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Dye removal by Adsorption using waste biomass: Sugarcane Bagasse

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Abstract
Dye removal from industrial effluents is an important environmental concern. Various physical and chemical treatment methods can serve this purpose, of which the most economical and effective one is adsorption. A variety of adsorbents are available naturally- rice husk, neem bark, clays etc. that can be used to remove dye from the discharged waste. In this study, adsorption efficiency of low cost adsorbent Sugarcane Bagasse is examined. The effect of different parameters like contact time, adsorbent dosage, initial concentration of dye, pH on the adsorption rate. The data perfectly fits Freundlich isotherm with second order kinetics.
Keywords: *Adsorption, Bagasse, Methylene Blue Adsorption, Dye removal.*

1. Introduction

Dyes are natural or synthetic, organic compounds that provide bright and lasting colour to other substances. They are used in various industries like the textile, leather, paper, rubber, plastic, cosmetics, pharmaceuticals, and food industries. Textile industries lie first in the dye usage. The wastewaters discharged from dyeing processes exhibit a high BOD, high COD, visible pollutants and high amounts of dissolved solids. Effluents discharged from dyeing industries are highly coloured and are toxic to aquatic life. Some dyes are mutagenic, carcinogenic and teratogenic. Therefore, it's a must to treat dye effluents before being discharged into the environment. Thus, there is a need to control an emission of dyes into the environment. The maximum permissible Chemical Oxygen Demand (COD) limit is 4.0 mg/L The maximum permitted Biological Oxygen Demand (BOD) content of < 100 to 300 mg/L according to USPH Standard [1]. The conventional wastewater treatment, which rely on aerobic biodegrading have low removal efficiency for reactive and other anionic soluble dyes. Therefore, due to inefficient biodegradation of dyes, this may not be an ideal choice for treating dyes in polluted water [2].

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. Many of them do not operate at low concentration of coloured compounds in the effluent. Also, these are very expensive and are not feasible for treating wide range of dyes in water. 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 [2]. Many studies were performed to study adsorption of various dyes on different adsorbents.

Abdullah et.al studied azo dye (methyl red) removal by adsorption using waste biomass: Sugarcane bagasse. 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 bagasse showed a better performance compared to formaldehyde treated sugarcane bagasse. For sulphuric acid treated and formaldehyde treated sugarcane bagasse, equilibrium attainment was achieved after 60 and 90 mins respectively. The percent adsorption efficiency of both decreased with the increase in initial dye concentration in the solution. The percent adsorption increased and equilibrium time decreased with increasing adsorbent doses. In the case of untreated sugarcane bagasse, maximum dye removal of 32.8% was recorded at pH 9. Significant increase in dye removal efficiency for formaldehyde treated sugarcane bagasse was observed between pH range of 3-7 [3].

Abdel et.al used raw sugarcane bagasse modified with propionic acid for the removal of methylene blue (basic) and orange II (acid) dyes from aqueous solutions. Maximum dye removal was attained after 60 min. The Langmuir isotherm provides a good model for the adsorption of methylene blue whereas the Freundlich isotherm is fit for the adsorption of orange II. A greater percentage of dye removal was observed in acidic medium (pH=2) in case of orange II whereas in (pH=7) in case of methylene blue dyes and increases with the increase of the dosage of adsorbent. Furthermore, the amounts of dye adsorbed at equilibrium, qe (mg g-1) for methylene blue and orange II were 59.5 and 25.5, respectively [4].

Mahesh et.al studied the removal of violet dyes using raw bagasse and chemically activated bagasse. This group of dye and adsorbent followed Freundlich isotherm. The percent adsorption of dye was decreased with increase in dye concentration. Raw bagasse was found more efficient than chemically activated form. The equilibrium is attained between 30-60 mins. The effect of increase in temperature was studied and it was found that increase in temperature decreases the rate of dye uptake [5].

2. Adsorption as Dye Removal Technique

Adsorption is a phenomenon in which gas or liquid molecules get adhered on the surface of porous solid. It is a surface phenomenon. The fluid molecule which gets adsorbed is called adsorbate. The porous solid on which the adsorbate gets adsorbed is called adsorbent. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physic-sorption or chemi-sorption. An adsorbent is a substance, usually porous in nature with high surface area that can adsorb substances onto its surface by intermolecular forces. Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption [6]. The adsorbents must also have a distinct pore structure that enables fast transport of the gaseous vapours. The efficiency of bagasse was studied using various dyes like methyl red, orange II etc were studied by using raw and chemically activated forms of bagasse in many researches.

3. Preparation Method of Materials

3.1 Preparation of Chemically Activated Sugarcane Bagasse Adsorbent

The bagasse was obtained from a nearby sugarcane mill. It was dried under the sunlight until all of the moisture in bagasse was evaporated and ground to fine powder. The bagasse was mixed with one third by weight of concentrated sulphuric acid for chemical activation 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 sieved, until the size between -80 to +230 mesh size was obtained, which will be used as chemically activated bagasse adsorbent for this study.

3.2 Preparation of Raw Sugarcane Bagasse Adsorbent

Cellulosic baggase obtained from sugarcane mill was soaked in distilled water for 48 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 bagasse adsorbent.

3.3 Preparation of Methylene Blue Adsorbate Solution

For this study, Methylene blue in powder form was obtained. The dye stock solution of 1,000 ppm is prepared by dissolving accurately weighed 1 g of dye in 1,000 mL of distilled water. The experimental solutions of desired concentrations are prepared by diluting the stock solution with distilled water.

4. Experimental Methodology, Results and Discussion

4.1 Effect of Initial Dye Concentration and Contact time

To evaluate the efficiency of adsorbents, laboratory experiments were conducted on aqueous solutions having initial dye concentration of 50, 75 and 100 ppm at room temperature and natural pH using 0.2 g of chemically activated bagasse in batches of 50 ml. At the end of pre-determined time intervals, adsorbent was removed by filtration and filtrate was analyzed for the residual concentration of Methylene Blue, spectro-photometerically at 655.8 nm wavelength.

The adsorption data is reported in terms of adsorption percentage using the following equation:

$$\%Dye\ Removal\ = \frac{(Co-C)}{Co} \times 100 \qquad (1)$$

Where, Co and C are initial and final dye concentrations (ppm) respectively.

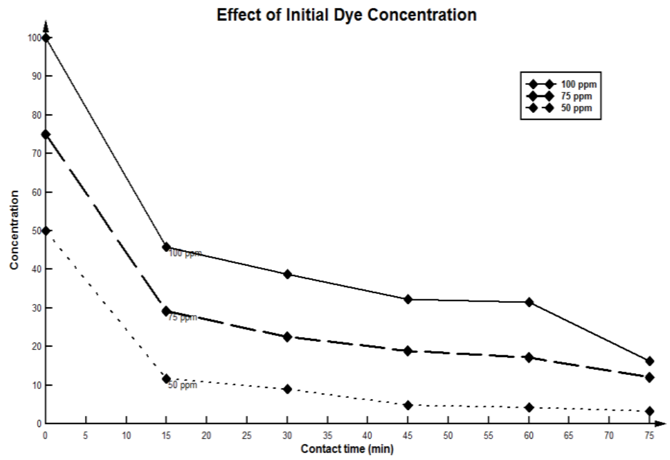

Figure 1 (a): Effect of initial dye concentration-concentration v/s contact time plot

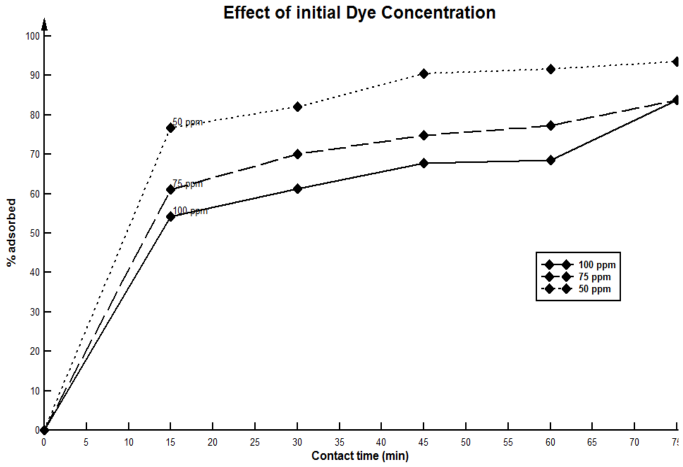

Figure 1 (b): Effect of initial dye concentration-% adsorbed v/s contact time plot

Figure 1 (a) and 1 (b) show the plots of effect of initial dye concentration on rate of adsorption. The graph shows the amount of dye adsorbed at various intervals of time which indicated the removal of dye (adsorbate) initially increases with time but attains equilibrium within 45 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. Chemically activated baggase could remove a maximum of 83.785% of Methylene Blue at initial dye concentration of 100 ppm, while for dye concentrations of 75 and 50 ppm, the adsorption of the dye were about 83.85 % and 93.51% respectively in 75 min.

The % adsorption of dye was decreased with increase in initial dye concentration. In this experiment, the rate of adsorption was greater for initial low concentration of 50 ppm due to decrease in resistance to dye uptake and consequently increase in mass transfer driving force. The formation of monolayer coverage on the surface of adsorbent was indicated by these results.

4.2 Effect of Adsorbent Dosage and Contact time

The adsorbent dose is another important parameter to optimize an adsorption system. The effect of adsorbent dosage on the adsorption of methylene blue has been investigated by using different doses of bagasse (chemically activated) varying from 0.2 to 1.0 g. The experiments were performed at constant initial dye concentration of 100 ppm, at room temperature and natural pH in batches of 50 ml. At the end of pre-determined time intervals, adsorbent was removed by filtration and filtrates were analyzed for the residual concentration of Methylene Blue using UV-VIS spectrophotometer.

Figure 2 shows effect of adsorbent dosage on rate of adsorption. An optimum equilibrium % removal rate of 95.61 was achieved with 12 g/L in 45 minutes by chemically activated bagasse. At 20 g/L there is slight increase in % adsorbed value but as we get nearly the same result, then going for 20 g/L instead of 12 g/L would be expensive. 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, by the fact that at lower adsorbent dose the dye is more easily accessible and because of this, removal per unit weight of adsorbent is higher.

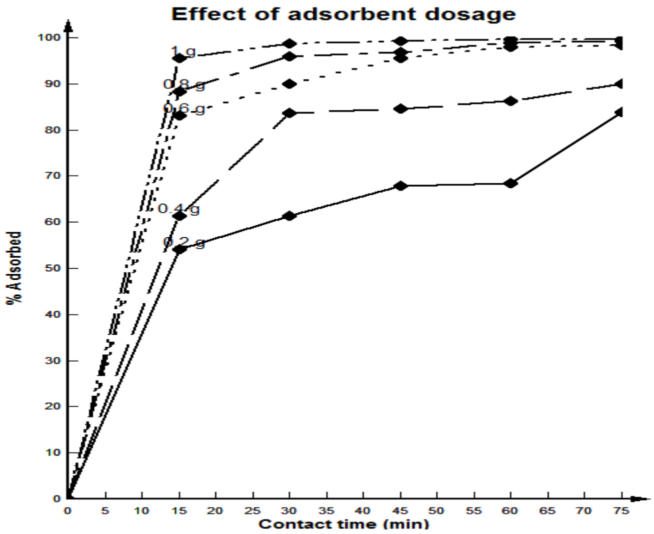

Figure 2: Effect of adsorbent dosage-%adsorbed v/s contact time plot

The % adsorption increased with increase in the adsorbent dosage. This was attributed to increased surface area and availability of more adsorption sites. The initial rise in adsorption with adsorbent dose was probably due to bigger driving force and larger surface area. The rate of adsorption has been found to be 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 was observed in % dye removal, which stated that adsorption and intra-particle diffusion took place simultaneously with dominance of adsorption. With rise in adsorbent dose, there was less proportionate increase in adsorption due to lower adsorptive capacity utilization of adsorbent.

4.3 Effect of pH

The effect of pH was studied carrying out batch experiments using 50 ml solutions of 50 ppm with adsorbent dosage of 8 g/L at room temperature, adjusting the pH values of the solutions from 1 to 9 with 0.1 M HCl or NaOH using a pH meter. After the time interval of 75 min the solutions were filtered and the filtrates were analyzed using UV-VIS spectrophotometer.

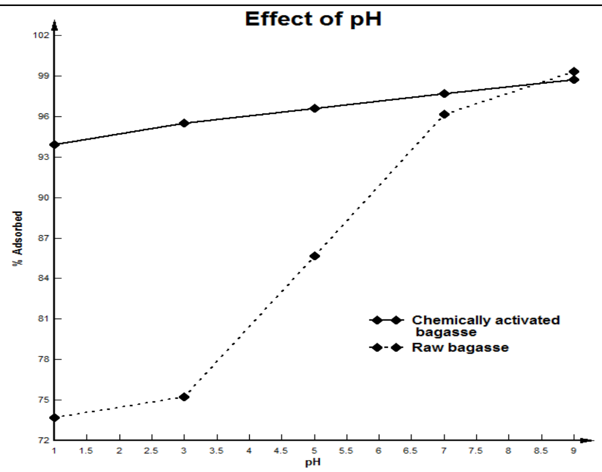

Figure 3: effect of pH-%adsorbed v/s pH plot

Figure 3 shows effect of pH on adsorption rate using chemically activated bagasse and treated raw bagasse. In general, the pH of the solution affects the charge of dye and of the adsorbent. In our case, it affects only the adsorbent since Methylene Blue does not have acid base properties. Methylene Blue remains positively charged. Thus the visible spectrum of Methylene Blue does not change as a function of pH.

It has been found that adsorption increases with increase in pH. This may be due to the fact that at higher pH values the surface of adsorbents becomes negative which enhances the adsorption of positively charged Methylene Blue ions through electrostatic force of attraction. The graph shows the

% adsorption of dye gradually increases with increase in pH in case of chemically activated bagasse, whereas there is a drastic increase in case of treated raw bagasse. The reason for this observation may be attributed to the replacement of weak positively charged ions and neutralization of negative ions during activation by conc. H_2SO_4.

4.4 Adsorption Isotherm

The experiments were studied at room temperature of 25 ºC to obtain the adsorption isotherm. Adsorption isotherm is a plot between amount of dye adsorbed (x) on the surface of adsorbent (m) and concentration (C) at constant temperature. The isotherm was plotted from the results obtained from the experiments on 50 ml batches at varying initial dye concentration using 0.2 g of adsorbent. The readings were taken at equilibrium time of 45 min.

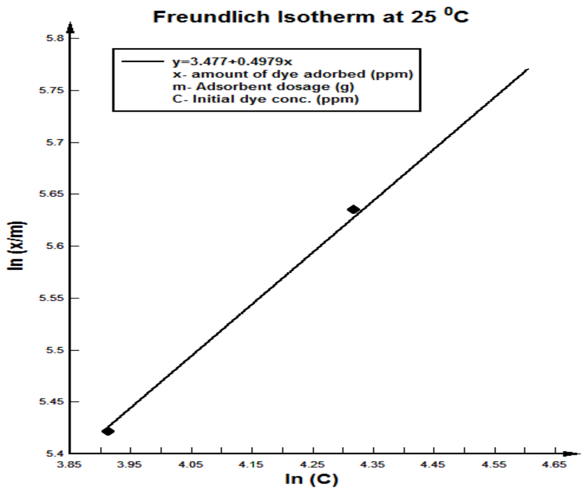

Figure 4: Adsorption isotherm

Figure 4 shows the adsorption isotherm plot. The linear plot of ln (x/m) vs. ln C tells that adsorption follows Freundlich isotherm model.

$$ln\left(\frac{x}{m}\right) = ln\ k + \left(\frac{1}{n}\right) ln\ C \qquad (2)$$

Where, C is the equilibrium concentration (ppm), x is the amount of dye adsorbed (g), m is the adsorbent dose used (g) and k and n are constants, incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively.

The plot was linearly fitted by the equation

$$Y = 3.477 + 0.4979X \qquad (3)$$

Where, Y= ln(x/m) and X= ln(C)

The plot indicated that adsorption followed second order kinetics as n=2 with adsorption coefficient (k) =32.362.

5. CONCLUSION

Removal of Methylene Blue from aqueous solution by adsorption with chemically activated bagasse has been experimentally determined and the following observations were made:

1. The amount of dye adsorbed initially increases with time but attains equilibrium within 45 minutes. Chemically activated baggase could remove a maximum of 83.785% of Methylene Blue at initial dye concentration of 100 ppm, while for dye concentrations of 75 and 50 ppm, the adsorption of the dye were about 83.85 % and 93.51% respectively in 75 min.

2. When dosage of adsorbent was studied it was found that in the first 15 min the adsorption rate rapidly increased and then it proceeded gradually till equilibrium time of 45 min. An optimum equilibrium percentage removal rate of 95.61 was achieved with 12 g/L by chemically activated bagasse of adsorbate concentration of 100 ppm.

3. Increase in pH increased the adsorption rate. Comparative study revealed that variation in adsorption rate with pH in case of chemically activated is less than treated raw bagasse. For pH values < 7 chemically activated bagasse was found to be more effective in dye removal whereas, for pH ≥ 7 both adsorbents were found to be equally efficient.

4. It followed Freundlich isotherm and indicated that adsorption followed second order kinetics as n=2 with adsorption coefficient (k) =32.362.

These preliminary studies state that adsorbents prepared from bagasse can be used effectively for the adsorption of dyes. Cost analysis for the preparation of activated carbon of bagasse has not been done since Bagasse 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 from aqueous solutions and industrial effluents.

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