

Evaluation of Adsorption Potential of the Agricultural Waste Areca Husk Carbon for Methylene Blue

A.Basker^{1*}, P.S. Syed shabudeen², and P. Vignesh kumar¹

¹Department of chemistry, Kalaignar Karunanidhi Institute of Technology, Coimbatore, Tamil Nadu, India.

²Department of chemistry, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India.

*Corres.author: baskerchemistry@gmail.com

Abstract: In this study, the ability of Areca Husk Carbon to adsorb Methylene blue (MB) dye from aqueous solution was investigated. Batch experiments were carried out for the adsorption of dye molecules onto AHC at room temperature. The influences of various factors such as particle size, adsorbent dosage, initial dye concentration, contact time, pH and temperature on the adsorption capacity was investigated and optimal experimental conditions was ascertained. Adsorption data were modeled using Langmuir, Freundlich and Temkin adsorption isotherms. Adsorption kinetics was verified by pseudo-first order, pseudo-second order and intra-particle diffusion 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 features of activated carbon were characterized by FTIR and SEM studies respectively. Main and interaction effects were analyzed by analysis of variance (ANOVA), F-test and p-values to define most important process variables affecting the dye adsorption. The results indicated that AHC could be employed as a low cost adsorbent in wastewater treatment for the removal of MB.

Keywords: Adsorption, Activated carbon, Areca Husk, Methylene Blue.

Introduction

Globally a huge quantity of dye effluents is produced from various industries is making a heavy demand for water resource. Several studies have been undertaken on the toxicity of dyes and their impact on ecosystems. These studies show that certain dyes degrade and that their derived products can be toxic and carcinogenic even at low concentrations. This resource needs to be conserved without toxicity and the industrial effluent is to be recycled. Therefore the concept of reuse, recycle and reduce have been very well conceived by industries, efforts in this direction need to be accelerated. So far, there is no viable technology available to treat the textile effluents and the sludge. A suitable technology with zero generation of sludge will therefore help to contain the problem of sludge disposal. The present study investigates to develop a low cost effective method of treatment of textile dye by using a solid agricultural waste, which is facing solid waste disposal problem is effectively and efficiently converted into an activated carbon and it is utilized to study the effectiveness of the removal of color from textile effluents. The color removal from textile effluent was attempted and the waste

water management studies were planned and executed. Industrial wastewater treatment from manufacturing, chemical industries was analyzed and the chemical properties of synthetic process and methodologies were formulated¹

There are several works of low cost non-conventional adsorbents have been carried out so far. Adsorbents used include agricultural solid wastes such as Walnut shell, Almond shell, Hazelnut shell and Apricot stones², Sludge ash³, Fine grinded wheat straw and Coarse grinded wheat straw⁴, Caulerpa racemosa⁵, Fly ash treated with HNO₃⁶, Neem leaf powder⁷, Raw beech saw dust⁸, Indian rosewood sawdust⁹, Wheat shells¹⁰, Natural Tripoli¹¹, Picea abies¹², Orange peel and Banana peel¹³, Cereal chaff, Jute processing waste and Yellow fashion fruit waste¹⁴, Salsola vermiculata leaves¹⁵, Cotton waste¹⁶, Pitch-pine saw dust Cherry saw dust and Oak saw dust¹⁷, Green grass¹⁸, Modified saw dust¹⁹, Mansonia wood saw dust²⁰, Parthenium²¹, Rice husk²², Olive pomice²³.

The aim of the present study is to prepare and characterize the quality and evaluate the efficiency of using AHC as an adsorbent for the removal of Methylene blue. After considering the efficiency of color 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 time, initial dye concentration, particle size, 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 carbon.

Materials and Methods

Methylene Blue

MB supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate and was not purified prior to use. Distilled water was employed for preparing all the solutions and reagents. MB has a molecular weight of 374 g mol⁻¹, which corresponds to the methylene blue hydrochloride with three groups of water. Chemical structure of the dye was shown in Figure 1.

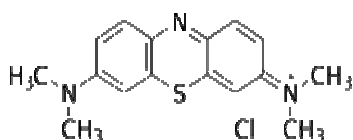


Figure 1. Structure of Methylene Blue

Preparation of activated carbon

One part by weight of each powdered raw material was chemically activated by treating with two parts by weight of concentrated sulphuric acid with constant stirring and was kept for 24 hours in a hot air oven at 75°C, the carbonized material was washed well with plenty of water several times to remove excess acid, surface adhered particles, water soluble materials dried at 200°C in hot air oven for 24 hours. The adsorbent thus obtained were grounded well and kept in air tight containers for further use.

Analysis of Methylene Blue

The concentration of MB in the supernatant solution after and before adsorption was determined using a double beam UV spectrophotometer (Shimadzu, Japan) at 665 nm. It was found that the supernatant from the activated carbon did not exhibit any absorbance at this wavelength and also that the calibration curve was very reproducible and linear over the concentration range used in this work.

Batch equilibrium studies

Batch experiments were carried out by shaking 100 ml of dye solution with 150 mg of adsorbent in a glass stoppered conical flask at a room temperature at the rate of 120 rpm. After agitation the solution centrifuged. Then the dye concentration in the supernatant solution was analyzed using a spectrophotometer by

monitoring the absorbance changes at a wavelength of maximum absorbance (665 nm) in these sorption experiments, the solution pH was used without adjusting.

Each experiment was carried out and average results are presented. Calibration curves were obtained with standard MB solution using distilled water as a blank. Mass capacity of adsorption q_e , is calculated from the difference between the initial and final concentration of MB.

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

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

Determination of functional groups

The FT-IR spectrum of MB onto AHC before and after adsorption was detected in the range of 4000 to 400 cm^{-1} was presented in Figure 2 and 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} were 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. Some of the peak was disappear due to the absorption of MB on AHC. Yet in Figure 3, the absorption bands at 1381cm^{-1} may be assigned to $\nu(\text{N-O})$ stretching, indicating that MB was adsorbed on the surface of AHC.

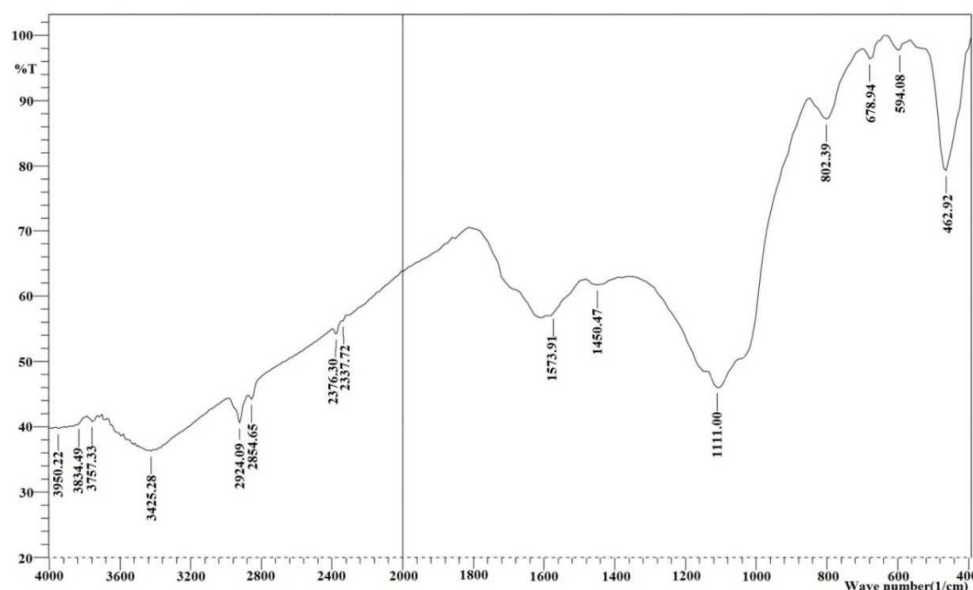


Figure 2. FTIR spectra of fresh AHC

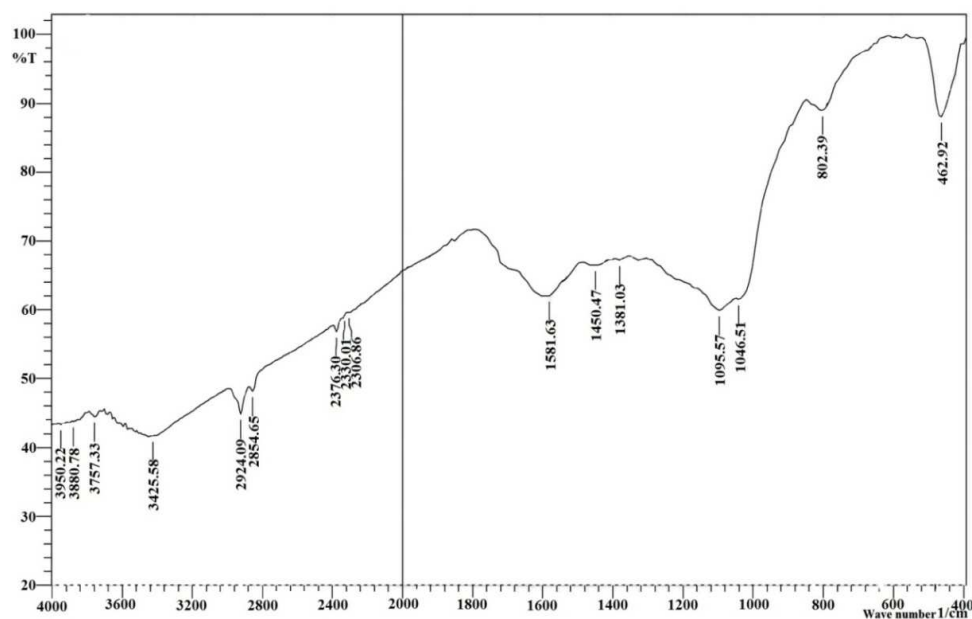


Figure 3. FTIR spectra of MB loaded AHC

SEM morphology

It is widely used to study the morphological features and surface characteristics of the adsorbent materials. Typical SEM photographs are shown in Figure 4. It reveals that the AHC has a rough surface with more porous and caves like structure.

The SEM Figure 5 shows the morphology of the loaded adsorbent, the surface of the adsorbent due to adsorption of the MB dye molecules, presumably leading to the formation of a monolayer of the dye molecule over the adsorbent surface is evident from the formation of the white layer and it is supported with FTIR spectra as shown in Figure 3.

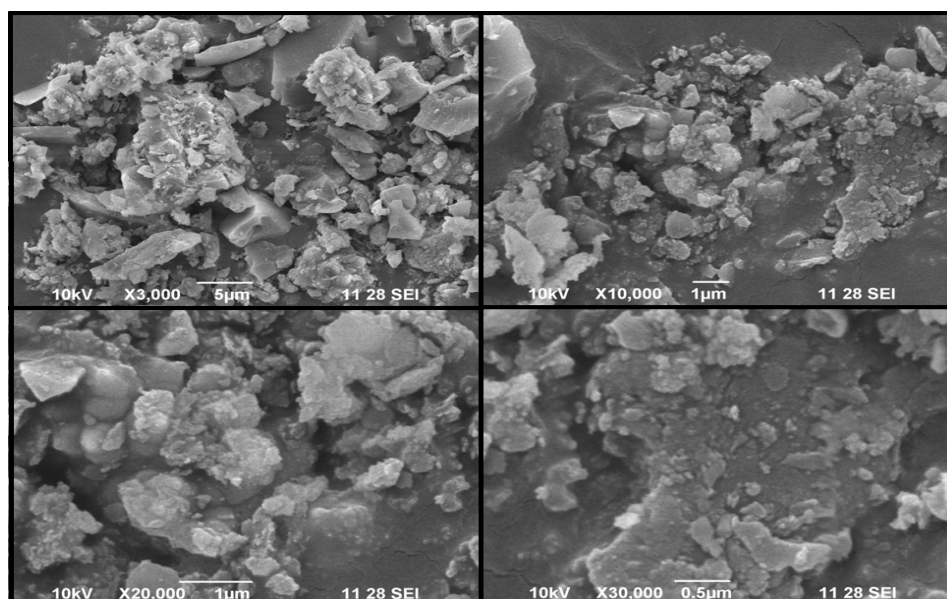


Figure 4. SEM image of Fresh AHC

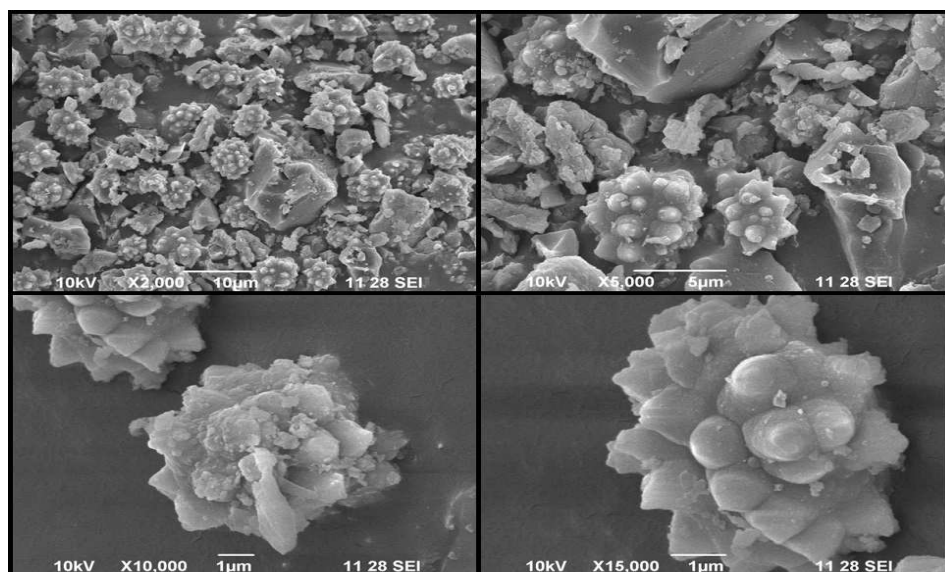


Figure 5. SEM image of MB loaded AHC

Influence of adsorbent dosage

In order to study the effect of adsorbent dosage on the adsorption of MB, a series of adsorption experiments was carried out with different adsorbent dosages at initial dye concentration of 10 mg L^{-1} . Figure 6 shows the effect of adsorbent dose on the removal of MB. Along with the increase of adsorbent dosage from 40-250 mg/L, the percentage of dye adsorbed increased. Above 150 mg of adsorbent dose the equilibrium of dye was reached and the removal ratios of dyes held almost no vary, so the AHC of 150mg was chosen for subsequent experiment.

Influence of particle size

The adsorption of MB was investigated at particle size 100,150, 250 BSS mesh, of the AHC and the results are represented in Figure 6 it seems that with the 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.

Influence of Contact time

The effect of contact time on removal of dye was shown in Figure 7. It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages 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.

Influence 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 MB removed respectively. The rapid adsorption removed respectively. 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 ratios, there are 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.

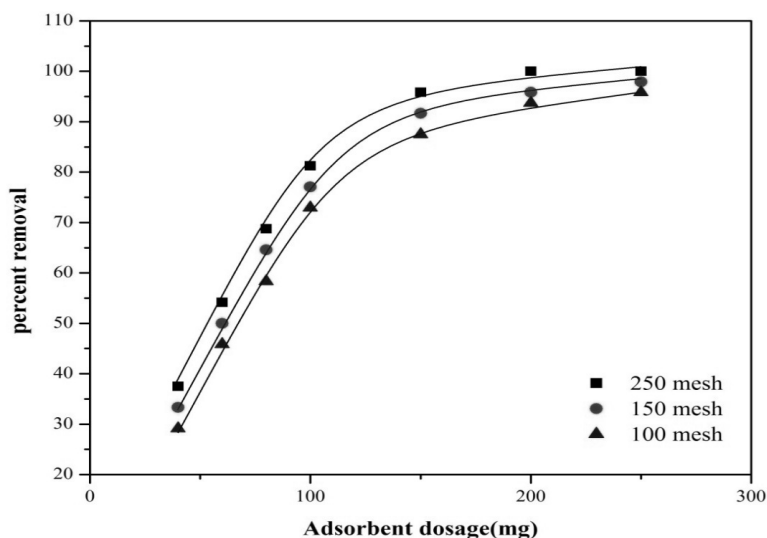


Figure6. Influence of adsorbent dosage and particle size on the removal of MB dye onto AHC

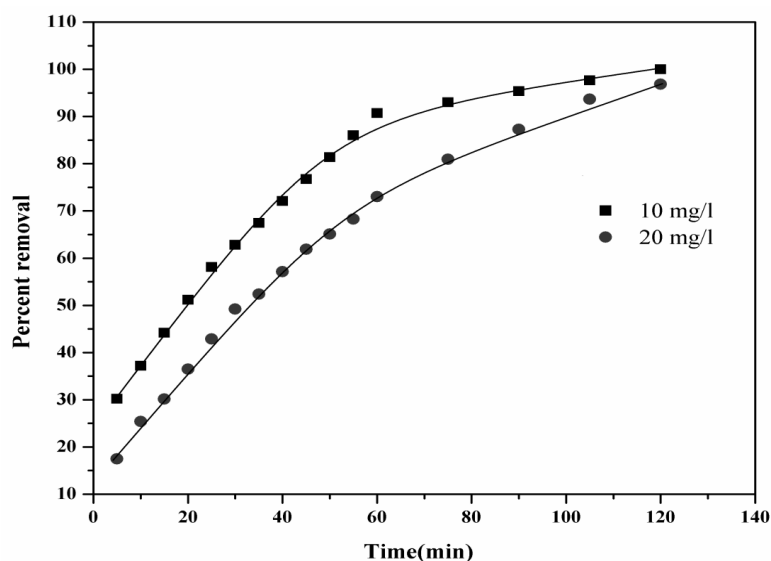


Figure 7. Influence of contact time on the removal of MB dye onto AHC

Influence of pH

The pH of the dye solution plays an important role in the whole adsorption process. As shown in Figure 9 a 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 MB at acidic pH might be due to the presence of excess H^+ ions competing with dye cations for the available adsorption sites.

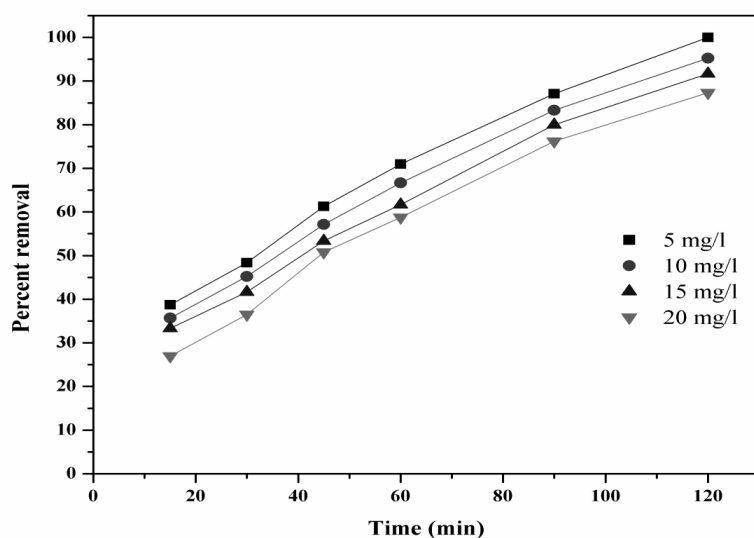


Figure 8. Influence of Initial dye concentration on the removal of MB dye onto AHC

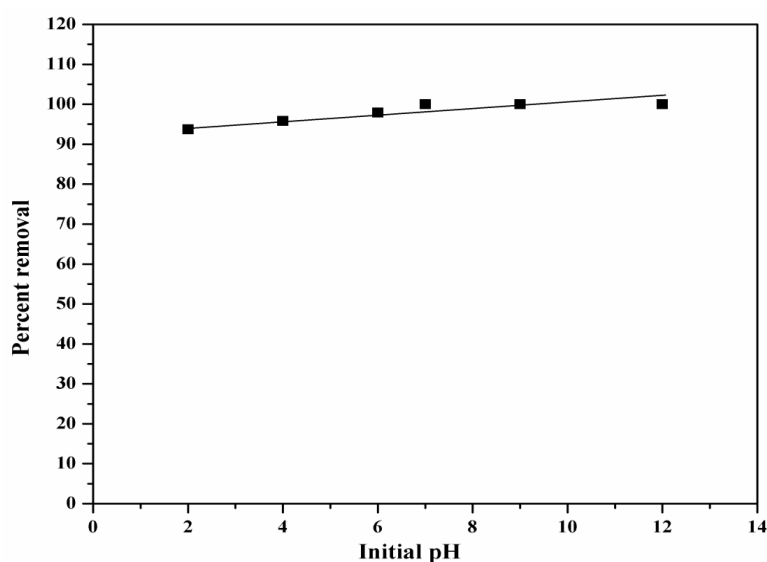


Figure 9. Influence of pH on the removal of MB dye onto AHC

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 three models i.e. pseudo first order, pseudo second order and intra- particle diffusion 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 MB by keeping other parameters constant.

Pseudo first order kinetic model

Lagergren proposed a pseudo-first order kinetic model as below²⁴. The integrated form of the model is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

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 $\log(q_e - q_t)$ Vs t . The correlation values of R^2 were 0.96 and 0.96 for 10 mg L⁻¹ and 20 mg L⁻¹ respectively.

The equilibrium adsorption capacities were 6.51 and 11.35 mg g⁻¹ respectively. The calculated equilibrium adsorption capacities were 5.65 and 10.27 mg g⁻¹. 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 MB from aqueous solution. The rate constant and other results obtained graphically were presented in Table 1.

Table 1 Kinetic Parameters for the adsorption of MB dye onto AHC

Model	Parameter	Initial Concentration	
		C ₀ = 10mg L ⁻¹	C ₀ = 20 mg L ⁻¹
Pseudo- first order	q _e (mg g ⁻¹)	6.51	11.85
	q _{calc} (mg g ⁻¹)	5.65	10.27
	k ₁ (min ⁻¹)	0.107	0.004
	R ²	0.96	0.96
Pseudo-second order	q _{calc} (mg g ⁻¹)	3.40	2.47
	k ₂ (g mg ⁻¹ min ⁻¹)	0.12	0.06
	h (mg g ⁻¹ min ⁻¹)	1.52	0.40
	R ²	0.96	0.92
Intra-particle diffusion	k _{int} (mg g ⁻¹ min ^{-0.5})	0.604	1.14
	C	0.848	0.480
	R ²	0.95	0.96

Pseudo-second-order kinetic model

Pseudo-second-order kinetic model²⁵ is given as:

$$\frac{dq}{dt} = k_2([q_e - q_t])^2 \quad (4)$$

After integrating we get

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where k₂ [g mg⁻¹ 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[mg g⁻¹ min⁻¹] is defined as:

$$h = k_2 q_e^2 \quad (6)$$

Where k₂ is the pseudo-second order rate constant of dye adsorption. The plot of t/q versus t of Eq.5 should give a linear relationship, from which q_{eq} and k₂ 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 k₂ were 0.12 and 0.06 g mg⁻¹ min⁻¹ for 10 mg L⁻¹ and 20 mg L⁻¹ respectively. In addition to the q_e calculated values and the experimental values q_e are not similar showing that the adsorption kinetics for the entire process did not follow the pseudo second order model.

It can be concluded that the pseudo first order model provided a good correlation for the adsorption of MB on AHC compared to the pseudo second order model.

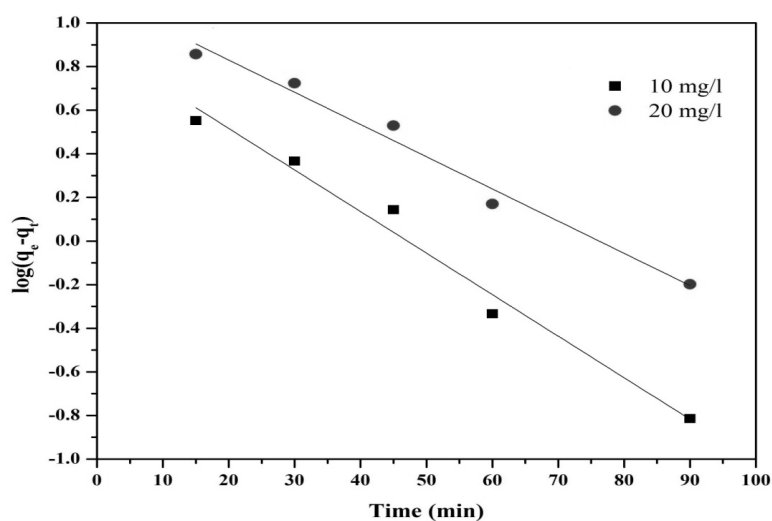


Figure10. Pseudo first order kinetics for the adsorption of MB dye onto AHC

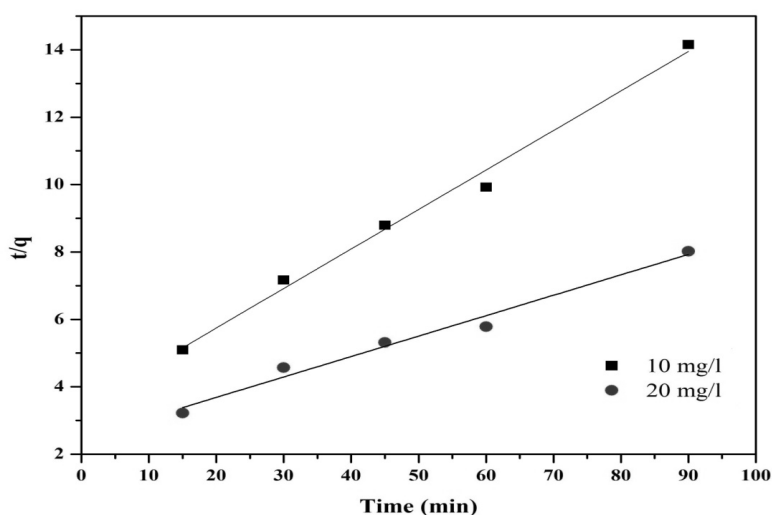


Figure11. Pseudo second order kinetics for the adsorption of MB dye onto AHC

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 Morris²⁶. The intra-particle diffusion equation is given as:

$$q_t = K_{int} t^{0.5} + C \quad (7)$$

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 $t^{0.5}$ (Figure 12). The calculated value of k_{int} is $0.604 \text{ mg g}^{-1} \text{min}^{-0.5}$ and C is 1.14. The correlation coefficient (R^2) values of 0.90 and 0.94 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

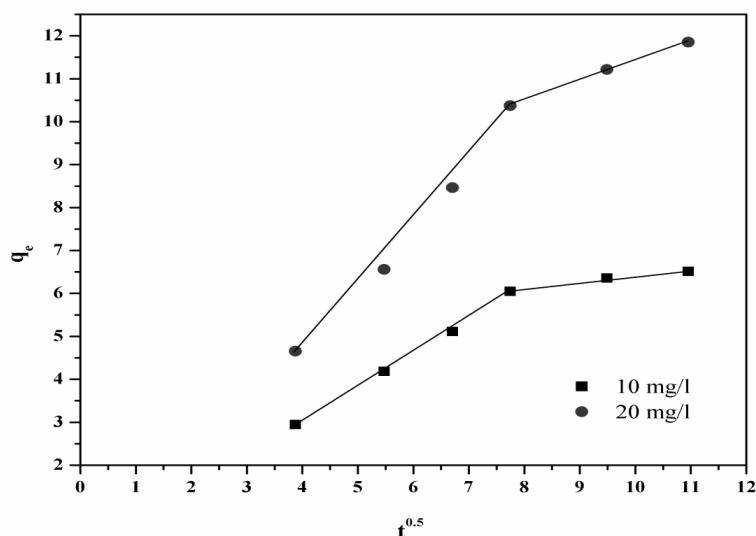


Figure12. Intra particle diffusion plots for the adsorption of MB dye onto AHC

Isotherm study

Langmuir isotherm

Langmuir isotherm model is based on assumption that a saturated monolayer of adsorbate molecules is present on the adsorbent surface²⁷, the adsorption energy is constant and there is no migration of adsorbate molecules in the surface plane when maximum adsorption capacity occurs. The linear transformation of the Langmuir equation is given by

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0} \quad (8)$$

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.

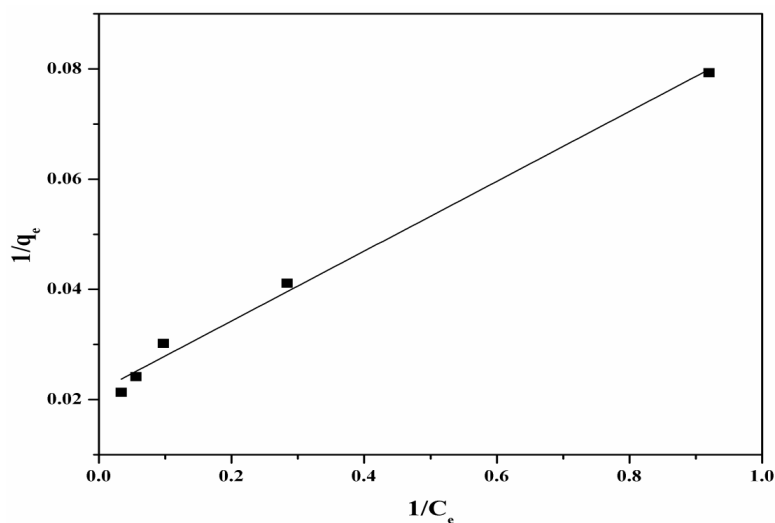


Figure13. Langmuir adsorption isotherm for the adsorption of MB dye onto AHC

A plot of $1/C_e$ versus $1/q_e$ is graphically represented in Figure 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.

$$RL = \frac{1}{(1 + b C_0)} \quad (9)$$

The data related to the equilibrium obeyed well with the Langmuir models. The maximum adsorption capacity of adsorption of MB by Langmuir isotherm was 46.3 mg g^{-1} . The value of R_L value lay between 0 to 1. It was inferred that followed Langmuir model and favourable for adsorption.

Freundlich isotherm

The Freundlich equation is used to determining the applicability of heterogeneous surface energy in the adsorption process²⁸. The empirical Freundlich equation is expressed as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)$$

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 ($R^2 = 0.98$). The values of K_f and n given in the Table 2. Values of n lie 1 to 10 indicate an effective adsorption. It also indicates the degree of favorability of adsorption.

The Freundlich adsorption capacity by this plot was 13.21 mg g^{-1} . Higher value of k_f indicates higher affinity for MB adsorption. From the results it was clearly observed that both models were well suited for adsorption of MB on AHC.

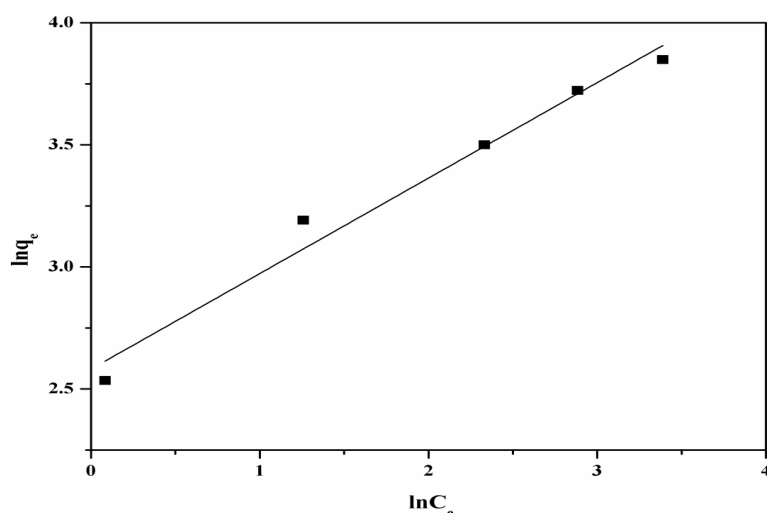


Figure14. Freundlich adsorption isotherm for the adsorption of MB dye onto AHC

Temkin isotherm

Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption²⁹. Linear form of Temkin equation is expressed as:

$$q_e = B \ln A + B \ln C_e \quad (11)$$

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 2.99 J g^{-1} which is uniformly distributed. The value of

constant B was 10.26 J mg^{-1} was heat of adsorption. The correlation coefficient of 0.97 obtained showed that adsorption of MB also followed the Temkin model.

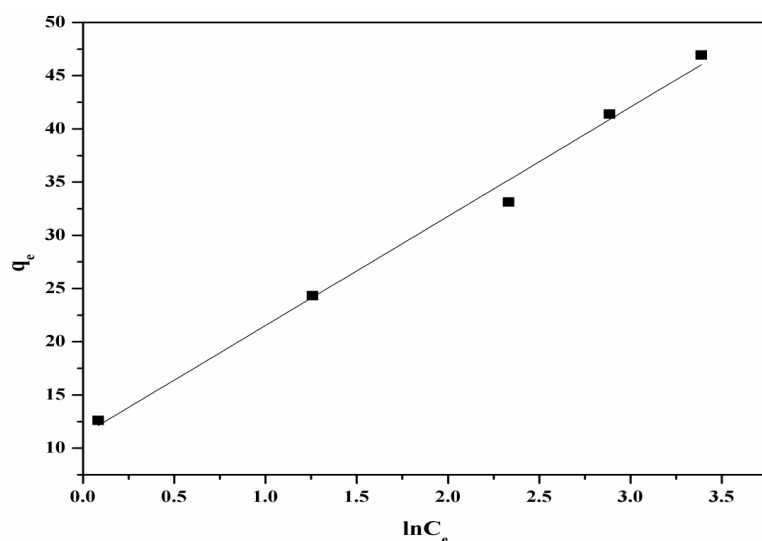


Figure15. Temkin adsorption isotherm for the adsorption of MB dye onto AHC

Thermodynamic study

Thermodynamic studies were conducted at various temperatures (300-320K). Parameters such as free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) which are used to decide whether the adsorption is a spontaneous process or not. Thermodynamic parameters can be calculated from the following equation.

$$\Delta G^\circ = -RT \ln K_d \quad (12)$$

Where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the temperature (K), and K_d is the distribution coefficient. If the value of ΔG° is negative, the chemical reaction can occur spontaneously at a given temperature. The K_d value was calculated using the following Eq.13.

$$K_d = \frac{C_e}{q_e} \quad (13)$$

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

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (14)$$

This equation can be written as

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

The thermodynamic parameters of ΔH° and ΔS° were obtained from the slope and intercept of the plot between $\ln K_d$ versus $1/T$ respectively from the Figure 16. The Gibbs free energy changes (ΔG°) were calculated from Eq.12, and the values of ΔG° , ΔH° , and ΔS° for the adsorption of MB onto AHC were given in Table 3. The negative values of ΔG° indicated the spontaneous nature of the adsorption process. The magnitude of ΔG° also increased with increasing temperature indicating that the adsorption was more favorable at higher temperatures. The value of ΔH° was negative, indicating the exothermic nature of the adsorption of MB onto AHC. The adsorption of MB on the AHC was a physical process because of the obtained ΔH° value between -38 to $-111.7 \text{ KJ mol}^{-1}$. Hence the adsorption equilibrium was rapidly attained and weak interactions between the MB and the functional groups on the surface of the adsorbent. In addition, the positive value of ΔS° suggested an increase in randomness at the solid/liquid interface during the adsorption of MB on the adsorbent

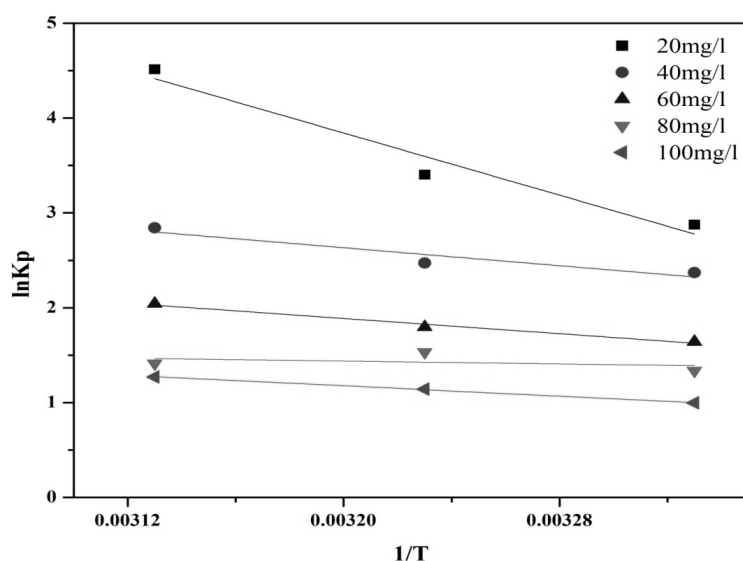


Figure16. Vant-Hoff isotherm plot for the adsorption of MB dye onto AHC

Table 2 Isotherm Parameters for the adsorption of MB dye onto AHC

Langmuir Isotherm		Freundlich Isotherm		Temkin Isotherm	
$q_0(\text{mg g}^{-1})$	46.32	$k_f(\text{mg g}^{-1})$	13.21	A	2.99
R_L	0.033	n	2.56	b	10.26
$b(\text{L mg}^{-1})$	0.34	R^2	0.98	B	243.09
R^2	0.99			R^2	0.97

Table 3 Thermodynamic Parameters for the adsorption of MB dye onto AHC

Conc (mg L^{-1})	T (K)	Kd	$\Delta G^\circ (\text{J mol}^{-1})$	$\Delta S^\circ (\text{J mol}^{-1} \text{K}^{-1})$	$\Delta H^\circ (\text{kJ mol}^{-1})$
20	300	19.275	-7171.9	348.318	-111.7
	310	19.565	-8483.3		
	320	19.855	-11260.1		
40	300	37.653	-5911.2	279.798	-89.9
	310	37.867	-6163.0		
	320	38.507	-7094.4		
60	300	53.134	-4092.5	194.321	-62.4
	310	54.030	-4482.8		
	320	55.224	-5093.9		
80	300	68.065	-3331.1	156.080	-50.2
	310	69.930	-3822.3		
	320	68.811	-3519.3		
100	300	80.263	-2487.6	118.343	-38.0
	310	82.456	-2848.6		
	320	84.211	-3163.9		

Analysis of variance

The results of analysis of variance (ANOVA) are given in Table 4-6. Statistical analysis of variance was performed to check whether the process parameters are statistically significant or not. The F-value for each process indicates which parameter has a significant effect on the MB removal. Since the Probability value is bigger than 0.05. At the level, the variances are not significantly different. Suppose the Probability value is smaller than 0.05. At the level, the variances are significantly different³⁰. Usually, the larger the F-value has the greater the effect on the MB removal. The influence of various parameters and their interaction on the removal percent was investigated by ANOVA analysis and performance characterized. The results of ANOVA

analysis for the removal of MB onto AHC are given in Table 4. Larger the F-value more is the effective parameter in the MB removal. The sequential order of the process variables is given below for MB removal onto AHC.

Temp>C₀ > PS> Dosage>Time> pH

From the above order temp, initial concentration, dosage and particle size play a major role in adsorption of MB onto AHC but pH and time shows that little effect compare to the other parametric study. From the Table5 kinetic and adsorption parameters shows at least two groups of the four have significant different means, since the p-value is smaller than 0.05. Some of the p values are found to be bigger than 0.05 in the Thermodynamic ANOVA parameters as shown in **Table 6** we can conclude that the four groups have equal variance, since the p-value is bigger than 0.05.

Table 4 ANOVA for Various parameters for the adsorption of MB onto AHC

Parameter	DF	SS	MS	F Value	Prob.>F
Dosage	8	44852.43	14925.62	987.64	0.000000320
Particle size	7	44852.43	14945.16	3523.83	0.000000322
Time	16	89367.22	29772.89	7972.11	0.000000021
Initial Conc.	6	30218.52	10071.61	8167.99	0.000002488
pH	6	57560.76	19186.23	27678.92	0.000000039

DF-Degree of freedom; SS-Sum of Squares; MS-Mean squares; F-Fischer.

Table 5 ANOVA for Isotherm and kinetic parameters for the adsorption of MB onto AHC

Parameters	Conc.(mg/l)	DF	SS	MS	F Value	Prob.>F
Isotherm	10	4	46.13	45.75	356.26	0.00032
	20	4	12.47	12.24	158.08	0.00108
Kinetics	10	4	1.23	1.21	152.19	0.00115
	20	4	0.74	0.73	162.58	0.00104

Table 6. ANOVA for Thermodynamic parameters for the adsorption of MB onto AHC.

Conc.(mg/l)	DF	SS	MS	F Value	Prob.>F
20	2	1.4008	1.3433	23.35	0.12992
40	2	0.1247	0.1123	9.11	0.20367
60	2	0.0817	0.0804	60.9	0.08113
80	2	0.0196	0.0028	0.17	0.75241
100	2	0.0371	0.037	685.04	0.02431

Conclusions

Activated carbon prepared from Areca Husk carbon was effectively employed as an adsorbent for the quantitative removal of MB from aqueous solution. The observed FTIR adsorbent spectral differences before and after adsorption indicated some of the peaks was disappearing due to the absorption of MB on AHC. Presence of pores was captured for AHC before adsorption through a scanning electron microscope. The adsorption capacity of the adsorbent was considerably affected by adsorbent dose, initial concentration, particle size, contact time, initial pH and Temperature. Maximum adsorption of MB was found at pH 7, AHC dosage 150 mg, initial dye concentration of 10 mg L⁻¹ and an equilibrium time of 120 min. The maximum adsorption capacity of areca husk carbon for MB was found to be 46.3 mg g⁻¹. Value of R_L was found to be 0.033 and

confirmed that the prepared activated carbon is favorable for adsorption of MB dye. The suitability of pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models for the sorption of MB onto AHC was also discussed. Kinetic data follow the pseudo-first order kinetic model.

Intra-particle diffusion model proves that pore diffusion plays major role in the dye adsorption. The calculated thermodynamic parameter shows the spontaneous and exothermic nature of the adsorption process. ANOVA indicated that the most considerable factor were temp, initial concentration, particle size and adsorbent dosage. The results showed the possibility of AHC for MB dye removal from aqueous solution as an alternative for most costly used adsorbent.

Acknowledgements

The authors are grateful to the Kumaraguru college of Technology for doing the research by providing some of the equipments for the research work.

References

1. Syed Shabudeen, P.S., Study of the Removal of Malachite Green from Aqueous Solution by using Solid Agricultural Waste, *Res.J.Chem.Sci.*, 2011, 1, 88-104.
2. Aygun, A., Yeniso-y-Karakas, S. and Duman, I., Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, *Micropor. Mesopor. Mater.*, 2003, 66, 189-195.
3. Weng, C.H. and Pan, Y.F., Adsorption characteristics of methylene blue from aqueous solution by sludge ash. *Colloids Surfaces A: Physicochem. Eng. Aspect.*, 2006, 274, 154-162.
4. Batzias, F.A., Sidiras, D.K., Schroeder, E. and Weber, C., Simulation of dye adsorption on hydrolyzed wheat straw in batch and fixed bed-systems, *Chem. Eng. J.*, 2009, 148, 459-472.
5. Cengiz, S. and Cavas, L., Removal methylene blue by invasive marine seaweed: *Caulerpa racemosa* var. *Cylindracea*. *Bioresour. Technol.*, 2008, 99, 2357-2363.
6. Wang, S., Boyjoo, Y., Choueib, A. and Zhu, Z.H., Removal of dyes from aqueous solution using fly ash and red mud, *Water Res.*, 2005, 39, 129-138.
7. Bhattacharya, K.G. and Sharma, A., Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder, *Dyes and Pigm.*, 2005, 65, 51-59.
8. Batzias, F.A. and Sidiras, D.K., Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems, *J. Hazard. Mater.*, 2004, 114, 167-174.
9. Garg, V.K., Amita, M., Kumar, R. and Gupta, R., Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rosewood sawdust: a timber industry waste, *Dyes and pigm.*, 2004, 63, 243-250.
10. Bulut, Y. and Aydin, H.A., Kinetic and thermodynamics of methylene blue adsorption on wheat shells, *Desalination*, 2006, 194, 259-267.
11. Atef, S. and Zaydien, A.L., Adsorption of Methylene Blue from Aqueous Solution onto a Low-Cost Natural Jordanian Tripoli., *American Journal of Environmental Sciences*, 2009, 5, 197-208.
12. Janos, P., Coskun, S., Pilarova, V. and Rejnek, J., Removal of basic dye (Methylene blue) and acid(Egacid orange) dyes from water by sorption on chemically treated wood shavings, *Bioresour.Technol.*, 2009, 100, 1450-1453.
13. Annadurai, G., Juang, R. and Lee, D., Use of cellulose based wastes for adsorption of dyes from aqueous solution, *J. Hazard. Mater.*, 2002, 92, 263-274.
14. Pavan, F.A., Lima, E.C., Dias, S.L.P. and Mazzocato, A.C., Methylene blue biosorption from aqueous solutions by yellow passion fruit waste, *J. Hazard. Mater.*, 2008, 150, 703-712.
15. Bestani, B., Benderdouche, N., Benstaali, B., Belhakem, M. and Addou, A., Methylene blue and iodine adsorption onto an activated desert plant, *Bioresour. Technol.*, 2008, 99, 8441-8444.

16. McKay, G., Ramprasad, G. and Pratapamowli, P., Equilibrium studies for the adsorption of dyestuffs from aqueous solution by low- cost materials, *Water air soil pollut.*, 1986, 29, 273-283.
17. Ferrero, F., Dye removal of low cost adsorbents: Hazelnut shells in comparison with wood sawdust, *J. Hazard. Mater.*, 2007, 142, 144-152.
18. Kumar, K.V. and Porkodi, K., Mass transfer, Kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*, *J. Hazard. Mater.*, 2007, 146, 214-226.
19. De, D.S. and Basu, J.K., Adsorption of methylene blue on to a low cost adsorbent developed from sawdust, *Ind. J. Environ. Protec.*, 1998, 19, 416-421.
20. Ofomaja, A.E., Equilibrium sorption of methylene blue using *mansonia* wood sawdust as biosorbents, *Desalination*, 2009, 3, 1-10.
21. Lata, H., Garg, V.K. and Gupta, R.K., Removal of a basic dye from aqueous solution by adsorption using *Parthenium hysterophorus*: An agricultural waste. *Dyes and Pigm.*, 2007, 74, 653-658.
22. Vadivelan, V. and Kumar, K.V., Equilibrium, Kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, *J. Colloid Interface Sci.*, 2005, 286, 90-100.
23. Banat, F., Al-Asheh, S., Al-Ahmad, R. and Bni-Khalid, F., Bench-scale and packed bed sorption of methylene blue using treated olive pomace and charcoal, *Bio resour. Technol.* 2007, 98, 3017-3025.
24. Syed Shabudeen, P. S., Daniel, S. and Indhumathi, P., Utilising the Pods of *Delonix regia* Activated Carbon for the Removal of Mercury (II) by Adsorption Technique *Int. J. Res. Che. & Environ.*, 2013, 3, 60-65.
25. McKay, G. and Ho Y.S., Pseudo-second-order model for sorption processes. *Process Biochem.*, 1999, 34, 451-465.
26. Webber W.J., In principal and application of water chemistry, edited by Faust S.D & Hunter, J.V, Wiley, New York, 1967.
27. Ozcan A. and Ozcan A.S., Adsorption of Acid red 57 from aqueous solutions onto surfactant –modified sepiolite, *J. Hazard. Mater.*, 2005, 125, 252-259.
28. Freundlich H.M.F., Over the adsorption in solution, *J. Phys. Chem.*, 1906, 57, 385-470.
29. Temkin, I.M.J., Pyzhev V., Recent modifications to Langmuir isotherms, *Acta Physicochim.*, 1940, 12, 217-225.
30. Ravikumar, K., Ramalingam, S., Krishnan, S. and Balu, K., Application of response surface methodology to optimize the process variables for reactive red and acid brown dye removal using a novel adsorbent, *Dyes and pigm.*, 2006, 70, 18-20.
