Studies on the utility of plant cellulose waste for the bioadsorption of crystal violet dye

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Abstract: *Several synthetic dyes employed in textile and food industries are discharged into aquatic environment. These visible pollutants in water damage environment, as they are carcinogenic and toxic to humans. The use of cost effective and ecofriendly plant cellulose based adsorbents have been studied in batch experiments as an alternative and effective substitution of activated carbon for the removal of toxic dyes from waste water. Adsorbents prepared from sugarcane baggase, were successfully used to remove certain textile dye such as crystal violet from an aqueous solution. The present investigation potentiate the use of sugarcane baggase, pretreated with formaldehyde (referred as Raw Baggase) and sulphuric acid (referred as Chemically Activated Baggase), for the removal of crystal violet dye from simulated waste water. Experiments were carried out at neutral pH with various parameters like dye concentration, temperature, contact time and adsorbent dosage. Efficiency of raw baggase was found better than chemically activated baggase for adsorption of crystal violet dye. The data obtained perfectly fits in the Freundlich adsorption isotherm.*

Key words: *Chemically activated baggase, Cellulose, Peel, Adsorption isotherm*
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Introduction

Dyes are extensively employed in various industries like textiles, leather, paper, plastic and cosmetics. The textile industry ranks first in usage of varieties of natural and synthetic dyes to color the fabrics (Saiful Azhar *et al.,* 2005; Dayaram, 2008). Triphenyl methane dyes are used extensively in textile industries for dying nylon, polyacrylonitrile-modified nylon, wool, silk and cotton. Some of the triphenyl methane dyes are used as medicine, biological stains and in paper and leather industries. The dyes released by the above referred industries cause serious water pollution (Lee *et al.*, 1999; Pappic *et al.*, 2000; Maurya *et al.,* 2008; Pant *et al.,* 2008). Conventional waste water treatment by aerobic biodegradation process has low removal efficiency for reactive and other anionic soluble dyes (Grag *et al.*, 2003). Therefore, due to inefficient biodegradation of dyes, aerobic degradation process may not be an ideal choice for treating dyes in polluted water. On the other hand, treatment of dyes by physical or chemical processes are very expensive (Raghuvanshi *et al.,* 2002) and are not feasible for treating wide range of dyes in water. Considering the merits and demerits of the above said process, bioadsorbtion is one of the effective strategies for removal of dyes from waste effluent. The efficient utility of adsorption process can be attributed due to its sludge free operation process and high percentage removal of wide range of dyes (Raghuvanshi *et al.,* 2002). Upsurge interest has been shown in the utility of various adsorbents derived from plant sources. Among various adsorbents used for dye removal, activated charcoal was found to be extensively used due to its excellent adsorption efficiency for organic compounds. However,

commercial grade activated charcoal and activated carbon are very expensive when employed at large scale (Maurya *et al.,* 2008). There is a 10-15% adsorbent loss during uptake capacity, due to these constraints several alternative low cost adsorbents have been employed. Among these, saw dust (Raghuvanshi *et al.,* 2002; Deo and Ali, 1993) peat, coal, lignin to wood (Raghuvanshi *et al.*, 2004) has low cost material. Other bioadsorbents like coconut coir, banana peel (Namasivayam and Kadirvelu, 1997), commercial activated carbon, wheat straw leaves, natural red soil (Pravin *et al.,* 2009) and even cow dung have been found to be very efficient, cost effective and eco-friendly. Activated carbon derived from male flowers of coconut tree has been used for the specific adsorption of crystal violet (Senthikumar *et al.,* 2006). Some expensive non-bioadsorbents like surfactant modified alumina (SMA) (Asok *et al.*, 2006) and polyacrylic acid bound magnetic nanoparticles are used for the adsorption of crystal violet dye (Liaomin-Hung *et al.,* 2004). In the present work we have attempted the use of sugarcane Raw Baggase (RB) and Chemically Activated Baggase (CAB) in the for bioadsorption of crystal violet dye. A cost effective process and efficient adsorption of dye pollutant have been noticed in the present work.

Materials and Methods

Cellulose based bioadsorbent like sugarcane baggase is selected. Baggase was obtained from sugarcane mill near Bangalore. In the preparation of CAB, four parts of cellulose sugarcane baggase were treated with three parts of concentrated sulphuric acid (Merck AR grade) by weight and placed in the oven for 35 hrs at 150-160°C. The carbonized material was then washed with distilled water to remove free acid and dried at 110-120°C

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for 24 hr. The treated material was then grounded, sieved using 100 and 200 mesh number screens, and the baggase powder retained on the 200 mesh number screen was used as CAB adsorbent.

Raw baggase was prepared by soaking cellulose sugarcane baggase in distilled water for 48 hr, then treated with formaldehyde (Merck AR grade) to preclude color interference during adsorption. The material was then dried in an oven at 100-110°C for 24 hr and pulverized to fine powder and used as RB adsorbent.

In the present work Freundlich (Freundlich uber die, 1906) adsorption isotherm model was used to predict the adsorption behavior for the adsorption of crystal violet dye on RB and CAB.

Freundlich equation (Robert, 1981) is given by the expression

$$C^* = k \, [v \, (C_0 - C^*)]^n$$

Where C_0 and C^* are the initial and equilibrium concentration of dye, g l^{-1}

v is the volume of solution Kg^{-1} of adsorbent, l g^{-1}

k and n are constants and these can be estimated by plotting a graph of

$$\ln C^* = \ln k + n \ln [\, v(C_0 - C^*) \,]$$

The plot of lnC* v/s ln [v(C$_0$ – C*)] gives a linear plot with intercept in ln k and slope n.

Experimental: Adsorbents (RB and CAB) of varying weight from 0.1 to 1.0 gm were taken separately in a conical flask containing 100 ml aqueous dye solution of known concentration and shaken well using an orbital shaker (Remi). Dye concentration (varied from 50-200 ppm) was measured at different time interval (15, 30, 60 and 90 min), at different temperatures (30, 40 and 60°C) at neutral pH. At the end of predetermined time intervals, mixtures were taken out and subjected to centrifugation (Remi) for 3000 rpm for 10 min, the supernatant collected was analysed for residual concentration of crystal violet dye at 400 nm using UV – VIS spectrophotometer (Elico). The amount of crystal violet dye adsorbed was calculated from the concentrations in solution before and after adsorption. All the experiments were performed in duplicate.

Results and Discussion

Effect of dye concentration: In that the percentage of dye adsorption increases initially and attains equilibrium within 30-60 min. RB and CAB adsorb the crystal violet maximum dye to a maximum of 92.38% (Fig. 1a) and 48.09% (Fig. 1b) respectively for initial concentration of 50 ppm at 30°C and adsorbent dose of 1g l^{-1}. The large fraction of the total dye concentration was removed after 30 min. The percent adsorption of dye was decreased with increase in dye concentration. In this experiment, the rate of
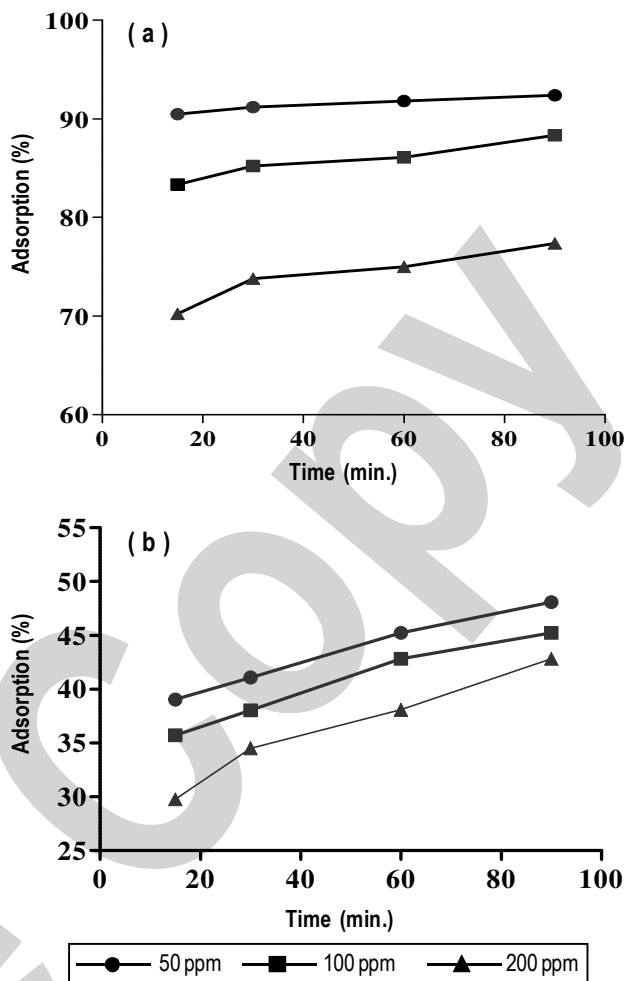

Fig. 1: Adsorption of crystal violet dye on (a) raw baggase (RB) and (b) chemically activated baggase (CAB) with reference to time

adsorption increases with time and gradually attains maximum adsorption, owing to continuous decrease in concentration driving force. It was also noticed that initial rate of adsorption was greater for initial concentration (50 ppm) due to decrease in resistance to dye uptake and consequently increase in mass transfer driving force. These results indicated the formation of monolayer coverage on the surface of adsorbent.

Effect of adsorbent concentration: The weight of the adsorbent was varied from 1.0 to 10 g l^{-1} for RB (Fig. 2a) and CAB (Fig. 2b) respectively on aqueous dye solution. The dye concentration was maintained constant at a concentration of 50 ppm. At 1.0 g l^{-1} of adsorbent dosage, there was a maximum adsorption of 92.38% for RB and 48.09% for CAB. The adsorption of dye on CAB was found to be meager when compared to RB. The highest and strongest adsorption of crystal violet to RB is probably due to the nature of preferential adsorption potential of carbon. In the preparation of CAB, cellulosic materials are transformed into carbonized material due to concentrated sulphuric acid treatment. These carbons may have mesopore structure which adsorbs medium size molecules like methylene blue (Raghuvanshi *et al.,*
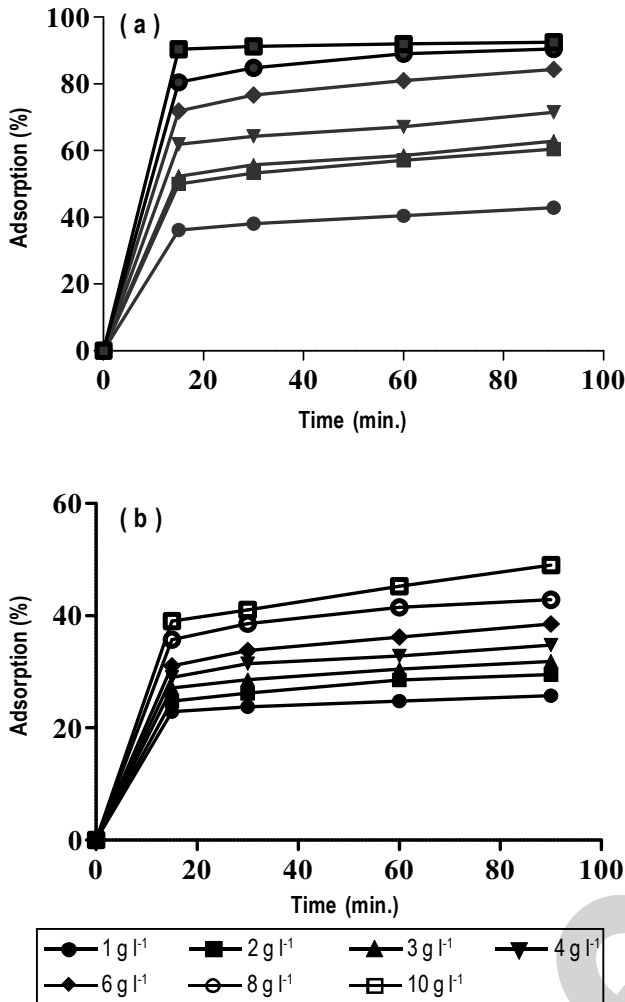
Fig. 2: Effect of various (a) raw baggase (RB) and (b) chemically activated baggase (CAB) with reference to time

Fig. 3: Adsorption of crystal violet dye on (a) raw baggase (RB) and (b) chemically activated baggase (CAB) with reference to temperature

2004), but not to sizable molecules like crystal violet. Contradictory to this, Senthikumar *et al.* (2006) reported that activated carbons prepared from male flowers of coconut tree could be used for the adsorption of crystal violet. In general, many carbons preferentially adsorb small molecules, due to these properties, non carbonized raw baggase are more useful adsorbent than carbonized baggase for the adsorption of crystal violet.

Effect of temperature on adsorption: The effect of adsorption rate was carried out at three different temperatures (30, 40 and 60°C) for adsorbent dosage of 1 g l^{-1} by varying dye concentration (50 to 200 ppm). In case of RB rate of dye uptake decrease from 90.47 to 82.85% with rising temperature from 30 to 50°C within 30 minutes for 50 ppm dye solution (Fig. 3a), indicating that the process is slightly exothermic in nature. This is probably due to a tendency of dye molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution (Gupta *et al.*, 1988) the same trend is observed for all dye concentrations. In case of CAB, although overall adsorption rate is poor, rate of dye uptake increased from 30.04
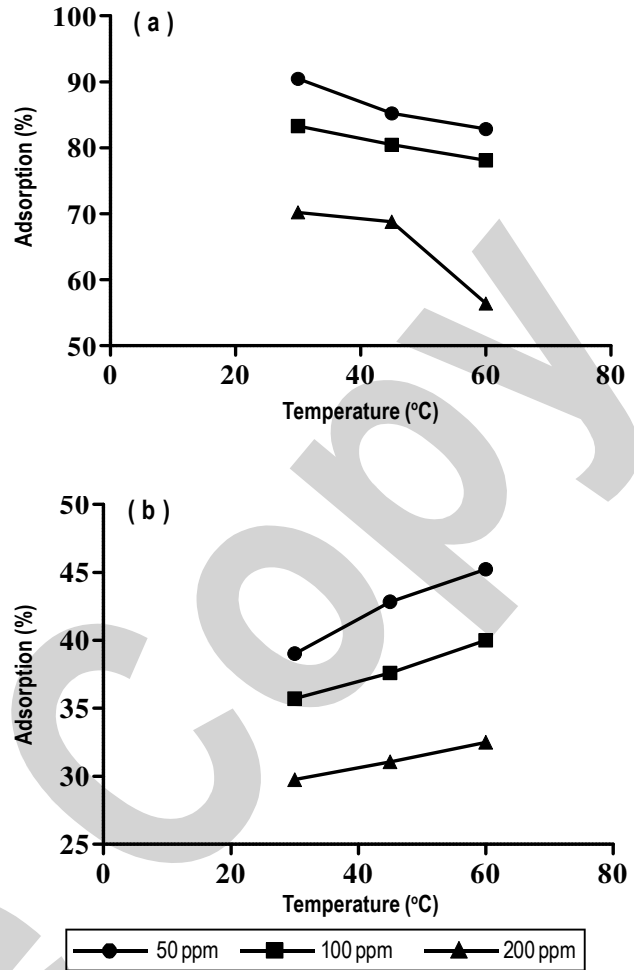
to 45.23% with rise in temperature from 30 to 50°C (Fig. 3b), because adsorption rate increases as the diffusion coefficient rises with temperature probably owing to the nature of molecules (Mekay *et al.*, 1988). However, there was decrease in adsorption with rise in dye concentration.

In adsorption isotherm for RB and CAB at equilibrium conditions, a Freundlich adsorption isotherm model is used for adsorption of crystal violet dye on RB and CAB.

The graph lnC* v/s ln [V(C$_0$ – C*)] was plotted for an RB and CAB as shown in figures (Fig. 4a and Fig. 4b). The linear plot with R^2 value of 0.9788 for RB and 0.8962 for CAB with deviation of 16%. The values of n and k is found be 1.2599 and 4.489 respectively for RB, 0.612 and 12.18 respectively for CAB. The value of n is greater than 1 for RB, which shows that RB is a very good adsorbent for adsorption of crystal violet dye. The value of n is lesser than 1 for CAB shows that CAB is poor adsorbent for crystal violet when compared to RB. The R^2 value is found to be 0.8962. Therefore the fit is not considered to be a best fit for CAB.

$$y = 1.2511x + 1.5018$$
$$R^2 = 0.9788$$

$\ln [v(C_0 - C^*)]$

$$y = 0.1628x - 2.5332$$
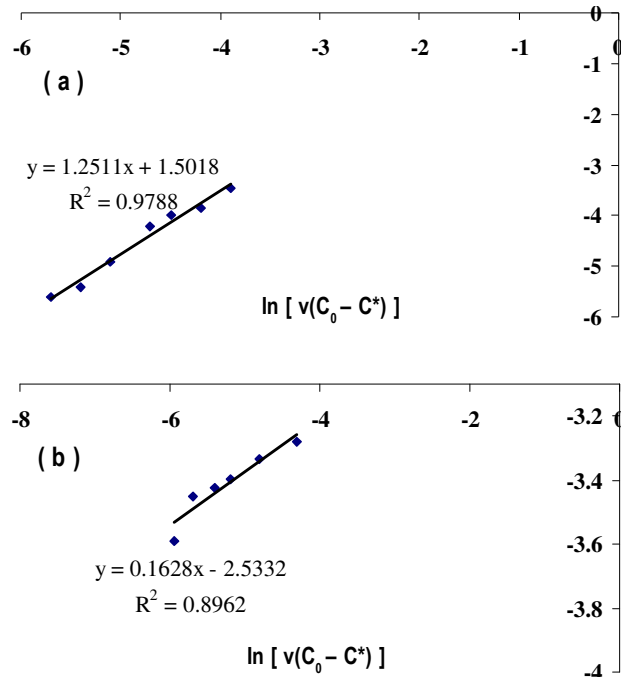$$R^2 = 0.8962$$

$\ln [v(C_0 - C^*)]$

Fig. 4: Adsorption isotherm for (a) raw baggase (RB) and (b) chemically activated baggase (CAB)

The RB was found to be suitable adsorbent for the adsorption of crystal violet dye for initial dye concentration of 50 ppm which is considered as optimum concentration for maximum adsorption. The temperature for optimum adsorption is between 30-40°C and adsorption process decreases with increase in temperature. The slope value n is greater than 1 for RB and lesser than 1 for CAB shows that RB is efficient adsorbent for crystal violet dye and CAB indicates that it is poor candidate for adsorption of crystal violet dye.

Acknowledgments

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