EQUILIBRIUM ADSORPTION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION USING SUGARCANE BAGASSE

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ABSTRACT

The present study includes the preparation of sugarcane baggase fibres for using as an adsorbent for the removal of methylene blue (MB) dye from an aqueous solution. Due to morphology, the surface area and porosity of these prepared nanofibres is very high which enhances the adsorption capacity. Equilibrium adsorption of methylene blue, a cationic dye has been studied using nanocellulosic fibers of sugarcane bagasse. The effects of major variables, governing the efficiency of the process such as, temperature, contact time, initial dye concentration, NCFs dosage, and pH were investigated. The experimental results have shown that the amount of dye adsorption increased with increasing the initial concentration, dose of adsorbent. The adsorption is small at low pH values of the solution but attains a maximum value at pH around 5. The adsorption capacity decreases gradually with increasing temperature. The Langmuir and Freundlich adsorption isotherms were used to model the adsorption equilibrium data and it was found that the system followed the Langmuir and Freundlich isotherms. The adsorption capacity of the NCF's of sugarcane bagasse was found to be 124.3mg/g, which is higher or comparable to the adsorption capacity of various adsorbents reported in the literature.

Keywords**:** *Methylene Blue, Cellulose fibers, Adsorption, FTIR*

1. Introduction

Due to rapid expansion in the chemical industry, there is an increase in the complexity of toxic effluents and metals. Heavy metal contamination has been a critical problem because metals tend to persist and accumulate in the environment. Toxic heavy metals cause many serious disorders like anemia, kidney disease, nervous disorders, and even death [1]. Many industries such as textile, paper, carpet and printing use dyes like methylene blue, malachite green, congo red and rhodamine B etc., to colour their products and discharge this wastewater into nearby land or rivers without any adequate treatment to remove harmful compounds. Dyes affect aquatic life because of reduced light penetration. Dyes are generally toxic, stable towards light and oxidizing agents and non- biodegradable [2]. Many of these compounds are carcinogenic also. The consumption of coloured water affects human beings as well as natural biological communities. Halogens such as chlorine (Cl) and bromine (Br) are widely used as antibacterial agents, but the direct use of halogens as bactericides has many problems because of their high toxicity and vapor pressure in pure form. Several methods which are being used for the removal of the contaminants like coagulation, filtration, boiling, distillation, reverse osmosis, water sediment filters, ion exchange, precipitation etc. which are expensive and inefficient in treating large quantities of waste water [3]. But for dyes effluents, adsorption process has been found to be more effective method. Few commonly used adsorbents are activated carbon, fly ash, activated clay, zeolite, green algae, rice husk, silica, saw dust etc. Although the activated carbon is the most effective because of their surface area, micro porous structure, the chemical nature of their surface, but there is need to produce for effective and cheaper adsorbents. Recently a number of low cost adsorbents have been used for removal studies of dyes [4].

Recent advances in nano scale science and engineering suggest that many of the problems involving water quality could be greatly diminished by using nano- particles because of their good adsorption efficiency especially due to the higher surface area and greater active sites [5] for interaction with coloured substance and metallic species. Polysaccharide materials, such as cellulose, [6] which is present in almost all plants, show quite low absorbency and retention [7] but after modification it show good values for both absorption and retention [8]. Adsorption has advantages over other methods for remediation of dyes from wastewater because its design is simple and it is sludge-free and can be of low capital intensive [9]. Cellulosic fibers are abundant, natural, renewable and biodegradable polymers, low denser, nonabrasive, combustible, non toxic, inexpensive [10]. This increasing interest in nanomaterials of plant origin and their unique properties have led to intensive research in the area of nano cellulosic materials [11, 12]. In recent years, adsorption techniques for wastewater treatment have become more popular with regard to their better efficiency in the removal of pollutants, especially coloured contaminants i.e. dye and heavy metal ions. Thus, now a day's, cellulose based nano fibers are widely used as adsorbents in purification of waste water. Industries such as textile, lather, paper, plastic [13, 14] releases the common pollutants include toxic organic compounds, dyes, detergents and surfactants, agro wastes like insecticides, pesticides and herbicides, disinfection byproducts, volatile organic compounds, plastics, inorganic compounds like heavy metals, noxious gases like NO_x, SO_x, CO and NH_3, and pathogens like bacteria, fungi and viruses [15], which affect the environment as well as the life of human beings.

Dyes are organic compounds consisting of two main groups of compounds, chromophores, which are responsible for color of the dye and auxochromes for intensity of the color [16]. Based on chromophores, there are 20–30 different groups of dyes like azo, anthraquinone, phthalocyanine and triarylmethane etc. There are several methods which can be used to treat dye wastewater. The technologies can be divided into three categories: biological, chemical and physical [17]. Similarly heavy metals (Chromium (Cr (VI)), Copper (Cu (II)), Cadmium (Cd (II)) and Nickel (Ni (II))) are also hazardous even at very low concentrations. Heavy metals cannot be degraded or destroyed. Aquatic systems are particularly sensitive to pollution possibly due to the structure of their food chains. In many cases harmful substances enter the food chain and are concentrated in fish and other edible organisms [18].

2. Experimental

2.1 Material

Sugarcane bagasse was used as raw material, collected from the nearby areas of locality. Other reagents used were: Sodium hydroxide (NaOH), Hydrogen peroxide (H_2O_2) and Hydrochloric acid (HCl). All the chemicals were purchased from Fisher Qualigens.

2.2 Adsorbate

The methylene Blue (MB) dye with chemical formula $C_{16}H_{18}N_3SCl$ (Fig. 1), molecular mass 319.85 g/mol and wavelength is 662 nm (measured value) as supplied by Fisher scientific [19]. At room temperature it appears as a solid, odorless, dark green powder, which yields a blue solution when dissolved in water. The hydrated form has three molecules of water per molecule of methylene blue [20, 21]. The MB was chosen in this study because of its known strong adsorption onto solids.

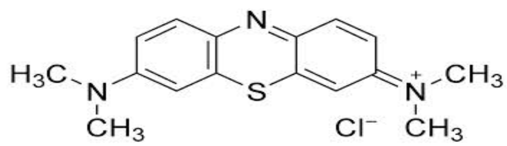


Fig. 1 Chemical structure of Methylene Blue Dye

2.3 Preparation of Adsorbent from SCB

Raw fibres were collected from local market of Sonepat, Haryana. Perfectly cleaned raw fibers of SCB are dried and chopped then placed into 2% (w/v) sodium hydroxide (NaOH) solution 24 hours at room temperature. Then alkali treatment was given to the fibres at three different concentrations i.e. 10, 12 and 14%. Bleaching of alkali treated samples was done using 300ml H_2O_2 solution. The content was heated upto 60^{o}Cfor approximately 5 hours followed by washing.after bleaching hydrolysis was done using 0.1 N of HCl in 100ml distilled water. Then these cellulosic fibers were to be put in oven at 35^{o}c to form it in dried manner.

3. Characterization

3.1 Fourier Transform Infrared Spectrometry (FTIR)

In FTIR, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted) [22, 23] .The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. This makes infrared spectroscopy useful for several types of analysis. The degree of crystallinity of the cellulose samples was determined using FTIR. Dried cellulose samples over phosphrous pentaoxide in a desiceator were made into a pellet with KBr powder (1:5,cellulose:KBr) and analyzed by weighed out within + 0.005 g range to present the quantitative aspect of the spectra, the ratio of the peak intenties at 1282 to 1202 cm^{-1} of the spectrum was used to determine the relative crystallinity of the cellulose samples [24].

The bands observed in FTIR spectra of as- received NCFs sample at 1671, 1467, 1128 cm-1 are associated with carboxylic groups.

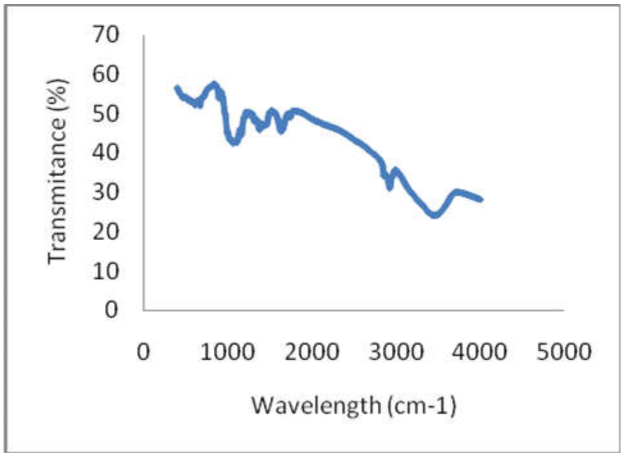


Fig. 2. FTIR spectra before adsorption.

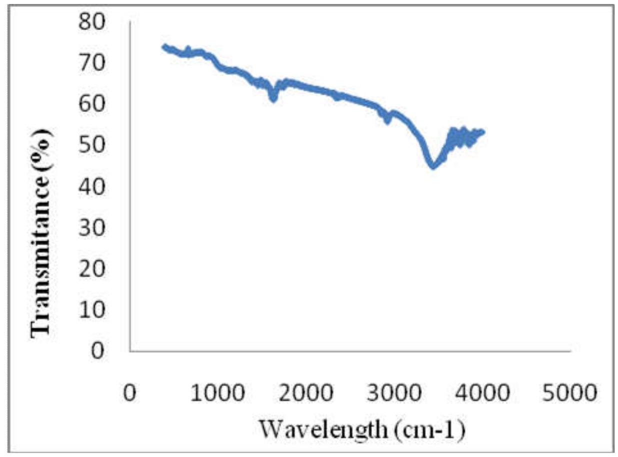


Fig 3. FTIR spectra after adsorption

FTIR spectra after adsorption of MB shows the elimination of 1128 and 1467 cm^{-1} bands and shifting of 1671 cm^{-1} band to the lower values of 1657 cm^{-1}. This suggests that the adsorption of MB takes place on the negative sites of the cellulosic fibers.

3.2 Equilibrium Adsorption of Methylene Blue

The batch adsorption was carried out by placing 0.1 g each of nanofiber in contact with 15 mL of MB solutions of different concentrations ranging from 100 mg/L to 1000 mg/L. After contact time for equilibrium to attain, the concentration of the solution was determined spectrophotometrically at a wavelength of 662 nm.

The amount of adsorption at equilibrium, q (mg/g), was calculated by

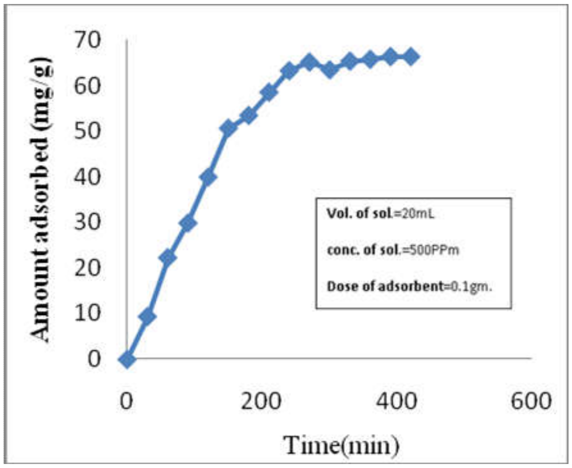
$$q = (Co - Ce)\frac{V}{W} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where q is the amount of methylene blue adsorbed by NCFs (mg/g), C and Ce (mg/L) are the initial and equilibrium dye concentration respectively. V is the volume of the solution (L) and W is the weight of adsorbent (gm).

4. Results and Discussion

4.1 Effect of Contact Time

The effect of time contact time is shown by (Fig. 4). The extent amount of dye adsorbed by NCFs increases with increase in contact time. It is seen that dye removal seems to occur in two phases. The first phase involved rapid dye uptake in the beginning and almost 50 % adsorption is completed within 150 min but attains a constant value after about 240 min. Further, the time required to achieve a definite fraction of equilibrium adsorption was found to be independent of initial concentrations. The time of contact for subsequent studies was kept for 240 min to make sure that the equilibrium was attained.



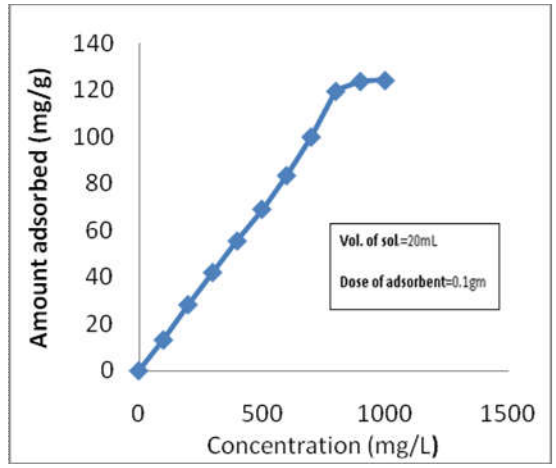


Fig.4 Effect of contact time on NCFs at temp. 40 °C Fig. 5 Effect of initial concentration on NCFs

4.2 Effect of initial concentration of MB Dye

As shown in Fig 5, when the initial MB concentration is increased from 100 to 700 mg/L the amount of MB adsorbed per unit weight of the NCFs (mg/g), at the constant temperature 40°C, increased from 13.2 to 100.1 mg/g after that equilibrium attained. Therefore, the extent of adsorption increases with increasing initial dye concentration.

4.3 Adsorption Isotherms

The adsorption isotherms of methylene blue from its aqueous solution on the NCFs adsorbent in the concentration range 100-1000mg/L are represented by the Table 1 and Fig 6. The two most common isotherms, namely Langmuir and Freundlich isotherm, were applied to analyze the adsorption equilibrium experimental data.

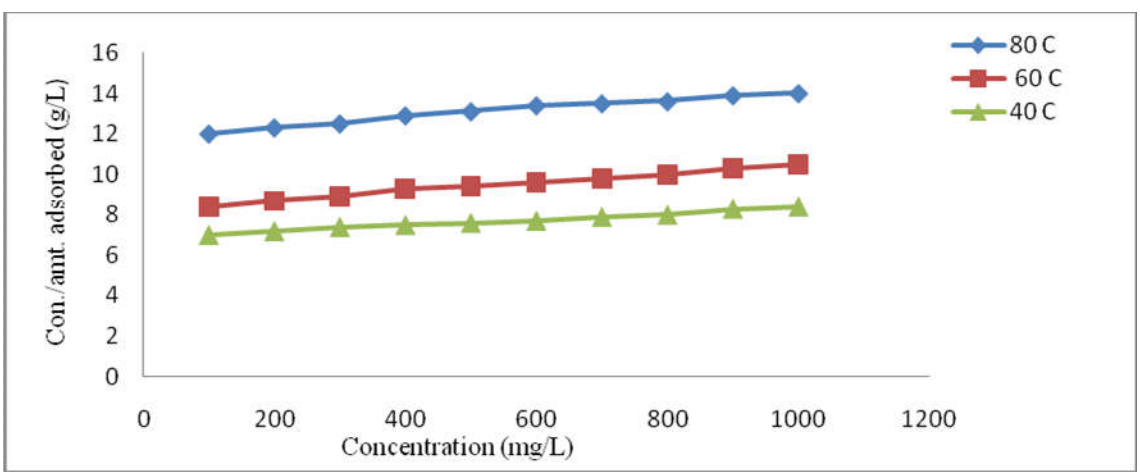


Fig. 6 Langmuir adsorption isotherms for the adsorption of MB on NCFs at different temperatures.

The linear form of the two isotherm equations can be expressed by equations (2) and (3).

$$\frac{C}{X} = \frac{1}{K_L X_m} + \frac{C}{X_m} \qquad (2)$$

$$\log X = \log K_F + \frac{1}{n}\log C \qquad (3)$$

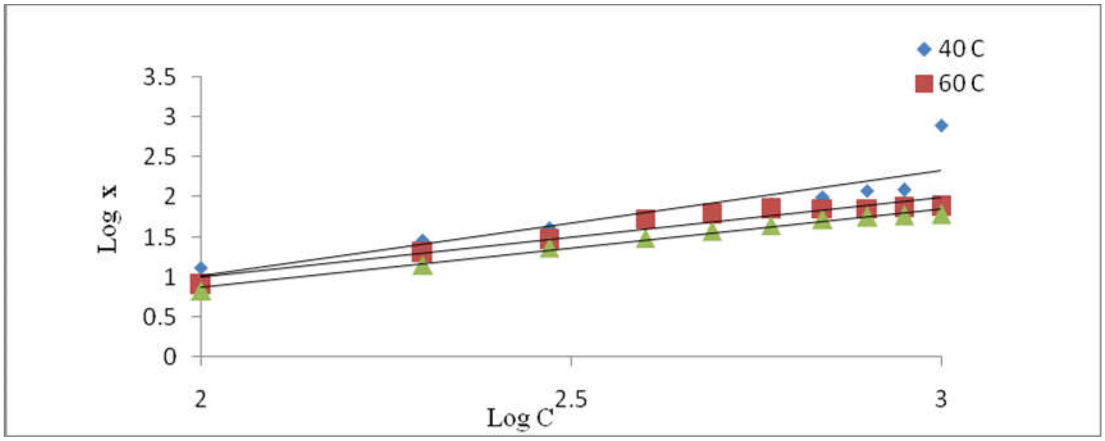


Fig. 7 Freundlich adsorption isotherm for the adsorption of MB on NCFs at different temperatures

Where x_m is the amount adsorbed (mg/g) at concentration C (mg/g), x_m is the monolayer adsorption capacity (mg/g) and k_L (L/mg) and k_F ((mg/g)(L/mg)$^{1/n}$) are two equation constants related to adsorption energy whereas n (g/L), in the Freundlich equation is a measure of energetic surface heterogeneity and adsorption intensity. The Freundlich constant n which should have value in the range of $0 < n < 1$ for favourable adsorption [25]. Favourable adsorption indicates that all the NCFs have energetically hetrogenous surface. The linear Langmuir and Freundlich adsorption isotherms of MB on adsorbent are shown in Fig 6 and Fig 7. The Langmuir and freundlich equation constants as calculated from the linear plots are given in Table 1.

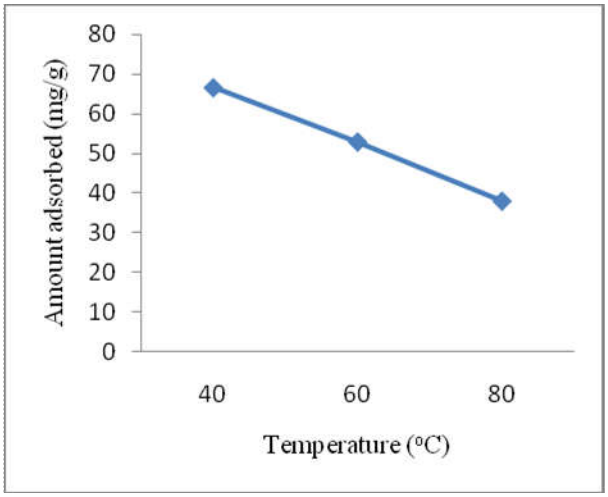
Table1.The Langmuir and Freundlich equation constants for the adsorption of MB on NCFs at different temperature

NCFs samples	Langmuir	Parameters	Freundlich	Parameters
	x_m (mg/g)	K_L (L/mg)	n (g/L)	K_F((mg/g)(L/mg)$^{1/n}$)
At 40°C	769.23	0.000191	0.95	15.85
At 60°C	384.61	0.00317	1	7.76
At 80°C	370.37	0.00231	0.95	5.25

4.4 Effect Of Temperature

To study the effect of temperature on the adsorption of dye adsorption by CNTs, the experiments were performed at temperatures of 40°C, 60°C, and 80°C. Fig. 8 shows the influence of temperature on the adsorption of dye onto

NCFs on different temperatures. It was found that the amount adsorbed decreases on increasing the temperature from 40°C to 80°C. A comparison of adsorption isotherms at 40°C, 60°C, and 80°C indicates that the process is exothermic in nature. This can be attributed to the fact that in case of physical adsorption, with increasing temperature the amount adsorbed decreases. Fig 9 shows that amount adsorbed at constant concentration 500 mg/L at different temperature.



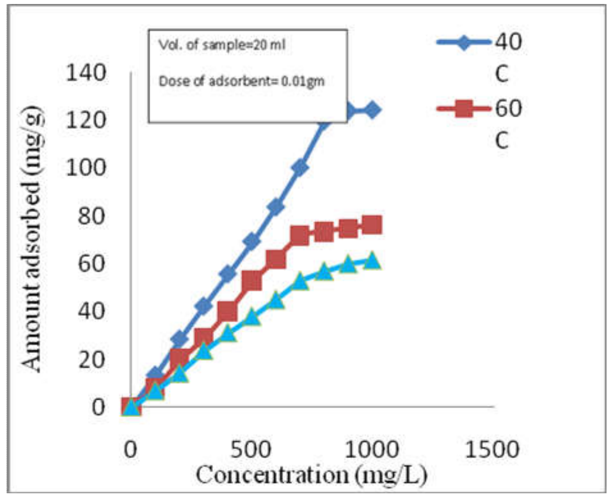


Fig. 8 Adsorption isotherms at different temp. Fig.9 Amount adsorbed at constant Concentration

4.5 Effect of pH

The effect of solution pH on adsorption of dye at pH range 1 to 7 as shown in Fig. 10. It is seen that the adsorption is small at pH between 1 and 3. A consistent increase in adsorption capacity of the NCFs was noticed as the pH increased from 2 – 5.5, whereas in the range 5.5 to 7, the adsorption amount was only slightly affected by pH.

As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H+ ions competing with dye cations for the available adsorption sites. Methylene blue adsorption usually increases as the pH is increased [26].

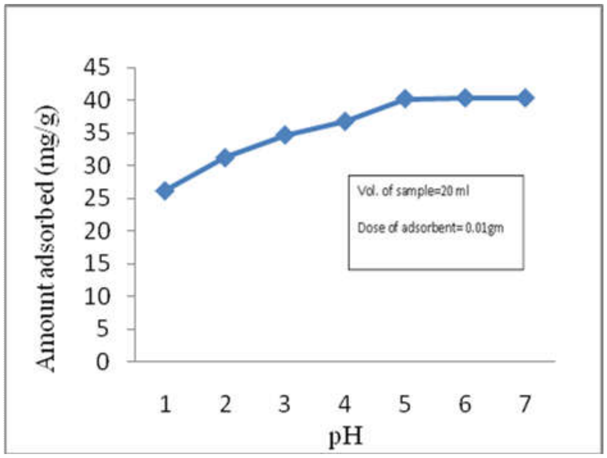


Fig. 10 Effect of pH

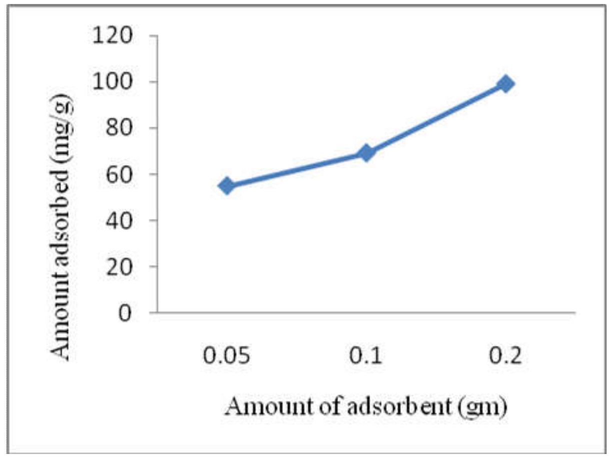


Fig. 11 Effect of adsorbent dose

4.6 Effect of Adsorbent Dose

Fig. 11 shows that more the amount of adsorbent, more was the adsorption of MB onto the surface of NCFs. This experiment was done at different amount of adsorbent i.e., are 0.05, 0.1 and 0.1 g**.**

5. Conclusion

Sugarcane bagasse (SCB) can be used as an adsorbent for removal of dye from waste industrial water. The removal of MB dye ions from aqueous solution by NCFs was found to be effective as the adsorption capacity of these adsorbent was 124.3 mg/g. The first phase involved rapid dye uptake in the beginning and almost 50 % adsorption is completed within 150 min but attains a constant value after about 240 min. The extent of adsorption increases with increasing initial dye concentration.

The equilibrium adsorption capacity of MB increases with decrease in temperature. This equilibrium adsorption data showed good fits to the isotherms of Langmuir and Freundlich. In view of the low cost of this material, the regeneration of the exhausted material need not be done, and it can be disposed of by burning.It is seen that the adsorption is small at pH between 1 and 3. A consistent increase in adsorption capacity of the NCFs was noticed as the pH increased from 2–5.5, whereas in the range 5.5 to 7, the adsorption amount was only slightly affected by pH.

From the observation of FTIR spectra of bagasse, the difference between these spectra before and after MB adsorption namely: reduction in the intensities for bands in the region between 1671, 1467, and 1128 cm^{-1}; a slight change in the shape of the broard band of 1128 cm^{-1} The other two frequencies 1671 and 1467 cm^{-1} were totally eliminated from the IR spectra.The results obtained from equilibrium studies of MB shows that it can be used as a low cost adsorbent for removing the dye from industrial waste water.

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