Adsorption Of Methylene Blue From Waste Water Using Activated Pongamia Pinnata POD Power: An Environmental Friendly Bioadsorbent

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Abstract:

Adsorption has been one of the most promising techniques for the removal of organic and inorganic contaminants. The present paper has been aimed to investigate and develop cheap adsorption methods for colour removal from wastewater using activated pongamia pinnata pod powder (APPPP) as an adsorbent, extracted from ground shells of pongammia pinnata pods (karanj tree). Systematic batch mode adsorption studies of Methylene Blue (MB) on activated pongamia pinnata pod powder (APPPP) were carried out as a function of process of parameters includes initial MB concentration, dose of adsorbent, pH, contact time, temperature and particle size. Kinetic parameters were performed at 30æ%C, using aqueous solutions of MB with 5×10^{-5} M concentration and 0.4g/L adsorbent dose. The adsorption behaviour of MB was studied using Freundlich, Langmuir, Tempkin and Dubinin-Radushkevich adsorption isotherm models. In thermodynamic analysis, free energy of adsorption ("Gæ%), enthalpy ("Hæ%), and entropy ("Sæ%) changes were calculated to predict the nature of adsorption. The kinetic measurements and estimated values for "Gæ% (- 2.224×10^{3}) over APPPP at 203K (30æ%C), suggest a spontaneous process involving pseudo first order kinetics controlled by particle diffusion process. Intra particle diffusion model showed boundary layer effect and larger intercepts indicates contribution of surface adsorption was high in rate controlling step. The proposed method of removal of MB from waste water holds a sustainable approach towards removal of toxic contaminants from water resources using an eco-friendly bioadsorbent in environment benign manner minimizing the use of harmful chemical adsorbents.

Keywords: Adsorption, Methylene Blue (MB), Activated pongammia pinnata pod powder (APPPP), Isotherms, Kinetics.

1. Introduction

Water pollution is one of the most important environmental problems facing by all over the world [1]. Pollution of the aquatic environment is mainly caused by the chemical compounds which are largely used worldwide. Among that "Dyes" are considered as an important chemical compound which is responsible for the water pollution. More than 10,000 dyes [2,3] have been widely used in different types of industries such as textile, rubber, paper, leather, plastics, pharmaceutical, cosmetic and food industries. Synthetic dyes are of great environmental concern because these are extensively used and their removal rate is very low during aerobic waste treatment. Methylene blue (MB) is a cationic dye having a variety of applications in medical science, chemistry, biology and dyeing industries. Its elongated exposure can cause some toxic effects such as vomiting, nausea, anemia and hypertension etc. Therefore there is a need to remove these types of contaminants from aquatic environment. The removal of dyes and other contaminants in an economic way has been become an important matter for researchers and

environmentalists. Different type of techniques has been reported by many researchers for this purpose [4,5]. Among that adsorption process is considered as a conventional method for treating dye-containing wastewater onto various type of adsorbing materials. This process is noted to be superior to other removal techniques because it is a simple, efficient and economically sustainable method. The aim of present investigation is to study the feasibility of the adsorbent prepared from Pongamia pinnata seed shell onto the removal of Methylene blue from the aqueous solution. Adsorption isotherm models, Kinetics study, diffusion models, and thermodynamic studies have also been investigated to evaluate experimental data.

2. Experimental

2.1 Development of adsorbent

Pods of Pongammia Pinnata were collected from the locally available pongammia pinnata trees in Madhav Institute of Technology and Science (MITS), Gwalior, India. The pod's shells were crushed, and sieved to obtain mesh sizes. Thereafter, Sieved biomass was treated with hydrogen peroxide (30%) at 60°C for 24 h to oxidize the adhering organic impurities and washed repeatedly with doubly distilled water. The resulting material was heated in an oven at 150°C and after that soaked in 1% NaHCO3 solution overnight to remove any acid. The obtained material was washed with distilled water and dried in oven at 150°C. The material was grounded and sieved to desired particle sizes.

2.2 Reagents and chemicals

Methylene blue (MB) was obtained from E. Merck, India and was used without further purification. A stock solution of MB dye of concentration 1mg/mL was prepared by dissolving 1g of MB dye in 1L of double distilled water. Experimental working solutions of desired concentration were obtained by appropriate dilution of the stock solution in double distilled water. The concentrations of MB in the solutions before and after equilibrium were determined by employing a systonic model S-922 spectrophotometer over the wavelength range of 340 to 960 nm. Sartorius CP224S analytical balance (Gottingen, Germany) and ultra sonic cleaner (Frontline FS 4, Mumbai, India) were used during the study. Measurements of pH of the solutions were carried out on a digital pH meter (DB 1011 India).

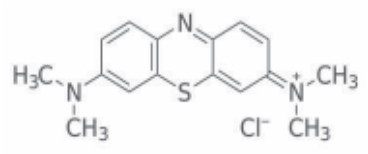


Figure 1: Structure of Methylene Blue

2.3 Adsorption and kinetic studies

Adsorption experiments were carried out in batch technique at room temperature (298±30K). In the batch method, a fixed amount of the adsorbent (0.4 g/L) was added to 30 ml of dye solution of different initial concentrations in range of 1×10^{-5} to 8×10^{-5} M in 100 ml conical flasks. The conical flasks were stirred continuously at constant temperatures. After equilibrium time (determined initially) the samples were withdrawn and the supernatant was filtered through Whatmann filter paper (No. 1) and the amount of MB adsorbed was monitored spectrophotometrically by measuring the absorbance at ëmax 650 nm. At time t =0 and equilibrium, the concentration retained in the adsorbent phase (qe, mg g$^{"1}$) was calculated by the following equation:

$$qe=(C0-Ce)W/V \quad (1)$$

Where C0 and Ce are the initial and equilibrium adsorbate concentrations (mg L$^{"1}$), respectively. V is the volume of solution (L) and W is the mass of adsorbent (g).

3. Results and Discussion

3.1 Adsorbent Characterization

The Developed APPPP was analyzed by Scanning electron microscope (SEM) and FTIR (Fourier transform infrared). The morphological structure of biosorbent activated pongamia pinnata pod powder (APPPP) was observed under SEM (JSM-6390, JEOL/EO) and the micrographs were recorded at acceleration voltage of 5–15 V. The result as shown in Fig. 2 (a) indicates that

the APPPP has small cavities on the surface or quite rough surface. These pores were 8 to 10 micro meters in diameter so these are classified as macropores. It has a porous texture that may provide bulky surface for the adsorption of the dye molecules. For FTIR analysis measurements were carried out by means of Varian Resolution Pro- FTIR spectrophotometer using KBr pelleting method. The FTIR spectra are shown in Fig. 2 (b). In Infrared spectra of APPPP shows strong peak absorbance at 3427 cm^{-1} and 3635 cm^{-1} due to presence of O-H stretching. Strong peak absorbance at 1658 cm^{-1} also indicated presence of carbonyl group. C-H stretching observed at 2921 cm^{-1} and 2851 cm^{-1}.

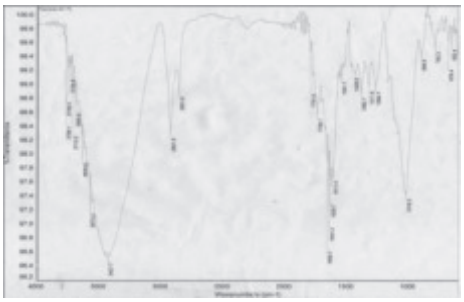


Figure 2 (a): Scanning Electron Microscope of APPPP

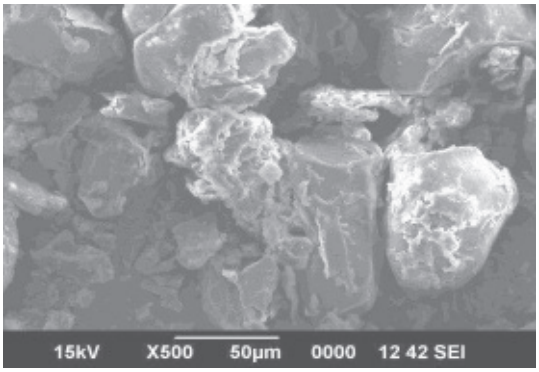


Figure 2 (b): FTIR analysis of APPPP

3.2 Optimization of the parameters affects the MB adsorption onto APPPP

Optimization of process has to be carried out to determine the optimal conditions showing maximum response. In the optimization of each parameter, a minimum and a maximum range was selected as the criteria for determining the optimum conditions showing the maximum response Table 1.

Table 1: Adsorption operational parameters with their range and optimum values

S.No.	Parameter	Range	Other optimum conditions	Optimumvalue
1.	Effect of dose of APPPP	0.1 g/L to 0.7 g/L	Initial MB concentration: 5×10^{-5} MInitial pH: 7.3 Temperature: 30^{O}C Contact time: 10 min	0.4 g/L
2.	Effect of MB concentration	1×10^{-5} to 8×10^{-5} M	Optimum dose of APPPP: 0.4 g/LInitial pH: 7.3 Temperature: 30^{O}C Contact time: 10 min	5×10^{-5} M
3.	Effect of temperature	30^{O}C to 50^{O}C	Initial MB concentration: 5×10^{-5} MOptimum dose of APPPP: 0.4 g/L Initial pH: 7.3 Contact time: 9 min	30^{O}C
4.	Effect of pH	6.5 to 12.5	Initial MB concentration: 5×10^{-5} MOptimum dose of APPPP: 0.4 g/L Temperature: 30^{O}C Contact time: 10 min	7.3
5.	Effect of contact time	2 to 14 minutes	Optimum dose of APPPP: 0.4 g/L Initial MB concentration: 5×10^{-5} M Temperature: 30^{O}CInitial pH: 7.3	10 minutes

4. Adsorption Isotherms

In the present study Langmuir, Freundlich, Tempkin and Dubinin Radushkevich (D-R) isotherms have been used to analyse the experimental data. The Langmuir isotherm is derived on the assumption of monolayer coverage of adsorbate over a homogenous adsorbent surface [6]. The linear form of the Langmuir isotherm is given as equation 2.

$$1/qe = 1/Q^0 + 1/bQ^0\ Ce \quad (2)$$

Where q_e is the amount adsorbed (mol/g), C_e is the equilibrium concentration of the adsorbate (mol/L), and Q^o and b is Langmuir constants related to maximum adsorption capacity and energy of adsorption relatively. Langmuir constants are calculated and values of these constants at different temperatures are given in Table 2.

Freundich isotherm is an empirical equation which is expressed [7] in linear form as:

$$\log qe = \log kf + 1/n \log Ce \quad (3)$$

Where, qe is the amount adsorbed (mol/g), C_e is the equilibrium concentration of the adsorbate mol/L), and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively (Table 2).

The Tempkin isotherm [8] has commonly been applied in the following form:

$$qe = RT/bT + \ln (ACe) \quad (4)$$

where RT/bT = B (J/mol), which is the Tempkin constant related to heat of sorption whereas A (L/g) is the equilibrium binding constant corresponding to the maximum binding energy. R (8.314 J/mol K) is the universal gas constant and

Table 2: Langmuir, Freundlich, Tempkin and Dubinin Radushkevich (D-R) adsorptio isotherms for MB over APPPP

Langmuir constants for MB over APPPP at different temperatures

Temp.(°C)	b	Q^o	bQ^o	R^2	%RSD#
30	1.277	1.839	2.418	0.995	0.986
40	2.832	1.314	3.721	0.902	0.912
50	3.597	1.788	6.434	0.965	0.908

Freundlich constants for MB over APPPP at different temperatures

Temp.(°C)	K_f	n	R^2	%RSD#
30	1.064	1.131	0.913	0.963
40	1.196	2.267	0.890	0.912
50	1.337	4.23	0.953	0.898

Tempkin constants for MB over APPPP at 30°C temperature

Temp.(°C)	B ($Jmol^{-1}$)	A (Lg^{-1})	B	R^2
30	0.085	2.626	1.2×10^3	0.980

Dubinin Radushkevich (D-R) constants for MB over APPPP at different temperatures

Temp.(°C)	B_D	E	q_D	R^2
30	7.057	0.094	40.68	0.977
40	4.478	0.157	23.74	0.967
50	3.650	0.193	19.43	0.858

T (K) is the absolute solution temperature (Table 2).

The D-R isotherm [9] was applied to estimate the porosity apparent free energy and the characteristics of adsorption (Table 2). The linear form can be represented as:

$$\ln qe = \ln qD - B\text{å}^2 \quad (5)$$

where, B is a constant related to the mean free energy of adsorption ($mol^2(kJ^2)^{-1}$), qD is the theoretical saturation capacity (mg/g), å is the polyani potential, and calculated as follows:

$$\text{å} = RT \ln (1+1/Ce) \quad (6)$$

5. Thermodynamic Parameters

Thermodynamic parameters obtained for adsorption systems were also calculated from Langmuir adsorption isotherms at different temperatures. Negative value of $\ddot{A}G^o$ indicates feasible and spontaneous nature of the ongoing adsorption process. Endothermic nature of the process was once again confirmed by the positive values of $\ddot{A}H^o$ (Table 3).

6. Adsorption Kinetic Studies

The pseudo-first-order kinetic model has been widely used to predict sorption kinetics. The

Table 3: Thermodynamic parameters of MB over APPPP

Adsorbent	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (JK^{-1} mol^{-1})
	30 °C	40 °C	50 °C	30 °C	30 °C
APPPP	-2.224× 10^3	-3.419× 10^3	-4.999× 10^3	3.469× 10^3	27.351

model given by Langergren and Svenska [10] is defined as:

$$\log (qe - qt) = (\log qe - kad \times t) /2.303 \quad (7)$$

Where, qe and qt (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (h), respectively and kad (1/h) is the adsorption rate constant. The values of kad and correlation coefficient, R^2 obtained from the plots for adsorption of MB on the APPPP are given in Table 4.

Table 4: Rate constants kad for MB over APPPP

Temp.(^{o}C)	kad	R^2
30	0.117	0.996
40	0.133	0.982
50	0.147	0.955

7. Conclusion

It is concluded from the results of the present study that the adsorption process is a very effective process for the decolorization of MB containing wastewater. pH plays a significant role in the process of methylene blue adsorption onto the APPPP. The equilibrium adsorption is practically achieved through a time of 10 min. Results show that Freundlich and Langmuir isotherms fitted well. Thermodynamic parameters such as standard enthalpy (ÄH°), standard entropy (ÄS°), and standard free energy (ÄG°) were determined. The negative value of ÄG° is -2.224×10^3 at 303 K (30°C), indicating towards a spontaneous process.

8. References

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