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Fast and Efficient Elimination of Malachite Green Dye by Activated Carbon Derived from Fresh Water Micro Algae: Kinetics and Thermodynamic studies

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Abstract
The adsorption process of "Malachite green (MG)" dye was carried out by graphitic activated carbon derived from fresh water micro algae calcined at various temperatures. The batch mode experiments were studiedwith algal residue activated carbonsamples calcined at 400, 500 and 6000 C (ARAC). At varying constraintslikepreliminary MG strength, interaction time, pH and temperature, ARAC(600)exhibited highest removal of MG (93.9%) having initial concentration 20 ppm, within 15 minutes at pH~9. The powdered XRD analysis of the sample indicated the presence of carbon with C(002) plane and the "scanning electron microscopy(SEM)" image presenteda presence of micro and macro-pores. The adsorption process fitted well to "Langmuir isotherm model"signifying monolayer adsorption with uniform energies and no migration of adsorbate in the plane of the surface. The adsorption of MG onto ARAC followed a "pseudo-second order kinetics" depicting chemisorption mechanism as the rate controlling step. The standard parameters of thermodynamics (ΔS0, ΔG0 and ΔH0) designated adsorption was endothermic and spontaneous. These results proved the fastness and high efficiency of ARAC as anencouraging adsorbent for dye exclusion that are frequently found in surface water.

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I. INTRODUCTION

Dyes and pigments have extensive use in various industries includes but not limited to textile, paper, plastics, rubber, tannery, paints, and cosmetics. Color is a highly visible contaminant; it opposes the accepted conception of clean waterand shields a protective coverage for other types of toxic waste. It blocks thediffusion of sunrays into subterranean layers of water by reducing the light needed for photosynthetic organism and depletes of dissolved oxygen in water. The production of dyes is very huge amounting to nearly 7×105 tons per annum around the world, and approximately 3.2% of dyes are wasted by manufacturing, processing operations of industries and the industrial effluentsoriginateserious environmental pollution[1]. The recycle of treated wastewater is essential because of the reason: high levels toxicity into finishing processes. The textile dyes are having complex structures that are stable to auto-degradation, and must be removed from the effluents before being consumed by human being

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and animals.“Malachite green (MG)”, a triarylamethane textile’s dye that is banned to beemployed as colorant in eatable.Conversely, it is employeddeviously as a food coloring agent andis responsible for liver carcinogenesis. As a standard dye, itis widely used inpaper,cotton, leather, wool,silkand jute products. Additionally, MG applied intoaquaculture as a disinfectant to treat parasites, fungal and bacteria.Being a type-II toxin, MG dye is mutagenic and carcinogenic to humans.By uninterrupted contact ofinhalation and ingestion MG causessimpleproperties on human beings’nervous system and brain. Due to these reasons, theremoval of MG from the surroundings has become very imperative.

The amputation of unsafe dyes has been agreed out by filtration membrane, photo catalyzed degradation, microbiological process, oxidation, coagulation, flocculation,ozonation and adsorption[2]. Amongst the various methods adapted for dye removal, adsorption has been widely used as it is inexpensive, non-cumbersome and insensitive to toxins [3].The degradation of MG dye was considered using nano-particles of silver and titania [4],magnetic carrageenan/silica hybrid [5], magnetic metal-organic framework (MOF) [6] carbon nanotubes [7] andgraphene family materials [8]. The bright side of adsorption technique is its versatility and its simplicity in practical forms. But in contrast, the materials which are absorbent in nature are either pricey or cannot be stimulated for the large-scale solicitations. Further,carbonaceous materials derived from graphene have been lately proved to be toxic themselves [9].

The use of non-toxic, efficient and low cost waste materials as alternative adsorbents has gained importance for large scale treatment of waste water. V. K. Gupta et. al,have reported theremoval of dyes by adsorption with natural materials such as coal, deoiled soya, fly-ash and blast furnace slag. Adsorption of MG by a cost effective activated carbon, rice husk activated carbon (RHAC), reported 93.75% removal of MG at preliminary concentration of preferably 100 mg/L.Additional recently, MG dye has been removed by biological treatment using activated pithphora sp.,desmodesmus sp., chlorella vulgaris Beijerinck and dunaliellasalinaTeodoresco extracted from fresh water micro algae.

Though the above studies showed good activity by micro algal extracts', they lacked nearly total removal of the dye, adsorption mechanism and repeatability of the materials.In this work, we have used the activated carbon that is derived from fresh water microalgae as an adsorbent that is used for rapid removal of MG dye with greater efficiency, and possible mechanistic pathwayswith repeatability are reported.

II. MAERIALS AND METHODS

A. Materials

The green micro algae was collected from Ansupa Lake, near Bhubaneswar, Odisha. The composed fresh water micro algae was cultured on University hostel waste water. After 10-days of cultivation, distilled water was used twice for its washing, then it was hot aired oven dried preferably at 80.0°C for 48.0 h.“Malachite Green”, a cationic dye bearingchemical formula “C23H25N2Cl”, molecular weight 364.63g/mol, wassuppliedfromLobachemie.The double distilled &deionised water was employed in preparing all the obligatory stock solutions of the desired concentration.

B. Synthesis of adsorbent

The dried algae was ground to fine particles with a size 15-50 micrometer. The fine particles of biomass werecalcined in muffle furnace by varying the temperature from 400-800°C for 5h with a temperature gradient of 2°C/min in presence of N_2 gas. The activated carbon derived from algal residue were labelled as ARAC(T) where T = 400, 500, 600, 700 and 800°C.

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C.Batch mode studies

Adsorption kinetics can be studied by batch adsorption testing. Amount of 00.02 g about adsorbent aresupplementary to 20mlof MGexplanation with multipleprimary concentrations ranging from 20 to100 ppm. The different starting pH of MG solutions had beenmaintained by adding 0.1 N HCl and 0.1 N NaOH and measured by a pH meter. The batch mode adsorption experiments with varying pH, initial concentration, contact time and temperature were carried out in a multi-stirrer at 300 rpm. After equilibrium was reached, the MG concentration was determined spectro-photometrically at a λmax of 621 nm. The capacity of MG removal efficiency andequilibrium adsorptionof ARAC was considered by using the mass balance equation (1) and (2)

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

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

Where qe(mg/g) isthequantity adsorbed pergram of adsorbent,C0 and Ce (mg/L) are initial and equilibrium concentration of MG, it is concentration of MG at time t, m (g) is amount of adsorbent, & V (L) is capacity of solution.

D. Zero point charge (pHZPC)

The enlargement of positive charge on adsorbent surface with donation of more proton isfavoured; if pH is less than "pHZPC value". Conversely, if pH is more than pHZPC then adsorbent surface is characterized with negative charge. Batch mode study was conducted to obtain pHZPC of ARAC samples[25]. Initially, in 20 mL 0.1 M NaCl solution 20 mg of ARAC was added and through addition of 0.1 M HCl and 0.1 M NaOH initial pH (pHi) of NaCl solution maintained by pH ~ 0.5–7.5. Equilibration of suspension was achieved by stirring for 24h at at 25 0C followed by filtration and thus final pH (pHf) had beencalculated. Repetition of the procedure had beenoptimisedby 0.01 M NaCl solutions. Fromplot of pHfvs. pHi values, the pHZPCvalue was calibrated and calculated as 3.1 .

E. Physico-chemical characterization

Variablepoint"N2" desorption-adsorption technique at liquid N2 temperature (77K) by "ASAP 2020 (Micromeritis)" was performed to determine BET surface area, normalporediameter and porecapacity of prepared ARAC samples. UV visible spectrophotometerof V-750 JASCO model was used for adsorbate analysis. Scanning electron microscopic (SEM) images was obtained at 6000X magnification ofacceleration voltage of15 kV (Hitachi SE900). X-ray Diffraction Studies of the algal carbon from fresh water algae was conducted by employing Rigakucorporation, Japan X-rayDiffractometer 40KV/30mA, Model D/Max ULTIMA III . ThepH meterfrom standardSystronics was used for pH measurement.

F. Determination of superficial functional assemblies of activated carbon

Boehm's-titrationand FTIR-spectrophotometer were performed, to analyze the active groups that were present on purely activated algal carbon surface and the resultant mainly consisted about acidic groups. For acidic group analysis the titration was followed by addition of 0.5 g of ARAC into several flasks containing 50 mL of 0.05 N NaHCO3, Na2CO3, &NaOHsolutions and the process was followed for basic groupsanalysis by 50 mL about 0.05 N HCl solution. Acidity test, after 24 h 10 mlof ARAC mix solution of each of NaHCO3, Na2CO3 and NaOHsolutions were filtered and titrated against 0.05 N HCl solution beforehand standardized Na2B4O7 solution. Basicity was calculated through the filtrate of ARAC mix HCl solution and was titrated against 0.05 N NaOH solution earlier standardized through H2C2O4 solution.

G. Desorption studies

The separation of 20 mg/l MG dye loaded

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ARAC solution had beenideally performed by centrifugation (REMI). The filtrate was collected by using 42-Whatmanfilter paper & washed moderatelythroughdeionised water foreradicating any un-adsorbed dye. Then the washed-out adsorbent was stirred at 300 rpm with 50ml of distilled water for 1 h, adjusted to changed pH values and kept for 40min. The desorbed MG dye was estimated by UV-Vis spectrophotometer.

III.RESULTS AND DISCUSSIONS

H. Spectral and surface characterizations

As shown in Fig. 1, themicroporosity nature ofactivatedcarbon derived from micro algaewasdemonstratedthroughquickadsorption by nitrogen ona low relative pressure (Fig. 1a) and has pore size below 20A°(Fig. 1b). In spite of microporosity, the presence offunctional groups(acidic and basic) within activated carbon contributes significantly towards its adsorption ability,providing selective attractionto cations ontocarbon surface. Theefficacy of thesurface charges that facilitates adsorption mechanism of ARAC is strongly influence by the functional groups.

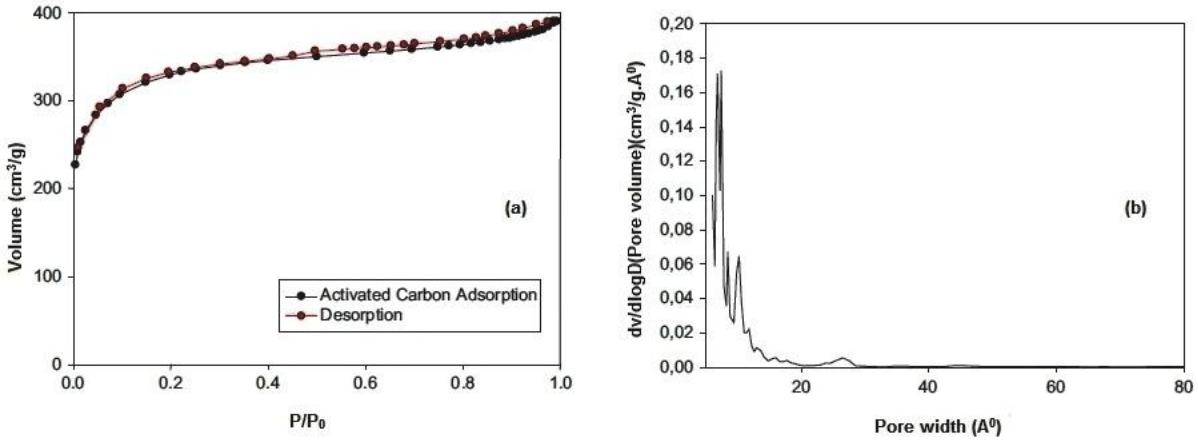
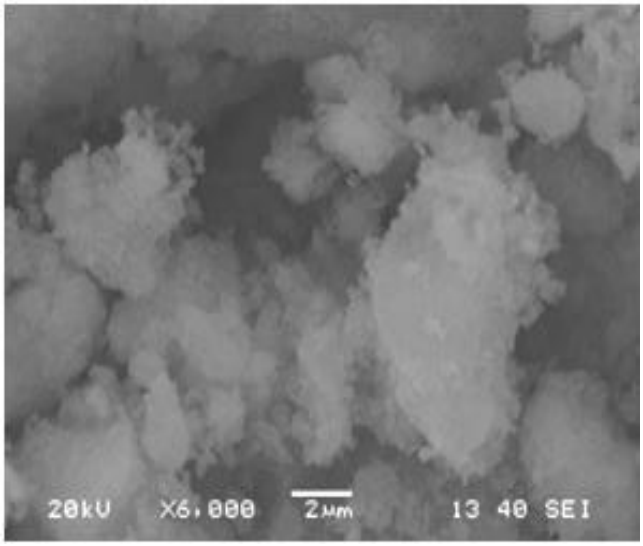


Fig.1. Nitrogen sorption curve (a) of ARAC(600), and (b) pore width value

I. SEM and XRD characterisation:

The surface morphology ARAC ischaracterisedabout SEM & XRD, as displayed in Fig.2(a) and Fig.2(b). Micrograph indicated the presence of crevices and pores having various sizes mostly in the micropore region. The XRD analysis showed peaks corresponding to 2θ = 200, 230 and250 corresponding to graphitic and reduced graphenic carbon. The peak at 2θ = 270 corresponds to the C(002) plane. As reported the higher temperature treatment hasproduced stacks of graphitic layers in the ARAC.



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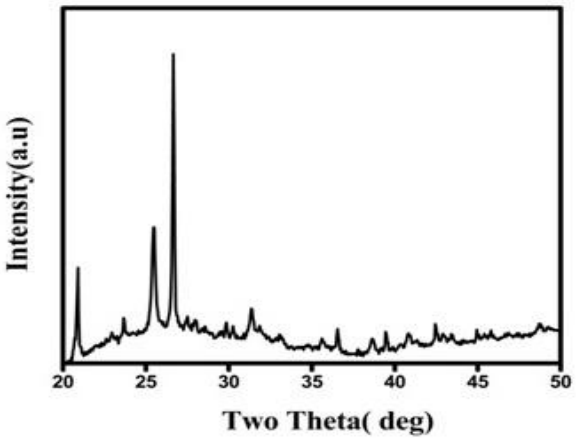

Fig.2 (a). SEM image of ARAC.
Fig.2(b). Powdered XRD pattern of ARAC.

J. Surface Chemistry

The FTIR spectroscopy analysis identifies the major active groups on the adsorbent and estimate the possible interaction of ARAC and MG. The obtained result from FTIR spectrum of ARAC showed the absorbance bands to have peaks at 3486, 2339, 1642, and 1154 cm−1. Reports from other investigators suggested the identification and presence of most of these bands for diverse carbon materials along with this band on around 3486 cm−1can be counted to–OH elongatingquivering of hydroxyl group.Band concerning on 2339 cm−1 has beencreditedfor the C≡C stretching. Peak on 1642 cm−1 has been identified as the C=O stretch of the carboxylic acid group. It was found that the peak concerning to 1154 cm−1 refers to the C–O changes in multiplegroups containing oxygen[28]

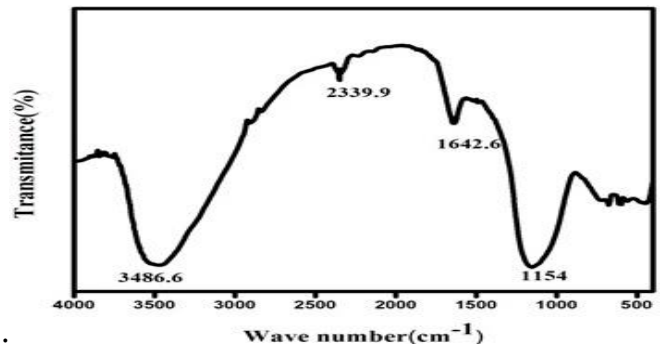

Fig.3. FTIR analysis of ARAC.

Table :1Assignment of infrared absorption bands

O-H stretching of hydroxyl group	3486
C≡C stretching of alkyne group	2339 1642
C=O stretching of lactones, ketones, and carboxylic anhydrides	1154
C-O groups stretching in ester, ether, or phenol group	

K. Effect of calcination temperature on number of surface active sites

Surface functional clusters in the pores of algal-activated-carbon have considerableinput towards the effectiveness of the adsorption process. These active groups are mostly carboxyl and phenolic groups that triggers surface charge & adsorption efficacy aboutalgal-activated-carbon. The microporosity nature of ARAC with maximum number of acidic functional groups is prevalent at a calcination temperature of 600°C[@]. As shown in Fig.5, the ARAC(600) removed a maximum 93% of MG dye compared to 84% and 83% for ARAC (400) and ARAC (500) respectively. Considerabledistinction exists on quantityabout itsbasic&acidicpurposefulassemblies with changing calcination temperature, satisfying the accurateness of the previouslyobserved pHpzc value of ARAC(600)which exists withinacidic range.

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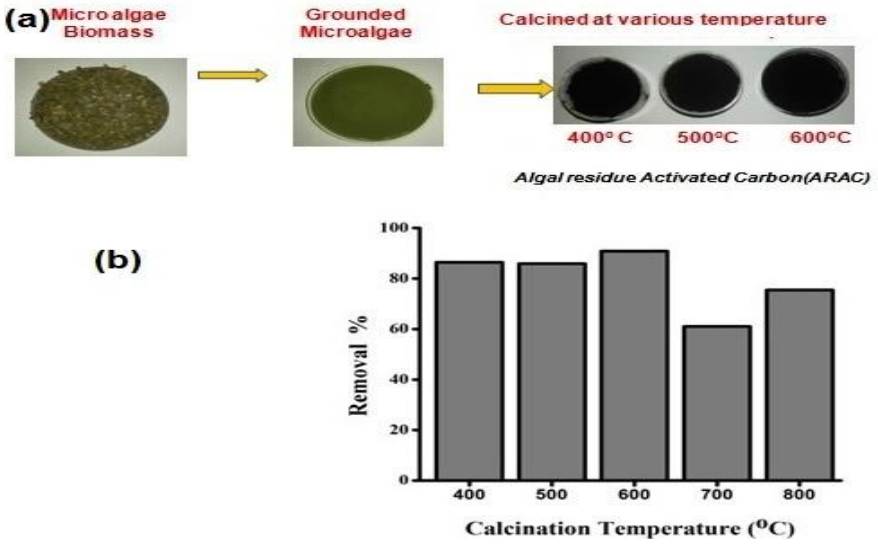

Fig.4.(a)Images of biomass before and after calcination,
(b)Removal percentage of MG dye by ARACcalcined at various temperatures.

L. Effect of adsorbent dose

In Fig.6 uptake of MG dye onto ARAC(600) decreased from 283 mg/g into 268 mg/g as amount about ARAC dosage improvedby 0.02 g to 0.08 g. Drop off in uptake of the dye may be credited to two factors. Firstly, the increase in the amount of adsorbent developed clumsiness inthe amount of sites which are active for optimum adsorption, thus decreasing the uptake of MG onto ARAC. Secondly, the acidic functional groups that were freely available to MG, encounter a competition of basic groups from active carbon with increase in their amount. Though there is increase in removal percentage of MG from 94% to 97% with increase in ARAC amount, the intake decrease is mainly due to surface and pore restrictions.

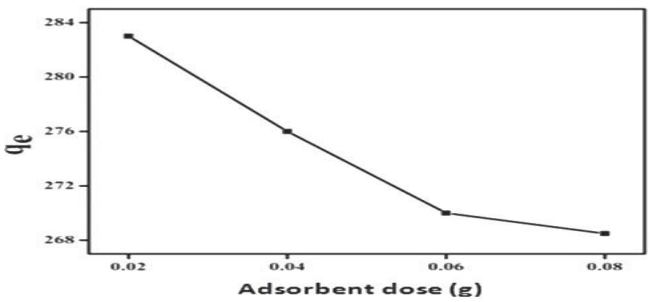

Fig.5. Uptake of MG with varying doses of ARAC (600).

J. Effect of pH

The pH valueshows a substantial role during adsorption process as it has huge impact on ionization degree of dye molecules&change in surface charges about the adsorbate ARAC. As Fig.6(a),illustrates the percentage removal onic dye i.e. MG onto ARAC have increased greater than before from 58% to 93% with an increase in from pH~2 to pH~10. After that the uptake remained constant with further increase in pH value. It is because of presence of positively charged H+ ions at lower pH thatcompeted with cationic MG dye thus decreasing the amount of adsorption. As schemed in Fig.8 higher pH values abundance about negatively charged OH- ions on surface of ARAC favouredtheadsorptionofpositively charged MG dye increasing the uptake for 93%.The presence of functional group on ARAC favours adsorption for the cationic dye i.e MG adsorption at pH>pHZPC. From the result, the pHZPC of discharge of ARAC(600) being 3.1.Above this pH the surface of ARAC(600)acquires more negative charge ion there by enhancing the acceptance of cationic dye MG due to electrostatic force of attraction.

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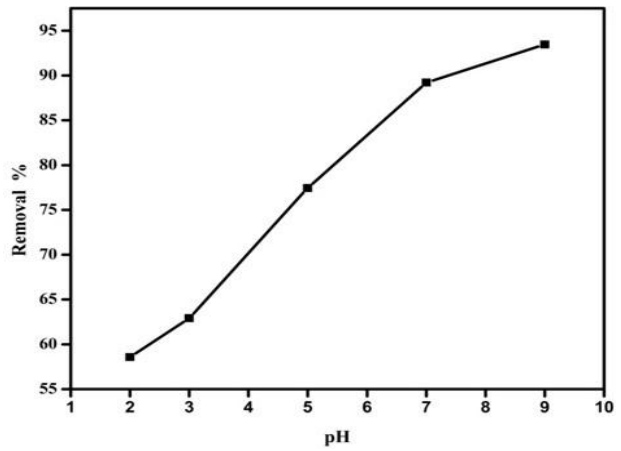

Fig.6 (a): Effect of pH on removal of MG by ARAC (600)

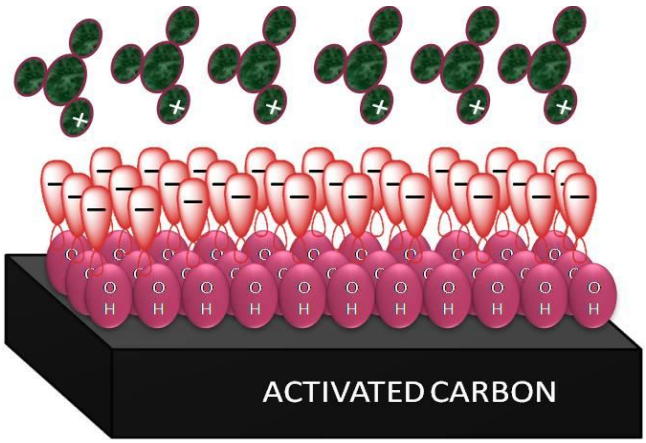

Fig.6(b): Mechanism of MG adsorption onto ARAC(600) at higher pH values.

K. Adsorption Isotherms

Langmuir and the Freundlich adsorption isotherms were considered for sorption isotherm analysis.

Langmuir isotherm

According to Langmuir sorption isotherm, sorption at a particular site ceases when considerable amount of adsorbate chemically occupies a fixed number of well-defined site. The significance is concerned to equivalent energy owned by all the sites with no lateral interface between adsorbate species. The Langmuir adsorption model is agreed as equation (3),

$$C_e/q_e = 1/Q_0 b + C_e/Q_0 \quad (3)$$

$C_e$equilibrium concentration about MG in solution (mgL^{-1}), $q_e$issolid phase concentration of adsorbateat equilibrium (mgg^{-1}),Q_0 indicates monolayer adsorption capacity (mgg^{-1})& b is Langmuir constant defined by adsorption energy.

The adsorption effectiveness had calculated about dimensionless equilibrium separation factor R_L, that is stated in equations (4),

$$R_L = 1/ 1+ bC_0, \quad (4)$$

where C_0 is starting concentration (mg/L). $R_L$rate gives shape for concerned isotherm to be either favourable adsorption ($0< R_L <1$) , unfavourable adsorption ($R_L>1$), linear adsorption ($R_L=1$) and irreversible adsorption ($R_L=0$).

Freundlich isotherm

Freundlich isothermsare mostly deployed in order to describe the multilayer nature of the adsorptionprogression. The continuation of sorption process is inclined towards the increase amount of adsorbate.This moderatelysuitable empirical can be employed for non-ideal sorption that includes heterogeneous sorption & that is expressed as equation (5),

$$q_e = K_F . (C_e)^{1/n} \quad (5)$$

.

The logarithmic form is given as equation (6),

$$\log q_e = \log K_F + n \log C_e \quad (6)$$

K_F is Freundlichsorption parameters(mg) and n is an empirical constant .High K_F and n value indicates about the binding capacity and affinity between ARAC and MG molecule. The value of n defines the nature of adsorption, high adsorption capacity ($2<n<10$), moderate adsorption ($1<n<2$) and small adsorption capacity ($n<1$).

Based on the application of both models i.e. Langmuir &Freundlichisotherm model to this study, implies existence of in cooperation monolayer adsorption and heterogeneous surface adsorption of

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MG onto ARAC(600). The value of regression coefficient obtained from these model used to discoverythe best fit, from the findings. Langmuir isotherm model is best fitted one. As shown in Fig. 7. The C_e/q_e Vs.$C_e$provides straight line through regression coefficient R^2 value 0.999 satisfying optimum adsorption.

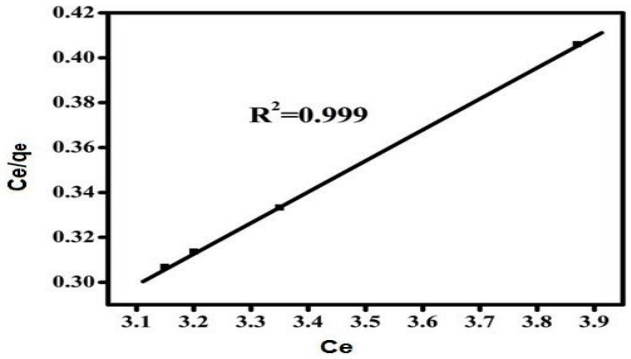

Fig.7. Adsorption isotherm of MG onto ARAC(600) fitted well to Langmuir model.

L. Special effectsabout agitation time & initial dye concentration

Outcomeabout agitation time on MG dye elimination by ARAC (600) asillustrated in Fig.8. Fraction of dye removal increasesthroughincrease in agitation time &after 20 min equilibrium had been attained toMG concentrationabout 100 mg/l used. During agitation 75% of MG was removed after 5 min that increased to 76.2% after 20 min and almost remained same through the upragein agitation time. Conversely, through increase into dye concentration through 20 for 100mg/l ratio about available surface becomes relatively low thereby decreasing the percentage MG removal from 95% to76%. It is obvious that initial attentiveness plays a vital role inpercentage removal aboutMG dye. Removal curves are distinct, even and constantleading to saturation. Similar studies have been reported as in table 2.

Table 2: Various studies on effects of concentration by various adsorbents.

Adsorbent	Pollutant	Increase in initial dye concentration range (mg/L)	Decrease in % removal efficiency	Reference
Chitosan/Alumina	Methyl orange	20 t- 400	99.53 to 83.55	[30]
Pine leaves	Methylene blue	10 - 90	96.5 to 40.9	[29]
Activated carbon derived from algal bloom	Cr(VI)	50 - 200	91.9 to 85.5	[32]
Sugarcane bagasse	Basic Blue 9	250-500	94 to55.5	[33]]
Rice husk	MG	10-30	82.5 to 71	[34]

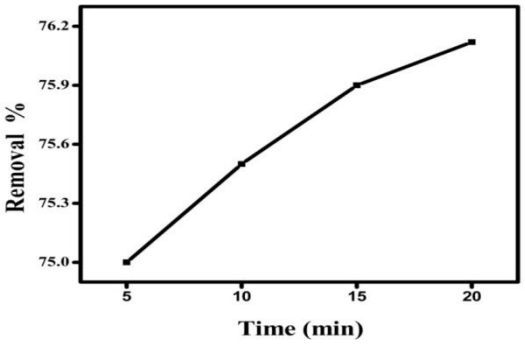

Fig.8. Agitation effect time onto removing of MG throughARAC(600).

M. Adsorption dynamics

The controlling mechanism was examined and detailed kinetic modelling for adsorption

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process was performed. The investigation of adsorption kinetics of MG dye by ARAC (600) in instruction to measure the rate & pathways of adsorption equilibrium, pseudo-first-order & pseudo-second-order mechanisms were verified.

Lagergren pseudo-first-order model may be applied for describing the adsorption rate by taking the calculated data experimental data and the regression coefficient is generally represented as equation(7).

$$\text{Ln}\,(qe - qt) = \ln qe - K1t \quad (7)$$

The pseudo-second-order kinetics in adsorption mechanism had been suggested throughMcKay andHo.Linear form of second order kinetics equations given in equation (8),

$$t / qt = 1 / K2\, qe2 + t / qe \quad (8)$$

qe is the quantityrelated to MG adsorbed per unit mass of ARACon equilibrium (mg/g), qt is quantity of MG adsorbed at time t (mg/g) , K1 is equilibrium rate constant of pseudo-first-order (min-1) , t is contact time (min) and K2 is the pseudo-second-order equilibrium constantrate (g/mg/min).

Plot of ln (qe – qt) versus time (t) fairly exhibit straight line by the R2 values above 0.90 as well as experimental and computed qe value (by intercept) does not concur, which notably disobeys Lagergren1storder kinetic model of MG adsorption.

The plot of t /qtwith t gives straight lines. Linearised plots of t / qt versus t having deterioration co-efficient (R2) standards more than 0.997 stabilizes a pseudo-second-order kinetics for MG adsorption by ARAC(600). Based on the result, the best fit model is pseudo-second-order by its relatively high correlation coefficient,R2 . Thus this model successfully describes that sorption process is controlled by chemisorptions, where the valence force are created by the exchange and sharing of electron between ARAC and MG dye.

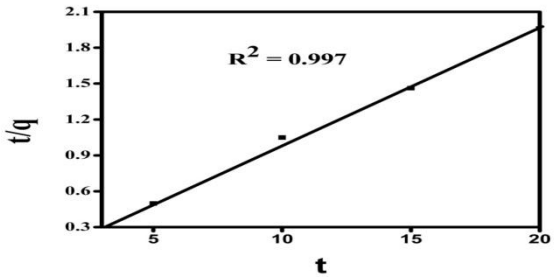

Fig.9: Kinetic studies of MG adsorption onto ARAC (600) that followed a pseudo-second order rate.

Table 3 :Kinetics studyparameterstobiosorption of MG onto ARAC

Time (min)	Co(mg/L)	Ce(mg/L)	Rate constant K_2 in 10^{-2} (L $mol^{-1}min^{-1}$)
5	20	3.35	4.4477
10	20	3.25	1.8377
15	20	3.19	1.6196
20	20	3.2	1.1894

N. Effect of Temperature

Temperature is notable controlling parameter since it influences the adsorbent by change in adsorption capacity. As illustrated in Fig.13. plot of removal percentage Vs. temperature indicated the removal of MG dye increased from 85% to 97% with upsurgeof temperature from 298 K to 318 K. This confirms adsorption of the dye onto ARAC(600) was favoured by temperature and the process was endothermic in nature. Due to increase in mobility about MG molecule and increase in number of active site of ARAC(600) .

O. Thermodynamics

Adsorption process is processed with the heat evolutionas more stabilization of adsorbate is attained on surface of adsorbent rather on bulk phase. In this research, the Henry's constant 'k', a

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temperature dependency factor abide with the van't Hoff equation (9),

$$d\ln k / dT = \Delta H / RT^2 \quad (9)$$

Where R is taken as the gaseous constant and T is taken as the temperature(Kelvin) and wherein, Δ H is the heat of reaction. The integrated form of the above equation is given by equation (10),

$$\ln k = \ln k0 + (- \Delta H / RT) \quad (10)$$

Thermodynamic contraints (ΔH) (ΔG), and(ΔS) explains about the spontaneity of the adsorption method and the inter-face of solid-solution (i.e ARAC-MG solution interface). Byvan'tHoff & Gibb's equations (11) & (12) correspondingly these parameters were furtheroptimized.

$$\Delta G = - RT \ln Ka \quad (11)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (12)$$

Ka is equilibrium contranits of adsorption.

It was observed about plot of lnKaVs 1/T (as dlnKa/dT = ΔH/RT2) change in enthalpy, ΔH is calculated. The parameters ΔS and ΔG are calculated from Eq. (11) and (12). From Table 5it is optimizedthat with increase in temp. there is decrement in value of ΔG from -11.59 KJ/mole (303 K) to -14.25 KJ/mole (323 K) which significantly increases the rate of adsorption. As displayed in Fig. 14. The plot "log K versus 1/T yielded straight line with regression coefficient R2 value 0.993 satisfying the optimum conditions of feasibility of the adsorption process".

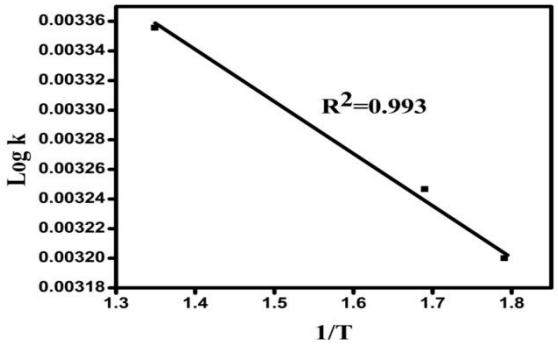

Fig.10:Vant' Hoff isotherm of MG adsorption onto ARAC(600).

Table 4: Comparision with other adsorbents

Source of AC (adsorbent)	Dye	Uptake amt.	Optimum Parameters	Adsorption Modelling	Reference
rice husk activated carbon (RHAC)	MG	94.91%	endothermic	Langmuir and Freundlich isotherms	Y.C.Sharma et.al, 2011
Durian seed activated carbon	MG	476.19mg/g	pH 8 , pseudo-second-order	Freundlich isotherm	M.A.Ahmed et al,; 2014
Lime peel activated carbon	MG	94.68%	Activation temperature796oC		M.A.Ahmad et al;2015
rubber seed coat based activated carbon(RSCAC)	MG	72.73 mg/g	pH 6	Langmuir isotherm model	M. N. Idrisa et.al, 2015
activated carbon produced from lemon peel	MG	66.67 mg/g	pseudo second-order rate	Langmuir model	S.Z. Mohammdia et.al, 2014

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Aactivated carbon from the wood of ThevetiaPeruviana(TPAC)	DB71	107.69 mg/g	Endothermic, pseudo- second order	Langmuir model	J. R. Baseri et.al, 2012
Activated Carbon Developed from Enteromorphaprolifera	RR23, RB171 and RB4	59.88, 71.94 and 131.93 mg·g−1	pH of 4.5 - 6.0, endothermic, Second-order kinetic	Freundlich isotherm	D. Sun et.al, 2013
Marine alga Caulerparacemosavar.cylindracea	MG	25.67mg g-1	Pseudo-second-order	Freundlich isotherm	Z.Bekci et al; 2008
Elaeagnus activated carbon (EAC)	(MG), (RB), (MB)	288.18, 281.69, 432.90 mg/g	Pseudo second-order kinetic model, endothermic.	Langmuir model	U¨nalGec¸gel et.al, 2016
Wood apple shell (WAS)	MG	80.645 mg/g	Endothermic,	Langmuir isotherm	S.Sartapeet.al, 2012
Pomegranate peel activated carbon (PPAC)	RBBR	94.36%	pH 2, pseudo-second-order,	Freundlich isotherm model	M. A. Ahmad et.al, 2014
Annonasqumosa seed (CAS)	(MG) (MB)	25.91 mg g−1 08.52 mg g−1	pH 6, pseudo-second-order	Langmuir model,	T. Santhi et.al, 2016
Rambutan seeds based activated carbon (RSAC)	MG	91.45%	Pseudo-second-order, Endothermic	Freundlich isotherm	M. A. Ahmad et.al, 2016
Brown marine algae turbinariaconoides	MG	66.6mg g-1	Pseudo-first-order, pH8	Langmuir isotherm	R.R kannan et al;2009
Dried cashew nut bark carbon	MG	20.09 mg g-1	pH 6.60		Parthasarathy et al; 2011
Biochar produced by liquefaction of sewage sludge	MG	49.3 mg g-1	Temperature 30oC		.L.Leng et al;2015
Antigononleptopus leaves powder	MG	89.50%	pH4 , exothermic	Langmuir isotherm	M.M.lanka et al;2017
MicroAlgae Residue Activated Carbon(ARAC)	MG	-99.90% 15 min.	Pseudo-second-order, Endothermic, pH ~9	Langmuir isotherm	This Work

Table 5: Thermodynamic parameters for the biosorption of MG onto ARAC

Temperature (K)	ΔG (kJ/mol)	ΔS (J/K/mol)	ΔH (kJ/mol)
298	-11.59	133.5	28.7
308	-12.92		
318	-14.25		

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IV. CONCLUSION

The substitution of natural adsorbents with advances materials for environmental remediation is the call of time. Activated carbon derived from fresh water micro algae was employed as a suitable adsorbent for MG dye elimination. ARAC(600) exhibited highest removal of MG (93.9%) having initial concentration 20 ppm, within 15 minutes at pH~9 and RT. The adsorbingmethod fitted well to Freundlichisotherm model indicatesmultilayer adsorption with uniform energies & no transmigration about adsorbate in plane of surface. Adsorption of MG onto ARAC followed pseudo-second order kinetics depicting chemisorption mechanism as rate controlling step. The standard thermodynamic parameters (ΔG,ΔH and ΔS) indicates the adsorption had been endothermic and spontaneous. These results proved the ultra-fastness and high efficacy of ARAC as a potential adsorbent for dye removal.

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MANUSCRIPT DETAILS

Paper Title: Fast and Efficient Removal of Malachite Green Dye by Activated Carbon Derived From Fresh Water Micro Algae: Kinetics and Thermodynamic studies

The transformed used of unwanted fresh water green microalgae into ARAC(600)resulted as a very good natural green biosorbent in removing MG at pH =9, initial concentration =20mg/Lwithin 15 min. The removal of MG was more efficient with the increase in calcination temperature to be 600oC. The uptake was more with increase in initial concentration and ARAC dose. It followed a Pseudo-second order kinetics and fitted well to Freundlich model. Therefore it is concluded that the utilization of unwanted green waste into an efficient algal based activated carbon can replace the need of highly cost activated carbon in adsorption process. Thus ARAC utilization enhances the efficacy of adsorption process for aqueous dye removal from surface water to be more greener and safer.

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