Research Paper
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Efficient removal of Methylene Blue on *Aeglemarmelos* leaves: Equilibrium, Kinetics and Thermodynamic Studies.

Chemistry

KEYWORDS : Activated Carbon, adsorption, equilibrium, kinetic, thermodynamics

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ABSTRACT

Activated carbon(ACBTL) was prepared by chemical activation of bael tree leaves (Aeglemarmelos) at 450 oC using phosphoric acid. Characterization of the sample was performed by using nitrogen adsorption isotherms, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The effects of major variables governing the efficiency of the process such as temperature, time, dosage and pH were investigated. Experimental results have shown that, the percentage removal increased with increasing temperature, time, dosage and pH.The adsorption kinetic data were analysed using pseudo-first-order and pseudo-second-order models. It was found that the pseudo-second order kinetic model was the most appropriate model, describing the adsorption kinetics. Equilibrium data were fitted to the Langmuir, Freundlich and Dubinin-Radushkevich models. The equilibrium data were best represented by the Langmuir isotherm model. Thermodynamic studies showed that the adsorption was spontaneous, endothermic and entropy controlled.

INTRODUCTION

The discharge of pollutants from various industries poses threat to Earth's biodiversity. Among various types of environmental pollutions water pollution is of major concern and for its occurrence dye-based industries are the main cause and foremost. Dyes are released into the environment, entering into aquatic ecosystem, deteriorating the water quality and thereby affecting the flora and fauna (1). Among these techniques, adsorption process is a procedure of choice for the removal of organic compounds from wastewater (2). Particularly the cationic dye Methylene blue produces serious environmental problems. Adsorption is the most effective method and activated carbon is the preferred adsorbent widely employed to treat waste water for all classes of dye (3). Methylene blue is widely used for printing calico, dyeing, printing cotton etc. Accidental large dose creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia (4).

Material and Method

Bael tree leaves were collected, washed, dried and ground to powder and oven dried at 110ºC. The dried mass was impregnated with orthophosphoric acid in the ratio of 5:1 (g H_3PO_4 /g Bael tree leaf powder) and allowed to carbonize at 450ºC in a muffle furnace for 1h.The carbon was washed to remove all the free acid until a constant pH was obtained and then dried at 110ºC overnight.

Results and discussion

Characterization of the adsorbent (ACBTL)

The activated carbon prepared from black gram husk exhibited a typical type IV isotherm according to IUPAC classification. According to the results of the BET the external surface area reported is 134.28 m^2/g. D_p value is 6.65nm indicating a great development of mesopores. SEM micrographs clearly revealed that wide variety of pores is present in the activated carbon. It is also found that there are holes and openings on the surface of the adsorbent, which would have more surface area available for adsorption. The FT–IR spectra of the activated carbon prepared by using phosphoric acid as the activating agent shown in Figure 1. The peak appearing at 3310.83cm^{-1} is attributed to the hydrogen bonding of the OH group of alcohol and phenols. The peak appearing at 1164.33 cm^{-1} is due to the stretching the vibration in alcohol (5).

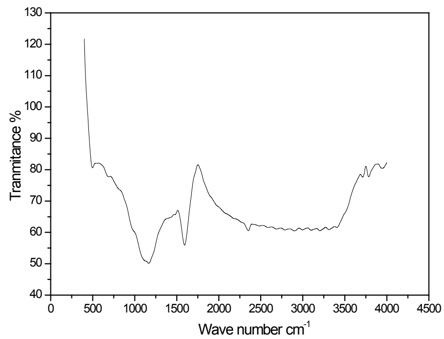

Fig.1 FT-IR analysis of ACBTL.

Adsorption and kinetic study

Batch experiments were carried out in order to evaluate the effects of amount of adsorbent, contact time, initial dye concentration and solution pH.In the adsorption experiments 50 ml of different concentrations of MB dye solution was taken in each of 100 ml volumetric flasks with fixed amount of adsorbent (ACBTL) in each flask. The flasks were then subjected to mechanical agitation in water bath shaker at a constant temperature until the equilibrium was reached. These solutions were centrifuged and the absorbance of the supernatant solution obtained was determined at the maximum wavelength (λ_{max} 663) with a UV-visible spectrophotometer. The percentage removal and the amount of dye adsorbed at equilibrium (q_e) were calculated by the following equations.

$$\text{Percentage removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

and the kinetic study with a series of 50 ml sample dye of known concentrations namely 12x 10^{-4} M, 14 x 10^{-4} M and 18 x 10^{-4} M were prepared and agitated. The solutions from the flask were centrifuged at different predetermined intervals of time 5 to 120 min and the supernatant solution from each flask was quantified spectrophotometrically. The amount of dye adsorbed (q_t) at time (t) was calculated from the equation as follows.

$$\text{Amount Adsorbed } (q_t) = (C_0 - C_t) \times \frac{V}{m} \quad (2)$$

Effect of adsorbent dose.
The effect of adsorbent dose on the percentage removal of MB dye was studied at an initial dye concentration of 18 x 10^{-4}M .The dye removal efficiency has increased from 27.78% to 99.53%. The percentage removal increased with adsorbent dosage up to a certain limit and then attained saturation. The optimum adsorbent dose is 0.14g.

Effect of contact time
Effect of contact time on the adsorption of MB was studied for different concentrations namely 12x10^{-4}, 14x10^{-4} and 18x10^{-4}M with fixed dose of 0.14g. This data reveals that as the contact time increases, rate of adsorption first increases and then becomes almost constant. This is due to the aggregation of dye molecules with the increase in contact time, which makes it almost impossible to diffuse deeper into the adsorbent structure at higher energy sites. The optimum contact time is found to be 120 min to study the other parameters.

Effect of concentration at different temperature.
The adsorption of MB dye was studied in the concentration range from 2×10^{-4}M to 24 ×10^{-4}M at fixed dose of 0.14g. It is seen that the percentage removal of MB dye decreases with increasing concentration. The percentage removal of the dye decreased due to non-availability of adsorption sites for the increased number of molecules.

Effect of pH.
The adsorption of dye onto adsorbent is highly dependent on the pH of the solution, which influences the structure of the dye and the surface properties of adsorbent. The effect of pH was studied with MB dye concentration of 18x10^{-4}M, adsorbent dose 0.14g of ACBTL and varying the pH by adding 0.1N of NaOH or HCl and shaken until the equilibrium was reached. The results show that as the pH increased from 2 to 12 the percentage adsorption of MB also increased.

Adsorption isotherm
The Langmuir adsorption isotherm assumes that monolayer coverage of the dye molecules onto surface of adsorbent with a finite number of adsorption sites. The adsorption capacity of any adsorbent can be determined by using Langmuir adsorption isotherm. The Langmuir adsorption isotherm equation can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \quad (4)$$

were q_e (mol/g) and C_e(mol/L) are the amount of dye adsorbed per unit weight of adsorbent and the concentration of the dye solution at equilibrium respectively (Fig.2).The favorability and feasibility of Langmuir adsorption isotherm was tested by using dimensionless constant called separation factor or equilibrium parameter (R_L) which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 is the initial MB dye concentration (mol/L) and K_L (L/mol) is Langmuir equilibrium constant. R_L values for the removal of MB dye is between 0.048 and 0.071 which indicates favorable adsorption isotherm. The mono layer adsorption capacity of ACBTL was found to be 6.464 x 10^{-4} mol/g.

As may be appreciated, the Langmuir model enables to represent properly the data for all the systems with R^2 values 0.998. It should be mentioned that the Freundlich model was also applied, but it led to a less adequate description of the results, as revealed by lower values of R^2.Dubinin-Radushkevich adsorption isotherm was employed from which the E value calculated (21.19 to 23.33) clearly indicates that adsorption of MB dye onto ACBTL is mainly through chemical process. The values of Q_m and K_L increased with an increase in temperature indicating that adsorption is favorable at higher temperature as well as the endothermic nature of adsorption process (Table1).

Table 1.Adsorption isotherm parameters for the adsorption of MB onto ACBTL

Adsorption Isotherm parameters	Temperature(K)		
Langmuir adsorption isotherm			
Q_m (mol/g)	6.464x 10^{-4}	6.818x 10^{-4}	7.331x 10^{-4}
K_L (L/mol)	6.485x 10^{4}	6.796x 10^{4}	9.812x 10^{4}
R^2	0.998	0.998	0.998
R_L	0.071	0.060	0.048
Freundlich adsorption isotherm			
K_f(mol/g)	2.068x 10^{-4}	2.115x 10^{-4}	2.198x 10^{-4}
R^2	0.970	0.956	0.998
DR- adsorption isotherm			
Q_m (mol/g)	0.973x10^{-4}	1.009x10^{-4}	1.157x 10^{-4}
K(mol²/KJ²)	1.112x 10^{-9}	1.009x 10^{-9}	1.002 x10^{-9}
E(kJ/mol)	21.19	22.26	23.33
R^2	0.983	0.950	0.961

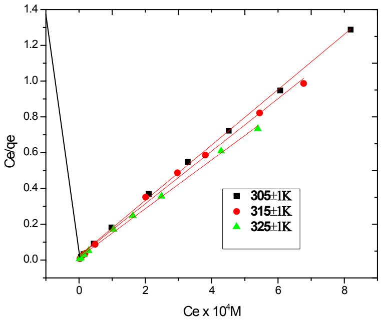

Fig.2.Langmuir plot of MB dye on ACBTL.

Adsorption kinetics.
Two kinetic models such as pseudo first order and pseudo second order equations were employed to evaluate the experimental data. The pseudo first order equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (10)$$

where k_1 (1/min) is the rate constant, $k_1$and q_e can be calculated from the slope and intercepts of log(q_e–q_t)versus time t. If the calculated q_e is not equal to the experimentally obtained q_e value, then the reaction is not likely to be pseudo first order reaction even when R^2 values are high. The plots of log (q_e-q_t) versus t gave straight lines with high correlation coefficients ranging from 0.981 to 0.988. Even though the correlation coefficients are relatively high, the calculated q_e values were not equal to the experimental q_e. Therefore the adsorption of MB dye onto ACBTL

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does not follow the pseudo first order reaction.

The pseudo second-order kinetic rate equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (11)$$

The plots of t/q_t versus t were straight lines for all the initial concentrations studied,

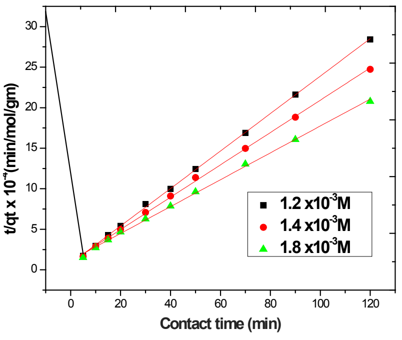

Fig.3. Pseudo second order kinetic plot for the adsorption of MB on ACBTL

Suggesting that the adsorption process followed the pseudo second order kinetic model. The correlation coefficients are nearly equal to unity (R^2 = 0.999) and the calculated q_e values agreed very well with the experimental q_e values. Therefore, the adsorption of MB dye onto ACBTL can be well described by the pseudo second order model and it is an indication of chemisorption process.

Thermodynamic parameters

Thermodynamic parameters such as standard free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were estimated to evaluate the feasibility and the endothermic nature of the adsorption process. These values were calculated by using the following relationships:

$$\Delta G^0 = -RT\, lnK_L \qquad (12)$$

The enthalpy ΔH^0 and entropy ΔS^0 values were determined from the following equations:

$$\Delta H^0 = -R \frac{T_2 T_1}{T_2 - T_1} ln \frac{K_{L1}}{K_{L2}} \qquad (13)$$

where K_L, K_{L1} and K_{L2} were the Langmuir constants at different temperatures, R was the universal gas constant (8.314 J/mol/K)

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \qquad (14)$$

The negative values of ΔG^0 (-29.13 to -31.05 KJ/mol) in the temperature range of 305–325 K, indicated that the process was of spontaneous in nature. The positive values of ΔH^0 (31.26 KJ/mol) and ΔS^0 (102.58) indicated that the adsorption process was of endothermic in nature and the adsorption mechanism was an entropy controlled process.

Conclusion

The percentage adsorption of MB dye was found to vary with contact time, adsorbent dose, and concentration of the dye, temperature and pH. The isothermal adsorption data fitted best to the Langmuir model confirming the monolayer coverage of MB onto ACBTL with a monolayer adsorption capacity. The adsorption kinetics of MB was found to follow the pseudo second order reaction model. The negative values of ΔG° indicate that the process is spontaneous. The positive values of ΔH^0 and ΔS^0 indicate that the adsorption process is of endothermic nature.

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