



ISSN (PRINT) : 2320 -1967
ISSN (ONLINE) : 2320 -1975



ORIGINAL ARTICLE

CHEMXPRESS 7(3), 76-85, (2014)

Thermodynamic and kinetic analysis on the removal of malachite green dye using activated Pistia Stratiotes leaves

S.Arivoli*, V.Marimuthu, T.Rose Judith

Department of Chemistry, Thiru.Vi.Ka, Government Arts College,
Thiruvarur-610003, Tamil Nadu, (INDIA)
E-mail : arivu3636@yahoo.com

Abstract : The research of the present work was to investigate the removal of Malachite Green from aqueous solution by using Pistia Stratiotes. Generally, dyes are used in chemical, textile, paper, printing, leather, plastics and various food industries. The need for the treatment of dye contaminated waste water passed out from the industry. In this study, Pistia Stratiotes Leaves was studied for its potential use as an adsorbent for removal of Malachite Green. The various factors affecting adsorption, such as initial dye concentration, contact time, adsorbent dose and effect of temperature, were evalu-

ated. 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 APSNC may be utilized as a low cost adsorbent for Malachite Green dye removal from aqueous solution. © Global Scientific Inc.

Keywords : Activated Pistia Stratiotes nano carbon (APSNC); Malachite green dye; Adsorption isotherm; Kinetics; Equilibrium models.

INTRODUCTION

Disposal of dyeing industry wastewater pose one of the major problems, because such effluents contain a number of contaminants including acid or base, dissolved solids, toxic compounds, and color. Out of these, color is the first contaminant to be recognized because it is visible to the human eye. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion. Possible methods of color removal from textile effluents include chemical oxida-

tion, froth flotation, adsorption, coagulation, etc. Among these, adsorption currently appears to offer the best potential for overall treatment, and it can be expected to be useful for a wide range of compounds, more so than any of the other listed processes. Recognizing the high cost of activated Nano Carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements. Such materials range from industrial waste products such as waste rubber tyres, blast furnace slag, and lignin to agricultural products such as wool, rice straw, coconut husk, saw dust, and peat mass.

In order to assess the ability of activated Nano Carbon for dye removal, malachite green (MG) has been selected for the present study.

MATERIAL AND METHODS

Preparation of activated nano carbon

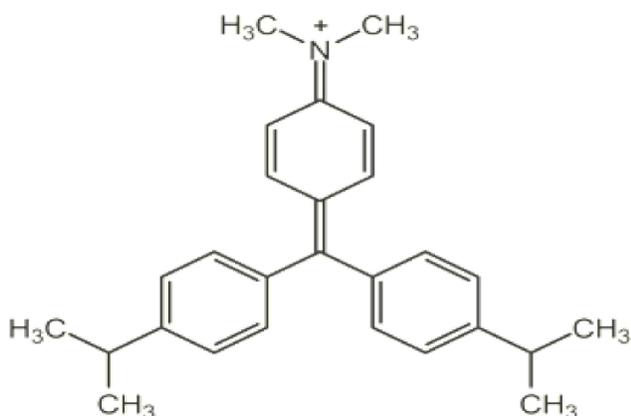


Pistia stratiotes (Akayat-tamarai)

Pistia Stratiotes Leaves used in this study was collected from the local Agriculture land of Thiruvapur, Tamilnadu, India. The raw biosorbent was cut into small sizes and then washed thoroughly with hot-distilled water followed by double-distilled water to remove any unwanted particles. It was then dried and activated in a muffle furnace at 1200 °C. The activated material was sieved to get uniform size particles <math><177\mu\text{m}</math> (80mesh). The same APSNC was used throughout the experiment.

Adsorbate

The stock solution of malachite green concentration 1000 mg/L was prepared by dissolving 1 g of malachite green in 1000 ml of double distilled water. Different concentration of dyes solution range from (25 to 125 mg/L) was prepared from the stock solution by appropriate dilution.



Material developments

Sorption studies were performed by the batch technique to obtain rate and equilibrium data. For isotherm studies a series of 50 mL Iodine flask were employed. Each test tube was filled with 50 mL of dye solution of varying concentrations and maintained at the desired pH and temperature. A known amount of adsorbent was added into each tube and agitated intermittently for a maximum period of 1 h. A 10-60 Minutes reaction period was found to be quite sufficient for equilibrium attainment for the dye. After this period the supernatant solution was centrifuged and the uptake of the dye was monitored spectrophotometrically at 425 nm. These concentrations were however decided after a good deal of preliminary investigation wherein the adsorbent was found to remove the dye to different extent. Sorption studies were carried out at 30, 40, 50 and 60 °C to find out the effect of temperature. The effect of pH was observed by studying the adsorption of dye over a pH range of 2-10.

Batch adsorption experiments

Batch adsorption was tested by adding 25 mg of APSNC to 50 ml of the dye solution of different initial concentration (25 to 125 mg/L) at a particular pH. The experiment was carried out using a wrist action shaker for the period of 60 min and 120 rpm using 250 ml stopper glass flasks at (30°C to 60°C). The residual concentrations of dyes in each sample after adsorption at different time intervals were determined by UV-Visible spectrophotometer. The equilibrium q_e (mg/g) was calculated by the following mass balance principle.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

Where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of dyes, V is the volume (L), M is the weight (g) of the adsorbent. The removal efficiency of the adsorbents on dyes was calculated by using the following expression.

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

Kinetic experiments

The batch kinetic^[9] experiments were basically similar to those used testing the adsorption equilibrium method. The dyes samples were taken at specific time

ORIGINAL ARTICLE

intervals and the concentration of dyes was similarly measured. The all kinetic experiments were carried out at 30, 40, 50 and 60°C with initial dye concentration (25, 50, 75, 100 and 125 mg/ L) the amount of adsorption at time t. The qt (mg/g) was calculated by.

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (3)$$

Where C_0 (mg/L) is the liquid phase concentration of dye at any time.

RESULTS AND DISCUSSION

Effect of contact time and initial dye concentration

The experimental results of adsorption of various dye concentrations with contact time are shown in Figure 1. This figure shows that the % removal initially increases and reaches the limiting value. So, that the equilibrium was established at 40 minutes. Hence all the remaining experiments were carried out at 40 min-

utes. The equilibrium data were given in TABLE 1 reveals that, the percentage removal was decreases with increase in initial dyes concentration. This was due to the number of available active sites was remains constant but the initial concentration of dyes increases, so that % removal decreases^[10,11].

Effect of adsorbent dosages

The effect of the APSNC doses was studied at 30°C by varying the amount of adsorbent dose 10-250 mg for the initial concentration of 50 mg/L Figure 2 reveals that increase in percentage removal of MG dye with increases in dose of adsorbent due to the increase in adsorbent surface area and the availability of more adsorption sites.

Effect of pH

The solution pH is one of the most important factors that control the adsorption of MG dye. To examine the effect of pH on the % removal of MG dye the pH of initial solution were varied from 2.0 to 10.0 by adding

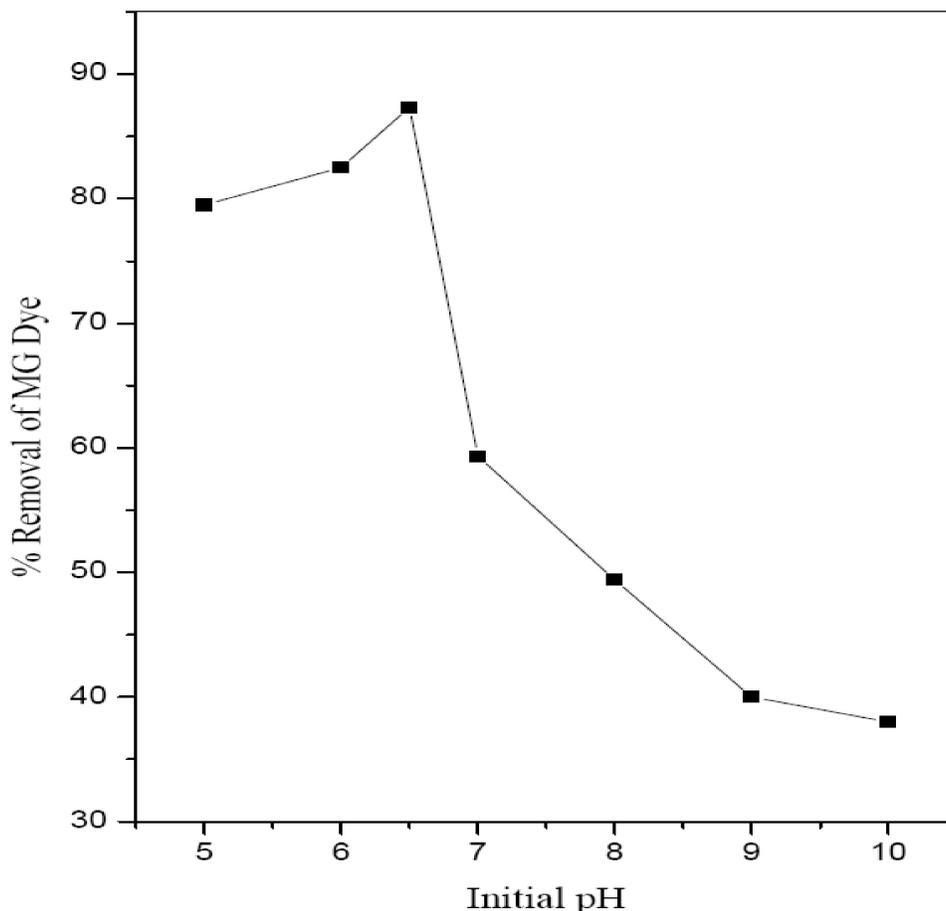


Figure 1 : Effect of contact time on the removal of MG dye [MG]=50 mg/L; temperature 30°C; adsorbent dose=25mg/50ml

TABLE 1 : Equalilibrium parameters for the adsorption of MG dye onto APSNC

M_0	Ce (Mg / L)				Qe (Mg / L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	2.36	2.58	2.04	2.36	45.26	44.82	45.91	45.26	90.52	89.65	91.82	90.53
50	6.23	6.32	4.24	4.01	87.53	87.34	91.50	91.97	87.53	87.34	91.50	91.97
75	12.34	10.35	11.13	10.74	125.30	129.28	127.73	128.51	83.53	86.18	85.15	85.67
100	26.74	24.84	11.13	20.36	146.51	150.31	177.73	159.26	73.25	75.15	88.86	79.63
125	42.95	38.74	22.87	31.84	164.09	172.50	204.25	186.31	65.63	69.00	81.70	74.52

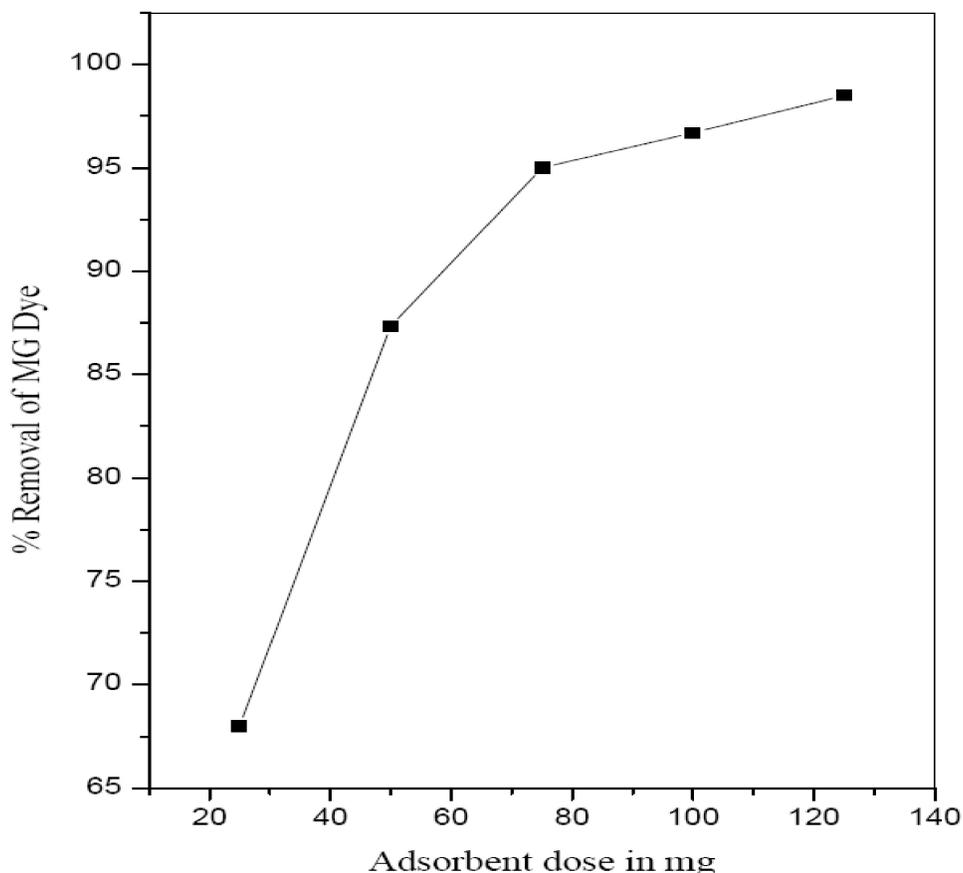


Figure 2 : Effect of adsorbent dose on the removal of MG dye [MG]=50mg/L; contact time 60min; temperature 30°C

NaOH or HCl in to them. The % removal increases as the pH increases up to 6.5. There after the % removal decreases. At pH 6.5 the optimum % removal takes place. So the remaining experiment was carried out at pH 6.5. The experimental result was shown in Figure 3.

Adsorption isotherm studies

To quantify the sorption capacity of the absorbent for the removal of dyes, the most commonly used isotherms, are the Freundlich and Langmuir isotherms and hence these were used in this study.

(A) Freundlich isotherm

Linear form of Freundlich isotherm model^[12] is rep-

resented by the equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where q_e is the amount of dyes adsorbed per unit weight of the adsorbent (mg/L) K_f is (mg/g(L/mg)) the measure of adsorption capacity and $1/n$ is the adsorption intensity. The value of K_f and n are calculated from the intercept and slope of the plot of $\log q_e$ Vs $\log C_e$ respectively. The constant K_f and n values are given in TABLE 2. In general the K_f value increases for a given adsorbate increases. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. The value of

ORIGINAL ARTICLE

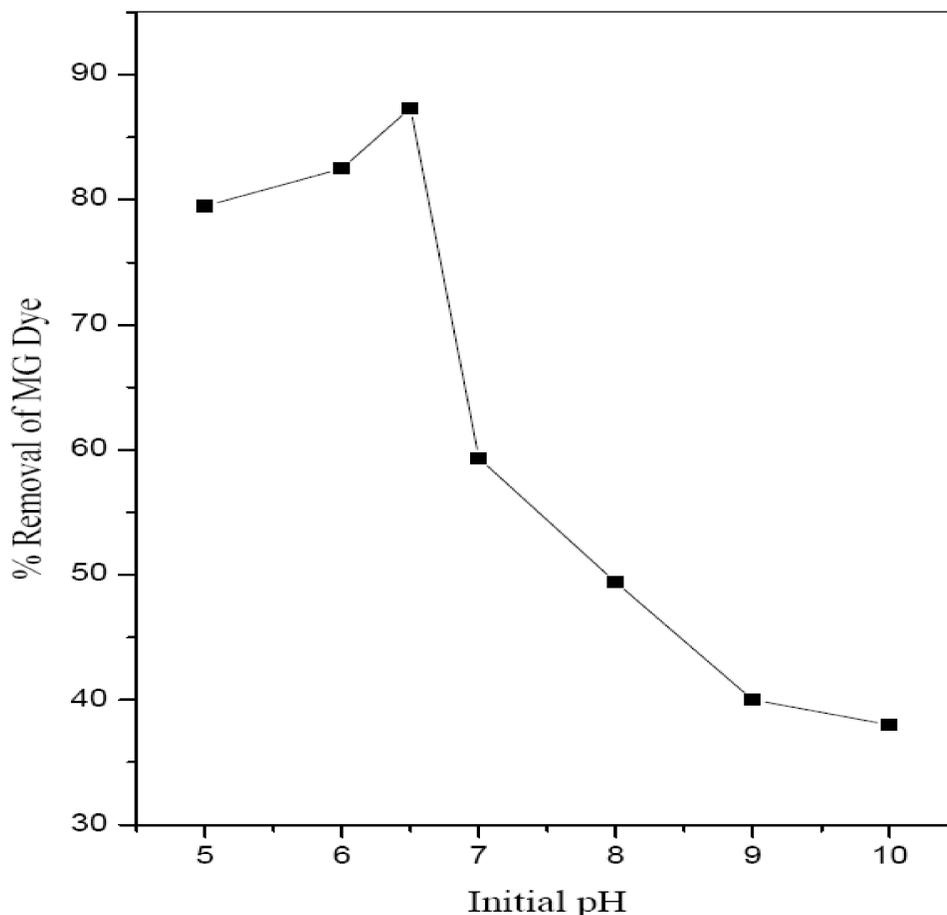


Figure 3 : Effect of initial pH on the removal of MG dye [MG]=50 mg/L; temprature 30 °C; adsorbent dose=25mg/50ml

$n > 1$ represents favorable adsorption condition^[7] (or) the value of n are in the range of 1 to 10 confirms the favorable condition for adsorption. The adsorption coefficient K_f of dyes on Pistia Stratiotes Leaves was found from 4.7157 to 4.7866 L/g. The K_f value indicates that the saturation time for adsorption of dyes is attained quickly due to the high affinity of activated Nano Carbon towards the adsorbate. The values of n were in the range of 1.6382 to 2.2913 (mg/L) for MG dyes adsorption. So Freundlich isotherm is suitable for this adsorption. The K_f values also indicate the multilayer adsorption were possible. This reveals that the activated Nano Carbon was more efficient for the removal of MG dyes.

(B) Langmuir isotherm

The Langmuir isotherm model^[13] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

$$C_e/q_e = C_e/q_{max} + 1/(b q_{max}) \quad (5)$$

TABLE 2 : Langmuir and Freundlich isotherm parameter for the adsorption of MG dye onto APSNC

Temp. (°C)	Langmuir Parameters		Freundlich Parameters	
	Q_m	B	K_f	N
30°C	191.09	0.1362	4.7157	2.2913
40°C	209.12	0.1172	4.5818	2.0787
50°C	297.26	0.0936	4.5806	1.6382
60°C	231.48	0.1208	4.7866	2.0326

Where C_e (mg/L) is the equilibrium concentration of the dye, q_e (mg/g) is the amount of dye per unit weight of adsorbent, Q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. Q_m is the amount of dye at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption or rate of adsorption. The linear plot of C_e/q_e against the equilibrium concentration C_e shows the Langmuir model. The Langmuir constant Q_m and b were determined from the slope and intercept of the Langmuir plot

and these values are given in TABLE 2. The feasibility of the Langmuir isotherm can also be expressed in terms of the dimensionless constant separation factor R_L ^[14,15] by the equation

$$R_L = \frac{1}{1 + b C_0} \quad (6)$$

Where C_0 (mg/L) is the initial concentration of adsorbent and b (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of the isotherm.

- $R_L > 1$ unfavorable
- $R_L = 1$ Linear
- $0 < R_L < 1$ Favorable
- $R_L = 0$ Irreversible

The R_L values lies between 0 and 1 indicate favorable adsorption for all initial concentration study. The calculated R_L values were given in TABLE 3. The calculated R_L values were with in the range of 0.0554 to 0.2993. So the adsorption of MG follows the Langmuir isotherm.

Thermodynamic study

Thermodynamic parameter such as change in free energy (ΔG^0) (KJ/mol), Enthalpy (ΔH^0) (KJ/mol) and entropy (ΔS^0) (JK/mol) were calculated by using the following equation (7,8) and (9)

$$K_0 = C_{\text{Solid}}/C_{\text{Liquid}} \quad (7)$$

$$\Delta G^0 = -RT \ln K_0 \quad (8)$$

$$\log K_0 = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (9)$$

Where K_0 is the equilibrium constant, C_{Solid} is the solid phase concentration at equilibrium (mg/L). C_{Liquid} is the liquid phase concentration at equilibrium (mg/L). T is temperature in Kelvin and R is the gas constant (8.314 J mol⁻¹K⁻¹). A graph was drawn between $\log K_0$ vs $1/T$. The ΔH^0 and ΔS^0 values obtained from the slope and intercept of van 't Hoff plots. These values were given

in TABLE 4. The negative ΔG^0 were indicate the adsorption is spontaneous in nature and also the magnitude of ΔG^0 indicate the adsorption is physical adsorption (ie, less than 70 KJ/mol). The value of ΔH^0 is positive, this indicates the adsorption is endothermic process. The positive ΔS^0 indicates increased randomness during the adsorption. This also support the adsorption was physical adsorption^[16,17]

Adsorption kinetics

The kinetics studies were done by using pseudo second order^[18] Elovich^[19,20] and intra-particle diffusion^[22] models.

(A) The pseudo-second-order kinetic model

The linear form of pseudo second order equation is expressed as

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (10)$$

Where k_2 (g/mg min) is the pseudo second order rate constant. For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ integrated form of Eq. (10) becomes:

$$(q_e - q_t) = \frac{1}{q_e} + K_2 t \quad (11)$$

This is the integrated rate law for a pseudo second order reaction. Equation (11) can be rearranged to obtain Eqs (12) which has a linear form:

TABLE 3 : Dimensionless separation factor (R_L) for the adsorption of MG dye onto APSNC

(C _i)	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.2269	0.2543	0.2993	0.2487
50	0.1279	0.1457	0.1760	0.1420
75	0.0891	0.1020	0.1246	0.0993
100	0.0683	0.0785	0.0965	0.0764
125	0.0554	0.0638	0.0787	0.0621

TABLE 4 : Thermodynamic parameter for the adsorption of MG dye onto APSNC

(C ₀)	ΔG^0				ΔH^0	ΔS^0
	30°C	40°C	50°C	60°C		
25	-5684.75	-5618.43	-6493.9	-6252.78	2.249	25.980
50	-4909.13	-5028.07	-6383.4	-6750.91	16.00	68.455
75	-4091.94	-4764.78	-4691.6	-4951.46	3.513	25.592
100	-2538.76	-2880.94	-5578.6	-3775.23	17.500	66.648
125	-1630.21	-2082.58	-4018.3	-2971.9	16.85	61.414

ORIGINAL ARTICLE

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

If the initial adsorption rate (h) (g/mg min) is

$$h = K_2 q_e^2 \quad (13)$$

Then Eqs. (12) and (13) becomes:

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (14)$$

Where k_2 (g/mg min) is the pseudo second order rate constant, q_e is the amount of dye adsorbed on the per unit mass of adsorbent (mg/g) at equilibrium, q_t is the amount of dye adsorbed at time "t". A Graph is drawn between t/q_t versus "t", the q_e and k_2 can be calculated from the slope and intercepts of the graph. The correlation coefficient value (γ) were also calculated. These values are given in TABLE 5. The correlation coefficient value (γ) for the pseudo second order was greater than 0.9900 (ie, $\gamma > 0.9900$) and also q_e value calculated from the model was almost equal to the experimental value. So the adsorption of MG follows pseudo second order model.

(B) The Elovich equation

The Elovich model equation is generally expressed as

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (15)$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g mg^{-1}) during any one experiment. To simplify the Elovich equation. Chien and Clayton assumed $\alpha\beta t \gg t$ and by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq.(15) becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (16)$$

If dyes adsorption fits the Elovich model, a plot of q_t vs. $\ln(t)$ yields a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The Elovich parameters α , β and correlation coefficient (γ) were given in TABLE 5. The initial adsorption rate (α) and desorption constant (β) increases with increase in initial concentration of MG dyes and also the correlation

TABLE 5 : The kinetic parameters for the adsorption of MG dye onto APSNC

C ₀	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q _e	K ₂	γ	h	α	β	γ	K _{id}	γ	C
25	30	49.90	23×10 ⁻³	0.994	7.59	55.10	0.1339	0.998	1.6249	0.992	0.1888
	40	47.72	19×10 ⁻³	0.995	10.69	952.98	0.2114	0.991	1.7457	0.994	0.1144
	50	48.39	16×10 ⁻³	0.997	10.52	1703.15	0.2241	0.993	1.7641	0.991	0.1057
	60	48.30	19×10 ⁻³	0.999	10.01	713.15	0.2030	0.992	1.7403	0.992	0.1186
50	30	95.49	24×10 ⁻³	0.998	16.18	199.04	0.0780	0.991	1.6513	0.991	0.1644
	40	93.32	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
75	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
100	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
125	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

coefficient (γ) were greater than 0.9900 (ie, $\gamma > 0.9900$). The Elovich model can also suitable for the MG adsorption onto APSNC.

(C) Intra-particle diffusion model

According to Weber and Morris suggested the intra-particle diffusion model is

$$q_t = K_{id} t^{1/2} + C \quad (17)$$

Where k_{id} is the intra-particle diffusion constant (mg/g min), and q_t is the amount of the dye adsorbed at time "t". According to Weber and Morris model, a graph is drawn between q_t and $t^{1/2}$, the line was passing through the origin. But here the intercept value indicates the lines were not passing through origin. This was due to that the intra-particle diffusion takes place along with some other process. This may be boundary layer adsorption or instantaneous adsorption.

Effect of the ionic strength on the adsorption of malachite green

The effect of sodium chloride on the adsorption of

malachite green on to APSNC is shown in Figure 4. In a low solution concentration of NaCl had less influence on the adsorption capacity. The partial neutralization of the positive charge on the adsorbent surface and a consequent compression of the electrical double layer by the Cl^- anion cause the increase in the adsorption of the malachite green at higher ionic strength. The chloride ions can also enhances adsorption of malachite green ion onto activated calcite by pairing of their charges and hence reducing the repulsion between the malachite green molecules adsorbed on the surface. The APSNC to adsorb more of positive malachite green dye^[16,17,22,23]

SEM and FTIR of APSNC

The SEM images of APSNC (Figure 4a and 4b) Shows the SEM micrographs of APSNC sample before and after dye adsorption. It is clear that APSNC has considerable numbers of heterogeneous layer of pores where there is a good possibility for dye to be adsorbed. The surface of dye-loaded adsorbent, however, clearly shows that the surface of APSNC is cov-

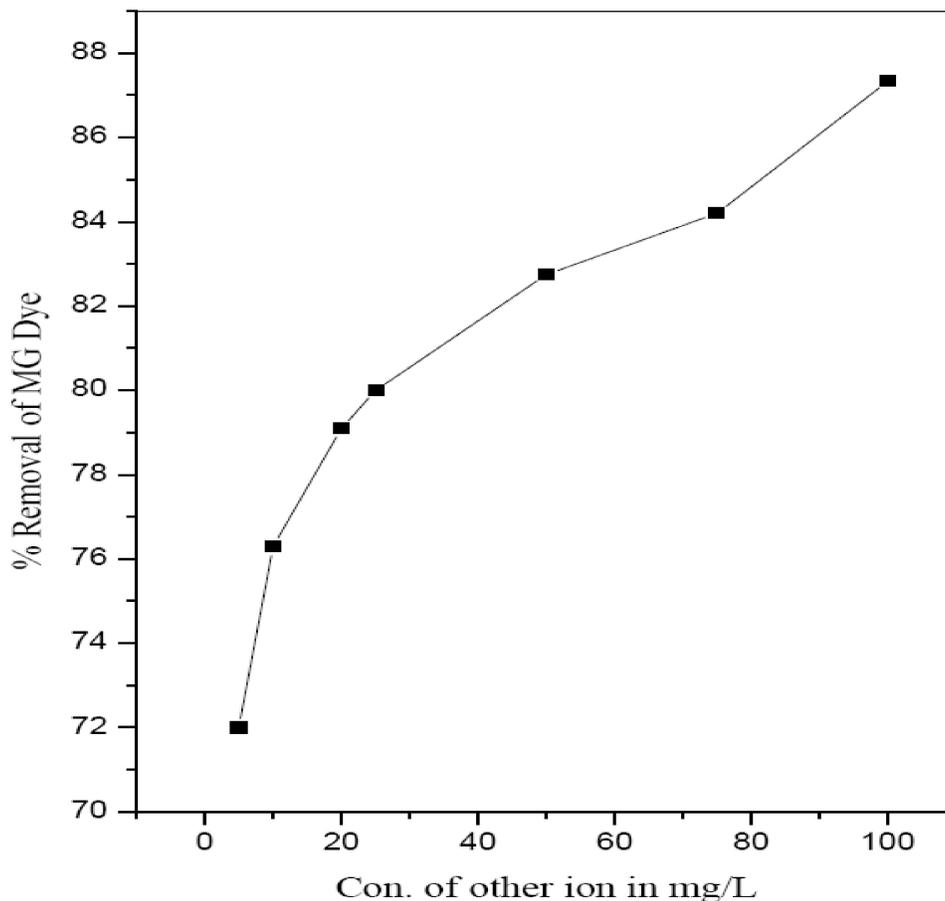


Figure 4 : Effect ionic strength on the adsorption of MG dye [MG]=50 mg/L; contact time=60 min; dose=25 mg/50 ml

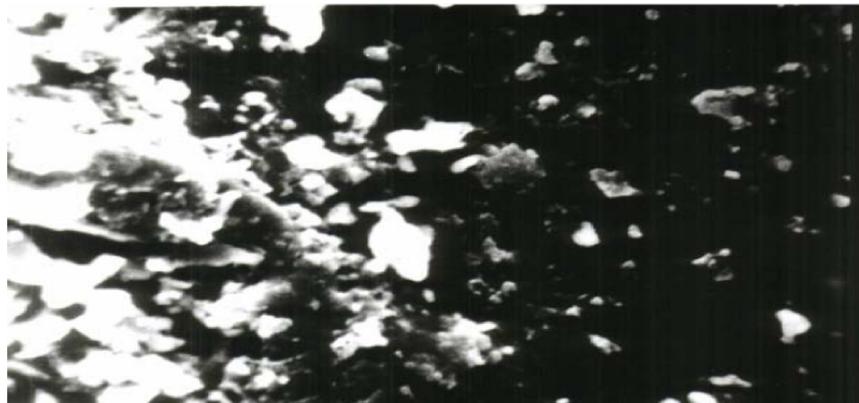
ORIGINAL ARTICLE

Figure 4a : SEM image of APSNC before adsorption

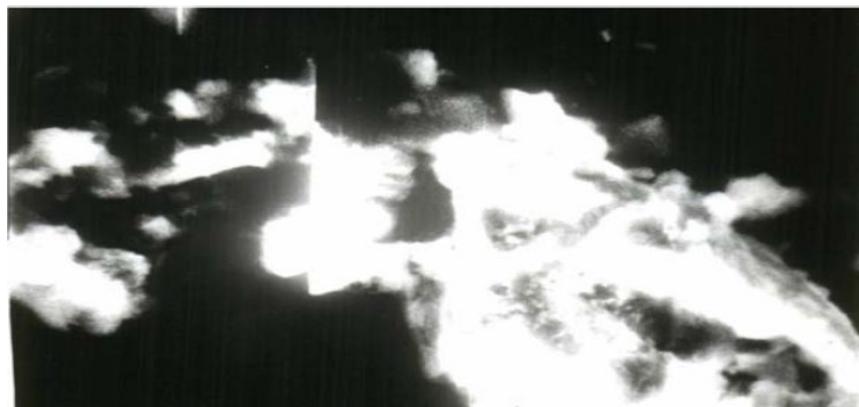


Figure 4b : SEM image of APSNC after the adsorption of malachite green

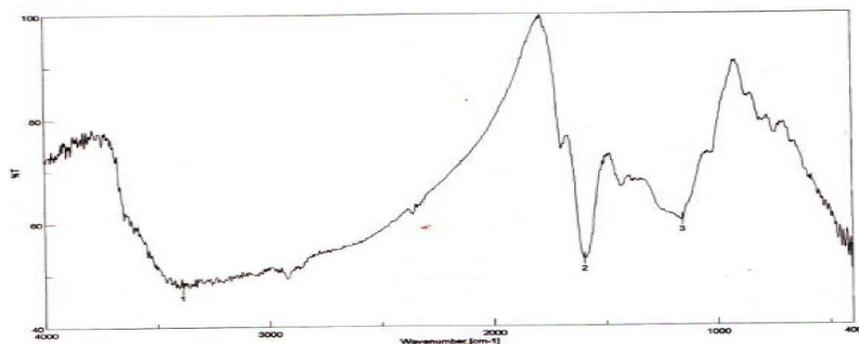


Figure 5a : FT-IR spectrum APSNC before adsorption

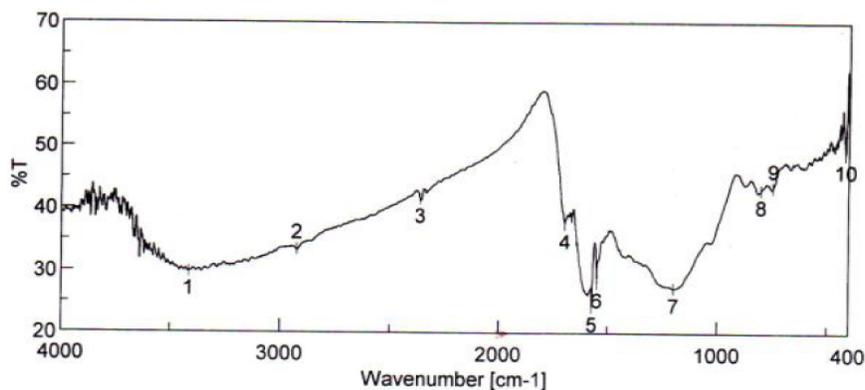


Figure 5b : FT-IR spectrum of APSNC after adsorption of malachite green

ered with dye molecules.

The FTIR spectrum of APSNC before and after adsorption (Figure 5a and 5b) shows that some peaks were shifted or disappeared and that new peak were also detected. These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of the APSNC in adsorption process.

CONCLUSIONS

The adsorption characteristics of MG dye onto Activated Nano Carbon are strongly affected by the initial dye concentration, initial pH and the adsorbent dose. The pH 6.5 was favorable for the optimum adsorption of MG dye by APSNC. The R_L values and other adsorption parameters indicate both Langmuir and Freundlich isotherms favorable for APSNC adsorption. The pseudo second order, Elovich and intra-particle kinetic model were found to applicable for the adsorption of MG onto APSNC reaction model. The thermodynamics parameters ΔG^0 , ΔH^0 and ΔS^0 values indicate the adsorption is endothermic and physical adsorption.

REFERENCES

- [1] B.Al Duri, G.Mckay, M.S.El Geundi, M.Z.Wahab Abdul; Three resistance transport model for dye adsorption onto Bagasse Pitch, *J. Environ. Eng. Div. ASCE*, **116**, 487 (1990).
- [2] S.J.Allen, G.Mckay, K.Y.H.Khader; Intraparticle diffusions of basic dye during adsorption onto Sphagnum Peat, *Environ. Pollut.*, **56**, 39 (1989).
- [3] N.L.Alpert, W.E.Kesi, H.A.Szymanaki; Theory and practice of infrared spectroscopy, 2nd Edition, Plenum, New York, (1970).
- [4] G.E.Boyd, A.W.Adamson, L.S.Meyers; The exchange adsorption of ions from aqueous solution by organic zeolites II, *Kinetics. J. Am. Chem. Soc.*, **69**, 2836 (1947).
- [5] J.Crank; The mathematics of diffusion, Clarendon Press, Oxford, (1956).
- [6] M.S.El-Geundi; Colour removal from textile effluents by adsorption technique, *Wat. Res.*, **25**, 271 (1991).
- [7] H.J.Fornwalt, R.A.Hutchins; Purifying liquids with activated carbon, *Chem. Eng. J.*, **73**, 179 (1966).
- [8] R.A.Freidal, J.A.Queiser; Infrared analysis of Bitumenous coal and other carbonaceous materials, *Anal. Chem.*, **28**, 22 (1956).
- [9] J.A.Gadsen; Infrared spectra of minerals and related inorganic compounds, Butterworths, London, (1975).
- [10] G.S.Gupta, G.Prasad, V.N.Singh; Removal of chrome dye from carpet effluents using coal II (Rate process), *Environ. Technol. Lett.*, **9**, 1413 (1988).
- [11] B.H.Hammed; A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solution, *Journal of Hazardous Materials*, **162**, 305-311 (2009).
- [12] C.Namasivayam, N.Munisamy, K.Gayathri, M.Rani, K.Renganathan; *Biores. Technol.*, **57**, 37 (1995).
- [13] H.Frendlich; The dye adsorption is losungen (Adsorption in Solution), *Z. Phys. Chem.*, **57**, 385-470 (1906).
- [14] I.Langmuir; The adsorption of gases plane surfaces of glass, mica and platinum, *J. Am. Soc.*, **579**, 1361-1403 (1918).
- [15] T.W.Weber, R.K.Chakravorti; Pore and solid diffusion models for fixed bed adsorbers, *J. Am. Inst. Chem. Eng.*, **20**, 228 (1974).
- [16] G.McKay, H.S.Blair, J.R.Gardner; Adsorption of dyes on chitin. I, *Equilibrium Studies, J. Appl. Polym. Sci.*, **27**, 3043-3057 (1982).
- [17] S.Arivoli, B.R.Venkataraman, T.Rajachandrasekar, M.Hema; *Res. J. Chem. Environ.*, **17**, 70-78 (2007).
- [18] S.Arivoli, K.Kalpana, R.Sudha, T.Rajachandrasekaran; *E.-J. Chem.*, **4**, 238-254 (2007).
- [19] Y.S.Ho, G.McKay; The kinetic of sorption of divalent metal ions on to Sphagnum moss peat, *Water Res.*, **34**, 735-742 (2000).
- [20] S.H.Chien, W.R.Clayton; Application of Elovich equation to the kinetics of phosphate release and sorption on soil, *Soil Sci. Sco, Am. J.*, **44**, 265-268 (1980).
- [21] D.L.Spark; Kinetics of Reaction in Pure and Mixed System in Soil Physical Chemistry, CRC, Press, Boca Raton, (1986).
- [22] W.J.Weber, J.C.Morris; Kinetics of adsorption on carbon from solution, *J. Sanitary Eng. Div.*, **90**, 79 (1964).