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Removal of organic pollutant from wastewater using Nano Carbon synthesized from wood waste biomaterial as an adsorbent

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ABSTRACT

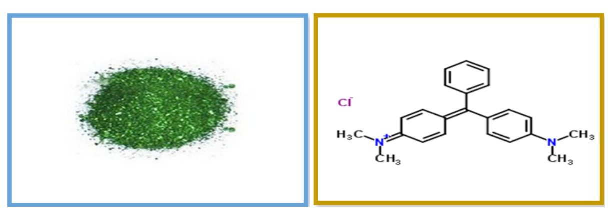
With the help of eco-friendly waste materials like Manila tamarind tree bark and shells (Pithecellobium Dulce), the malachite green dye has been removed from wastewater in this investigation. The maximum adsorption of dye was achieved at pH 6.7 in the research work. The removal percentage of Malachite green dye was found to be dependent on the initial concentration of dye solution, and the maximum removal percentage was found to be 85% at 25 mg/L of Malachite green dye. The experimental methods were carried out using the batch adsorption technique. The pH parameter, temperature, adsorption dose, and contact time for the removal of Malachite green dye were studied. The Freundlich, Langmuir, and Temkin methods were used to calculate equilibrium adsorption data. The thermodynamic parameters such as a change in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were determined. The negative values of ΔG^0 indicated that the process of dye removal was spontaneous at all values of temperature. Further, the values of ΔH^0 indicated the endothermic nature of the process of dye removal from the wastewater.

Key words : *Manila tamarind, Malachite green dye, pH parameter, Thermodynamic parameters, and Adsorption isotherms*

Introduction

Many types of synthetic dyes are widely used in various textile industries, paper, leather, rubber, food, and plastic industry in order to give desired colours to the cloth materials. Nearly 10,000 types of dyes have been employed commercially. About 10-15% of dyes are present in wastewater when dying the process, and hence the toxic dyes may cause severe health issues for human beings when they enter the human body through the food chain (Hameed and El-Khairy, 2008; Mall *et al.*, 2005; Kumar *et al.*, 2005).

Malachite green is an organic compound. It can be used in the dye industry. It is traditionally used as dyes in the materials of silk, plastic, leather, and paper. But it is more toxic it can enter into the environment, and it may cause an undesirable effect on living things.



Structure of Malachite Green

The toxic dyes should be treated before being discharged into nearby water bodies with that in mind. We have chosen the bio-waste material as an adsorbent for the removal of organic pollutants like malachite green using the Batch adsorption technique with effective parameters like carbon dose, contact time, and thermodynamic studies (Bayramoglu and Arica, 2013; Zhang *et al.,* 2008). Recently, the adsorption technique is extensively in the treatment of wastewater. Because this technique has been found to be low cost, reusable, eco-friendly, and highly efficient than reverse osmosis, coagulation, Electrodialysis, and chemical oxidation process.

In this research investigation, Nano-carbon was used as an adsorbent for the removal of organic pollutants like Malachite green from wastewater. Nano-carbon is prepared from Manila tamarind tree bark. The botanical name of *Manila tamarind* is *Pithecellobium dulce*, which belongs to the *Fabaceae* family. It is popularly known as kodukkapuli in Tamil and is also called monkeypod, or a black bead in English. It is located in agricultural areas along ridges and wells. Manila tamarind has a sweet and sour taste. The pods of kodukkapuli are not sold in the market places but are sold by street vendors going around the streets selling them to school students (Figure 1).

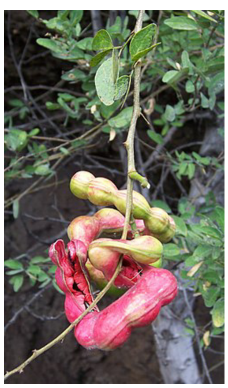


Fig. 1. Manila Tamarind pods

In this research investigation work, Nanocarbon was used as an adsorbent for the removal of organic pollutants like Malachite green from wastewater. Nanocarbon is prepared from Manila tamarind tree barks and shells. The botanical name of *Manila tamarind* is *Pithecellobium dulce*, which belongs to the *Fabaceae* family. It is popularly known as kodukkapuli in Tamil and is also called monkeypod, a black bead in English. It is located in agricultural areas along ridges and wells. Manila tamarind is a sweet and sour taste. The pods of kodukkapuli are not sold in market places but it is sold by street vendors going around the street places and tasted by school students.

Methodology

Preparation of Adsorbate for the removal of Environmental Pollutants

The wastewater was collected from the nearby Plastic industry of Pondicherry, India.

Reagents and Instruments for the removal of organic Pollutants

The sodium hydroxide and Hydrochloric acid solution will be used in this investigation. The UV- Visible double beam spectrophotometer and pH measurements like a digital pH meter will be employed in adsorption studies.

Preparation of adsorbent

The manila tamarind bark and shells (Figure 1) were collected nearby the village of Villupuram (District), Tamilnadu, India. The purified tree bark and shell were dried well and charred with a calculated amount of concentrated Sulphuric acid, which was maintained at 260 °C for 8 hours. Thereafter, the resultant activated carbon was thoroughly washed with the excess quantity of distilled water, and it was again dried at 150 °C for one hour. It was soaked in 5 % sodium bicarbonate and allowed to stand for a day to remove any residual acid (Ghosh *et al.,* 2015). The carbonized fabric was heated at 1100 °C for six hours in a muffle furnace. Finally, the dried powder has been sieved with the help of a mesh to get Pithecellobium Dulce Activated Nano Carbon [PDANC], which is shown in Figure 2.

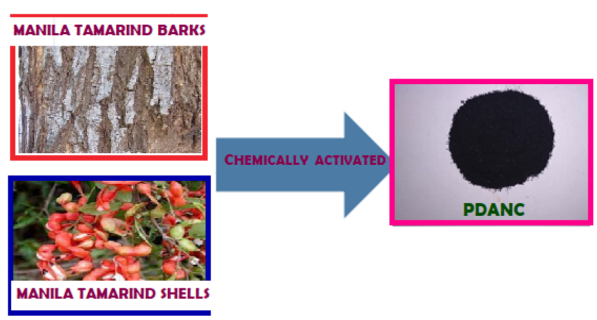


Fig. 2. Nano Carbon obtained from Manila tamarind barks and shells

Batch Adsorption Technique

The batch adsorption technique will be experimentally done by using 50 ml wastewater of different initial concentrations in Erlenmeyer 250 ml flasks. The tests should be determined at a different temperature between 30 to 60 °C. The pH for the removal of pollutants like malachite green onto Nano-carbon was studied. This method will be performed in a mechanical shaker with a period of time intervals. The pH values of the initial wastewater solution (50 mgl^{-1}) will be adjusted using 0.1M HCl or NaOH solution. The adsorbent should be mixed with wastewater and agitated for the sample until to obtain equilibrium. After the agitation wastewater will withdraw at different time intervals in the ranges between 10 to 65 minutes and centrifuged at 120 rpm for 10 minutes. The removal percentage of environmental pollutants will be determined by the following equation 1 & 2 [10].

$$Percentage\ removal = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \ldots\ldots 1$$

$$Q = \frac{C_i - C_t}{m} \times V \ldots\ldots 2$$

Where C_i and C_t are the initial and liquid-phase concentrations of pollutants in solution at a time 't' ($mg\ l^{-1}$) and Q is the number of pollutants adsorbed on the adsorbent at any time (mgg^{-1}), m(g) is the mass of the adsorbent sample used and V is the volume of the pollutants in solution (L).

Results and Discussion

Contact time for the adsorption of malachite Green

The effect of contact time for Malachite green adsorption onto Nano-carbon was studied at different time intervals. The adsorption data obtained for the removal of malachite green dye were observed by a decrease in the concentration of adsorbate solution within the adsorption medium and contact time. The time is necessary to attain the equilibrium for the removal of pollutants at different concentrations. The removal percentage of malachite green dye increased rapidly upto reach at 50 minutes due increase in surface area in the PDANC adsorbent (Fig. 3).

Adsorbent dose for the adsorption of Malachite Green

The effect of different adsorbent doses will be employed between the ranges of 5, 10, 15, 20, 25 and 30 mg. The results obtained from this study are shown in Figure 3. The amount of malachite green dye adsorbed per gram reduced with an increase in the dosage of PDANC. This reveals that the direct and equilibrium capacities of Rh-B are functions of the activated adsorbent dosage, which is shown in Figure 4.

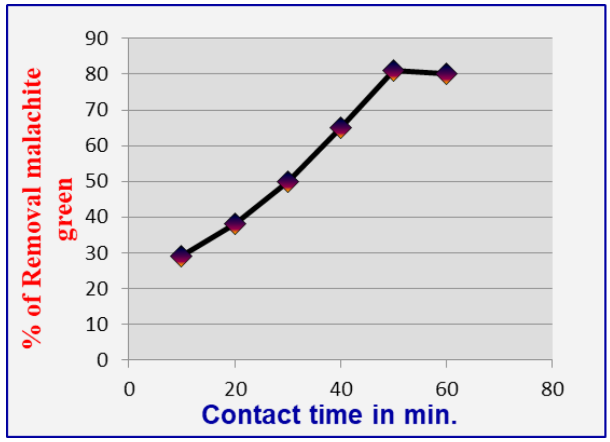


Fig. 3. Contact time for the adsorption of Malachite Green

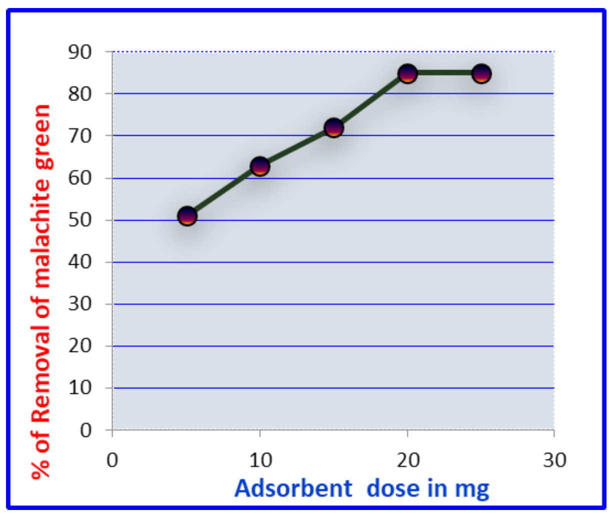


Fig. 4. Adsorbent dose for the adsorption of Malachite Green

Isotherm Models for Adsorption Studies

Freundlich adsorption isotherm for the removal of MG dye

The assumption is that the adsorption sites are dispersed exponentially with respect to the heat of adsorption. The Freundlich adsorption isotherm is expressed by the following equation.

$$qe = K_F C_e^{1/nF} \quad ...\ 3$$

It can be linearized in the following equations:

$$\ln q_e = \ln K_F + \frac{1}{nF} \ln C_e \quad ..\ (4)$$

In this equation, q_e is the quantity of dye adsorbed at equilibrium (mg/g) and C_e is the concentration of adsorbate in the liquid phase at equilibrium (ppm). K_F (L/g) and 1/nf are the Freundlich constant related to adsorption capacity and adsorption intensity, respectively. The Freundlich constants K_F-and 1/nF (Figure 5) will determine from the slope and intercept of the $\ln q_e$ Vs plot (ln Ce) (Anbalagan and Juliet, 2004). The values are given in the following Table 2.

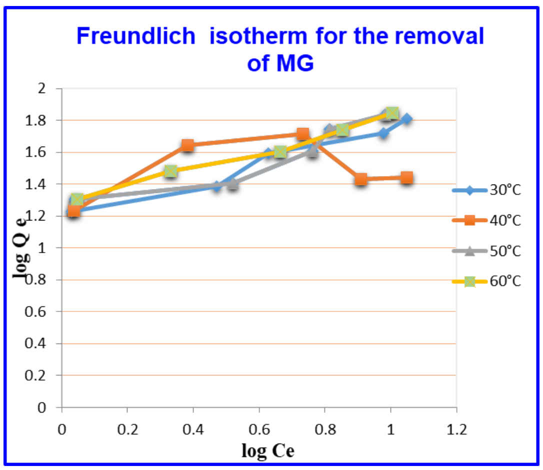


Fig. 5. Freundlich adsorption isotherm for the removal of MG dye

Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the postulation of the adsorption spots that have an equal attraction for the adsorbate (Rajachandrasekar *et al.*, 2006). The Langmuir adsorption isotherm for a linear form is given by the following expression.

$$\frac{C_e}{q_e} = \frac{1}{q_m KL} + \frac{C_e}{q_m} \quad ....5$$

In this expression, q_e is the quantity of pollutant adsorbed at equilibrium (mg/g), C_e is the concentration of pollutants in the wastewater at equilibrium (ppm), q_m is the maximum pollutant uptake (mg/g), and K_L is the Langmuir constants associated to adsorption capacity and the energy of adsorption (mg/g). The values of C_e/q_e versus C_e (linear plot) will be employed in the determination of the value like q_m and K_L. The value of K_L decreased with an increase in temperature. A high value of K_L specifies a high adsorption affinity (Figure 6). The values are listed in the following Table 2. The Langmuir isotherm in terms of a dimensionless constant separation factor (RL) is expressed by the following equation.

$$R_L = \frac{1}{1 + KLC_0} \quad ...\ ...\ ...\ ...\ ...\ ...\ 6$$

In equation 6, C_0 is the initial pollutant concentration (ppm)

The values of dimensionless separation factor (R_L) for pollutant removal will calculate at different concentrations and temperature (Santhi *et al.*, 2010).

Thermodynamically Parameters

The thermodynamic parameters such as free energy

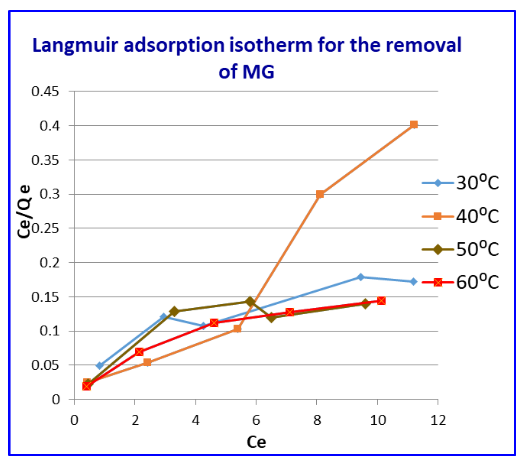


Fig. 6. Langmuir adsorption isotherm for malachite green

Table 1. Equilibrium Parameters for the Removal Organic Pollutant (Malachite Green Dye)

MG°	C_e (mg/l)				Q_e (mg/g)				Dye removed (%)			
	Temperature											
	30	40	50	60	30	40	50	60	30	40	50	60
10	1.081	1.000	1.100	1.118	17.12	17.22	20.19	20.11	89.32	98.23	96.89	99.25
20	2.954	2.416	3.309	2.145	24.48	4413	25.58	30.52	86.23	89.56	90.45	92.35
30	4.251	5.401	5.801	4.621	39.52	52.22	40.59	40.22	83.11	85.56	87.23	89.27
40	9.451	8.114	6.517	7.118	52.84	26.97	54.46	55.46	80.35	80.26	83.56	85.26

Table 2. Adsorption Isotherm Models for the Removal Organic Pollutant (Malachite Green Dye)

MG	T	Langmuir			Freundlich			Dimensionless separation factor				
		r2	Qm	b	r2	Kf	n	10	20	30	40	50
	30	0.09824	101.10	0.8095	0.9023	3.702	1.778	0.321	0.199	0.152	0.109	0.089
	40	0.9521	99.03	0.3361	0.9107	3.865	2.041	0.224	0.172	0.122	0.096	0.081
	50	0.9751	95.16	0.3826	0.9139	4.238	2.235	0.330	0.149	0.101	0.080	0.065
	60	0.9524	91.40	0.4054	0.9127	4.326	2.602	0.215	0.125	0.081	0.074	0.0152

change (ΔG), enthalpy changes (ΔH), and entropy change (ΔS) were determined from the following equations.

$K_c = C_{Ae}/C_e$ …………….. (7)

$\Delta G^0 = -RT \ln K_c$ …..……. (8)

$\text{Log } K_c = \Delta S^0/2.303R - \Delta H^0/2.303RT$ ………….. (9)

In these above equations, C_e is the equilibrium concentration in solution in mg/L and C_{Ae} is the equilibrium concentration on the sorbent in mg/L and K_c is the equilibrium constant. The values of ΔH° and ΔS° were obtained from the slope and intercept for the plot of log K_c against 1/T. +the values are given in the following Table 3. The negative values of ΔG at various temperature were obliviously indicate that adsorption process was in spontaneous nature. The positive values of ΔH and ΔS were clearly showed that adsorption was endothermic process.

Analytical evidence for the adsorption of Malachite Green dyes

Analytical techniques are essential for studying the adsorption of Malachite Green dyes. In this investigation, the adsorbent was analyzed by using a Fourier Transform Infrared spectrum, which is showed in Figure 7. Various adsorption peaks are displayed before the adsorption of malachite green onto PDANC (Chen *et al.*, 2019).

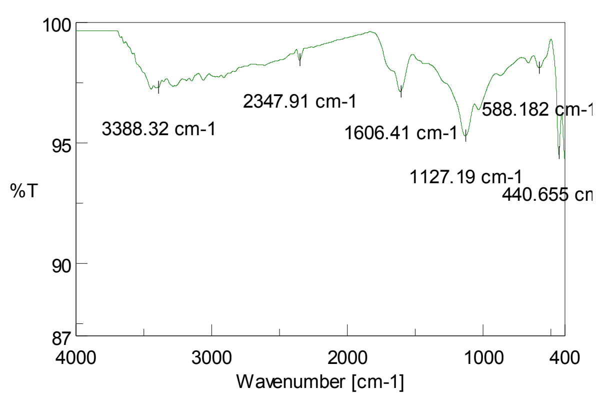


Fig. 7. FTIR Spectrum of Before adsorption of [PDANC]

Table 3. Thermodynamic Parameters for the Removal Organic Pollutant (Malachite Green Dye)

[MG]	ΔH°	ΔS°	G°			
			30°C	40°C	50°C	60°C
10	40.25	130.5	-6404.3	-6827.4	-7304.8	-8016.5
20	7.837	50.22	-5630.8	-6240.3	-6560.7	-7010.8
30	5.230	30.24	-4612.1	-5020.5	-5320.2	-6135.7
40	7.221	40.28	-3526.4	-2612.4	-4520.1	-5326.4

Conclusion

The experimental values were analyzed by using Langmuir and Freundlich adsorption isotherm models for the removal of organic contaminants such as malachite green from wastewater. The thermodynamic parameter values clearly indicate that the adsorbent employed has considerable potential for the adsorption of malachite green from wastewater based on the values of ΔG, ΔH, and ΔS. The adsorption characteristics have been analyzed by the use of Fourier transformer spectroscopy.

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