Global Journal of Environmental Research 4 (3): 175-182, 2010
ISSN 1990-925X

Adsorption Removal of Methyl Red from Aqueous Solutions with Treated Sugarcane Bagasse and Activated Carbon- *a Comparative study*

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Abstract: The use of sugarcane bagasse, an agro industry waste, to remove methyl red dye from the wastewater is studied in this review. It investigates the potential use of sugarcane bagasse pretreated with formaldehyde and sulphuric acid. The adsorption capacities of both formaldehyde treated and sulfuric acid treated bagasse were examined at varying pH, initial dye concentration, adsorbent dosage, contact time and temperature. To compare the performance of treated sugarcane bagasse with commercially available powdered activated carbon, similar experiments were conducted with powdered activated carbon. The effect of pH, adsorbent dosage, initial dye concentration and temperature on removal of dye was examined for different contact times. It was observed that the adsorption efficiency of sulfuric acid treated bagasse was higher than that of formaldehyde treated bagasse. Also, the adsorption capacity was observed to be higher for lower initial dye concentrations. As pH of the dye solution was increased, the adsorption efficiency got increased. It was found that the dye removal was increased with the increment of adsorbent dosage. Also, the optimization study was carried out to get optimum conditions for the treatment process. This study demonstrates that treated sugarcane bagasse is an effective and cheap adsorbent for the removal of dyes from the aqueous solutions and the possibility of using it for a simple and inexpensive method of dye removal from wastewaters in a batch or stirred tank reactors. The data obtained may be useful for designing an economical and optimized treatment process using batch or stirred tank reactors for the removal of methyl red dye from industrial effluents.

Key words: Adsorption · Methyl red dye · Sulfuric acid · Formaldehyde · Sugarcane bagasse · Contact time · Adsorbent dosage etc

INTRODUCTION

The textile industry, a major consumer of water for several of its wet processing operations, is a major producer of effluent wastewater containing organic surfactants, salts, acids, alkalis, solvents and dyes as some of its main constituents. Dyes, although present in only small amounts are highly detectable and thereby capable of causing serious problems of an aesthetic nature in the receiving water bodies. In fact, most of the commercially used dyes are resistant to biodegradation, photodegradation and even oxidizing agents. Unless otherwise properly treated, these dyes can significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to certain forms of aquatic life due to the presence of metals and chlorides in them.

Dyes have also been known to interfere with certain municipal wastewater treatment operations such as ultraviolet disinfection, etc. A major contributor to color in textile wastewater is usually the washing operation after dyeing, during which as much as 50 percent of the dye might be exhausted into the effluent.

Given the inadequacy of biological methods for effective dye removal, adsorption has come to stay as one of the popular physical/chemical methods successfully employed for decolorization. Adsorption process is advantageous because of its sludge free clean operation and completely removed dyes, even from the diluted solutions. The emphasis has of late, however shifted towards low-cost adsorbents which can serve as viable alternatives to the more expensive activated carbon.

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The most widely used adsorbent is activated carbon. The adsorption capacity of activated carbon is on the higher side. But it is very expensive and also regeneration results in the loss of adsorbent which is undesirable.

In recent years, many studies have been carried out to find out inexpensive alternatives such as coir pith, banana pith, rice husk, clay, groundnut shell, maize cob, peat, orange peel, coconut husk, wheat straw dust etc. The use of treated sugarcane bagasse has also been studied as an adsorbent for the colour removal from aqueous solutions. Instead of just disposing the bagasse as a waste, the efficient utilization can be made to remove the dyes from the wastewaters. Related to this, the utilization of sugarcane bagasse (treated with formaldehyde and sulfuric acid) for the removal of methyl red dye from aqueous solutions has been dealt here in this review.

In this study, the adsorption of methyl red on formaldehyde and sulfuric acid treated bagasse has been compared with activated carbon to develop the economical process of dye removal using cheap and eco-friendly adsorbent.

Nowadays, there are numerous low cost, commercially available adsorbents which are used for the dye removal. However, the adsorption efficiencies of these adsorbents are not very high. This has lead to the further research on the use of low-cost, easily available adsorbents with very high efficiencies.

MATERIALS AND METHODS

Experimentation

Preparation of Adsorbents: The steps involved in the preparation of *formaldehyde treated bagasse and sulphuric acid treated bagasse are as follows.*

Raw bagasse was obtained from the nearby sugar mill. It was dried under the sunlight until all the moisture evaporated. Then it was ground to a fine powder in a grinder. The ground bagasse was sieved. The average particle size of the powder used was 0.1456 mm. This ground bagasse was later treated with 1% formaldehyde in the weight to volume ratio of 1:5 at 50°C for 4 hours. It was filtered out using Buchner funnel, washed with distilled water in order to remove free formaldehyde and was kept in oven at 80°C for 24 hours.

Sulfuric Acid Treated Bagasse: In this the bagasse fibers were treated with sulphuric acid in the ratio of 1:1 and then heated in a muffle furnace for 24 hours at 150°C. The heated bagasse was washed with distilled water and soaked in sodium bicarbonate solution overnight to remove free sulphuric acid. It was then dried in an oven at 150°C for 24 hours. Later it was ground and sieved. The size obtained was 0.1523 mm.

Dye Solution Preparation: The dye used for this experiment was methyl red. Methyl red dye crystals were dissolved in alcohol to get a clear solution. Stock solution was prepared by dissolving a weighed quantity of the dye in distilled water.

The test solutions needed for the experiment were obtained from successive dilutions.

pH variation was done by using sodium hydroxide (for basic pH range) or hydrochloric acid (for acidic pH range). pH range used for this study was between 2 and 10. The concentration of the dye in the solutions was determined by measuring the absorbance values before and after the treatments at 617 nm using UV spectrophotometer, model 117 and comparing with the standard calibration curve.

Adsorption Experiment: A known desired quantity of the adsorbent was added to 100 ml of the dye solution of known concentration and known pH in 250 ml BOD bottles at room temperature and the solutions were kept for shaking in a rotary orbital shaker. Samples were withdrawn from the shaker at different time intervals. The adsorbents were separated from the solution by employing a centrifuge for a period of 5 minutes. The absorbance of the supernatant solution was found out by UV spectrophotometer to estimate the final dye concentration. Experiment was repeated for different initial dye concentration (50-250 ppm), adsorbent dosage (0.2-1.0 mg/100 ml), pH (2-10) and for different temperatures (40-50°C).

RESULTS AND DISCUSSIONS

pH Variation: pH of the solution was varied from 2 to 10. For different pH values the percentage removal of the dye was recorded. Table 1 gives the percentage removal of dye with different adsorbents at different contact times. The values are given for initial dye concentration of 100 mg/l and adsorbent dosage of 0.4 g/100 ml.

Effect of pH: The adsorption efficiency was greatly affected by pH variation. It was seen that for formaldehyde treated bagasse the dye adsorption considerably increased as pH was varied from 2 to 6. At pH 2, the percentage of dye removal was very low, 54.7% for 100 ppm and it increased to 71.87% for 100 ppm as pH was made 6.

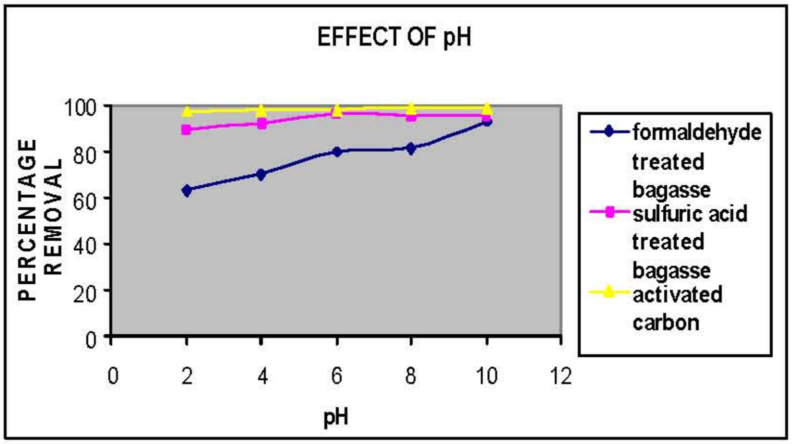

Fig. 1: Effect of pH on dye removal.
(Initial Dye Concentration=100 mg/l; adsorbent dosage=0.4 g/100 ml, contact time= 75min.)

Formaldehyde Treated Bagasse

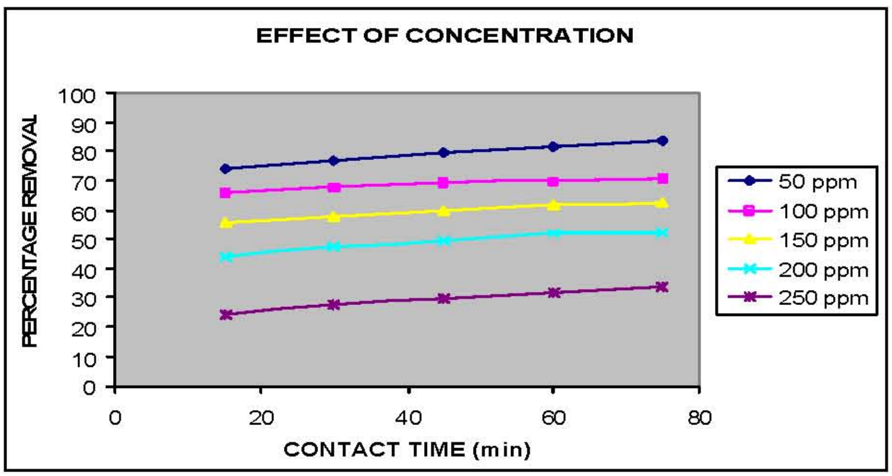

Fig. 2: Effect of initial dye concentration.
(Adsorbent dosage=0.4 g/100 ml, initial pH=7.0.)

Sulfuric Acid Treated Bagasse

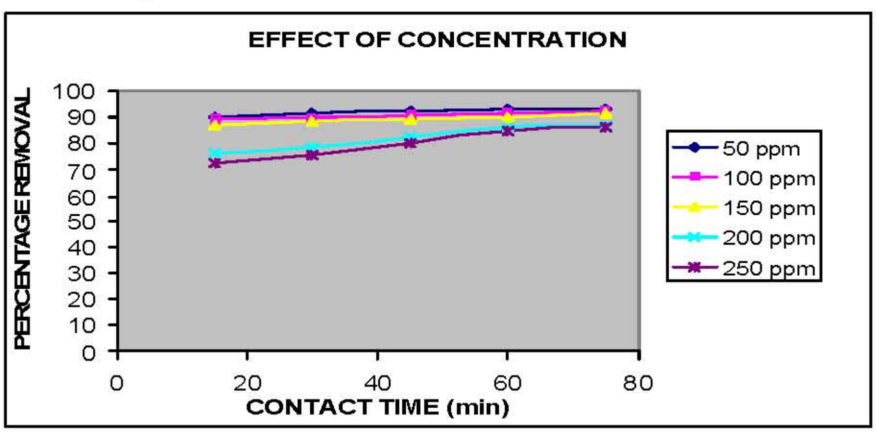

Fig. 3: Effect of initial dye concentration.
(Adsorbent Dosage=0.4g/100 ml, initial pH=7.0)

Activated Carbon

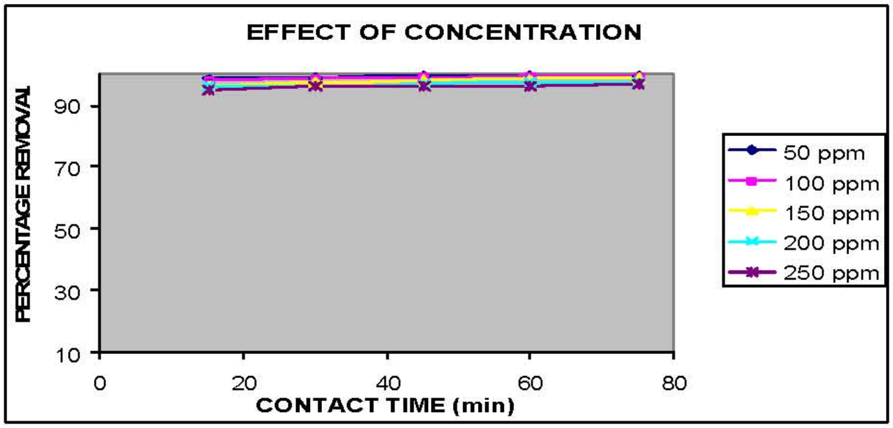

Fig. 4: Effect of initial dye concentration.
(Adsorbent dosage=0.4 g/100 ml, initial pH=7.)

Formaldehyde Treated Bagasse

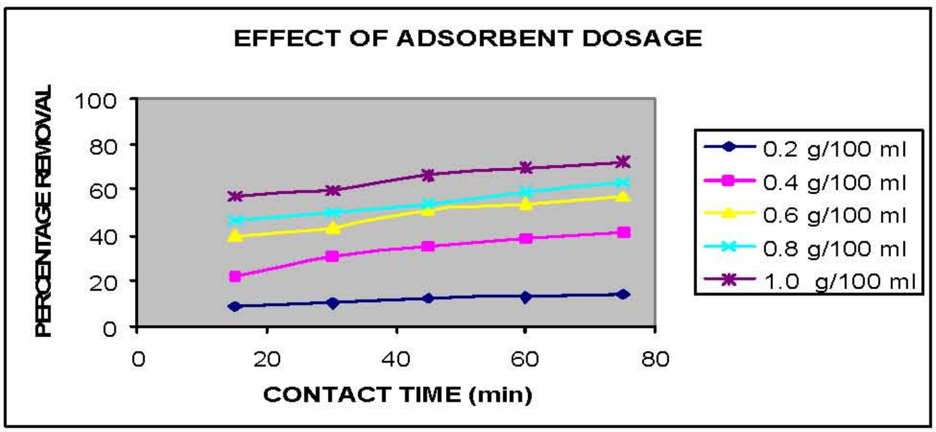

Fig. 5: Effect of adsorbent dosage on dye removal by formaldehyde treated bagasse.
(Initial dye concentration=250 mg/L, initial pH=7.0)

Sulfuric Acid Treated Bagasse

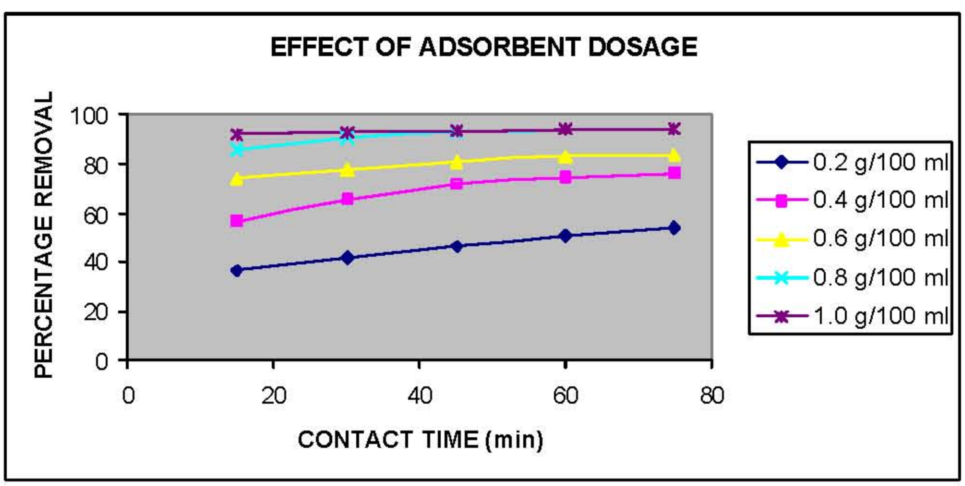

Fig. 6: Effect of adsorbent dosage on dye removal by sulfuric acid treated bagasse.
(Initial dye concentration=250 mg/L, initial pH=7.0.)

Activated Carbon

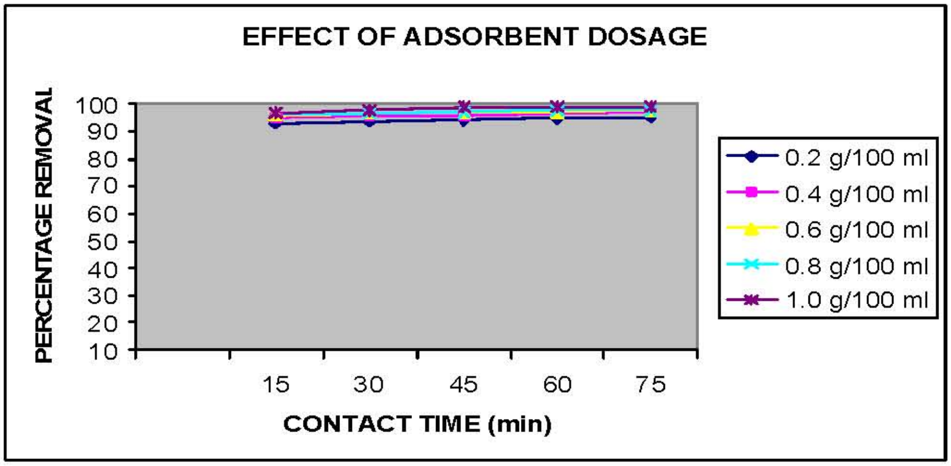

Fig. 7: Effect of adsorbent dosage on dye removal by activated carbon. (Initial dye concentration=250 mg/L, initial pH=7.0)

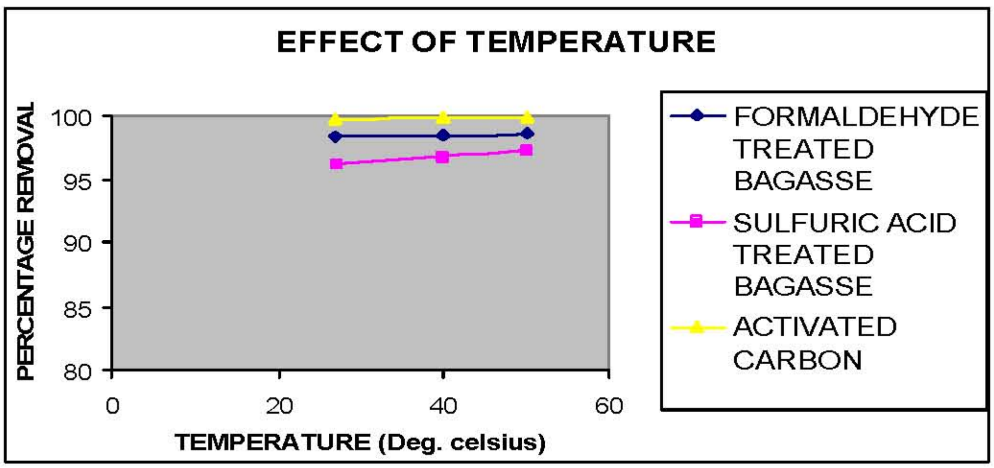

Fig. 8: Effect of temperature on methyl red dye removal.

Formaldehyde Treated Bagasse

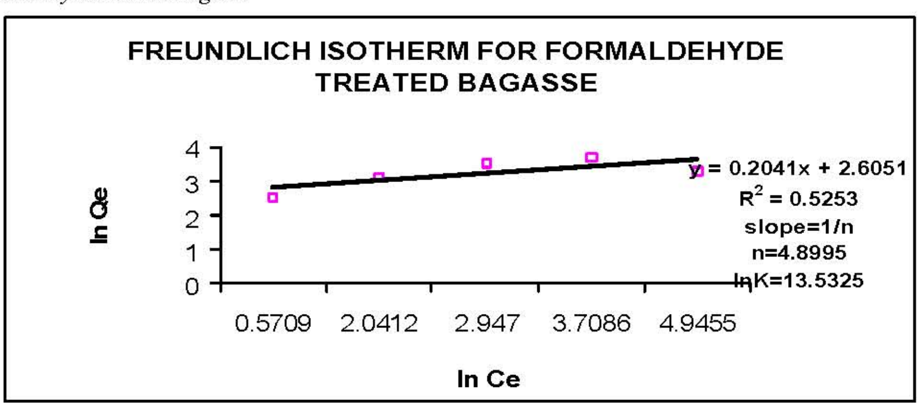

Fig. 9: Freundlich isotherm for formaldehyde treated bagasse. (Initial dye concentration=50ppm, initial pH= 10, adsorbent dosage= 0.4g/100ml.)

Sulfuric Acid Treated Bagasse

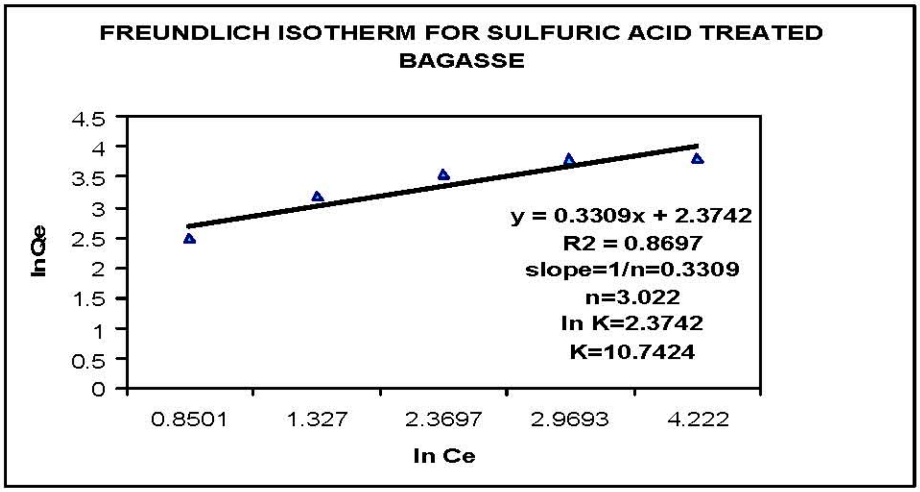

Fig. 10: Freundlich isotherm for sulfuric acid treated bagasse.
(Initial dye concentration=100 ppm, initial pH=6, adsorbent dosage=0.4 g/100 ml)

Activated Carbon

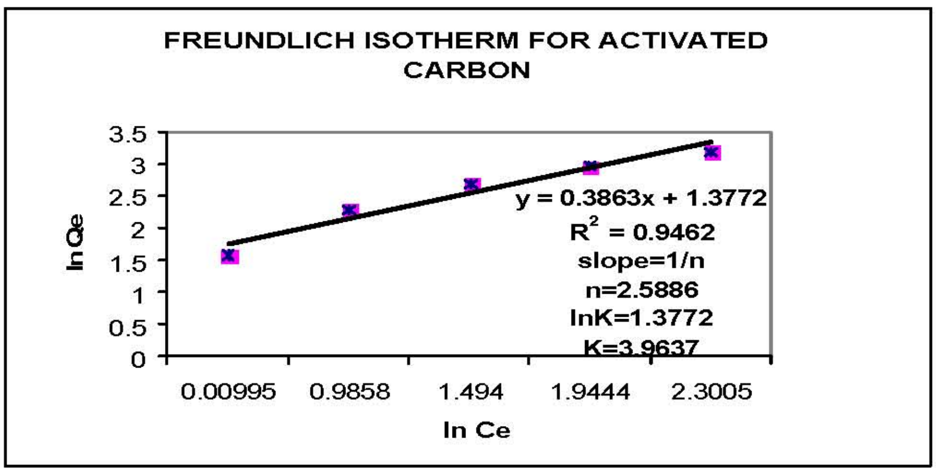

Fig. 11: Freundlich isotherm for activated carbon.
(Initial dye concentration=250 ppm, pH= 7, adsorbent dosage=1.0 g/100 ml)

From the Freundlich isotherm studies, the values of the constants obtained for different adsorbents are as follows.

For formaldehyde treated bagasse:

$n = 4.8995$, $K = 13.5325$, $R^2 = 0.5253$

For sulfuric acid treated bagasse:

$n = 3.022$, $K = 10.7424$, $R^2 = 0.8697$

For activated carbon:

$n = 2.5886$, $K = 3.9637$, $R^2 = 0.9462$

From the constants obtained we can say that the adsorption was moderately good.

For sulfuric acid treated bagasse, percentage removal increased from 81.76 to 90.2 as pH was increased from 2 to 10. As the pH of the solution increased, the percentage removal increased. The increased pH favored the adsorption for both formaldehyde and sulfuric acid treated bagasse. But for activated carbon the adsorption was not affected much by pH variation thereby percentage removal almost remaining same for all pH values.

Concentration Variation: Concentration of the solution was varied from 50 ppm to 250ppm. For different initial dye concentration values the percentage removal of the dye was recorded.

Effect of Concentration: For the formaldehyde treated bagasse, the increment in the dye removal was observed as the concentration was decreased. There was a significant rise in the dye removal as concentration was decreased from 250 ppm to 50ppm. The dye removal was increased from 23.87% to 74.2%.

Nearly the same pattern was obtained for the sulphuric acid treated bagasse. The highest percentage of dye removal was recorded for 50 mg/l and 75 minutes contact time as 93.4 percent. But for the activated carbon, initial dye concentration did not seem to affect much. It was on the higher side for all the initial dye concentration. The dye removal was higher than that for other two adsorbents used almost nearing 100% for all the initial dye concentrations.

The values are given for initial pH of 7.0 and adsorbent dosage of 0.4 g/100 ml.

Adsorbent Dosage Variation: Adsorbent dosage was varied from 0.2 to 1.0 g/100 ml. For different adsorbent dosages, the percentage removal of the dye were recorded. The values are given for initial dye concentration of 250 mg/l and initial pH of 7.0.

Effect of Adsorbent Dosage: For all the three adsorbents used for this study, the dye removal increased as the adsorbent dosage was increased. Increase in the adsorbent dosage provided increment in pores available for the adsorption and also the surface area got increased. Hence, the enhancement in the adsorption efficiency was seen with the increment in the adsorbent dosage.

For the formaldehyde treated bagasse, the dye removal was increased from 14% to 71.86% and for the sulfuric acid treated bagasse it was increased from 53.87% to 94.1% as the adsorbent dosage was increased from 0.2 to 1.0 g /100 ml.

For the activated carbon, the lowest percentage of dye removal was recorded for adsorbent dosage of 0.2 g /100ml and 15 minutes contact time.

Temperature Variation: Temperature was varied from 27°C to 50°C. For different temperature values the percentage removal of the dye was recorded.

Effect of Temperature: The temperature was varied from 27°C to 50°C. The experiment was carried out in a constant temperature water bath. First the optimum conditions were found out. Then, at these conditions the effect of temperature was studied. It was seen that as the temperature was increased, the dye removal was increased.

For the activated carbon, the temperature did not seem to have much effect on dye removal. It was almost 100% for all temperatures. But for the formaldehyde and sulfuric acid treated bagasse, the dye removal increased as the temperature was increased. For the formaldehyde treated bagasse, the percentage of dye removal increased from 98.27% to 98.61%, as the temperature was increased from 27°C to 50°C. The optimum temperature for the sulfuric acid treated bagasse was found to be 50°C.

Isotherm Studies: The isotherm studies were carried out for optimum conditions which were obtained. Using equilibrium concentration (Ce), Qe values were calculated. Amount of dye adsorbed per unit weight of the adsorbent

$$Qe = (Co - Ce).\ V/W \text{ mg/g};$$

where

Co = Initial dye concentration in mg/l; Ce = equilibrium dye concentration in mg/l;

V = Volume of the solution in ml;

W = Amount of the adsorbent used in gm.

Then Freundlich isotherm equation was used to find the constants K and n.

$$Qe = k\ Ce^{1/n}$$

$$\ln Qe = \ln K + 1/n \ln Ce.$$

A graph of ln Qe Vs ln Ce was plotted, the slope of the curve gives 1/n and intercept gives ln K, which gives the adsorptive capacity of the adsorbents.

CONCLUSION

In this review, the efficiency of using sugarcane bagasse as an adsorbent and as a substitution to activated carbon has been studied. Also the comparison between activated carbon and sugarcane bagasse treated with formaldehyde and sulfuric acid has been made. As a comparison, the activated carbon showed better performance than formaldehyde and sulfuric acid treated bagasse. Also, sulfuric acid treated bagasse showed better result than formaldehyde treated bagasse for all contact times, pH, adsorbent dosage and all initial dye concentrations.

The parameters varied were pH, contact time, initial dye concentration, adsorbent dosage and temperature. Initial pH range of 6 to 10 was favorable for both formaldehyde and sulfuric acid treated bagasse. The dye removal was found to be maximum for lower initial dye concentrations.

The adsorption efficiency was found to be maximum over the adsorbent dosage range of 0.6 to 1.0 g/100 ml. For the adsorbent dosage of 1.0 g/100ml, the dye removal was highest for all the three adsorbents used in this study. The uptake of the dye increased with increasing contact time. Also, the adsorption capacity was increased as the temperature was increased from 27°C to 50°C. The adsorption was also maximum at temperature of 50°C. The data generated was suitable to plot Freundlich isotherm.

Even though the adsorption capacity of treated sugarcane bagasse is less than that of activated carbon, it is cheaply available. It is an agro-industry waste. With this cheap and ecofriendly adsorbent considerable dye removal can be achieved. So, it can be substituted for expensive activated carbon. With the experimental data obtained in this study, it is possible to design and optimize an economical treatment process for the dye removal from industrial effluents.

ACKNOWLEDGEMENT

The authors wish to acknowledge with sincere thanks to Rohan Angadi, Pavankumar, Fayaz A Lathif and Vishal Wadone who worked diligently and for their selfless and consistent efforts to get through this task. We also express our sincere appreciations and gratitudes to Dr. Jagadeesh, Dept. of Microbiology, University of Agricultural Sciences, UAS Dharwad for providing us the valuable inputs as and when required.

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