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Degradation of Methylene Blue Dye Using Activated Carbon Obtained From Bio-Waste

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Abstract: Activated carbon (AC) was derived from waste Jack fruit leaves by chemical activation with KOH followed by pyrolysis at 600 °C for 5 hours in closed crucible in muffle furnace. The structural and morphological analysis of as synthesized activated carbon was done by Raman spectroscopy, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The synthesized activated carbon has been used for removal of Methylene Blue (MB) dye from an aqueous solution. Batch adsorption experiments were carried out as a function of contact time, initial dye concentration and adsorbent dose. The adsorption data of MB dye was analysed by Langmuir and Freundlich adsorption isotherms .It was observed that Langmuir model can be best fitted with regression coefficient R^2 =0.9959 as comparison to R^2 =0.875 for Freundlich Isotherm. The results indicate that adsorption of MB on activated carbon followed by Langmuir model with maximum monolayer adsorption capacity was found to be 84.03 mg/g.

Keywords: Activated, carbon, Bio-waste, Dye degradation, Isotherm

I. INTRODUCTION

Cosmetics, leather, paper, printing and textile finishing industries use dyes in order to colour their products and pour a lot of collared wastewater into the environment. Dyes even in low concentrations affect the aquatic life and ecological balance of the area [1-3]. All the dye wastes, produced from different sorts of commercial enterprises have harmful impact on microbial inhabitants and may be toxic and even deadly to mammals. These dyes have the potential to cause diseases such as allergic eczema, skin problem, mutations and cancer [4-5]. There are several effective methods reported for the removal of dyes from the wastewaters such as adsorption [6], coagulation [7], advanced oxidation [8], and membrane separation [9] which have been put to use for the removal of synthetic dyes from wastewater. Among all these processes adsorption is the most effective process for waste water treatment. The activated carbon is one of the best adsorption materials available for the waste water treatment. Activated carbon gives cost effective solution on an industrial scale. The highly expensive and poor performance of activated carbon derived from polymer and other synthetic materials leads to research in alternative sources of carbon from natural sources such as different agricultural wastes. There are many reported bio-waste derived activated carbons such as agricultural plant-based materials like date palm leaves [10], oak leaves [11], rice husk [12], fluted pumpkin stem [13], tung fruit husk [14], oil palm shells [15] and orange peel [16].

In the present work, adsorption capacity of jackfruit derived activated carbon was investigated, using methylene blue as a model basic dye. Jackfruit is typical plant which is common in backyards and waste places. The jackfruit derived activated carbon shows excellent adsorption capacity for methylene blue dye. Due to its abundant availability and affordability, it can be used as an effective adsorption material in the industry. The objective of this study was to examine the adsorption characteristics of jackfruit leaves derived activated carbon and to study adsorption models like Langmuir and Freundlich isotherms of the same.

A. Materials

II. EXPERIMENTAL PROCEDURE

The waste Jack fruit leaves ware collected from various places and washed with soap solution followed by 3-4 times washing with distilled water to removes the impurities. The washed leaves were then allowed to dry in sunlight for 24 hrs. After drying, leaves ware activated with KOH at a weight ratio of 1:1 (Leaves: KOH) for 24 hrs. The activated leaves were crushed with the help of grinder to get fine powder. The activated leaf powder was then put into the closed crucible and placed into the muffle furnace for carbonization process. The temperature was raised with ramping rate of 20 °C/min up to 600°C and annealed at that temperature for 5 hrs. The crucible was then allowed to cool at room temperature. The black color powder was washed with distilled water and dilute HCl to maintain the pH of material at 7. Finally the product dried at 120° C in vacuum oven for 12 hrs and placed into airtight bottle for further experiment.



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Methylene blue was purchased from Sigma Aldrich and used as received without any further purification. The stock solution of MB (1000 mg/l) was prepared in distilled water. Various concentrations of MB dye were prepared with the help of distilled water. The 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm MB solutions were used for experiments.

B. Structural and Morphological Characterizations

The Raman spectra of activated carbon were characterized with Renishaw microscope with laser wavelength 632 nm in the back scattering geometry. The laser power on the sample was \sim 2 mW and the detector used was CCD synapse with thermoelectric cooling to -70°C. A 50X objective was used to focus the laser beam and to collect the Raman signal. The FESEM images were recorded using Model JEOL JSM-6360 Field emission Scanning Electron Microscope with tungsten filament as electron source. The TEM images were recorded using TECNAI G2-20-TWIN transmission Electron microscope operating at 200 kV. The UV-visible spectra were recorded on JASCO, V-670 UV–Visible spectrophotometer.

III.RESULTS AND DISCUSSION

The Fig. 1(a) shows the typical Raman spectra of activated carbon with three separate peaks located at 1337 cm⁻¹, 1584 cm⁻¹ and 2674 cm⁻¹ corresponding to D, G and 2D band respectively. The presence of G band is described to sp^2 type of carbon with E^{2g} vibrating modes and D band indicates the presence of defects in the activated carbon.



Fig.1: Typical Raman Spectra for Activated carbon

The Fig 2 (a and b) shows the SEM images of activated carbon. The typical SEM images of activated carbon are porous in nature. The porous nature is more useful for the adsorption process for dye adsorption. The Fig. 2(c-d) shows the typical TEM images for activated carbon which shows the thin layers of activated carbon with containing full of cavities.



2: (a-b) Typical FESEM images and (c-d) Typical TEM images for activated carbon.



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A. Contact time study

In the contact time between adsorbent and adsorb ate is one of the most important parameter that particularly affect the performance of degradation rate of MB dye. The UV-VIS absorption spectrum for different Concentrations of MB dye is shown in Fig. 3(a). The Fig. 3(b) shows the absorption spectra of MB dye degradation in 30 ppm solution as function of time. The 0.03 g activated carbon was added in to 100 ml of 30 ppm Mb dye. The solution of 2 ml was pipette out with 5 minutes of time interval and filtered out. Then this solution was analysed with the help of UV-VIS spectrometer. The Fig. 4 (b) clearly shows that, the percentage removal of MB dye from aqueous solution increasing with increasing contact time. At the end of 25 min we get ~ 99 % degradation of MB dye from aqueous solution respectively.



Fig.3: (a) The UV-VIS absorption spectra for different Concentrations of MB dye, (c) The UV-VIS spectra for activated carbon for (b) Contact time study, (c) Initial concentration study, (d) adsorbent doses study.

B. Initial MB concentration

The effect of initial concentration of MB dye concentration on the removal percent and removal efficiency on various adsorbents is studied in fig.3(c) and 4(c). This investigation is carried out by keeping 0.03g carbon dose and 5 min degradation time constant. The carbon dose was added in to 100 ml of the prepared different concentrations (10 ppm to 50 ppm) of MB dye solution. The solution of 2 ml was pipette out after 5 min time interval and filter out. Then this solution was analysed with the help of UV-VIS spectrometer. This result shows that the percentage removal of the MB dye from aqueous solution was found to be decrease with increasing initial dye concentrations from 10 to 50 ppm witch is clearly indicated in term of percentage removal in Fig.4 (c).

C. Adsorbent dosage study

The effect of adsorbent dosage studies were carried out by varying the percentage of carbon in the MB dye solution from 0.01 g to 0.05 g respectively by keeping 30 ppm MB dye solution and 5 min degradation time constant. The activated carbon samples were added in 100 ml of 30 ppm MB solution. The solution of 2 ml was pipette out and filtered after 5 min. This solution is analysed with the help of UV-VIS spectra. The Fig.3 (d) shows that with increasing adsorbent dose of activated carbon, the adsorption percentage of MB also increases. Fig. 4(d) clearly shows it in terms of percentage removal. All the experiments were carried out at room temperature (30° C) at constant stirring rate of 600 RPM on magnetic stirrer.



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Fig.4(a) Calibration plot for MB dye solution at various concentrations. (b) The degradation of MB dye in terms of % for (b) Contact time study,(c) Initial concentration study and (d) adsorbent doses study.

D. Langmuir isotherm model

The linear form of Langmuir expression is in equation 1 [5]

$$C_{e}/Q_{e} = C_{e}/Q_{0} + 1/bQ_{0}$$
(1)

Where, C_e is the equilibrium concentration of dye solution (mg/l), Q_e is the amount adsorbed equilibrium (mg/g), Q_0 is the monolayer adsorption capacity (mg/g), and b is the Langmuir adsorption constant (L/mg) which is related to the free energy of adsorption. The Langmuir model was fitted to the experimental data as shown Fig. 5 (a). The values of Q_0 and b were calculated from the slope and intercept of the linear plots are presented in Table 1.

 TABLE I

 The isotherm data of Langmuir Contents, Freundlich Constants and maximum adsorption capacity of activated carbon.

Source name	Langmuir Constants			Freundlich Constants		
	Q _o (mg/g)	b (l/mg)	R ²	n	k _f (mg/g)	R ²
Present Work	84.03	8.43	0.9959	19.54	0.875	6.673

E. Freundlich isotherm model

The Freundlich isotherm model can be expressed in linear form as equation (2) [17]

$$lnQ_{g} = \ln k_{f} + \left(\frac{1}{n}\right) * lnC_{g}....(2)$$

Where, k_f and n are the Freundlich adsorption isotherm constants, which indicate the capacity and intensity of the adsorption respectively. The Freundlich model was fitted to the experimental data as shown in Fig. 5 (b). The maximum adsorption capacity of activated carbon was found to be ~ 84.03 mg/g.



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Fig. 5: (a) Langmuir isotherm, (b) Freundlich isotherm of MB dye on activated carbon.

IV.CONCLUSIONS

In conclusion, the activated carbon was synthesized from waste Jack fruit leaves. It was successfully used as an adsorbing catalyst for removal of Methylene blue dye from aqueous solution. The maximum adsorption capacity of was found to be ~ 85.05mg/g at room temperature.

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