

ADSORPTIVE REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION USING ARECA HUSK CARBON

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ABSTRACT

The Present study explored the feasibility of using agro-waste Areca Husk as adsorbent for the removal of Malachite green from aqueous solution was investigated. Batch adsorption experiments were conducted to study the effect of sorbent dosage, particle size, contact time, initial dye concentration, pH and temperature for the removal of dye. Adsorption data were modeled using Langmuir, Freundlich, Temkin and Dubnin-Radushkevich adsorption isotherms. Adsorption kinetics was verified by pseudo-first order, pseudo-second order, intra-particle diffusion, Elovich and Bangham models. The kinetic adsorption data fitted the pseudo-first order kinetic model well and also followed the intra-particle diffusion model. Thermodynamic parameters have also been evaluated. The structural and morphological of activated carbon were characterized by FTIR and SEM studies respectively. The results have established good potentiality for the carbons particles to be used as a sorbent for the removal of MG from waste water.

Keywords: Adsorption, Kinetics, Malachite green, Thermodynamics, Areca Husk.

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INTRODUCTION

Every year millions of tonnes of agricultural by-products are generated. Fallen areca nut leaves, areca nut bunch waste and areca nut husk are the major by-product areca nut cultivation about 1317 tonnes of dried leaves, 822 tonnes of dried areca nut bunch waste and 224 tonnes of areca nut husk are estimated to be available annually in India. These are either wasted or burnt inefficiently in their loose form causing air pollution. Handling and transportation of these materials is difficult due to their low bulk density. These wastes can provide useful energy by converting in to adsorbent. In recent years, attention has been focused on the utilization of native agricultural by-products as sorbent^{1,2}. Generally, the sorption capacity of native agricultural by-products is low. In order to improve the sorption capacity of these materials, the agricultural by-products were converted into activated carbon³. Malachite green is mainly used to colour the material like silk, wool, jute, leather, cotton, paper and other industries. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenicity and respiratory toxicity. Histopathological effects of MG include multi-organ tissue injury. Significant alterations occur in biochemical parameters of blood in MG exposed fish. Residues of MG and its reduced form, leucomalachite green have been reported from serum, liver, kidney, muscles and other tissues as also from eggs and fry. Toxicity occurs in some mammals, including organ damage, mutagenic, carcinogenic and developmental abnormalities.

The aim of the present study is to prepare, characterize and evaluate the efficiency of using AHC as an adsorbent for the removal of MG. After considering the efficiency of dye removal, the study was extended for other adsorbate and such study has not been attempted earlier. The adsorption study was carried out systematically involving various parameters such as contact time, initial dye concentration, adsorbent dosage, particle size, pH and temperature. The data generated over this study have been tabulated and discussed. The cost of this activated carbon is estimated and which is 10 times less than that of commercially available activated carbons.

EXPERIMENTAL

Preparation of the Areca Husk adsorbent

The husk of Areca nut was obtained from an agriculture farm land Coimbatore (Tamil Nadu). It was cut into small pieces, dried in sunlight, then kept 75°C for 24 hours in hot air oven. The dried material was digested with H₂SO₄ in the ratio 1:1 and kept at room temperature overnight. Then it was washed with doubled distilled water to remove the excess acid and kept in hot air oven at 85°C for 12 hours. Then it was taken in an iron vessel in muffle furnace and the temperature was gradually raised to 550°C for an hour, ground well by using ball mill and then sieved into particle size of 100,150 and 250 BSS Mesh size sand kept in air tight containers for further use.

Preparation of MG dye solutions

MG supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate and was not purified prior to use. MG has a molecular weight of 364.9 g mol⁻¹. Chemical structure of the dye was shown in Fig.1. Distilled water was employed for preparing all the solutions and reagents. The dye stock solutions were prepared by dissolving accurately weighed dyes in distilled water upto the concentration of 1000 mg L⁻¹. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

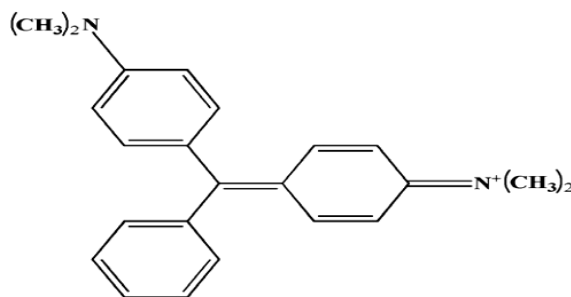


Fig.-1: Chemical structure of Malachite Green

Experimental methods and measurements

MG solutions were prepared with distilled water. Batch experiments were carried in a glass beaker by shaking a fixed mass AHC (150 mg) with 100 ml diluted solution (20-100 mg L⁻¹). After agitation, the solution was centrifuged at 1200 rpm with a required time at 27°C. Then the dye concentration of the supernatant solution was analyzed using a spectrophotometer by monitoring the absorbance changes at a wavelength of maximum absorbance (618 nm) in these adsorption experiments, the solution was used without adjusting pH. Each experiment was carried out duplicate and the average results are presented. Calibration curves were obtained with standard MG solution using distilled water as a blank. Mass capacity of adsorption q_e is calculated from the difference between the initial and final MG.

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

Where C_0 and C_e (mg L⁻¹) are the liquid-phase concentrations of dye at initial and equilibrium respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

SEM morphology

It is widely used to study the morphological features and surface characteristics of the adsorbent materials. Typical SEM photographs are shown in Fig. 2. It reveals that the AHC has a rough surface with more porous and caves like structure and it is supported with FTIR spectra as shown in Fig.3.

Determination of functional group

The FT-IR spectrum of MG on AHC before and after adsorption was detected in the range of 4000 to 400 cm^{-1} was presented in Fig.3. The band observed at 3425.58cm^{-1} was assigned to a $\nu(\text{O-H})$ stretching vibration. The absorption band at 2854.65 and 2924.09cm^{-1} can be attributed to the stretching vibrations of $\nu(\text{C-H})$ bonds in alkane and alkyl groups where carbon is bonded with hydrogen bonds. Adsorption bands at 2337.72 and 2376.30cm^{-1} corresponds to $\nu(\text{N-H})$ stretching. The band at 1573.91cm^{-1} shows the asymmetric $\nu(\text{-COO-})$ stretching. The band at 1450.47cm^{-1} may be attributed to the aromatic $\nu(\text{C=C})$ stretching vibration. At 1111.00cm^{-1} , the band is highly intense $\nu(\text{C-O})$ and is related to the $\nu(\text{C-O})$ stretching vibration of the bonds in ester, ether, or phenol groups. The band corresponding to 802.39cm^{-1} in the fingerprint area indicates a mono substituted aromatic structure. The weak absorption band at 678.94cm^{-1} corresponds to the $\nu(\text{O-H})$ vibration in the benzene ring. The band at 462.92 and 594.08cm^{-1} which were associated with the in-plane and out-of-plane aromatic ring deformation vibrations common that is quite common for activated carbon.

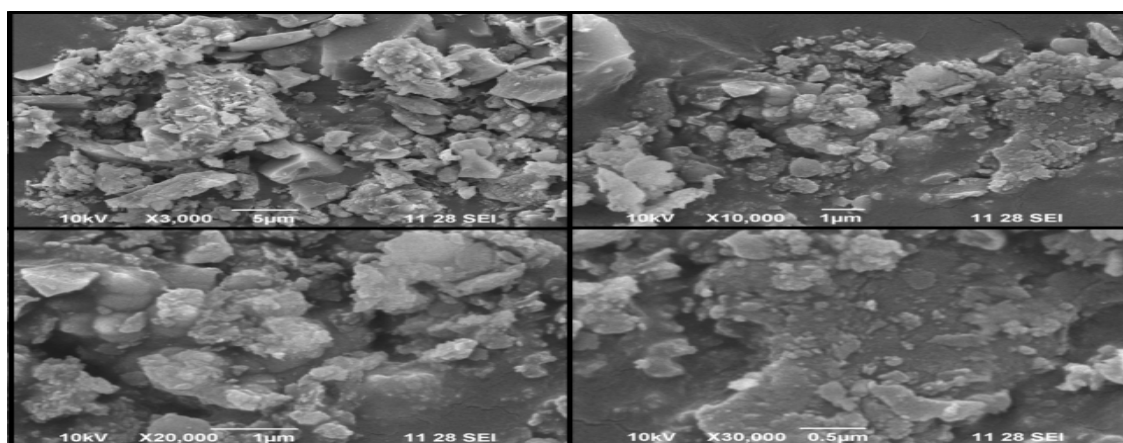


Fig.-2: SEM image of Fresh Areca Husk Carbon (AHC) at various magnifications

Effect of adsorbent dosage

The dependence of dye adsorption on carbon dose was studied by varying the amount of carbon from 100 to 250 mg / 100ml of the solution, keeping other parameters (pH, agitation speed and contact time) constant for the initial dye concentrations of 10 mg L^{-1} and which show the MG removal efficiency for different carbon doses. From fig. 4 it can be observed that removal efficiency is generally improved with increasing the carbon concentration upto a certain value and then, there is no further increase of adsorption. The removal efficiency of MG with the increase in carbon concentration is due to the greater surface area with more functional groups consequent to the increase in the number of carbon particles with more number of exchangeable sites for adsorption and saturation which occurred as a result of non-availability of exchangeable sites on the adsorbent. The increased removal at high dosages is expected due to the increased adsorbent surface area and availability of more adsorption sites. The removal of MG from the solution was noted at a initial concentration of 10 mg L^{-1} . The percentage of dye adsorbed increases along with the increase of adsorbent dosage from 50-250 mg L^{-1} . Above 150 mg of adsorbent dose the equilibrium of dye were reached and the % removal of dyes held almost no vary, so the AHC of 150mg was chosen for subsequent experiment.

Effect of particle size

The adsorption of MG was investigated at particle size 100,150 and 250 BSS mesh of the AHC and the results are represented in fig.4 it seems that with decrease in particle size the adsorption process increases to some extent. This could not be due to any substantial increase in surface area. It appears that large dye molecules are not able to penetrate to some of the interior pores of the particles when their size is large. Apparently access to all pores is facilitated as particle size becomes smaller resulting in higher adsorption.

As the particle of size 250 BSS mesh exhibit maximum adsorption capacity, all further detailed studies were done with this size only.

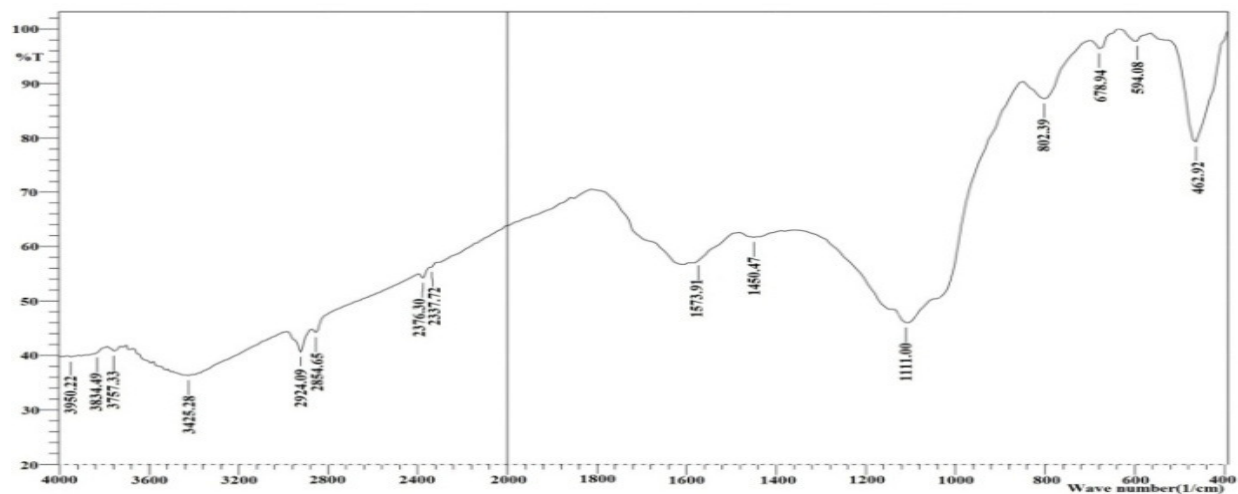


Fig.-3: FTIR spectra of fresh AHC

Effect of Contact time

The adsorption experiments were now carried out for different contact times with a fixed adsorbent dose (0.15 g) at room temperatures (Fig.5). It is observed that the uptake of the dye increases with time. The extent of adsorption is rapid in the initial stage and becomes slow in later stage till saturation is allowed. The final dye concentration did not vary significantly after 2 hours from the initial stage of adsorption process. This shows that equilibrium can be assumed to be achieved after 2 hours of contact time was found sufficient to acquire equilibrium. It is basically due to saturation of the active site which does not allow further adsorption. The adsorption rate was found to decrease with increase in time.

Effect of Initial dye concentration

The study of initial dye concentration was studied by varying the dye concentration from 5 to 20 mg L⁻¹ leads to a decrease in the percentage of the MG removal as shown in Fig.5. The rapid adsorption takes place in the first 30 min. Then the adsorption rate was decreased gradually and the adsorption reached equilibrium. This is because at low adsorbate/adsorbent ratio, the number of sorption sites in the AHC but as the ratio increases the adsorption sites are saturated, resulting to decrease in the sorption efficiency. At high initial concentration, the gradient between the solution sample and the centre of particle enhances dye diffusion through the film surrounding the particle and in the porous network of the AHC.

Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process. As shown in Fig.6 consistent increase in adsorption capacity of the AHC was noticed as the pH increased from 2 - 6, whereas in the range 2 - 10, after 6 the adsorption amount was only slightly affected by pH. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye cations due to electrostatic repulsion. In addition, lower adsorption of MG at acidic pH might be due to the presence of excess H⁺ ions competing with dye cations for the available adsorption sites.

Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The adsorption study was tested for five models i.e. pseudo first order, pseudo second order, intra- particle

diffusion, Elovich and Bangham's model. The experiments were carried out for time intervals varied from the 0 to 120 min at constant temperature, with 10 mg L⁻¹ and 20 mg L⁻¹ of MG by keeping other parameters constant.

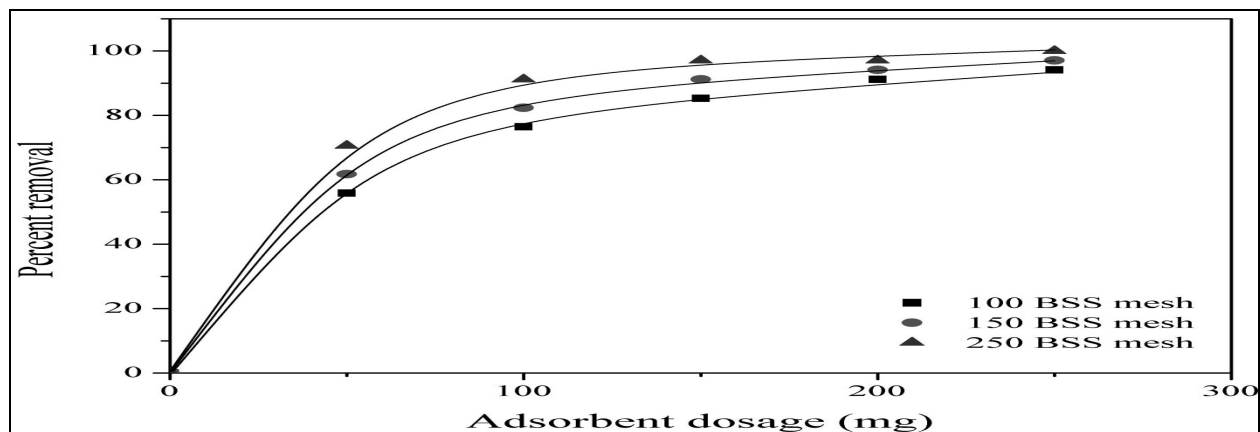


Fig.-4: Effect of adsorbent dosage and particle size on the removal of MG dye onto AHC

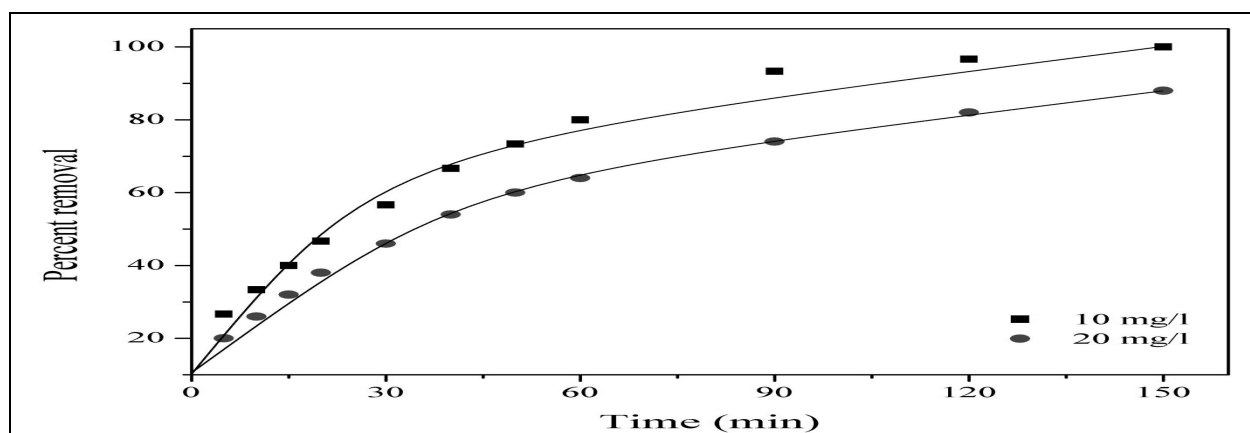


Fig.-5: Effect of contact time on the removal of MG dye onto AHC

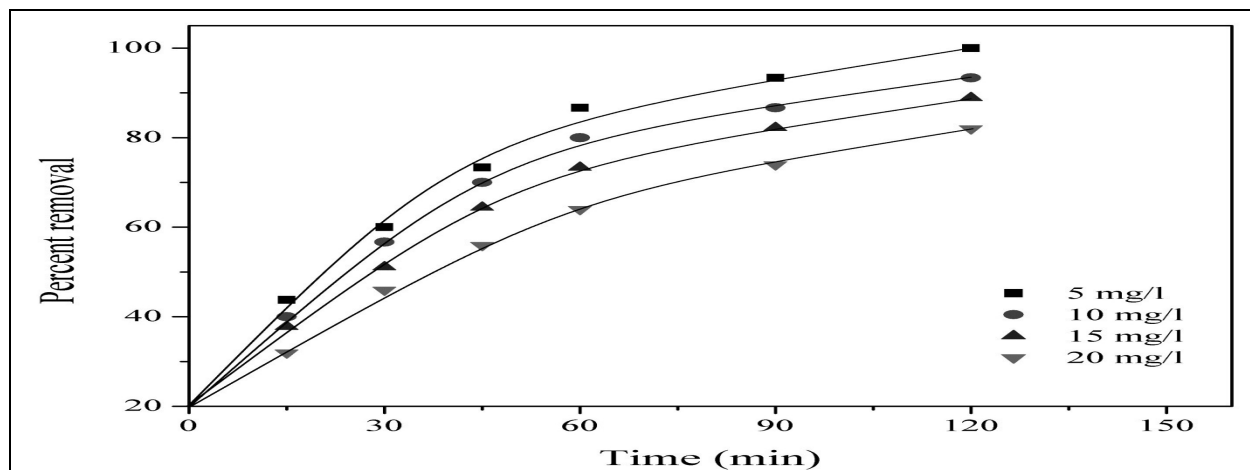


Fig.-6: Effect of Initial dye concentration on the removal of MG dye onto AHC

Pseudo first order kinetic model

Lagergren proposed a pseudo-first order kinetic model as given below⁴-

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption and q_t is the adsorption capacity at time 't' (mg g^{-1}). The rate parameters k_1 and q_e can be directly obtained from the intercept and slope of the plot of $\log(q_e - q_t)$ versus time t. The correlation values of R^2 were 0.9923 and 0.9936 for 10 mg L^{-1} and 20 mg L^{-1} respectively. The equilibrium adsorption capacities were 6.67 and 12.53 mg g^{-1} respectively. The calculated equilibrium adsorption capacities were 7.65 and 10.25 mg g^{-1} for 10 mg L^{-1} and 20 mg L^{-1} respectively. The calculated and experimental results reveal that, the pseudo-first order model provided a better approximation to the experimental kinetic data than the pseudo-second order model for adsorption of MG from aqueous solution.

Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is based on the assumption that the sorption follows second order chemisorption⁵. Pseudo-second-order kinetic model is given as-

$$\frac{dq}{dt} = k_2 ([q_e - q_t])^2 \quad (3)$$

After integrating we get -

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where k_2 [$\text{g mg}^{-1} \text{min}^{-1}$] is the rate constant of the pseudo-second order adsorption and q_t is the adsorption capacity at time 't' (mg g^{-1}).

The initial sorption rate h [$\text{mg g}^{-1} \text{min}^{-1}$] is defined as-

$$h = k_2 q_e^2 \quad (5)$$

Where k_2 is the pseudo-second order rate constant of dye adsorption. The plot of t/q versus t of eq(4) should give a linear relationship, from which q_{eq} and k_2 can be determined from the slope and intercept of the plot are listed in the Table-1. The correlation values are close to the unity. The rate constant k_2 were 0.1276 and 0.0721 $\text{g mg}^{-1} \text{min}^{-1}$. The calculated equilibrium adsorption capacities were 0.54 and 0.65 mg g^{-1} for 10 mg L^{-1} and 20 mg L^{-1} respectively. So, we conclude that the pseudo-second order is not totally adequate to describe the adsorption process.

Intra-particle diffusion model

There are essentially three consecutive mass transport steps associated with the adsorption of solute from the solution by an adsorbent. These are (i) film diffusion, (ii) intra-particle or pore diffusion, and (iii) sorption into interior sites. The third step is very rapid and hence film and pore transports are the major steps controlling the rate of adsorption. In order to understand the diffusion mechanism, kinetic data was further analyzed using the intra-particle diffusion model based on the theory proposed by Weber and Morris⁶. The intra-particle diffusion equation is given as-

$$qt = K_{int} t^{0.5} + C \quad (6)$$

Where q_t is the amount of AHC adsorbed (mg g^{-1}) k_{int} , the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$) and C is the intercept is listed in Table 1. k_{int} was determined from the slope of the plot of q_t versus $t^{0.5}$ (fig. 10). The calculated value of k_{int} is (0.52 - 0.88) $\text{mg g}^{-1} \text{min}^{0.5}$ and C is (0.85 - 0.93). The correlation coefficient (R^2) values of 0.9608 and 0.9869 for the AHC. The high R^2 value indicates that intra-particle diffusion might play a significant role in the initial stage of the adsorption. The value of intercept give an idea about the thickness of boundary layer i.e., larger the intercept greater is the boundary layer. The

double nature of plot may be explained by the fact that the initial portion is boundary layer diffusion effect while the final linear portion is the result of intra particle diffusion.

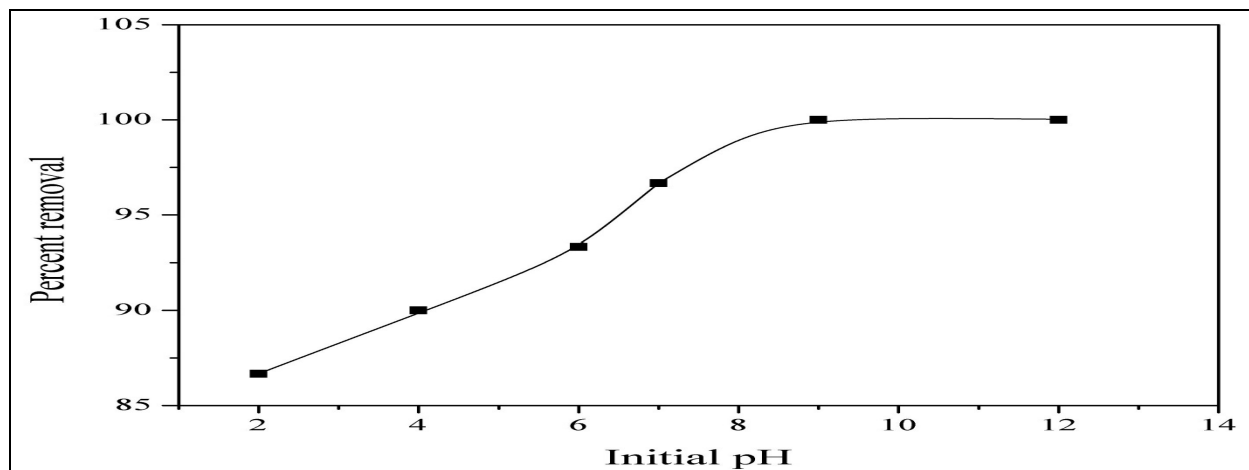


Fig.-7: Effect of pH on the removal of MG dye onto AHC

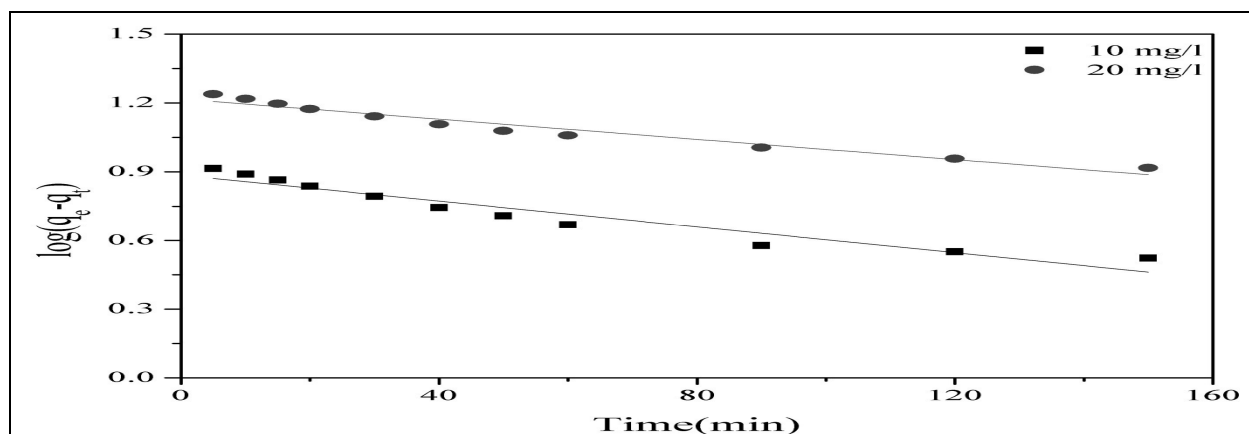


Fig.-8: Pseudo-first order kinetics for the adsorption of MG dye onto AHC.

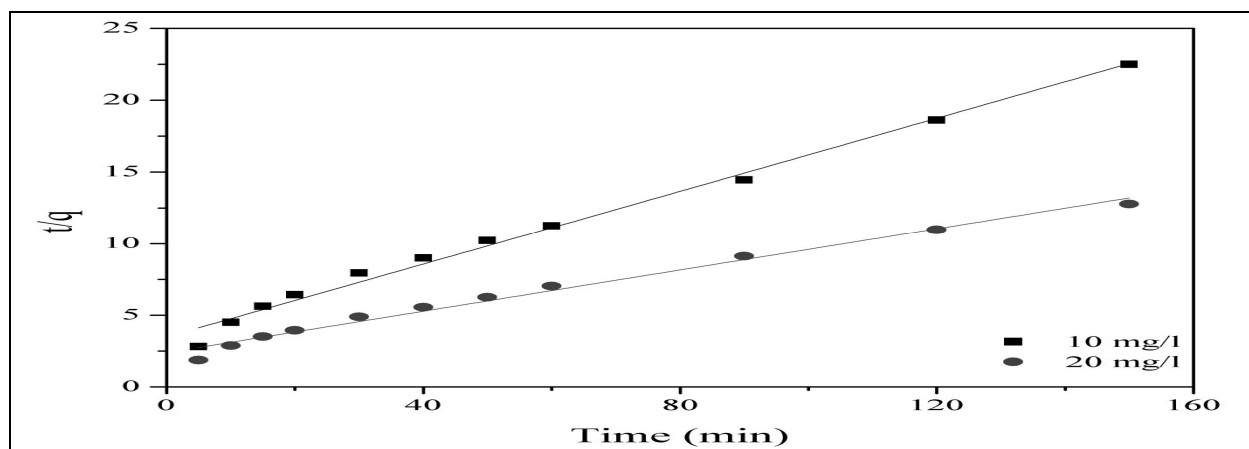


Fig.-9: Pseudo-second order kinetics for the adsorption of MG dye onto AHC

Table-1: Kinetic Parameters for the adsorption of MG dye onto AHC

Kinetic model	Model coefficients		
		$C_0 = 10\text{mg L}^{-1}$	$C_0 = 20\text{ mg L}^{-1}$
Pseudo- first order	$q_e (\text{mg g}^{-1})$	6.67	12.53
	$q_{\text{cal}} (\text{mg g}^{-1})$	7.65	10.25
	$k_1 (\text{min}^{-1})$	0.0051	0.0038
	R^2	0.9923	0.9936
Pseudo-second order	$q_{\text{cal}} (\text{mg g}^{-1})$	0.54	0.65
	$k_2 (\text{g mg}^{-1} \text{min}^{-1})$	0.1276	0.0721
	$h (\text{mg g}^{-1} \text{min}^{-1})$	1.4936	0.4119
	R^2	0.9930	0.9880
Intra-Particle diffusion	$k_{\text{int}} (\text{mg g}^{-1} \text{min}^{-0.5})$	0.52	0.88
	C	0.85	0.93
	R^2	0.9608	0.9860
Elovich	α	0.2484	0.0542
	B	0.6215	0.3548
	R^2	0.9761	0.9749
Bangham's	K_b	0.0320	0.0257
	A	0.4344	0.4642
	R^2	0.9844	0.9939

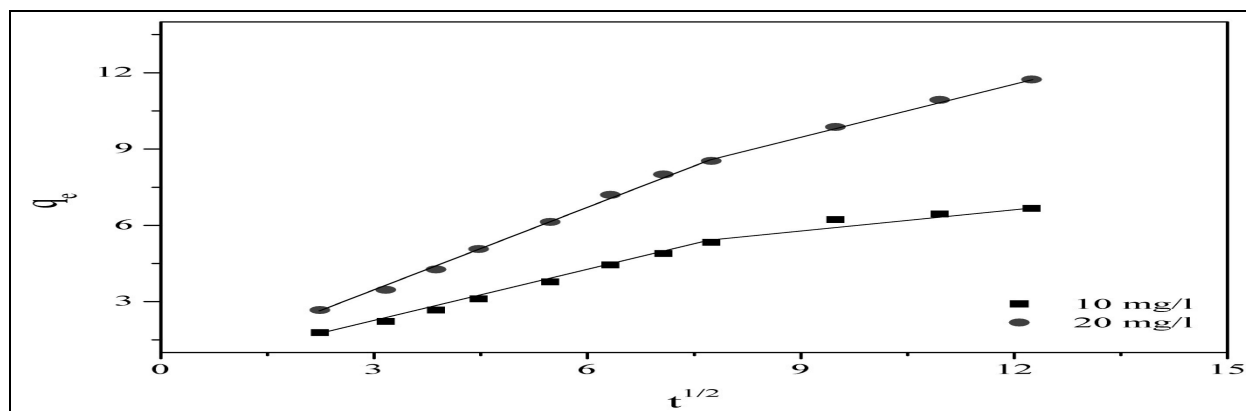


Fig.-10: Intra-particle diffusion plots for the adsorption of MG dye onto AHC.

Elovich model

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate–adsorbent⁷. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation⁸. The linear form of this equation is given by:

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \quad (7)$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}). The Elovich coefficients could be computed from the plots q_t vs $\ln t$. The initial adsorption rate α and desorption constant β were calculated from the intercept and slope of the straight-line plots of q_t against $\ln t$ as shown in Fig.11. The kinetic constants obtained from the Elovich equation were presented in table 1. It will be seen that applicability of the

simple Elovich equation for the present kinetic data indicates that the Elovich equation was able to describe properly the kinetics of MG onto AHC.

Bangham's model

Bangham's model equation is generally expressed as follows⁹-

$$\log \log \left[\frac{C_i}{C_i - C_s q_t} \right] = \log \left[\frac{K_b C_s}{2.303 V} \right] + \alpha \log t \quad (8)$$

Where C_s is the weight of adsorbent used per litre of solution (g/L), α (<1) and k_b are constants $\log[C_i/C_i - C_s q_t]$ was plotted against $\log t$. The MG adsorption fits the Bangham's model α and k_b constants were calculated from the intercept and slope of the straight line plots. If the experimental data is represented by this equation then the adsorption kinetics are limited by the pore diffusion¹⁰. The kinetic constants obtained from the Bangham's equation were listed in table1. It will be seen that the value of α and k_b varied as a function of the solution temperature. Thus, on increasing the temperature, the value of α decreased and the value of k_b increased. The experimental data give a good correlation ($R^2 = 0.9844$ & 0.9939). In addition, it was found that the correlation coefficients for the Bangham's model are higher than those obtained for Elovich model. This result still confirmed that the pore diffusion is only rate-controlling step.

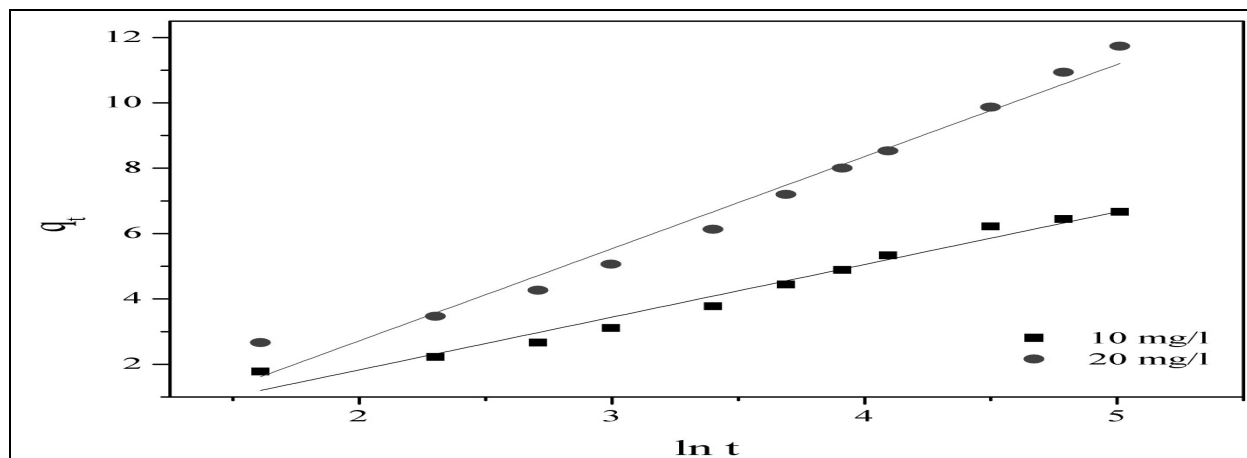


Fig.-11: Elovich plot for the adsorption of MG dye onto AHC

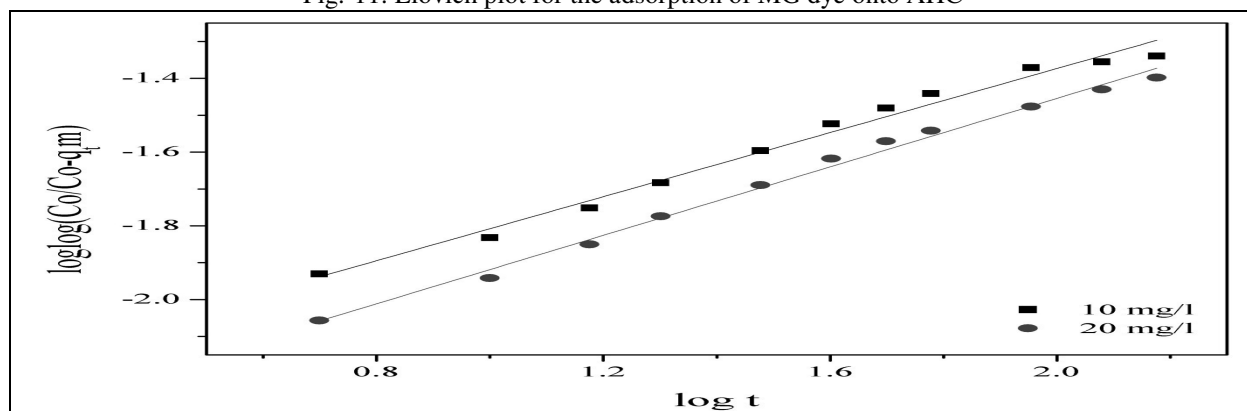


Fig.-12: Bengamn's plot for the adsorption of MG dye onto AHC

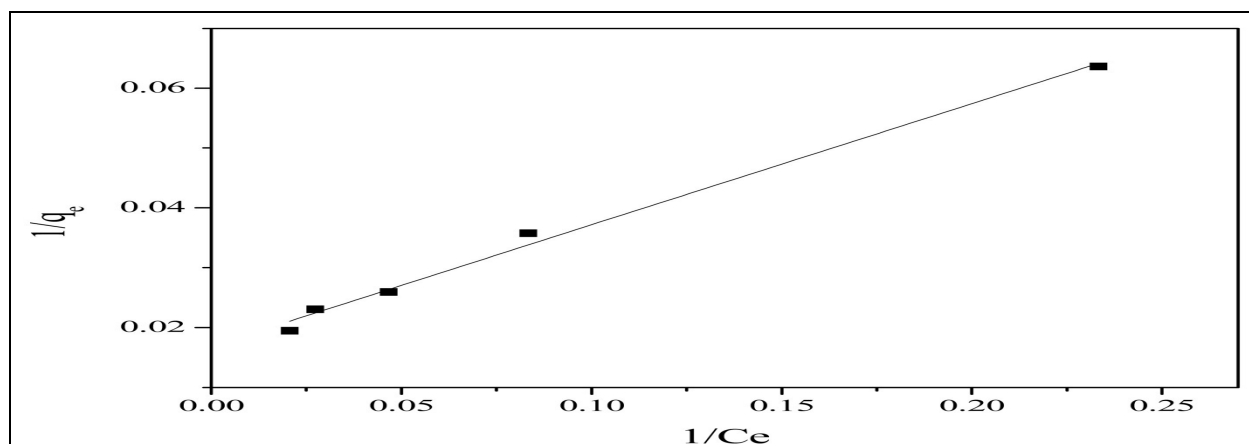


Fig.-13:Langmuir adsorption isotherm for the adsorption of MG dye onto AHC

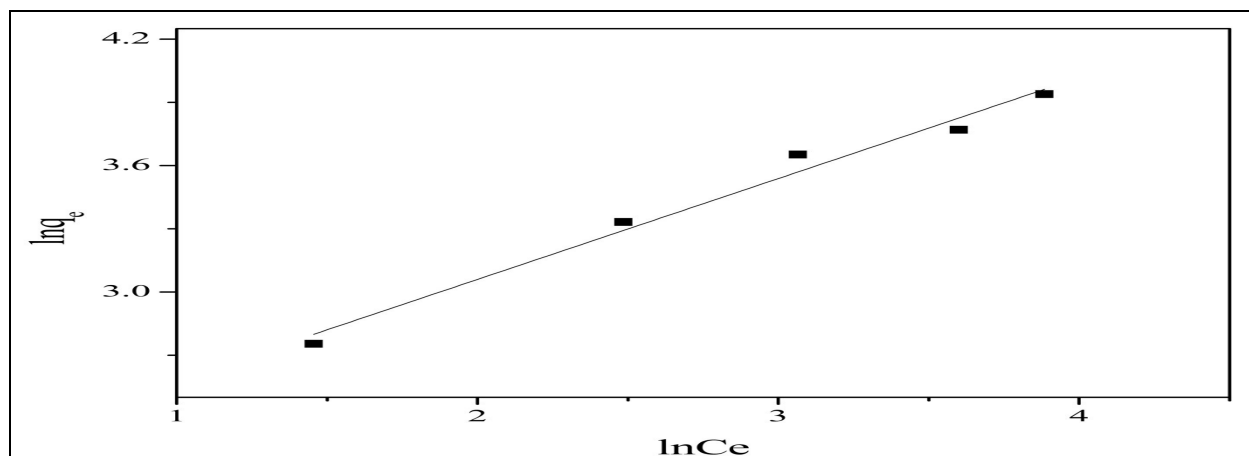


Fig.-14:Freundlich adsorption isotherm for the adsorption of MG dye onto AHC

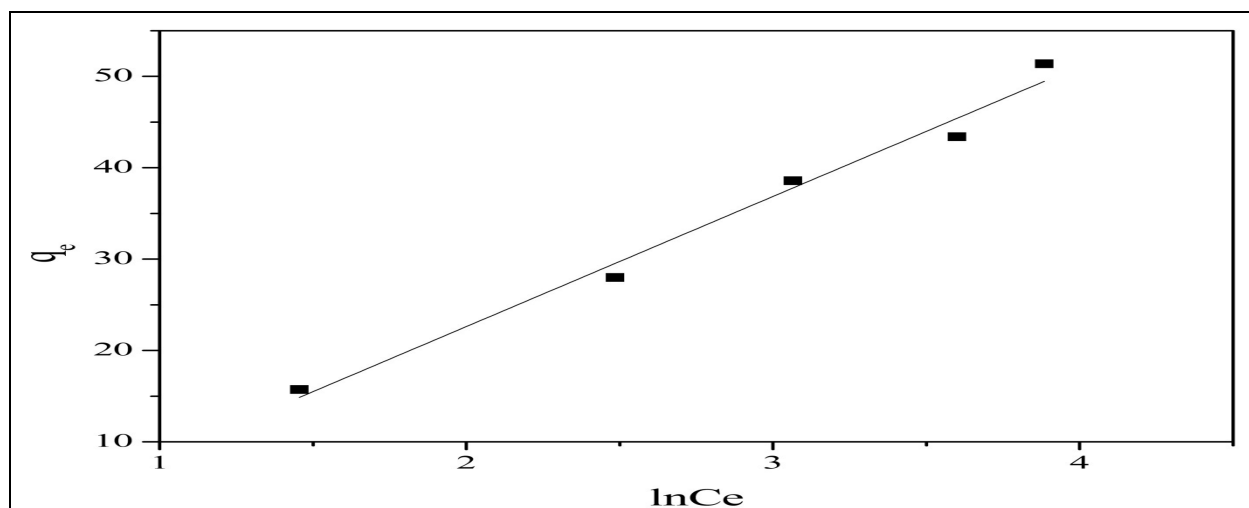


Fig.-15:Temkin adsorption isotherm for the adsorption of MG dye onto AHC

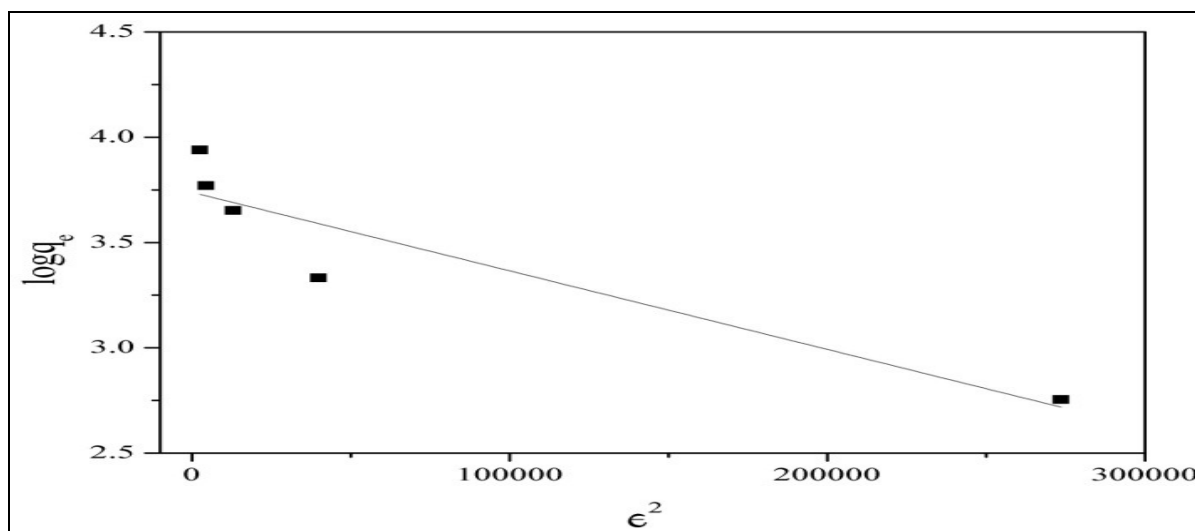


Fig.-16: Dubnin-Radushkevich adsorption isotherm for the adsorption of MG dye onto AHC

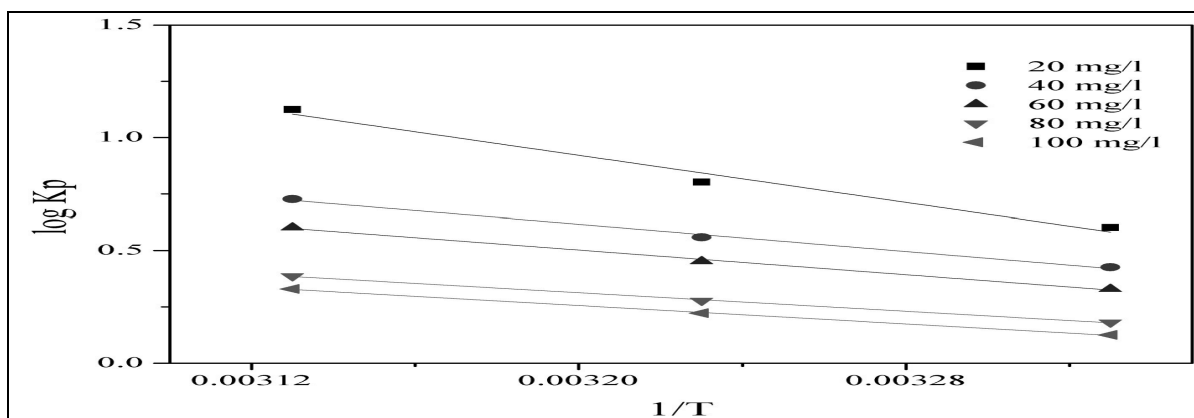


Fig.-17: Vant-Hoff isotherm plot for the adsorption of MG dye onto AHC

Adsorption isotherm

Langmuir isotherm

Langmuir isotherm model is based on assumption that a saturated monolayer of adsorbate molecules is present on the adsorbent surface, the adsorption energy is constant and there is no migration of adsorbate molecules in the surface plane when maximum adsorption capacity occurs¹¹. The linear transformation of the Langmuir equation is given by-

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_e} \quad (9)$$

Where q_0 is the maximum amount of adsorbate per unit mass of adsorbent form a complete monolayer on the surface (adsorption capacity), C_e denotes equilibrium adsorption concentration in solution, q_e is the amount adsorbed per unit mass of adsorbent and b is the binding energy constant. A plot of $1/C_e$ versus $1/q_e$ is graphically represented in Fig.13. The values of Q_0 and b were calculated from the intercept and slope respectively and the results are presented in Table 2. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L also known as the separation factor that is given by the following equation-

$$R_L = \frac{1}{(1 + b C_0)} \quad (10)$$

The data related to the equilibrium obeyed well with the Langmuir models. The maximum adsorption capacity of adsorption of MG by Langmuir isotherm was 59.20 mg g⁻¹. The R² value 0.9943 suggests that the Langmuir isotherm provides a good fit to the isotherm data. The value of R_L was 0.2026 which indicates the favour of adsorption i.e. formation of monolayer of MG on the surface of AHC.

Freundlich isotherm

The Freundlich equation is used to determining the applicability of heterogeneous surface energy in the adsorption process¹². The empirical Freundlich equation is expressed as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (11)$$

Where k_f is measure of adsorption capacity (mg g⁻¹) and n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1), unfavorable (1/n > 1). The plots of ln q_e vs ln C_e showed good linearity (R² = 0.9838). The values of K_f and n given in the Table-2. Values of n lies 1 to 10 indicate an effective adsorption. It also indicates degree of favorability of adsorption. The Freundlich adsorption capacity by this plot is 8.14 mg g⁻¹. Higher value of k_f indicates higher affinity for MG adsorption. From the results it was clearly observed that both models were well suited for adsorption of MG on AHC, but the regression factor as well as the calculated and experimental values correlates more correctly with the Langmuir values, on this basis it could be concluded that, MG form monolayer on the surface of AHC.

Table-2: Isotherm Parameters for the adsorption of MG dye onto AHC

Isotherm model	Model coefficient	
Langmuir	q ₀ (mg g ⁻¹)	59.20
	R _L	0.2026
	b(L mg ⁻¹)	0.0833
	R ²	0.9943
Freundlich	k _f (mg g ⁻¹)	8.16
	n	2.08
	R ²	0.9838
Temkin	A	0.6620
	B	14.24
	b	175.05
	R ²	0.9850
Dubnin-Radushkevich	K(mol ² kJ ⁻²)	0.0023
	q _m (mol g ⁻¹)	0.0186
	E (kJ mol ⁻¹)	14.58
	R ²	0.9590

Table-3: Thermodynamic Parameters for the adsorption of MG dye onto AHC

Conc. (mg/l)	T (K)	K _d	ΔG° (J mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔH° (kJ mol ⁻¹)
20	300	17.1	-1501.7	74.42	-23.8
	310	18.1	-1999.4		
	320	19.0	-2805.8		
40	300	2.7	-1062.5	52.08	-16.7
	310	3.6	-1393.2		

	320	5.3	-1813.3		
60	300	2.1	-820.7	40.57	-13.0
	310	2.8	-1128.1		
	320	4.0	-1501.7		
	320	4.0	-1501.7		
80	300	1.5	-452.5	22.82	-7.3
	310	1.9	-694.4		
	320	2.4	-965.6		
	320	2.4	-965.6		
100	300	1.3	-311.6	16.23	-5.2
	310	1.7	-553.3		
	320	2.1	-820.7		
	320	2.1	-820.7		

Temkin isotherm

Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption¹³. Linear form of Temkin equation is expressed as:

$$q_e = B \ln A + B \ln C_e \quad (12)$$

Where $B = RT/b$, b is the Temkin constant related to heat of sorption q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Therefore, a plot of q_e versus $\ln C_e$ enables one to determine the constants A and B . From Table-2, AHC has maximum binding energy 0.6620 Jg^{-1} which is uniformly distributed. The value for constant B is 14.24 J mg^{-1} is heat of adsorption. The correlation coefficient of 0.9850 obtained showed that adsorption of MG also followed the Temkin model.

Table-4: Adsorption capacity of various adsorbents with MG

Adsorbent	Q_0 (mg/ g)
Rattan sawdust ¹⁶	62.7
Areca Husk ¹⁷	59.2
Lemon peel ¹⁸	51.7
Laboratory grade AC ¹⁸	42.2
Silica gel ¹⁹	39.7
Rubber wood sawdust ²⁰	36.3
Hen feather ²¹	10.7
Acid activated low cost AC ²²	9.7
Arundo donax root carbon ²³	8.7
AC commercial grade ¹⁸	8.3
Bentonite clay ²⁴	7.7
Neem sawdust ²⁵	4.2

Dubinin-Radushkevich isotherm

The linearised form of the D-R isotherm equation as follows¹⁴-

$$\ln q_t = \ln q_m - K \epsilon^2 \quad (13)$$

$$\epsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (14)$$

Where K is a constant related to the adsorption energy of adsorption per mole of the adsorbate ($\text{mol}^2 \text{J}^{-2}$), q_m is the theoretical adsorption capacity (mol g^{-1}) and ϵ is the Polanyi potential, R ($\text{J mol}^{-1} \text{K}^{-1}$) is the universal gas constant and T (K) is the absolute temperature. Hence by plotting $\log q_e$ versus ϵ^2 it is

possible to obtain the value of q_m from the intercept and the value of K from the slope. Values of q_m and K are presented in Table-2. The constant $K(0.0023)$ gives an idea about the mean free energy E (KJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship.

The mean free energy of adsorption (E) was calculated using the following relation-

$$E = \frac{1}{\sqrt{2K}} \quad (15)$$

It is defined as the free energy change when 1 mole of adsorbate is transferred to the surface of the solid from infinity in solution. The value of E is very useful in predicting the type of adsorption. If the value is less than 8 KJ mol^{-1} , then the adsorption is physical in nature due to weak Vander Waals force and if it is in between $8\text{-}16 \text{ KJ mol}^{-1}$, then the adsorption is due to exchange of ions. The value of E was found to be 14 KJ mol^{-1} for the removal of MB onto AHC.

Thermodynamic study

In order to investigate the effect of temperature on the uptake of MG the process was carried out at different temperatures ranging from 300K, 310K and 320K. The temperature affected the equilibrium uptake as shown in Fig.16. The equilibrium MG adsorption capacity of both the adsorbents were better at higher temperatures as the adsorbed amount of MG increased with the rise in temperature. Higher uptake at high temperature is due to the increase in molecular diffusion or may be attributed to the availability of more active sites on the surface of the related with several thermodynamic parameters including free energy change (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) which is used to decide whether the adsorption is a spontaneous process or not¹⁵. Thermodynamic parameters can be calculated from the following equation-

$$\Delta G^0 = -RT \ln K_d \quad (16)$$

Where R is the universal gas constant ($8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$), T the temperature (K), and K_d is the distribution coefficient. If the value of ΔG^0 is negative, the chemical reaction can occur spontaneously at a given temperature. The K_d value was calculated using the following Eq. (17)-

$$K_d = \frac{C_e}{q_e} \quad (17)$$

Where q_e and C_e are the equilibrium concentrations of MG (mg L^{-1}) on the adsorbent and in the solution, respectively. The enthalpy change (ΔH^0) and entropy change (ΔS^0) can be calculated from the following equation-

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (18)$$

This equation can be written as-

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (19)$$

The thermodynamic parameters of ΔH^0 and ΔS^0 were obtained from the slope and intercept of the plot between $\log K_d$ versus $1/T$ respectively from the Fig.16. The Gibbs free energy changes (ΔG^0) were calculated from Eq. (18), and the values of ΔG^0 , ΔH^0 , and ΔS^0 for the adsorption of MG onto AHC were given in Table-3. The negative values of ΔG^0 indicated the spontaneous nature of the adsorption process. The magnitude of ΔG^0 also increased with increasing temperature indicating that the adsorption was more favorable at higher temperatures.

The negative values of ΔH^0 indicate that the exothermic nature of the adsorption of MG onto AHC. Further, negative ΔG^0 values indicate spontaneous nature of the adsorption process and positive ΔS^0 values indicate the affinity of the adsorbent of dye.

CONCLUSION

This study investigated the equilibrium and the dynamics of the adsorption of MG onto activated carbon prepared by Areca Husk. The adsorption capacity of the adsorbent was considerably affected by initial concentration, adsorbent dose, particle size, contact time, temperature and initial pH. The adsorption of MG was exothermic in nature with the adsorption capacity increasing with increasing temperature. The Langmuir and D-R adsorption models were used for the mathematical description of the adsorption equilibrium of MG onto AHC. The experimental data fitted well to the D-R adsorption isotherm. The kinetics of adsorption MG on AHC was studied by using five kinetic models. The adsorption proceeds according to the pseudo-first order model which provides the best correlation of the data in all cases and the experimental $q_e(\text{exp})$ values agree with the calculated ones. Also, it was observed that the intra-particle diffusion was not the only rate-controlling step. According to Elovich and Bangham model, the results show that the rate could be enhanced by increasing the adsorption temperature. Negative ΔH and positive ΔS values indicate that the adsorption of MG onto AHC was exothermic. MG has good affinity towards the adsorbent and the increasing randomness at the solid solution interface during the adsorption process.

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