimental methods and measurements

In each adsorption experiment, 100 ml of dye solution of known concentration and pH was added to 400 mg of adsorbents (untreated, formaldehyde treated and sulphuric acid treated sugarcane bagasse) in a 250 ml round bottom flask. This was done at a room temperature (29±1^{o}C). The mixtures were then stirred on a rotary orbital shaker (Heidolph, Model: Unimax 1010) at 160 rpm. The initial pH of the mixtures were varied between 2-9, this was controlled by the addition of dilute HCl or NaOH solutions.

Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution. Therefore, samples were withdrawn from the shaker every 15 or 30 minutes and the adsorbent was separated from the solution by centrifugation at 4500 rpm for 5 min. In order to determine the residual dye concentration, the absorbance value of the supernatant solution was measured before and after the treatment, at 617 nm with Shimadzu UV Visible spectrophotometer (Model UV mini 1240).

Two main system variables, initial dye concentration in the test solution and adsorbent dosage, were varied to investigate their effects on the adsorption kinetics. Blank runs, with only the adsorbents in 100 ml of distilled water, were conducted simultaneously at similar conditions to account for any colour leached by the adsorbents and adsorbed by glass containers. Samples were diluted with distilled water if absorbance values exceeded 0.900. Each experiment result was an average of three independent adsorption tests.

RESULTS AND DISCUSSIONS

Effect of initial dye concentration

The influence of the initial concentration of methyl red in the solutions on the rate of adsorption on sulphuric acid treated, formaldehyde treated and untreated sugarcane bagasse was studied. The experiments were carried out at fixed adsorbent dose (400 mg/100 ml) in the test solution, 29±1^{o}C room temperature, pH (7.0) and at different initial concentrations of methyl red (50, 100,150, 200 and 250 mg/L) for different time intervals (15, 30, 45, 60, 90 and 120 min). Results are shown in Table 2. It is evident that the percent adsorption efficiency of sulphuric treated, formaldehyde treated and untreated sugarcane bagasse decreased with the increase in initial dye concentration in the solution. However, for sulphuric acid treated and formaldehyde treated sugarcane bagasse, equilibrium attainment was achieved only after 60 and 90 mins, respectively. This may be due to the fact that sulphuric acid and formaldehyde treated sugarcane bagasse have macro and micro pores, resulting in longer contact time between the dye molecules and the adsorbent. In the process of dye adsorption, initially dye molecules have to encounter the boundary layer effect before diffusing from boundary layer film onto adsorbent surface. This is followed by the diffusion of dye into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time. The time profile of dye uptake is a single, smooth and continuous curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the adsorbent [20].

Effect of adsorbent dose

The adsorption of methyl red on sulphuric acid treatment and formaldehyde treated sugarcane bagasse were studied by changing the quantity of adsorbent (0.2, 0.4, 0.6, 0.8 and 1.0 g/100 ml) in the test solution while keeping the initial dye concentration (250 mg/L), temperature (29±1^{o}C) and pH (7.0) constant. Experiments were carried out at different contact times for 120 mins. As shown in Table 3, the percent adsorption increased and equilibrium time decreased with increasing adsorbent doses. The adsorption increased from 59.4 to 96.3%, as the sulphuric acid treated dose was increased from 0.2 g to 1.0 g/100 ml at equilibrium time (120 min). For formaldehyde treated sugarcane bagasse, adsorption increased from 17.5 to 74.5% as the adsorbent dose was increased from 0.2 to 1.0 g/100 ml. Maximum dye removal was achieved within 90-120 min after which methyl red concentration in the test solution was almost constant. Increase in the adsorption with adsorbent dose can be attributed to the increase in adsorbent surface area and availability of more adsorption sites.

Table 2: Effect of methyl red concentration on the dye adsorption

Initial dye concentration (mg/L)	Percent dye removal with time (min)					
	15	30	45	60	90	120
Sulphuric acid treated sugarcane bagasse						
50	90.1	92.5	92.8	93.4	94.0	96.2
100	89.5	90.2	90.8	92.1	93.3	93.9
150	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
Formaldehyde treated sugarcane bagasse						
50	77.0	78.8	80.3	82.3	84.5	85.9
100	66.8	68.0	69.9	70.5	71.8	73.3
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
Untreated sugarcane bagasse						
50	43.0	50.4	52.2	53.0	53.8	54.1
100	38.6	42.8	45.6	46.1	47.2	47.5
150	36.2	40.6	43.6	44.2	46.4	46.8
200	30.8	33.0	36.7	37.1	37.6	38.2
250	25.3	26.7	28.1	29.2	30.3	31.6

Table 3: Effect of adsorbent dose on the dye adsorption

Adsorbent dose (g/100 mL)	Percent dye removal with time (min)					
	15	30	45	60	90	120
Sulphuric acid treated sugarcane bagasse						
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
Formaldehyde treated sugarcane bagasse						
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	72.4	74.5
Untreated sugarcane bagasse						
0.2	18.5	19.8	20.5	22.5	23.0	23.8
0.4	25.3	26..8	28.3	29.7	30.6	31.8
0.6	32.0	33.4	35.8	36.9	38.2	39.9
0.8	42.5	44.6	47.6	48.6	49.8	52.4
1.0	52.6	55.8	58.7	61.4	63.4	64.6

Effect of pH

In order to study the effect of pH on methyl red adsorption on formaldehyde treated sugarcane bagasse and sulphuric acid treated sugarcane bagasse, experiments were carried out at 250 mg/L initial dye concentration with 400 mg/100 ml adsorbent mass at room temperature of 29±1^{o}C for 3 h equilibrium time. Results are presented in Figure 2. In the case of untreated sugarcane bagasse, maximum dye removal of 32.8% was recorded at pH 9. Between pH range of 2-6, the percentage of dye removal was nearly equal, ~ 20%. Significant increase in dye removal efficiency for formaldehyde treated sugarcane bagasse was observed between pH range of 3-7. Although dye adsorption efficiency for sulphuric acid treated sugarcane bagasse is higher than the untreated and formaldehyde treated sugarcane bagasse, it was not significantly affected by pH. This may be due to hydrolysis of the adsorbent in water, which creates positively charged sites [20]. Overall, the dye adsorption by sulphuric acid treated was 79-96% in the studied pH range followed by formaldehyde treated (52-95%) and untreated sugarcane bagasse (15-33%).

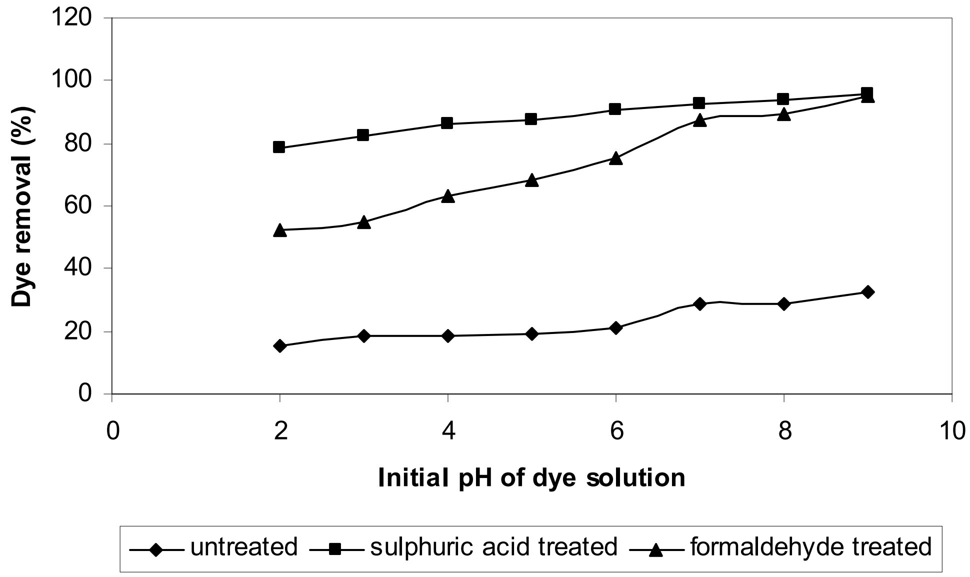

Figure 2: Effect of pH on methyl red adsorption
(initial dye concentration = 250 mg/L; adsorbent dose = 400 mg/100 mL; equilibrium time = 3 h)

CONCLUSION

Sugarcane bagasse is a common biomass waste material and is easily available at a small price. The removal of methyl red from simulated wastewater using chemical treatment of sugarcane bagasse with sulphuric acid and formaldehyde has been investigated under different experimental conditions in batch mode. The adsorption of methyl red was dependent on the adsorbent dose and the methyl red concentration in the wastewater. The results show that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of methyl red. Sulphuric acid treated sugarcane baggase showed a better performance compared to formaldehyde treated sugarcane baggase. This study proved that sugarcane bagasse is an attractive option for dye removal from dilute industrial effluents.

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