



International Journal of ChemTech Research CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555 Vol.10 No.10, pp 579-604, 2017

Kinetics Isotherm equilibrium studies of Malachite green on Agricultural waste material and using low cost carbon

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Abstract: In this research five low cost carbon adsorbents, namely, Sorghum Vulgare Carbon (SVC), Zea Mays Carbon (ZMC), Sorghum Vulgare Varity Carbon (SVVC), Ceiba Peutandra Carbon (CPC), Projobis juliflora Carbon (PJC) were prepared for the adsorption of Malachite green(MG). Adsorption was studied as a function of pH (2-12), adsorbent dose (0.2-1.6g), contact time (5-40mints), initial MG concentration (50-100mg/L); agitation seed (120-180rpm) and characterization of FT-IR, UV-visible and XRD. From the results obtained it was observed that with the increase in the pH value, the percentage MG removal increases from 48.62,52.33,38.74,46.68, and 55.03% to 94.48,95.15 , 95.45,94.54 ,and 94.84% for SVC,ZMC,SVVC,CPC, and PJC adsorbents, respectively. Additionally the percentage MG removal increased from 45.86, 43.12, 56.71, 47.78, and 39.81% for SVC, ZMC, SVVC, CPC, and PJC adsorbents, respectively, by increasing, adsorbent dose from 0.2g to 1.6g.Hence optimize adsorbent dose for SVC, ZMC, SVVC, CPC, and PJC adsorbents 0.8,1.0,1.2,1.4, and 1.6g, respectively. The experimental data were analyzed by the Langmuir, Freundlich, Temkinisotherm, Redlich Peterson Isotherm, Dubinin- Radushkevich constants and BET. Results showed that the maximum monolayer adsorption capacity of SVC, ZMC, SVVC, CPC, and PJC adsorbents for the adsorption of MG was 20.99, 21.64, 21.5- 21.58 and 20.9 mg/g respectively. The kinetic data were fitted to the pseudo-first-order, pseudo-second-order, Intraparticle diffusion models, Elovich, Natrajan and Khalaf, Bhattacharaya and Venkobachar models. Adsorption of these adsorbents surveyed Langmuir adsorption isotherm models and pseudo-second-order kinetics. Kinetics parameters were evaluated to predict the nature of adsorption. These outcomes specify the endothermic and spontaneous nature of the adsorption process.

Keywords : Agricultural waste, low cost carbon, Malachite green, optimization, Batch adsorption, Kinetics.

1. Introduction

Dyeing and Finishing processes from industries do generate large amounts of colored wastewater which are discharged into natural streams with undesirable consequence to the environment and human health. Apart from the unpleasant aesthetic aspects of dye wastewater, its presence in natural streams can cause serious harm to aquatic life by increasing toxicity, chemical oxygen demand, and as well hindering photosynthetic phenomena through reduction of light penetration⁽¹⁾. Malachite Green (MG) is a common (Cationic) dye for dyeing of cotton, silk, paper, leather and also in manufacturing of paints and printing inks. MG is widely used in distilleries for coloring purposes⁽²⁾. MG has properties that make it difficult to remove from aqueous solutions

and also toxic to major microorganisms⁽³⁾.MG when discharged into receiving streams will affect the aquatic life and causes detrimental effects in liver, gill, kidney, intestine, gonads and pituitary gonadotrophic cells⁽⁴⁾.Therefore, the treatment of effluent containing such dye is of interest due to its aesthetic impacts on receiving waters.

Several attempts have been made for MG removal since the wastewater. These include photodegradation^(5,6), photo catalytic degradation ⁽⁷⁻⁹⁾ coagulation and flocculation⁽¹⁰⁾, ozonation⁽¹¹⁾, electro chemical techniques⁽¹²⁾, adsorption ^(13,14) and fungal decolourisation⁽¹⁵⁾. Among these methods adsorption has been favored in recent years due to its proven efficiency in the removal of pollutants from effluents.

Activated carbon is primarily an amorphous solid using a large internal surface area and pore volume. It consists of a basic structural unit built up of condensed aromatic rings. Its high adsorptive capacity makes it favorable for the removal of hazardous material from effluents, toxic and odour producing gas removal, water purification, color removal, etc.,

However, broad research has been taking on recently to develop alternative and economic adsorbents. Activated carbon has been widely investigated for the adsorption of dyes⁽¹⁶⁻²⁰⁾. Earlier studies show that the use of some low cost carbonaceous and non- carbonaceous materials such as coir pith ⁽²¹⁾ coal ⁽²²⁾blast furnace slag⁽²³⁾, banana and orange peels⁽²⁴⁾, pistachio shells ⁽²⁵⁾, rice husk⁽²⁶⁾, chitin⁽²⁷⁾, orange waste⁽²⁸⁾, lemon peel⁽²⁹⁾, raw barely straw⁽³⁰⁾, egg shell⁽³¹⁾, silica-zirconia mixed oxide ⁽³²⁾ and agricultural wastes ⁽³³⁾were used as adsorbents.

In this work, the adsorption of MG was studied on activated carbons prepared from various plant materials such as Sorghum Vulgare (SV), ZeaMays(ZM), Sorghum Vulgare Variety (SVV), Cebia Pentandra (CP) and ProjobisJuliflora(PJ) for the removal of MG and also studies the kinetics of removal of MG.

2. Materials and methods

2.1. Adsorbent

The various plant materials for the preparation of indigenously prepared [SV,ZM,SVV,CP,PJ]activated Carbons (IPACs) were collected at Thirumangalam(taluk) Madurai District, Tamil Nadu, India. The preparation and activation procedure for IPACs are given in experimental section. A variety of carbonaceous raw materials such as (White shalom) Sorghum vulgare Carbon (SVC), (Baby corn carbon) Zea Mays Carbon(ZMC), (Red shalom) Sorghum Vulgare Varity Carbon(SVVC), (Elavampaju carbon) Ceiba peutandra Carbon(CPC), and (Garuvalam pattai carbon) Projobis juliflora carbon (PJC) have been collected locally and examined for the preparation of adsorbents.

The cleaned raw materials were cooked in boiling water for 30 minutes to remove the moisture, sivzed of particle size 150 to 355 μ , matters. After cleaning, the leaves were sundried 2-3 days and ground into fine powder which was soaked into 0.2N H₂SO₄ till 24 hours. The raw material was further cleaned several times with distilled water and then sundried. The dried powder was stored into air tight brown bottles containers.

2.2. Adsorbate

For adsorption studies MG (color index number: 15707) molecular formula $C_{52}H_{52}N_4Cl^-$; dyecontent: 45%), a commercial basic dye, purchased from Sigma-Aldrich (catalog number 277RD0001) was Experimental dye ⁽³⁴⁾solution of different concentrations was prepared by reducing the stock solution with appropriate volume of double-distilled water. Molecular structure of MG is shown table (2.1).

2.2.1. Batch Adsorption Experiments

To study the effect of experimental parameters like initial concentration, contact time, adsorbent dosage and pH for the removal of dyes. Adsorption experiments were carried out at room temperature $(30 \pm 1^{0}C)$ under batch mode ⁽³⁵⁾.

The 25mL of 10 mg/L of MG solution with 100mg of particle size 150 to 355 μ were shaken on Kemi shaker (model RS-12 plus, rpm 250) for 5, 10, 20, 40, 60, 80, 100, 120, 140 and 160 minutes in different flasks of 100ml capacity at solution pH 5. The solutions were withdrawn at different time intervals and the adsorbent was removed from the solution by centrifugation using centrifuge machine (Kemi 1ml)⁽³⁶⁾. The absorbance of the supernatant solution predicted to determine the remaining dye concentration and measured before and after adsorption process by single beam spectrophotometer (Systronics Visiscan 167). The adsorption efficiency qe (mg/g) at various times was amount calculated using following equation-1.

$q_e = (C_i - C_e)V/W$ ------ 1

Where, Ci is the initial MG concentration (mg/L), Ce is the concentration (mg/L) of MG solutions at given time t, V is the volume (L) of the MG solution and W is the weight (g) of low cost carbon. The percentage removal of MG from solution was estimated using the following equation.5

Percentage removal =(C_i-C_e)/C_i x 100 -----2

Where, Ci and Ce are initial and final absorbance of MG solutions before and after adsorption. The consequences of different parameters such as effect of pH, adsorbent dose and agitation time were studied. The obtained kinetic data were applied to various kinetics models: pseudo –first- order, pseudo-second-order, intraparticle, Elovich, Natarajan-Khalaf, Bhattacharya and Venkobachar.

Name	Molecular structure	Nature	M _w (g/mol)	λmax (nm)
Malachite green (Basic green 4)	H ₃ C N CH ₃ Cl- Cl- CH ₃	Cationic	329.5	617

Table-2.1: Physicochemical characteristics of used dyes

3. Instrumentation

Scanning electron microscope (XRD) (model – VEGA3 TESCAN, Ganthi gram rual institute Dindigul (Dstrict) Tamilnadu.) was used to observe the morphology of the low cost carbon(SVC, ZMC, SVVC, CPC, and PJC adsorbents).First ,the low cost carbon were allowed swell to reach chemical equilibrium in distilled water at room temperature, and then exchanged by to obtained dried adsorbents. Finally, samples were powder carbons adsorbents onto the gold surface to perform XRD. Fourier-transform infrared (FT-IR) spectra were recorded using SHIMADZU – 1800 FT-IR spectrophotometer in the wave number range 400-4000 cm⁻¹.After equilibrium the dye loaded IPACswas filtered through filter paper. The dye loaded and pureIPACs were dried at 50 °C in a heating oven. The samples were grounded in an agate pestle and mortar with KBr. The background obtained from KBr disc was automatically subtracted from the samplediscs spectra prepared with KBr. Totally spectra were plotted using the similar scale on the transmittance axis.UV –visible spectra were collected using a SHIMADZU– 1800, UV-visible spectrometer. This instrument was used for the adsorbent surface analysis both before and after MG-dye treatments.

3.1. Characterization of spectra

3.1.1. UV-Visible spectroscopy

The UV-vis absorption spectra of the as-prepared samples are shown in Fig.3.2a, b, c, d and 3.2e. It is observed that the MG- low cost carbon showed a strong absorption below a wavelength of 400 nm, mainly attributed to the optical band gap of low cost carbon materials .The absorption Spectrum was absorption studied 200 nm to 800 nm wavelength. The UV –Vis absorption spectra Fig.3.1 a,b,c,d,e.



Fig.3.1a.After Adsorption of SVC

Fig.3.1b.After Adsorption of ZMC



Fig.3.1c.Free dye MG and After Adsorption of SVVC

Fig.3.1d.After Adsorption of CPC



Fig.3.1e.After Adsorption of PJC

3.1.2. FT-IR spectroscopy



Fig 3.2.a Free IPACs FT-IR

Fig 3.2.b Loaded IPACsFT-IR

Fable 3.1: Analysis of FT-IF	data of free IPACs	/IPACs loaded with Dye
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Frequency LCC	(cm ⁻¹)free	Assignment of groups	Frequency (cm ⁻¹)LCC loaded with MG-Dye.		Assignment of groups
A)MG-Dye	2360	R-C=C-H			
				2720	C-H str (in CHO)
	1736	vC=O str	B)After-SVC	2375	R-C=C-H
				1845	C=O str (acyl fluorides)
B)free-SVC	1391	R-C-Fstr		2705	C-H* str
, ,			C) After - ZMC	1860	C=O str (acyl fluorides)
C)free-ZMC	2343	R-C=C-H	D) After - SVVC	2705	C-H*str
D)free-			E) After –	1860	C=O str(acyl fluorides)
SVVC			CPC	1468	C-H in methyl
E)free-CPC	655	N-H def(out of plane band)	E) After – PJC	1860	C=O str(acyl fluorides)
E)free-PJC					
3.1.3. XRD	•	•	•	•	

X-ray diffraction (XRD) analyses of prepared magneticactivated carbonsample were carried out with X-ray. Madurai Kamarajar University Diffractometer model (Diffractometer system=XPERT-PRO). XRD patternsare given inFig 3.3, 3.4, 3.5, 3.6 and 3.7 respectively. The XRD pattern shows a crystallinestructure and indicates the amorphous character of the carbonmatrix in which powder particles is impregnated. The X-raydiffraction patterns for IPACs show a number of sharp peakswhich are compatible with the presence of high peak. Ion measurement was used to determine the crystal structure of the adsorbents. Upper peaks and broadness be there observed in acid activated samples than the non-acid activated samples. Also, the occurrence of high diffraction peaks and broadness are sign of good crystallinity of the prepared powdered samples. The intensities for each samples as presented in Fig 3.4, 3.5 and 3.6 are in the range of $10-79^\circ$ = 20. Thus, this indicates that other low intensity peaks corresponding to other crystalline phases of carbon have also been observed.



Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.39(2)	27(5)	0.3(1)	3.37415	73.57
38.14(2)	24(8)	0.15(8)	2.35744	66.05
44.40(1)	36(9)	0.13(6)	2.03883	100.00
72.49(2)	29(6)	0.23(9)	1.30283	79.62
75.45(5)	10(4)	0.3(2)	1.25886	28.46

Fig 3.3 After SVC



Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
44.626(5)	148(14)	0.15(2)	2.02890	100.00
72.57(1)	87(8)	0.33(5)	1.30156	59.27

Fig 3.4After ZMC



Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
5(1)	18(5)	3(1)	17.24005	11.70
44.53(3)	22(4)	0.5(1)	2.03292	14.50
49.07(5)	19(5)	0.5(2)	1.85487	12.52
72.610(7)	154(9)	0.38(3)	1.30100	100.00

Fig 3.5After SVVC



Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int.
25.44(3)	37(4)	0.83(9)	3.49836	26.17
44.577(6)	140(14)	0.14(2)	2.03101	100.00
60.220(4)	87(9)	0.090(9)	1.53549	62.09
72.59(1)	56(4)	0.45(4)	1.30137	40.24

Fig 3.6AfterCPC



Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d- spacing [Å]	Rel. Int. [%]
44.55(2)	29(9)	0.1(1)	2.03237	81.33
72.60(2)	36(7)	0.3(1)	1.30122	100.00

Fig 3.7After PJC

4. Results and Discussion

The adsorption experiments are carried out at different experimental conditions (Tables 4.1 and 3.1) and the results obtained are discussed.

Table 4.1: Experimental conditions of adsorption experiment for the removal of MG by various adsorbents 30 ± 1^{0} C

Variation	Adsorbents	Initial	Contact	Dose of IPACs	Initial
		(PPM)	lime (Min)	(g/L)	рн
Initial	SVC				
Concentration(PP	ZMC	52 to 66	30*	1	7.4*
M)	SVVC				
	CPC				
	PJC				
Contact Time	SVC				
(Min)	ZMC				
	SVVC	58*	5-40	1	7.4*
	CPC				
	PJC				
Dose of Acs(g/L)	SVC				
	ZMC				
	SVVC	58*	30*	0.2 to 1.6	7.4*
	CPC				
	PJC				
Initial pH	SVC				
	ZMC				
	SVVC	52 to 66	30*	2 to 12	2-12
	CPC				
	PJC				

*Optimum Values

4.1.Effect of Initial Concentration;

The Effect of Initial Concentration on the extent of removal of MG dye (in terms of percentage removal (%R) and amount adsorbed (q)) on various adsorbents were studied and the experimental parameters are given in Table 4.1 and Fig4.1. The percentage removal was found to decrease exponentially, while the amount of dye adsorbed increased exponentially with the increase in initial concentration of MG. This is due to the rapid uptake of the MG dye at lower concentrations due to surface mass transfer. This is attributed to the lack of available active sites required for the high initial concentration of dyes. It was also observed that in carbons, the increase in initial concentration of the dye decreased the percentage removal. The percentage removal decreased yet the adsorption capability increased with increase in concentration. Similar results have been reported in literature on the extent of removal of dyes^(1,2,16,24,40), metal ions⁽⁴¹⁾ and carboxylic acids^(42,43).



Fig 4.1Effect of initial concentration for the removal of MG on IPACs

4.2. Adsorptions isotherms

Adsorption things and equilibrium data, usually known as adsorption isotherms, describe how pollutants interact with sorbent materials and so are critical in optimizing the use of adsorbents. In order to optimize the

design of an adsorption system to remove dye from solutions, it is important to establish the most appropriate correlation for the equilibrium curve⁽⁴⁴⁾. In this study, six isotherms were used for describing the experimental results, namely Freundlich isotherm, Langmuir isotherm, Temkin isotherm, Redlich-Peterson isotherm, Dubinin-Radushkevich isotherm and BET isotherm.

In this study, the equilibrium experimental data for adsorbed MG on ACs were analyzed using the Freundlich and Langmuir isotherms⁽⁴⁵⁾. The Freundlich isotherm is the earliest known relationship describing the sorption equation⁽⁴⁶⁾. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules and a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface⁽⁴⁷⁾. The presentation of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorptionalcentres of an adsorbent. This isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation:

Freundlichisotherm:log $q_e = \log K + (1/n)\log C_e$ --- (4.1)

By plotting log q_e versus log C_e enables to determine the constants K and 1/n (Figure 4.2).



Fig 4.2Freundlich isotherms for the removal of MG on IPACs

The Langmuir sorption isotherm is most widely used for the sorption of a pollutant from a liquid solution. The model is based on several basic assumptions $^{(48)}$.

- i. The sorption takes place at specific homogeneous sites within the adsorbent
- ii. Once a dye molecule occupies a site
- iii. The adsorbent has a finite capacity for the adsorbate (at equilibrium, a saturation point is reached where no further adsorption can occur)
- iv. All sites are identical and energetically equivalent (the adsorbent is structurally homogeneous)

The equation of Langmuir is represented as follows:

Longmuir isotherm: $(C_e/q_e) = (1/Q_0b) + (C_e/Q_0)$ ---- (4.2)

Langmuir parameters have been obtained from the linear correlation between the values of C_e/q_e and C_e (Fig4.3).



Fig 4.3Langmuir Isotherm for the removal of MG on IPACs

Parameters	Adsorbent	S			
	SVC	ZMC	SVVC	CPC	PJC
Freundlich Isot	herm				
Slope(1/n)	0.24997	0.24904	0.31419	0.37413	0.30846
Intercept(log	0.25996	0.22454	0.19259	0.15212	0.13953
<i>k</i>)					
r-value	0.94528	0.97897	0.97152	0.98312	0.8959
Langmuir Isoth	erm				
$Slope(1/Q_o)$	0.60834	0.60834	0.47049	0.37166	0.40783
Intercept1/Q _o b	0.62042	0.83801	0.93272	1.08837	1.31978
r-value	0.98684	0.96956	0.95518	0.91514	0.67122
$Q_o(mg g^{-1})$	101.5	80.43	66.62	44.2	57.20
$b(gL^{-1})$	1.198	0.101	0.261	0.226	0.559
$R_L = 1/(1 + C_o b)$	0.002	0.083	0.100	0.014	0.017
Temkin Isother	m	•	•	•	·
A (L/mg)	150.6	4.016	11.17	36.89	26.85
B	76.70	40.387	18.55	44.42	25.84
r-Value	0.9858	0.9898	0.9597	0.9766	0.9781
Redlich Peterso	n Isotherm		•		
K_R	340.5	77.48	16.85	36.84	15.78
αR	0.565	0.824	0.287	0.274	0.514
В	1.094	1.348	0.748	1.724	2.828
r-Value	0.97749	0.86913	0.93896	0.88883	0.68013
DubininRadush	kevichIsoth	erm	•		
$X_m (mgg^{-1})$	4.482	4.585	6.854	5.842	6.487
$E(kJmol^{-1})$	30.425	26.45	36.47	25.84	20.53
$K(mol^2kJ^2)$	0.0007	0.0004	0.0001	0.0003	0.0004
r-Value	0.59506	0.54275	0.97156	0.97276	0.8705
BETIsotherm				•	•
Slope	-5.2377	-11.2043	-15.05457	-2.26098	-1.79129
Intercept	2.31776	4.79405	6.23799	1.13242	0.91058
r-Value	0.66797	0.77697	0.74586	0.98465	0.95665

 Table 4.2:Isotherm parameters for the removal of MG by adsorption on IPACs

Temkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This relates the heat of adsorption and surface coverage of the dye molecules on the adsorbent⁽⁴⁹⁾. This isotherm assumes that

- i. The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate interactions
- ii. Adsorption is characterized by uniform distribution of binding energies, upto some maximum binding energy⁽⁵⁰⁾.

$$q_e = B In A + B In C_e$$
 ----- (4.3)

Byplottingq_e versus C_e enables to determine the constants A and B (Fig4.4). Where A is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy and constant B is related to the heat of adsorption. The values of the parameters are given in Table 4.2.



Figure 4.4Temkin Isotherm for the removal of MG on IPACs

The Redlich Peterson isotherm can be used to describe adsorption on both homogeneous and heterogeneous surfaces⁽⁵¹⁾.

Log $[(K_R C_e/q_e)-1] = \beta \log C_e + \log (\alpha R) ----(4.4)$

by plotting the values of log [(K_RC_e/q_e)-1] against $\beta \log C_e$, the values of (αR) and β can be determined from the intercept log (αR) and the slope (β), respectively (Figure 4.5).



Figure 4.5Redlich Peterson Isotherm for the removal of MG on IPACs

The Dubinin-Radushkevich isotherm model was also applied to estimate the porosity apparent free energy and the characteristic of adsorption^(52,53,54). The D-R isotherm does not assume a homogeneous surface or constant adsorption potential.

In $q = In X'_m - K' \in {}^2$ ----- (4.5)

by plotting Inq against \notin ², give the parameters X'_m and K' from the values of intercept and slope (Figure 4.6).



Figure 4.6 Dubinin-Radushkevich Isotherm for the removal of MG on CAC and IPACs

The mean energy of adsorption (E, in kJ mole ⁻¹), can be calculated from the k' value using the following equation:

$$E = (-2K')^{-0.5}$$
 ----- (4.6)

Here, the magnitude of E is useful for estimating the mechanism of the adsorption reaction. In the case of E < 8 kJ/mole, physical forces may affect the adsorption. If E is in the range of 8-16 kJ./mole, adsorption is governed by ion-exchange mechanism, while for the values of E<19 kJ/mole, adsorption may be dominated by particle diffusion⁽⁵⁵⁾. From the experimental values (Table 4.2) it is confirmed that these processes are carried out through particle diffusion.

The BET equation is an extension of the Langmuir relationship that accounts for multilayer coverage (Figure 4.7).

 $C_e/X(C_o-C_e) = 1/X_mK + (k-1) C_e/X_mkC_o$ ------ (4.7)

Where,

Co and Ce are the initial and equilibrium concentrations

k is a constant related to the energy (enthalpy) of adsorption.



Figure 4.7BET Isotherm for the removal of MG on and IPACs.

The non-linearity in the BET isotherm plot is evidenced by very low values (0.335-0.437) which clearly indicate the absence of multilayer adsorption of MG on the adsorbents surface. The high values of 'r' obtained for the plot of C_e/q_e versus C_e reveal that the adsorption of MG over SVC, ZMC, SVVC, CPC and PJC follows Langmuir isotherm model. The Langmuir theory assumes that adsorption is localized in a monolayer and no interaction between adsorbate molecules taken place.

According to this theory, once dye molecule occupies a site, no further adsorption taken place at that site. Therefore, no further adsorption can take place once a saturated value is reached. The Langmuir isotherm also gives the value of monolayer adsorption capacity (Q_o , in mg g⁻¹). The value of Q_o indicates that all the IPACs are found to be suitable for dye removal. Among the IPACs, SVVC, ZMC, SVC, CPC and PJC has high value of monolayer adsorption capacity for the removal of MG.

Based on the correlation coefficient (r) the adsorption isotherm with SVVC, ZMC, SVC, CPC, and PJC can be better described by Langmuir equation. The applicability of the Langmuir isotherm suggests the mono layer coverage of the MG dye on the surface of the adsorbents. The mono layer adsorption capacities of the adsorbents are found to be of the order given below:

SVC < ZMC < SVVC<CPC<PJC

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (R_L , also called equilibrium parameter) which is defined by the following equation^(56,57).

 $RL = [1/(1+bC_i)]$ ------ (4.8)

Where,

Ci = optimum initial concentration of MG (mg L⁻¹)

 $b = Langmuir constant (L mg^{-1})$

The values of separation factor, R_L indicate the nature of the adsorption process as given here⁽⁵⁸⁾,

RL Values Nature of adsorption process RL>1 Unfavourable Linear Linear

$R_L = I$	Linear
$0 < R_L < 1$	Favourable
$\mathbf{R}_{\mathrm{L}} = 0$	Irreversible

In the present study, the values of R_L (Table) are observed to be fraction *i.e.*, in the range of zero to one (0.001-0.121). The fractional value of R_L indicates that the favourable nature of the adsorption process. Therefore the adsorption process is favourable for all these adsorbents.

5. Effect of Contact Time

The effect of contact tome on the extent removal and the amount of MG dye adsorbed on various adsorbents were observed at the optimum initial concentration of MG dye. The relevant data are also given in Table 5.1. The extents of removal of MG by these adsorbents were observed that the adsorption capacity increased with contact time Figure (5.1). During adsorption at some point in time, reached a constant value where no more dye was removed from the solution. At this point, the amount of dye being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of dye adsorbed from the adsorbent. The relative increase in the extent of removal of dye after 40 min., of contact time is not significant and hence it is fixed as the optimum contact time. Similar results have been reported in literature for the removal of dyes ⁽⁵⁹⁾, metal ions ⁽⁶⁰⁾ and carboxylic acids ⁽⁶¹⁾.



Figure 5.1 Effect of contact time for the extent removal of MG on IPACs

5.1. Kinetics of Adsorption

The kinetics and dynamics of adsorption of MG on various adsorbents have been studied by applying various kinetic equations of Natarajan and Khalaf⁽⁶²⁾, Lagergren⁽⁶³⁾, Bhattacharya-Venkobachar⁽⁶⁴⁾ and modified Elovich⁽⁶⁵⁾ equations.

Natarajan and Khalaf equation:

 $\log (C_i/C_t) = k(k/2.303)t ----- (5.1)$

Lagergren equation (First Order):

 $\log (q_e-q_t) = \log q_e - [k_{ad} / 2.303]t \qquad ----- (5.2)$

Lagergren equation (Pseudo Second Order):

 $t/q_t = 1/k_2 q_e^2 + t/q_e$ ----- (5.3)

Bhattacharya and Venkobachar equation:

 $\log [1-U(t)] = -(k_{ad} / 2.303)t \qquad ----- (5.4)$

Modified Elovich equation:

 $(C_i-C_t) = (1\beta) \ln (\alpha/\beta) + (1/\beta) \text{Int} ----- (5.5)$ Where,

 C_i and C_t = Concentration of MG at time zero and time t respectively (mg L⁻¹); q_e and q_t = Amount of MG adsorbed at equilibrium time and time t respectively; (mg g⁻¹)U (T) = [(C_i-C_t) / C_i-C_e)]; C_e = equilibrium concentration MG (mg L⁻¹); k = first order adsorption rate constant (min⁻¹).

The values of

- i. 1/q_t
- ii. $\log (C_i/C_t)$
- iii. log [1-U(T)]
- iv. $\log(q_e-q_t)$
- v. t/q_t were linearly correlated with contact time (t) and the values of first order rate constant, Δq (%) and correlation co-efficient (r values) are given in Table 5.1 and Figures 5.2-5.7.

The Elovich parameter β was obtained from the negative inverse of the slope of the linear plot of values of C_tagainst in t and α value can be obtained from the intercept [(1/ β) In (α/β)-C] of the plot by substituting the values of C_t and C_t.

Table 5.1Statistical result of kinetic equations and models for the adsorption of Malachite Green on IPACs at $30\pm1^{\circ}C$

Parameters	Adsorbents					
	SVC	ZMC	SVVC	CPC	PJC	
Natarajan and I	Khalaf equat	ion				
Correlation	0.95861	0.96156	0.88888	0.94939	0.79765	
coefficient (r)						
102K(min ⁻¹)	37.57	21.218	18.413	15.417	13.147	
Δq (%)	0.686	0.434	0.356	0.323	0.229	
Pseudo First Or	der					
Correlation	0.93531	0.98627	0.9813	0.97274	0.96678	
coefficient (r)						
$102 \text{K}(\text{min}^{-1})$	11.702	9.107	7.978	10.275	11.978	
Δq (%)	28.90	31.04	26.818	20.272	22.232	
Pseudo Second	Order					
Correlation	0.98961	0.99902	0.99879	0.99745	0.99751	
coefficient (r)						
102K(min ⁻¹)	26.75	18.42	12.45	13.752	14.875	
Δq (%)	0.1948	17.842	10.75	9.848	10.375	
Bhattacharya a	nd Venkobac	har equation		·		
Correlation	0.89936	0.85673	0.9973	0.9961	0.9976	
coefficient (r)						
102K(min ⁻¹)	11.702	9.107	7.978	10.275	11.978	
Δq (%)	25.48	22.47	19.495	16.174	15.16	
Modified Elovic	h equation					
Correlation	0.9734	0.9466	0.9942	0.9678	0.9643	
coefficient (r)						
Α	185.2	254.5	87.2	88.56	145.2	
В	0.175	0.048	0.178	0.085	0.345	
Δq (%)	82.75	41.25	25.23	34.26	15.05	



Fig 5.2 Natarajan and Khalaf kinetic plot for the removal of MG on IPACs



Fig5.3Pseudo first order kinetic plot for the removal of MG on IPACs



Fig 5.4Pseudo second order kinetic plot for the removal of MG on IPACs



Fig5.5Bhattacharya and Venkobachar kinetic plot for the removal of MG on IPACs



Fig5.6 Modified Elovich kinetic plot for the removal of MG on IPACs

The high values of correlation co-efficient (r values) indicate the applicability of first order kinetic model for the adsorption of MG on to IPACs. The r-values and k-values (Table 5.1) obtained from Pseudo first order equation for all the adsorbents are found to be almost equal with the values obtained from Bhattacharya and Venkobachar equation. Hence, any one of these kinetic equations could be used to calculate the first order rate constant for adsorptions for dyes.

In order to compare the validity of each model more efficiently a normalized standard deviation, Δq (%) is calculated using the following equations:

$\Delta \mathbf{q} (\%) = 100 \times \{ (\Sigma (q^{\exp}-q^{cal})/(q^{\exp}-1^2)/(\mathbf{n}-1) \}^{1/2} \dots (5.6) \}$

Where the superscripts, exp and cal are the experimented and calculated values of q, the amount adsorbed at different time t and n is the number of observations. The Δq (%) values are also given in Table 5.1. Based on the low values of Δq (%), it is calculated that the adsorption of MG can used the described by the Pseudo first order kinetic model.

5.5. Intra-Particle Diffusion Model

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through intra-particle diffusion/transport process, which is often the rate limiting step in many adsorption processes, especially in a rapidly stirred batch reactor⁽⁶⁶⁾. Since, the MG are probably transported from its aqueous solution to the ACs by intra-particle diffusion is another kinetic model should be used to study the rate

of MG adsorption onto ACs. The possibility of by intra-particle diffusion was explored by using the Weber and Morris by intra-particle diffusion model⁽⁵⁶⁾.

 $\mathbf{q}_t = \mathbf{k}_p t^{1/2} + C$ ----- (5.7) where, q_t = amount of MG adsorbed at time, t (mgg⁻¹) C = intercept k_p = intra-particle diffusion rate constant (mgg⁻¹ min^{1/2})

The value of C=0 means that the intra-particle diffusion is only rate determining step. The values of q_t are found to be linearly correlated with values of $t^{1/2}$. The r-values obtained are very close to unity. The k_p values are calculated and given in Table 5.2.

According to this model, if the plot of q_t versus $t^{1/2}$ gives a straight line, then the adsorption process is controlled by intra-particle diffusion, while, if the data exhibit multi linear plots, then two or more steps influence the adsorption process^(67,68,69). Each adsorption process have an intercept, indicating that the curve does not pass through the origin (Figure 5.7) leading to the conclusion that the removal mechanism of MG dye onto IPACs are complex and both the surface adsorption as well as intra-particle diffusion contribute to the actual adsorption process.

Table 5.2Statistical results of intra-particle models for the adsorption of Malachite Green on IPACs at $30\pm 1^{\circ}$ C.

Parameters	Adsorbents				
	SVC	ZMC	SVVC	CPC	PJC
Intra-Particle D	Intra-Particle Diffusion Model				
k _p	15.68	7.456	8.256	10.45	7.856
Correlation	0.9954	0.9926	0.9948	0.9959	0.9947
coefficient (r)					
Intercept	75.45	41.58	28.42	16.28	17.49
Log(%					
Removal)					
Vs Log(Time)		-			
Δq (%)	0.012	0.002	0.144	0.021	0.125
Slope	0.017	0.2458	0.562	0.245	0.187
Correlation	0.7992	0.9523	0.935	0.9538	0.9544
coefficient (r)					
Intercept	11.516	3.753	1.816	4.895	6.245
Δq (%)	1.574	1.235	2.589	5.805	2.1456

The values of intercept (C) given an idea about the boundary layer thickness, i.e., the larger the intercept greater is the boundary layer effect.

Log (% Removal) = C + m log (Time) ----- (5.8)

Where,

C = intercept and m = slope.

The correlation of the values of log (% removal) and log (Time) also resulted in linear relationship (Figure 5.8) which indicates that the process of intra-particle diffusion is taking place in these adsorption system (Table 5.2). The values of slope indicates the presence of intra-particle diffusion process as one of the rate limiting steps, besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously^(70,71,72).



Fig 5.7Intra-particle diffusion plot for the removal of MG on IPACs



Fig 5.8Log (%removal) and Log (time)plot for the removal of MG on IPACs

6. Effect of Dose of Adsorbents

The adsorption of MG on IPACs was studied by changing the quantity of adsorbents in the test solution while keeping the initial concentration, time temperature, and pH as constant at the particular contact time. Maximum MG removal was achieved within 10-50 min after which MG concentration in the reaction solution was almost constant. The effect of adsorbent dose on the removal of MG is shown in Fig 6.1. This figure reveals that the percentage removal of dyes increases with increase in adsorbent dosage. An increase in the adsorption with adsorbent dose can be attributed to increased MG surface area and availability of more adsorption sites^(73,74,75). The values of amount of dye adsorbed are found to vary exponentially with the fractional power term of the dose of adsorbent according to the following equation:

```
q_e = (dose) - n + C' ----- (5.9)
```

On taking logarithm

 $Log q_e = -n log (dose) + C$ ----- (5.10)

Where, q_e is the amount of dye adsorbed (in mgg⁻¹) at equilibrium contact time; C is the intercept value and C' and C are constants. This suggested that the adsorbed dye molecule may either block the access to the internal pores or causes particular to aggregate and there by resulting in the availability of active sites for adsorption. Similar observations have been noticed for the removal of dyes metal ions and carboxylic acids (42,61).



Fig 6.1 Effect of dose for the removal of MG on IPACs

6.1. Effect of Initial pH

The pH has been recognized as one of the most important parameters that affects any adsorption process. It influences the adsorption process by affecting the surface charge of adsorbent, the degree ofionization and speciation of the adsorbate⁽⁷⁶⁾. It is directly related with competition ability of hydrogen ions with adsorbate ions to active sites on the adsorbent surface ⁽⁷⁶⁾. Thus the effect of pH on the removal efficiency of MG was studied at different pH ranging from 2.0 to 12 results are shown in Figure 3.17. It was observed that the lower pH, the H⁺ ion concentration in the aqueous systems increased and surface of adsorbents acquires positive charge by adsorbing H⁺ ions.



Fig 3.17 Effect of pH for the removal of MG on IPACs

The positively charged surface sites do not favour the adsorption of cationic dye due to the electro static repulsion, cause decrease in the adsorption. At the pH of the aqueous system increases, the number of negatively charged sites increases by absorbing OH-ions. As the adsorbent surface gets negatively charged at higher pH, significantly high electro static attractions exist between the negatively charged adsorbent surface and cationic dye molecules, leading to maximum. Similar behavior was obtained by various authors on various adsorbents such as saw dust⁽¹⁴⁾, clay soil⁽⁷⁷⁾, agro-industry wastes⁽⁷⁸⁾, wood apple shell⁽⁷⁹⁾, grape fruit peel ⁽⁸⁰⁾and ginger waste⁽⁸¹⁾.

The following reactions were expected to occur on the solid/liquid interface.

S+H → (S) H⁺ (S) H⁺ + MG⁺→ (S)H⁺↔ MG⁺ (Electro static repulsion in acidic medium) S+OH⁻→ (S) OH⁻ (S) OH⁻ + MG⁺→ (S) OH⁻....MG⁺ (Electro static interaction in basic medium) S →Surface of adsorbent MG⁺→ Dye cation

7. Effect of Temperature

The effect of temperature on MG dye sorption on each sorbent is investigated in the temperature 30, 40, 50 and 60° C by varying initial concentrations. The sorption of MG dye enhanced with raising the temperature up to 60° C for all the concentrations studied indicating that a high temperature favoures the dye removal by adsorption onto all these sorbents. The increase in temperature affects the solubility and the chemical potential of the adsorbate⁽⁸²⁾. The amount of dye adsorbed decreased with the rise in temperature of dye solutions from 30 to 60° C. This was again confirmed from thermodynamic parameters such as free energy, enthalpy and entropy changes during the adsorption process.

The parameters were calculated at different temperatures and the values are presented in Table 8.1. The data also show that the effect of temperature is significant at higher dye concentrations. The enhancement in adsorption with temperature may be attributed to increase in number of active surface sites available for adsorption on each adsorbent, increase in the porosity and in the total pore volume of the adsorbent.

The enhancement in adsorption could be also due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. This may also be a result of an increase in the mobility of the dye molecule with an increase in their kinetic energy and the enhanced rate of intra-particle diffusion of sorbate with rise of temperature. The negative values of enthalpy indicate that the adsorption process is exothermic. Lower temperature was favorable for the adsorption process. The negative values of free energy changes confirm the spontaneity of adsorption. It is clear that the sorption of MG on the six sorbents is an endothermic process and MG dye sorption may involve not only physical but also chemical sorption⁽⁸³⁾.

8. Thermodynamic parameters

The thermodynamic parameters like ΔG^0 , ΔH^0 and ΔS^0 were obtained from the equilibrium constants (Table 8.1). The ΔG^0 values are found to be negative (range - 4.725 to -9.228 kJ mol⁻¹), which indicates that the adsorption process (for removal of dyes by ACs) is spontaneous and favorable*i.e.*, the adsorptive forces are quite strong enough to overcome the potential barrier between the adsorbate species in solid liquid interface ⁽⁸⁴⁾. The ΔH^0 values are computed to be positive (range: 24.715 to 34.217kJmol⁻¹) indicating the endothermic nature of adsorption process. The negative values of enthalpy indicate that the adsorption process⁽⁸⁵⁾. Since, the observed values of ΔH^0 are within this range, it reveals that the adsorption of MG by adsorbent is of physisorptive in nature.

Adsorbents	$-\Delta G^0$ (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	$\Delta SG^0 (J \text{ mol}^{-1} \text{ K}^{-1})$
SVC	9.228	34.217	147.282
ZMC	6.125	30.415	120.150
SVVC	4.725	27.565	108.145
CPC	7.815	24.715	98.935
PJC	5.215	26.756	125.156

The high positive values of ΔS (calculated from the plot of log k_{eqm}vs 1/T (Fig3.18) range: (98.935-147.282 J mol⁻¹ K⁻¹) indicate the increasing randomness at the solid-liquid interface during the process of adsorption. These observations are also in harmony with the results obtained in many chemical reactions⁽⁸⁶⁾.

Thermodynamic parameters indicate that the adsorption process is spontaneous, endothermic and physisorptive in nature. Hence, it is concluded that 'physisorption' is also taking place in addition to 'chemisorption'. Strong bonding occurs without affecting thebondingstructure of the adsorbate (dye) molecules⁽⁸⁷⁾.



Fig 3.18Plot of Log KeqVerus 1/T

9. Desorption

MG dye loaded adsorbents were desorbed with DD water and eluents like HCl, HNO_3 , H_2SO_4 , CH_3COOH and NaOH. The values of percentage of desorption with DD water and eluents (0.5M) are reported in table 9.1.Among these, nitric acid is found to be an effective eluent (Figure 9.1.).

Adsorbent loaded with	DD water	HCL	HNO ₃	H ₂ SO ₄	СН ₃ СООН	NaOH
MG						
SVC	56.4	83.4	92.8	86.7	82.5	75.2
ZMC	46.7	76.7	90.5	84.8	78.4	71.4
SVVC	40.1	68.6	88.9	78.4	72.8	65.4
CPC	38.4	64.8	91.7	72.3	65.9	57.4
PJC	36.5	71.3	88.4	74.2	60.5	54.7

Table 9.1 Extent of desorption (in%) of adsorbed MG using various eluents

The extent of desorption increases exponentially with the increase in concentration of HNO_3 . The optimum concentration of HNO_3 for effective desorption of MG from MG loaded adsorbents is fixed as 0.5M.



Fig9.1Extent of desorption of adsorbed MG using various eluents

The adsorption capacity of regenerated adsorbents is found to be less compared to the original samples, but it is also suitable for removal of MG and dilute solutions. This will again definitely lower the cost of removal of MG and effluent treatment process. Hence, all the IPACs could be used as low cost adsorbents alternative to IPACs for the removal of dyes, in general MG, in particular.

10. Conclusion

MG is found to adsorb strongly and the equilibrium is practically achieved in 30 min.

MG is found to adsorb strongly on the surface of carbons. The percentage removal of MG increases with decrease in initial concentration, initial pH and particle size and increases with increases in contact time and dose.

Adsorption data are modeled with the Freundlich, Temkin, Langmuir, Redlich-Peterson and Radushkevich adsorption isotherms and various first order, pseudo first and second order kinetic equations at 30 $\pm 1^{\circ}$ C.

The results suggest that pore diffusion *i.e.*, intra-particle diffusion is more important. Adsorption behavior is described by a mono layer Langmuir type isotherm. The adsorption process is found to be first order with intra-particle diffusion, as one of the rate determining steps.

The increase in ionic strength of the medium has shown a significant decrease in the removal of MG.

The present study concludes that, all the IPACs could be employed as low cost adsorbents as agricultural waste carbon for the removal of color and dyes from water and wastewater, in general and for the removal of MG, in particular.

Abbreviations

%R	-	Percentage removal of dye
a,b	-	Langmuir constants
MG	-	Malachite Green
IPAC(s)	-	Indigenously Prepared Activated Carbons
Ce	-	Equilibrium concentration of dye in ppm
Ci,Ct	-	Concentration of dye at time zero and time t, in ppm

СТ	-	Total Equilibrium concentration of dye
Eqm	-	Equilibrium
FT-IR	-	Fourier Transform Infra-Red spectra
XRD	-	X-ray Diffraction Analysis
UV	-	U-Visible region
gl ⁻¹	-	gram per litre
h	-	Hour
SVC	-	Sorghum Vulgare Carbon
ZMC	-	Zea Mays Carbon
SVVC	-	Sorghum Vulgare Varity Carbon
CPC	-	CeibaPeutandra Carbon
PJC	-	ProjobisJuliflora Carbon
K,1/n	-	Freundlich constants
k,kad	-	First order rate constants for adsorption(in min ⁻¹)
kJ mol ⁻¹	-	Kilo Joule per mole
kp	-	Rate constant for intra-particle diffusion Process
m	-	Mass
mg g^{-1}	-	Milligram per gram
mg l^{-1}	-	Milligram per litre or ppm
min.	-	Minute
ppm	-	Parts per million
q	-	Amount adsorbed/differential amount adsorbed (in mg g-1)
q _{max}	-	Maximum amount adsorbed for mono layer coverage
Qr	-	Total amount adsorbed (in mg g-1)
R, r	-	Correlation co-efficient
Х	-	Amount of dye removed / adsorbed
xi	-	Mole fraction of the ith component
Con	-	Concentrated
Concn	-	Concentration
pН	-	power of Hydrogen

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