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Removal of Malachite Green from aqueous solution using low cost adsorbent

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A B S T R A C T

This study investigated the potential use of a low-cost Vitex negundo stem for removal of Malachite Green (MG) dye from an aqueous solution. Batch studies were performed to evaluate the influence of various experimental parameters like adsorbent dose, effect of pH, initial dye concentration at different temperature and different contact time.The experimental data were fitted into the pseudo-second order kinetic model. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherm models. The objective of the present work suggests the AAVNSC may be utilized as a low cost adsorbent for malachite green dye removal from aqueous solution.

Introduction

Generally, dyes are organic compounds used as colouring products in chemical, textile, paper, printing, leather, plastics and various food industries. Discharge of coloured wastewaters into natural water bodies is not desirable, as they are aesthetically displeasing and prevent reoxygenation in receiving waters by cutting off penetration of sunlight. The colour also upsets the biological activities in water bodies (Mittal and Venkobachar, 1989). In addition most of the dyes used as colouring materials are toxic to aquatic organisms (Gong *et al.*, 2005). Contamination of water bodies with dyeing industry effluents has caused great environmental problems. Malachite green is a common basic dyestuff of triphenyl methane series used for dyeing silk and wool. The need for the treatment of dye contaminated waste water passed out from the industry.This has initiated a search for effective and economic treatment techniques to offer significant reduction in cost than other such methods as electrolysis, membrane filtration, chemical coagulation, oxidation, etc.

Adsorption is one of the most effective and widely used techniques for the removal of dyes from aqueous solutions. In recent years several investigators have concentrated their work on low-cost and non-conventional adsorbent materials to achieve the economically feasible and effective treatment of wastewaters containing dyes.

The present study is undertaken to evaluate the efficiency of activated carbon prepared from Vitex negundo stem for the removal of Malachite Green (MG) from aqueous solutions.

Materials and methods

Materials

Vitex negundo stem was carbonized with concentrated sulphuric acid in the weight ratio of 1:1(W/V). The carbonization and activation was completed by heating for 5 hours in a muffle furnace at 400°C. The resulting carbon was washed with distilled water until a constant pH of the slurry was achieved. Then the carbon was dried for four hours at 100°C in a hot air oven.

The dried material was grinded to a fine powder and stored in vacuum desiccators. All Chemicals used were of high purity, commercially available AR grade. Stock solutions of 1000 mg / L of dyes were prepared using doubly distilled water.

Adsorption experiment

The adsorption experiments are carried out in a batch process at 30, 40, 50, and 60^{o}C. A known weight of adsorbent was added to 50mL of dye solutions with an initial concentration of 50–250mg/L. The contents were shaken thoroughly using a mechanical shaken rotating at 150rpm.intervals and the residual dye concentration was measured. The solution was then filtered at preset time.

Effect of adsorbent dosage

Various doses of the adsorbent were mixed with dye solution and the mixture was agitated in a mechanical shaker.

The adsorption capacities for different doses were determined at define time intervals by keeping all other factors constant.

Effect of initial concentration of dye

In order to determine the rate of adsorption, experiments were conducted with different initial concentration of dyes ranging from 50-250mg/L. All other factors were kept constant.

Effect of contact time

The Effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by keeping initial concentration, dosage, pH and temperature constant.

Effect of pH

Adsorption experiments were carried out at pH 2-10.

The acidic and alkaline pH of the media was maintained by adding the required amount of dilute HCL and NaOH.

All other factors were kept constant while carrying out the experiment. The pH of the sample was determined using a portable pH meter.

Effect of temperature

The adsorption experiments are carried out at four different temperatures viz., 30, 40, 50, and 60^{o}C in a thermostat attached with a shaker.

Results and Discussions

Effect of contact time and initial dye concentration

The experimental results of adsorptions of Malachite green (MG) dye on the activated carbon at various concentrations (50-250mg/L) with contact time are shown in figure 1. The equilibrium data were collected in table 1, reveals that, percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in dye concentration. This means that the adsorption is highly dependent on initial concentration of the dye. Because, at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low, subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration (Suguna Devi *et al.,* 2002). Equilibrium was established at 50 minutes for all concentrations. Figure 1 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on the carbon surface (Senthikumar *et al.*, 2005).

Effect of adsorbent dose

The effect of AAVNSC dose on MG adsorption was studied with varying amounts of the adsorbent dose ranging from 10-250mg/50ml for MG concentration of 50 mg/L. The percentage removal of MG increased with increasing in adsorbent dose, this was due to the increase in the surface area and availability of more adsorption sites. The 60% to 95 % of MG dye removal were takes place in the adsorbent range of 25-250 mg/50ml. The results are shown in figure 2. Hence the entire studies are carried out with the adsorbent dose of 25mg/50 ml of the adsorbate solution (Vadivelan and Vasanthkumar, 2003).

Effect of pH

The influence of pH on the MG dye adsorption onto AAVNSC was studied while the MG dye concentration, contact time and amount of adsorbent were fixed. The variation of MG dye adsorption on AAVNSC over a pH range of 2.0-10.0 was shown in figure 3. The result reveals that the adsorption of the MG dye increases with an increase in pH of the solution from 2.0 to 6.5 and then rapidly decreased. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is in turn influenced by the solution pH. The pHzpc value for AAVNSC was 6.2. At pH values below pHzpc, the adsorbent had net positive charge and would therefore, be prone to electro statically repel cations (Stephen Inbaraj and Sulochana, 2002). MG is a cationic basic dye as denoted by the presence of the positive nitrogen ion in its structure. On dissolution, the oxalate ion enters the aqueous solution ensuring that the MG dye has an overall positive charge. The positive charge on the cationic dye should ensure that it is attracted by an anionic adsorbent**.**

Adsorption isotherm

A study of adsorption isotherm is basic requirement for the design adsorption systems. The isotherm indicates the relation between the mass of dye adsorbed at constant temperature per unit mass of the adsorbent and liquid base concentration of dye. It can be generally expressed standard isotherms like Langmuir and (Langmuir, 1918) and Freundlich (Freundlich, 1906).

The linear plot of log C_e/q_e versus C_e, suggested that the present system follows the Langmuir isotherm. The calculated adsorption isotherm parameters were given in table 2. From these results indicate that the adsorption capacity (Q_m) and adsorption intensities linearly increased with increasing temperature. The values of (Q_m) concludes that the maximum adsorption corresponds to a saturated monolayer of dyes molecules on the adsorbent surface with almost constant energy. Furthermore, it confirms the endothermic nature of the adsorption process involved in the system. In order to confirm the favorability of the adsorption process, the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L). The R_L values calculated at different temperatures were given in table.3. From the results of R_L value confirm the favorable adsorption of this model (Yupeng Guo and Jingzhu Zhao, 2005).

The Freundlich equation was also applied to the adsorption of MG dye onto AAVNSC. Linear plots of log Q_e versus log C_e shows that the adsorption obeys Freundlich Isotherm. The Freundlich constants related to adsorption capacity (K_F) and intensity of the reaction (n) were given in table.2. The K_F and n values increase with increase in temperature which indicates slight possibility of chemisorption through percolation. Values of n>1 indicates that adsorption is much more favourable.

Adsorption kinetics

The kinetics of sorption describes the solute uptake rate, which in turn governs residence time of sorption reaction. The pseudo-second–order, Elovich and intra-particle diffusion model were applied for the mechanism of MG onto AAVNSC. The kinetic parameter values of these models have been given in table.4. From the kinetic data, the pseudo- second –order rate constant decreased with increase in the initial dye concentration. The equilibrium sorption capacity (q_e) and the initial sorption rate increased with increasing the initial dye concentration. The correlation coefficient (γ) value is greater than 0.9900. From the results it can be suggested that the adsorption of MG on AAVNSC system follows the pseudo- second-order kinetics.

The same experimental data were used for the Elovich model, the initial adsorption rate (α), desorption constant (β) and the correlation coefficient (γ) were calculated. From the Elovich model shows that the initial adsorption (α) increased with temperature similar to that of initial adsorption rate (h) in the pseudo second order kinetic models. The correlation coefficient (γ) value is greater than 0.9900. The initial adsorption rate constant (α) value was high at lower dye concentration. The desorption constant (β) decreases with an increase in the initial dye concentration from 50 to 250 mg/L.

The data for the adsorption of MG dye onto AAVNSC was tested to the intra-particle diffusion model, and the results were presented in table 4.6.4. The intercept C value increased with increasing dye concentration which indicates an increase in the thickness of the boundary layer. The lines were not passing through the origin, therefore some other adsorption process affect the intra-particle diffusion. The intercept value indicates the boundary layer effect while the high correlation coefficient (γ) value indicates intra-particle diffusion (Weber, 1967). All the correlation coefficient (γ) values were higher than 0.9900. So the intra-particle diffusion takes place along with the boundary layer effect.

Table.1 Equilibrium parameters for adsorption of MG dye onto AAVNSC adsorbent

MG_0	Ce (Mg / L)				Qe (Mg / g)				Removed (%)			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
50	1.23	1.26	1.43	1.09	44.30	47.07	47.92	47.81	93.28	94.37	93.65	94.18
100	3.08	3.84	3.11	3.02	88.23	90.00	93.26	93.00	86.03	94.30	92.66	92.98
150	11.23	11.25	10.52	9.04	124.7	121.18	124.90	130.04	83.38	86.18	86.65	87.89
200	25.26	22.06	19.01	19.22	147.4	153.46	179.98	160.75	71.23	66.73	89.09	81.17
250	39.27	30.76	22.26	31.26	133.2	144.06	205.23	178.47	64.51	68.70	82.48	71.08

Table.2 Langmuir and freundlich isotherm parameter for adsorption of MG dye onto AAVNSC

TEMP. (°C)	LANGUMUIR PARAMETERS		FRUENDLICH PARAMETERS	
	Q_m	b	K_f	n
30°	168.82	0.19	4.10	2.52
40°	181.88	0.22	4.30	2.12
50°	228.85	0.18	5.32	2.18
60°	221.08	0.24	5.48	2.45

Table.3 Dimensionless seperation factor (RL) for adsorption of MG dye onto AAVNSC

(C_0)	TEMPERATURE °C			
	30°C	40°C	50°C	60°C
50	0.13	0.14	0.17	0.13
100	0.08	0.13	0.14	0.09
150	0.06	0.09	0.08	0.07
200	0.03	0.04	0.05	0.04
250	0.02	0.03	0.04	0.02

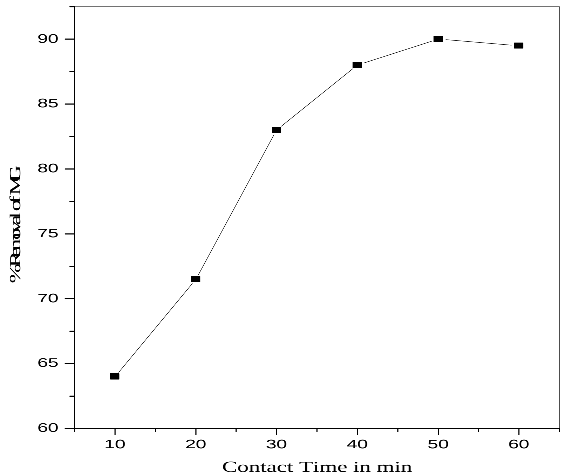


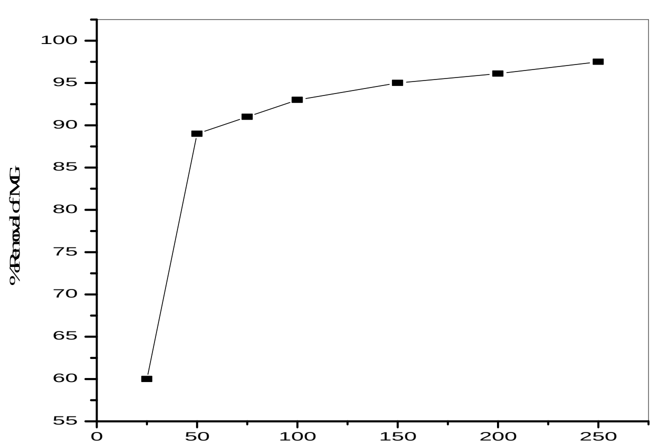
Fig:1- Effect of Contact Time on the Removal of MG Dye
[MG]=50 mg/L;Temprature 30°C;Adsorbent dose=25mg/50ml

Table.4 The kinetic parameters for the adsorption of MG dye onto AAVNSC

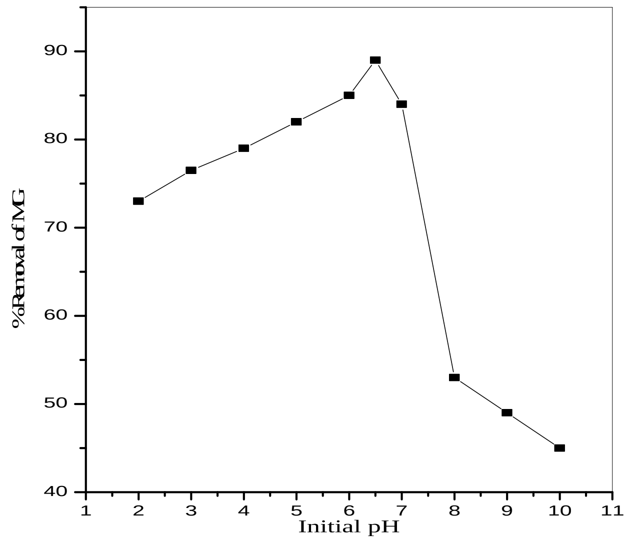
C_0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
50	**30**	48.90	23×10^{-3}	0.994	7.59	55.10	0.1339	0.998	1.6249	0.992	0.1888
	40	46.72	19×10^{-3}	0.995	10.69	952.98	0.2114	0.991	1.7457	0.994	0.1144
	50	47.39	16×10^{-3}	0.997	10.52	1703.15	0.2241	0.993	1.7641	0.991	0.1057
	60	46.30	19×10^{-3}	0.999	10.01	713.15	0.2030	0.992	1.7403	0.992	0.1186
100	**30**	94.49	24×10^{-3}	0.998	16.18	199.04	0.0780	0.991	1.6513	0.991	0.1644
	40	92.32	20×10^{-3}	0.997	24.52	1797.23	0.1056	0.992	1.7403	0.992	0.1162
	50	97.90	18×10^{-3}	0.998	19.69	1120.61	0.0972	0.991	1.7378	0.991	0.1229
	60	97.15	16×10^{-3}	0.992	21.55	4137.60	0.1138	0.993	1.7704	0.993	0.1034
150	**30**	134.87	23×10^{-3}	0.994	23.70	759.65	0.0649	0.997	1.6724	0.991	0.1360
	40	139.42	23×10^{-3}	0.991	22.36	563.68	0.0605	0.994	1.6705	0.992	0.1427
	50	136.05	20×10^{-3}	0.992	28.77	1961.5	0.0716	0.994	1.7129	0.991	0.1193
	60	137.01	20×10^{-3}	0.991	30.46	2303.4	0.0721	0.995	1.7219	0.991	0.1172
200	**30**	158.46	23×10^{-3}	0.992	27.23	759.73	0.0541	0.997	1.6105	0.991	0.1395
	40	164.24	25×10^{-3}	0.991	27.42	478.14	0.0483	0.999	1.6033	0.992	0.1527
	50	166.11	11×10^{-3}	0.993	29.79	943.42	0.0526	0.998	1.6390	0.993	0.1361
	60	171.53	23×10^{-3}	0.991	30.70	836.48	0.0498	0.997	1.6469	0.992	0.1398
250	**30**	173.00	18×10^{-3}	0.992	39.92	5381.16	0.0613	0.998	1.6176	0.993	0.1081
	40	185.49	22×10^{-3}	0.994	32.47	1013.47	0.0470	0.999	1.5877	0.992	0.1366
	50	195.87	16×10^{-3}	0.991	30.53	515.61	0.0402	0.996	1.5754	0.998	0.1546
	60	201.29	23×10^{-3}	0.992	34.10	1003.97	0.0429	0.997	1.6185	0.995	0.1383

Table.5 Thermodynamic parameter for the adsorption of MG dye onto AAVNSC

C_0	ΔG°				ΔH°	ΔS°
	30° C	**40° C**	**50° C**	**60° C**		
50	-8212.00	-8363.64	-8349.44	-8300.5	9.08	63.37
100	-6234.41	-6703.03	-6132.00	-6423.48	17.15	81.40
105	-5129.30	-5124.78	-5879.06	-5229.47	7.39	40.04
200	-3463.30	-4567.02	-5768.43	-3888.23	15.20	65.03
250	-2638.01	-2328.32	-3980.44	-3199.06	17.89	64.32



Fig;2- Effect of Adsorbent dose on the removal of MG Dye
[MG]=50mg/L;Contact Time 50min;Temprature 30^{o}C



Fig;3- Effect of Initial pH on the removal of MG Dye
[MG]=50 mg/L;Temprature 30°C;Adsorbent dose=25mg/50ml

Thermodynamic Studies

The adsorption capacity of the AAVNSC increased with increase in the temperature of the system from 303-333K. The ΔH° and ΔS° values obtained from the slope and intercept of Van't Hoff plots were presented in table 5.

The positive values of ΔH° and ΔS° suggested endothermic reaction, while the negative values of free energy change (ΔG°) indicate that the adsorption is spontaneous. The positive values of ΔS° have also suggested the increased randomness at the solid-solution interface during desorption of MG on AAVNSC. In desorption of the MG dye, the adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than was lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system (Harapriya and Mohapatra, 2005).

Desorption studies

Desorption studies help to elucidating the nature of dye adsorption and the recycling of the spent adsorbent. Desorption can be carried out using neutral pH water, alkali, mineral acid and organic acid like acetic acid. The effect of various reagents used for the desorption studies indicates that hydrochloric acid is good regenerating agent for MG dye. This confirms the physical force of attraction between AAVNSC adsorbent and MG dye. The desorption of dye MG by mineral acid shows that the adsorption was through physisorption (Arivoli, 2007)

Conclusion

The present study has shown the effectiveness of using AAVNSC in the removal of malachite green dye from aqueous solutions. Acid Activated Vitex Negundo Stem has a great role in modern life to clean environment. An adsorption test has been carried out for industrial pollutants (malachite green) under different experimental conditions in batch mode. The adsorption of malachite green was dependent on adsorbent surface characteristics, adsorbent dose, malachite green concentration, time of contact and temperature. A study of the kinetic models on sorption showed that sorption fitted the pseudo second- order kinetics model. The values of ΔH°, ΔS°and ΔG° show that the adsorption on AAVNSC was a spontaneous and endothermic process. So AAVNSC acts as a good adsorbent for adsorption of MG dye from aqueous solution.

References

Arivoli, S. 2007. Kinetic and thermodynamic studies on the adsorption of some metal ions and dyes on to low cost activated carbons, Ph.D., Thesis, Gandhigram Rural University, Gandhigram-India.

Freundlich, H.M.F. 1906. Uber die adsorption is losungen. *Z. Phys. Chem.*, 57: 385–470.

Gong, R., Ding, Y., Li, M., Yang, C., Liu, H., Sun, Y. 2005. Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. *Dyes Pigments,* 64: 187–192.

Harapriya, Mohapatra., Gupta., 2005. *Biores. Technol.*, 96: 1387.

Langmuir, I. 1918. The adsorption of gases plane surfaces of glass, mica and platinum. *J. Am. Soc.*, 579: 1361–1403.

Mittal, A.K., Venkobachar, C. 1989. Studies on adsorption of dyes by sulphonated coal and Ganoderma Lucidum. *Ind. J.Environ. Hlth.*, 31: 105.

Senthikumar, S., Varatharajan, P.R., Porkodi, K., Subburaam, C.V. 2005. Adsorption of methylene blue carbon onto jute fibre carbon, *J. Colloid Interface Sci.*, 284: 79.

Stephen Inbaraj, R., Sulochana, N. 2002. Basic dye adsorption on a low-cost carbonaceous sorbent–Kinetic and equilibrium studies. *Ind. J. Chem. Technol.*, 9: 201.

Suguna Devi, S.R., Sathish Kumar, M., Shanthi, K., Kadirvelu. K., Pattabhi. S. 2002. Removal of direct- T-blue-R from aqueous solution onto carbonized sugarcane bagasse waste. *Ind. J. Environ. Prot.*, 22(5): 500–505.

Vadivelan, V., Vasanthkumar, K. 2005. Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk. *J. Colloid Interface Sci.*, 286: 91.

Weber, W.J. 1967. Principle and application of water chemistry. Faust, S. D. and Hunter, J. V. (Eds). Wiley, New York.

Yupeng Guo, Jingzhu Zhao, Hui Zhang, Shaofeng Yang, Zichen Wang, Hongding, Xu. 2005. *Dyes and Pigments*, 66: 123.