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Discovery

Dye removal on low cost adsorbent media developed from Pine cone

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ABSTRACT

The author has made an attempt to develop a low-cost adsorbent from pine cones, a widely available bio-waste, and to check its suitability through batch study with synthetic Methylene Blue aqueous solution as adsorbate. The effect of initial dye concentration, adsorbent dose, adsorbent particle size (Geometric mean size) and contact period on percentage removal efficiency and adsorption capacity were analysed. Bulk density test and FTIR spectral analysis were also conducted on adsorbent. The analysis of FTIR spectra indicates the involvement of functional groups like, OH-, C≡C, N=O etc. in methylene blue dye adsorption process. The spectral shift and the peak variation provides considerable support to the MB dye adsorption on the adsorbent material. The results of the present study were very encouraging. The AC developed from pine cone showed high removal efficiency. Maximum removal of 96.85 percent was observed with adsorbent of geometric mean size 212.13 µm, when 100 mg/L concentrated Methylene Blue solution was treated with it. The dye removal efficiency increased from 49.05 percent to 96.32 percent and the adsorbate adsorbed per unit mass of adsorbent was found to be decreasing from 2.49 to 0.99 mg/g, as the adsorbent dose increased from 20 g/L to 100 g/L.

Key words: Pine cone, Activated carbon, adsorbent, Methylene Blue, Unit adsorption capacity, Percentage removal efficiency

1. INTRODUCTION

Surface water and groundwater contamination due to dye Industries is common in India, mainly in Rajasthan, Tamil Nadu and Gujarat etc. Industries like textile industries, paper mills, leather industries, cosmetic industries, medicine manufacturers and so on, uses dyes in their processes to impart colour to their products, and a major part of it gets wasted through the effluent discharge. Investigation report shows that textile industry alone produces nearly 200 billion litres of coloured effluent annually and 15-20 percent of this comes from dyeing section (Rita Kant (2012)). Dyes are even toxic to aquatic organisms and reduce their population in surface water sources. The high colour imparted to water by these dyes reduces sunlight penetration into water and thereby affects the self purification capacity of water sources. To avoid these problems the dying industry effluents should be treated before disposal. The adoptable treatment methods include, coagulation flocculation, filtration, membrane processes, ultra-filtration, reverse osmosis, nano-filtration and micro-filtration, adsorption, ozone treatment, electrochemical processes etc. (C. Allegre et. al. (2006)). Among these all methods adsorption is considered as a cost effective and easy to operate technique for the removal of almost all kinds of dyes, particularly non-degradable dyes (M. Danish et. al. (2014)). The author has made an attempt to develop a low-cost adsorbent as activated carbon from pine cone through physical modification is used in this study to remove Methylene Blue dye from synthetically prepared solution. This paper is trying to represent the effect of various operating parameters, including particle size of adsorbent material, on the dye removal efficiency and adsorption isotherm studies. The physicochemical data of adsorbents obtained from FTIR and bulk density test results were also presented in it.

2. MATERIALS

2.1. Equipments

Accurate weighing of materials was performed using an analytical balance with precision of ±0.0001 g (Model: A&D GR-200 (max 210 g min 10 mg e=1mg d= 0.1 mg)). Drying of materials was carried out in an electric oven (Model: SECOR INDIA). Desiccators were used to bring the dried adsorbent medium to the room temperature. The hot Porcelain dishes, in which the drying operations were carried out, were handled using tongs. The dye in the sample was measured spectrophotometrically using a spectrophotometer (Model: DR-2800, HACH, USA). FTIR (Fourier Transform Infrared) spectra were obtained on FTIR spectrometer (Model: Perkin Elmer Spectrum-65, SP-65, USA).

2.2. Reagents and Stock Solution

All the chemicals used in the study were of analytical reagent grade and used without further purifications. All the experiments were carried out at room temperature and standard atmospheric pressure. Methylene Blue dye was used as an adsorbate in this set of study. The molecular weight of Methylene Blue is, MW = 319.65 g mol^{-1}. Fig. 4.1 shows the structure of Methylene Blue dye (G Mckay, J. F. Porter and G. R. Prasad (1999)).

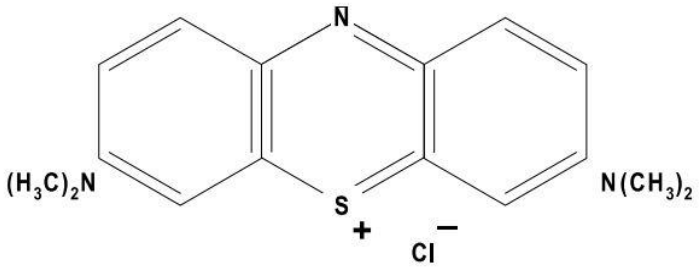

Figure 2.1 Structure of Methylene Blue

2.3 Preparation of Sorbents

Pine cones were collected from NIT Hamirpur campus. It was cleaned thoroughly with distilled water and dried at 65^0C for 24 hours in a hot air oven. This was again burnt in a container with holes on the top of the container, to allow the fumes to escape, up till the rising fume stops, and it took around 3 hours. Allowed it to cool to the room temperature, ground and sieved through IS sieves 4.75mm, 2.36 mm, 2 mm, 1.18 mm, 600 µm, 425 µm, 300 µm and 150 µm with the help of the sieve shaker. Washed them thoroughly using distilled water, dried them in the oven for 24 hours and stored them in container after cooling down to the room temperature using desiccators, to use as an adsorbent. Adsorbents of GM size 504.98 µm, 357.07 µm and 212.13 µm were opted for this study after initial removal efficiency analysis.

2.4. Experimental Methods

The physical characteristics of adsorbent were studied using FTIR spectral analysis and bulk density test. Batch kinetic studies were carried out at room temperature using MB aqueous solution as adsorbate and different sized adsorbents. The absorbance of the effluent was measured using spectrophotometer in one hour intervals until closer observations were found, i.e. until equilibrium was attained. This was repeated by varying initial concentration of MB solution (100 mg/l, 200 mg/l and 300 mg/l), and with adsorbent of geometric mean size 504.98 µm, 357.07 µm and 212.13 µm. The effect of adsorbent dosage, initial dye concentration and contact period on percentage removal and dye adsorbed per unit adsorbent were analyzed with the result obtained. The adsorbate adsorbed per unit mass of adsorbent was calculated using the equation given below.

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where, q_t (mg/g) is the amount of dye adsorbed per unit weight of adsorbent, C_0 and C_t (mg/L) are initial and final concentration of the MB solution respectively, V (L) is the volume of dye solution and m (g) is the weight of adsorbent.

The percentage dye removal efficiency was calculated using the equation given below:

$$\%\ \text{removal efficiency} = \frac{(C_0 - C_t)}{C_0} * 100$$

3. RESULTS AND ANALYSIS

3.1. FTIR Spectroscopy

Fourier transform infrared (FTIR) spectroscopy gives structural and compositional information on the functional groups present in the samples. The activated carbon sample (10 mg) was ground with 200 mg of KBr (spectroscopic grade) in a mortar, and then pressed into 10 mm diameter disks under 10 tonnes of pressure and high vacuum for 10 minute to prepare the specimen for FTIR spectroscope, (Olugbenga Solomon Bello *et al.* (2010)).

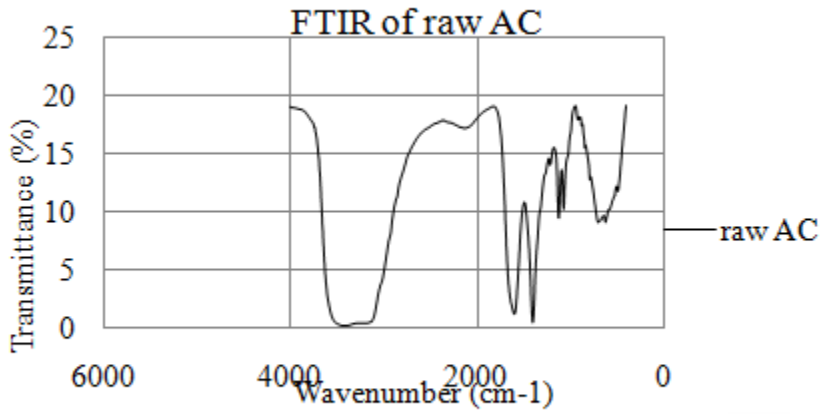

Figure 3.1 FTIR Spectra of Activated Carbon before Adsorption

The FTIR spectra of AC before treatment or the raw AC is shown in the Fig. 3.1, that of MB treated AC is shown in Fig 3.2 and the spectral variation after adsorption is displayed in Fig. 3.3, and it was found to be having a number of peaks in it, which indicates the complex nature of AC prepared from pine cones. The broad adsorption peak observed at 3430cm^{-1}, indicates the presence of hydroxyl group with stretched bonding. The stretch vibration peak at 2124cm^{-1} implies an alkyl C≡C. The presence of C=O was assured by the peak at 1602cm^{-1}. The peak at 1400 cm^{-1} may be due to the presence of carboxylic group. The peak at 1214cm^{-1} and 1069cm^{-1} may be due to asymmetric and symmetric stretching vibration, corresponding to C-O-C bond, respectively. The peak at 1122cm^{-1} indicates C-O bond, 918 cm^{-1} stipulates an OH bending vibration and 697cm^{-1} shows a C-C bond in the AC.

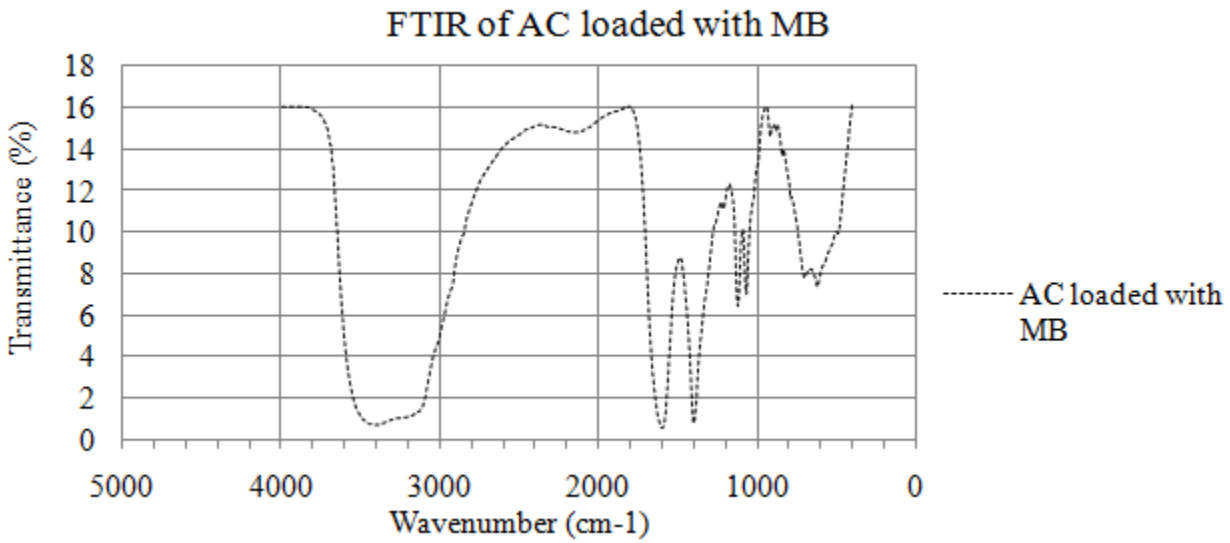

Figure 3.2 FTIR Spectra of Activated Carbon after Adsorption

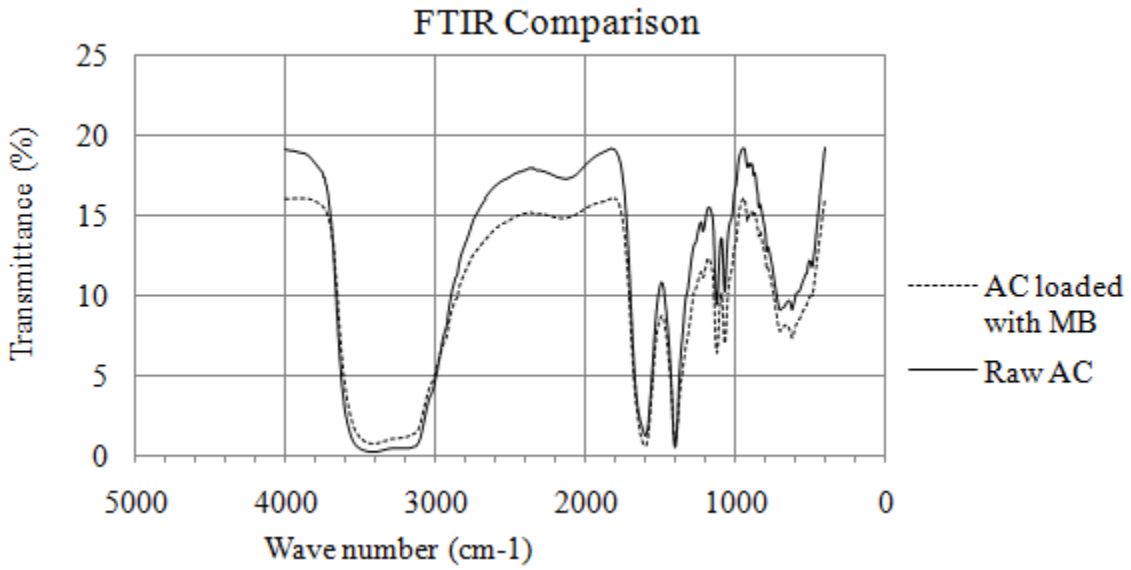

Figure 3.3 Showing Spectral Deviation of AC after Adsorption from Raw AC

The adsorption capacity of adsorbents depends upon porosity as well as chemical reactivity of functional groups at the surface. This reactivity creates an imbalance between forces at the surface when compared to those within the body, thus leading to molecular adsorption by the van-der-Waals force (P. SenthilKumar *et al.* (2010)). Thus functional groups have considerable involvement in adsorption process.

Table 3.1 FTIR Spectral Characteristics of Pine Cone Derived Adsorbent Before and After Adsorption

IR Peak	Wave number (cm^{-1})		Differences	Assignment
	Before adsorption	After Adsorption		
1	3431	3421	-10	OH^- stretching
2	2124	2147	23	C≡C stretching
3	1598	1602	4	N=O stretching
4	1214	1215	1	C-O-C Stretching
5	697	700	3	C-C bending

The FTIR spectra of AC were shifted after adsorption of MB dye on it. The peak at 2124 got clearly vanished after adsorption process and a new peak was introduced at 918 cm^{-1}, which may be due to the stretching C-N group. The variation in FTIR spectra of AC before and after adsorption of MB is clearly visible in Fig. 3.3. The Table 3.1 represents the spectral analysis of AC, which shows

that -OH group and other functional groups can be the potential sites involved in MB adsorption. Similar observations were made by Avisha Chowdhury, Avijit Bhowal and Siddhartha Datta (2012).

3.2. Batch Study

3.2.1 Effect of Adsorbent Dose

A 50 ml of MB solution of 100 mg/L initial concentration was made into contact with 1 g, 2 g, 3 g, 4 g and 5 g of adsorbent of GM size 212.13µ. The effect on percentage removal in the case of adsorbent of GM size 212.13 µm is shown in Fig. 3.4.

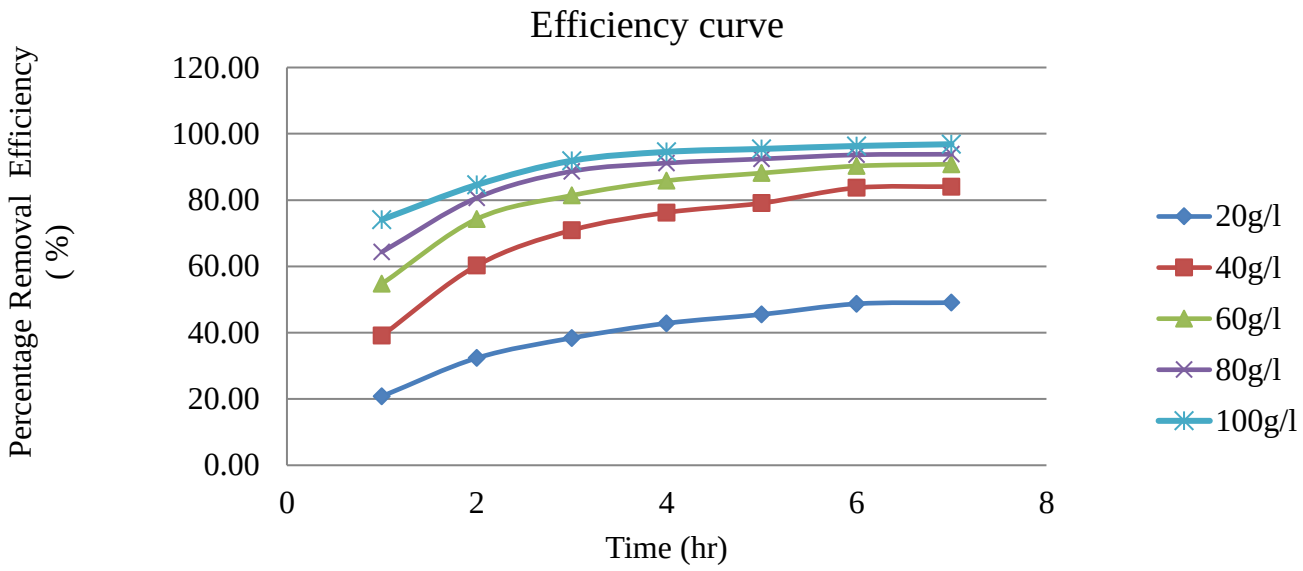

Figure 3.4 Removal Efficiency of Adsorbent of GM Size 212.13 µm

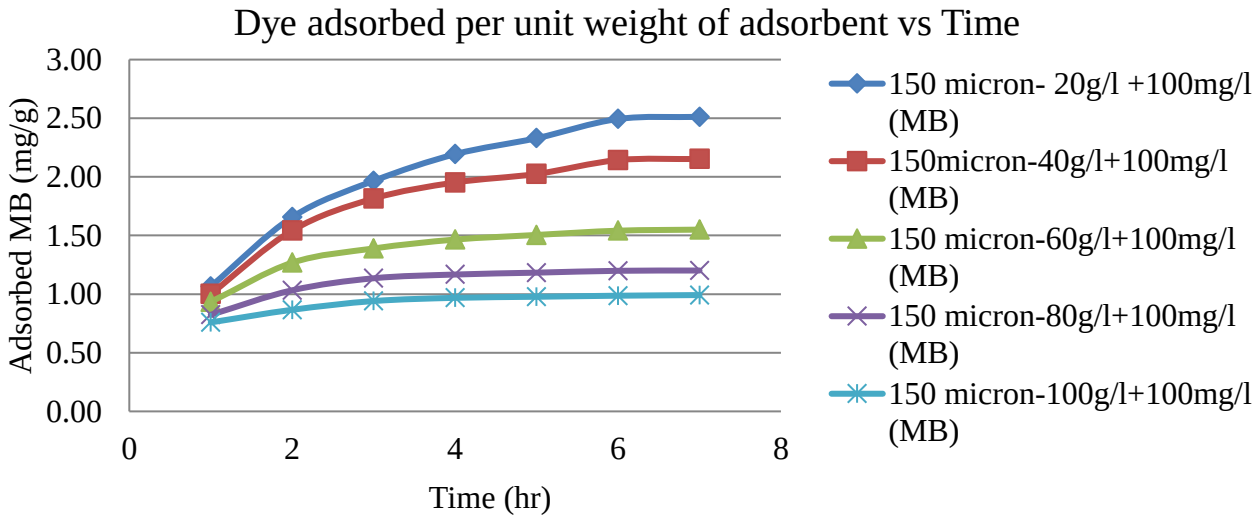

Figure 3.5 Variation of Dye Adsorbed Per Unit Mass of Adsorbent with Increase in Adsorbent Dosage and Time in the case of Adsorbent with GM Size 212.13 µm

The percentage removal efficiency was found to be increasing with increase in adsorbent dose, while the dye adsorbed per unit weight of adsorbent was found to be decreasing, and both of the parameters were found to be increasing with increase in contact period. Similar observation was made by Reza Ansari (2012), on saw dust, and Papita Saha (2010), on tamarind fruit shell, were also found to be following such pattern. The equilibrium was attained after 6hour. The dye removal efficiency of 212.13 GM sized adsorbent was increased from 48.69 percent to 96.32 percent with the increase in adsorbent dosage from 20 g/L to 100 g/L after 6 hours of contact period. The graphical representation is displayed in Fig. 3.4. The variation of unit adsorption capacity with time for adsorbent of GM size 212.13 µm is shown in Fig. 3.5.

3.2.2 Effect of Initial Dye Concentration

The percentage dye removal was found to be decreasing with increase in initial dye concentration and MB dye adsorbed per unit weight of the adsorbent (q) was found to be increasing. Graphical representation of the data is presented in Fig. 3.6 and Fig. 3.7.

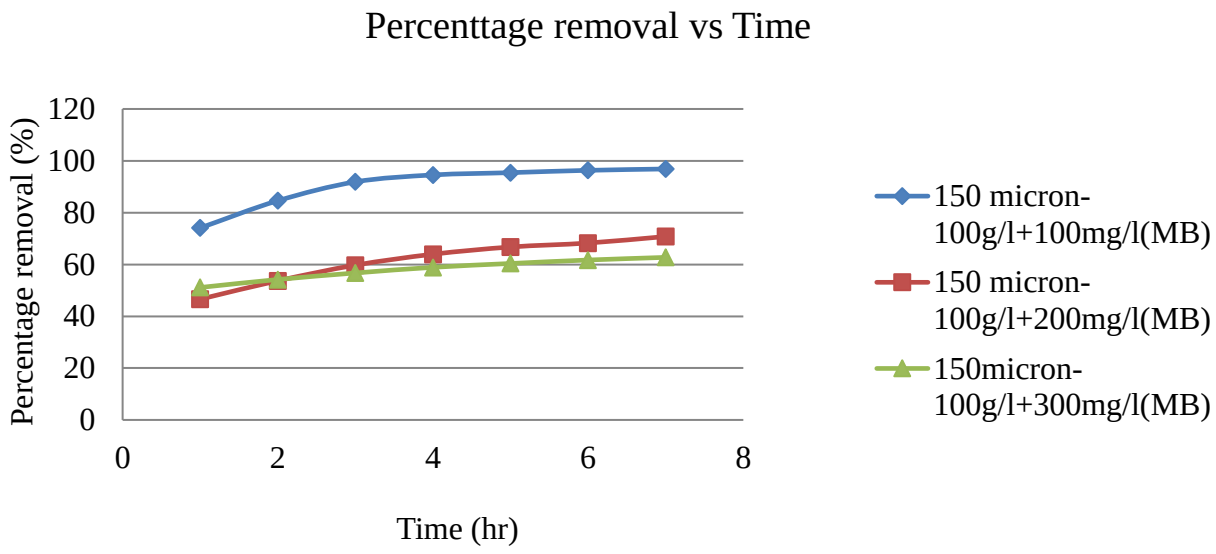

Figure 3.6 Effect of Initial Dye Concentration on Percentage Removal with Passage of Time

The removal efficiency was decreased from 96.85percent to 62.73percent and 'q' got increased from 0.99 mg/g to 1.87 mg/g, with increase in influent concentration from 100 mg/L to 300 mg/L at 7 hours of contact period, where the GM size of the adsorbent was 212.13 µm. The pattern of data obtained by G. M. Ratnamala, K. Vidya Shetty, G. Srinikethan(2012) resembles the results of the current work.

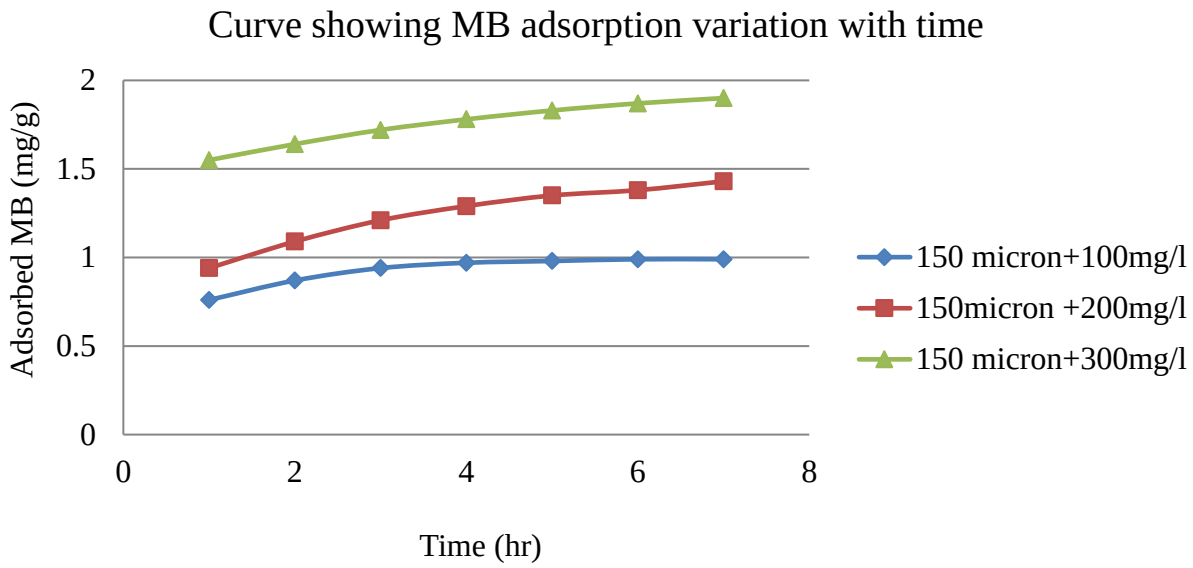

Figure 3.7 Effect of Initial Dye Concentration on Mass of Adsorbate Adsorbed Per Unit Mass of Adsorbent

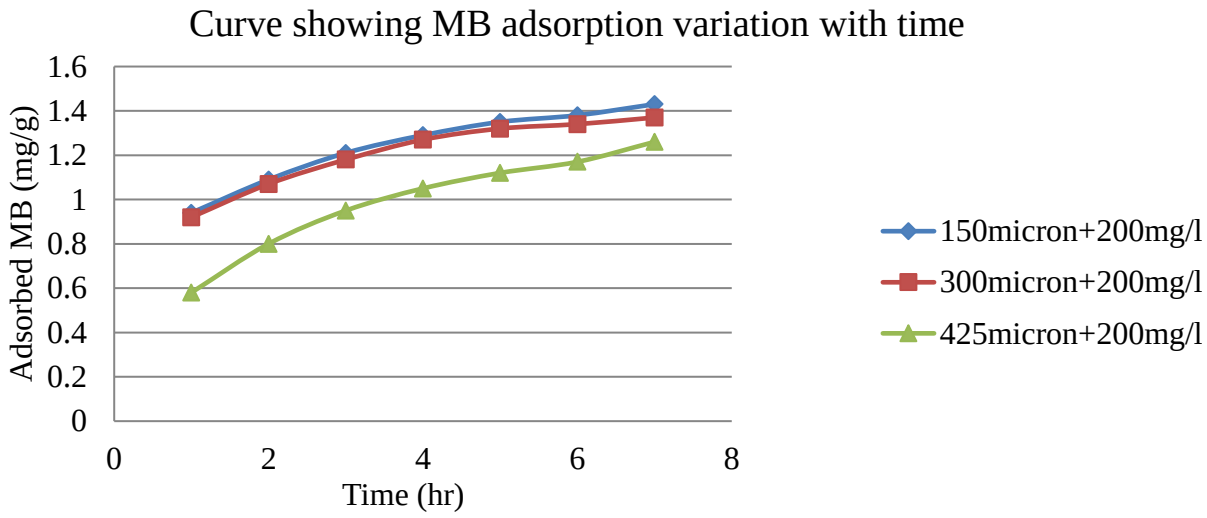

Figure 3.8 Effect of Size of Adsorbent on Mass of Adsorbate Adsorbed per Unit Mass of Adsorbent (q)

3.2.3 Effect of adsorbent size

Adsorbent retained on 425 µ, 300 µ and 150 µ IS sieves or geometric mean sizes 504.98 µm, 357.07 µm and 212.13 µm respectively, were treated with MB solution of 100 mg/L initial concentration. The equilibrium was attained after 6 hours. The results indicates that the size of the adsorbent is inversely proportional to its removal efficiency, i.e. percentage removal was found to be decreasing with increase in adsorbent particle size, and adsorbate adsorbed per unit adsorbent was also showing same pattern. Fig. 3.8 shows the graph**.**

Adsorption is a surface phenomenon and the observation supports the theory. Since the surface area increases with decrease in particle size, the percentage dye removal increases. Adsorbate adsorbed per unit weight also follows the similar trend in this case. Dye removal efficiency obtained for adsorbent geometric mean sizes 504.98µm, 357.07µm and 212.13µm were 96.32 percent, 94.73 percent and 92.76 percent respectively. The Fig. 3.8 shows the graphical representation of the data.

Through the batch study a maximum removal efficiency of 96.85 percent was obtained with adsorbent of GM size 212.13 µm, when MB solution of 100mg/L concentration was treated with an adsorbent dosage of 100g/l for 7 hours of contact period.

4. CONCLUSION

The present investigation was able to develop a low-cost adsorbent from locally available pine cones for removal of dye. There were following conclusions drawn from studies:

1.Adsorbent with GM size 212.13 µm has shown highest dye removal efficiency among all the three sizes of adsorbents.

2.Adsorbents of GM size 212.13 µm, 357.07 µm and 504.98µm has shown an equilibrium adsorption capacity of 2.49 mg/g, 2.37mg/g and 1.81 mg/g and removal efficiency of 96.85 percent 95.08 percent and 92.76 percent respectively at 20 g/L adsorbent dosage.

3.The FTIR spectra shows the involvement of functional groups like, OH^- stretching, C≡C stretching, N=O stretching, C-O-C Stretching, C-C bending etc. in adsorption phenomena. A clear shift in spectra is observed in-between the spectra of AC before and after adsorption process. The peak at 2124 cm^{-1} got clearly vanished after adsorption process and a new peak was introduced at 918 cm^{-1}, which may be due to the stretching C-N group. This strongly supports, MB dye adsorption being the reason for FTIR spectral shift.

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