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Study of the Removal of Basic Dye From Aqueous Solution by Using Solid Agricultural Waste

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Agricultural solid waste, namely Kapok hull was activated by sulphuric acid (1:1 ratio) for removing malachite green (basic) dye from aqueous solution. Batch kinetic and isotherm experiments were conducted to determine the sorption and desorption of the malachite green from aqueous solution with activated carbon. The factors affecting the rate of adsorption involved in the removal of dye for initial dye concentration, agitation time, carbon dose, particle size and pH variation have been studied at various temperature ranges at 300, 318 and 330 K. The experimental data was analyzed for possible agreement with the Lagergran, Langmuir and Freundlich adsorption isotherm equations. The intraparticle diffusion rate constant, adsorption rate constants, diffusion rate constants and diffusion coefficients were determined. Intraparticle diffusion was found to be the rate limiting step. The structural and morphological of activated carbon were characterized by XRD and SEM studies, respectively. Response surface method using Box-Behnken design of experiments was adopted and gives a mathematical model for the adsorption of dye stuff.

KEYWORD

Activated carbon, Adsorption, Particle size, X-ray diffraction, Scanning electron microscope.

INTRODUCTION

Among various industries, textile industry is equally considered as an intensive water consuming activity besides utilizing a wide variety of chemicals and dyes. Water resource needs to be conserved 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. Effluent discharged from the textile industries mixes with sewerage system or neighbouring water receiving bodies. The coloured wastewater interferes in the photosynthetic activity of plants since, it impedes solar radiation penetration and thereby affects ecosystem. Conventional wastewater treatment processes do not remove the dyes and colours, as they are fairly stable to light, heat and resist biodegradation because of their complex molecular structures. 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

Table 1. *Characteristic of KHAC*

Parameter	Obtained result
pH solution	6.7
Moisture content, %	2.4
Ash content, %	1.856
Decolorizing power, mg/g	22.5
Ion-exchange capacity, meq/g	0.0415
Surface area, m^2/g	158-228
Apparent density, g/L	0.42
Particle size, µm	125
Volatile matter, %	12.0
Fixed carbon, %	86.0
Calcium, %	16.0
Sodium,mg/g	7.0
Potassium, mg/g	13.0
Water soluble matter, %	2.0
HCl soluble matter (0.25N), %	7.0
Phenol number, mg	11.2

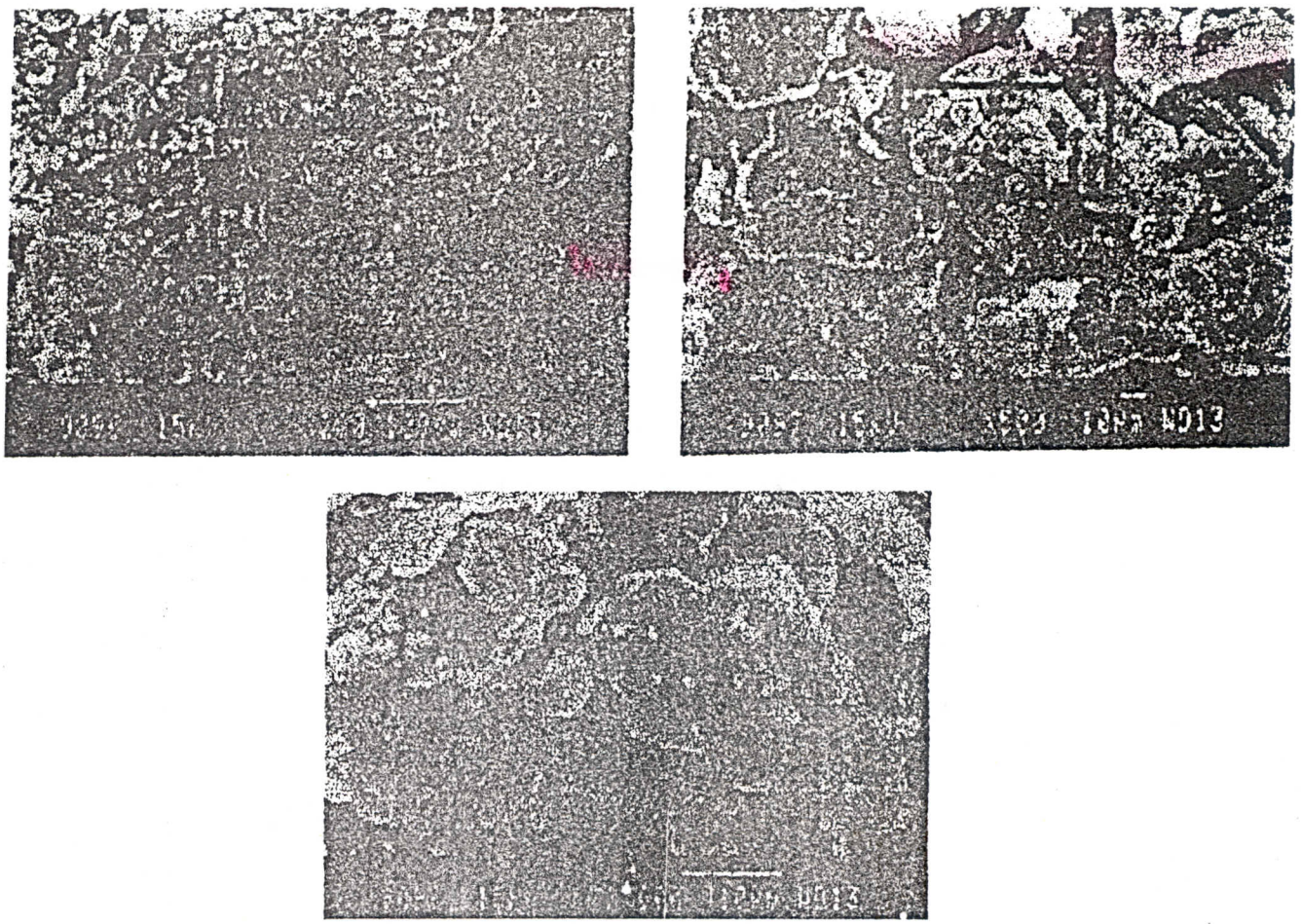


Figure 1. *SEM photograph of Kapok Hull activated carbon (KHAC) at various magnifications (x200, x500 and x2000)*

Table 2. *Effect of adsorbent dosage and particle size on the removal of malachite green (100mg/L) at 300K*

Carbon	% Removal			Log X/M			Log Ce		
dose	250	150	100	250	150	100	250	150	100
100	18	18	16	-2.745	-2.745	-2.796	-0.086	-0.086	-0.076
200	20	20	20	-3.000	-3	-3	-0.097	-0.097	-0.097
300	22	25	25	-3.135	-3.079	-3.079	-0.108	-0.125	-0.125
400	30	30	28	-3.125	-3.125	-3.155	-0.155	-0.155	-0.143
500	35	34	32	-3.155	-3.167	-3.194	-0.187	-0.18	-0.167
600	38	37	36	-3.198	-3.21	-3.222	-0.208	-0.201	-0.194
700	43	42	40	-3.212	-3.222	-3.243	-0.244	-0.237	-0.222
800	50	49	48	-3.204	-3.213	-3.222	-0.301	-0.292	-0.284
900	55	53	50	-3.214	-3.23	-3.255	-0.347	-0328	-0.301
1000	61	56	52	-3.215	-3.252	-3.284	0.409	-0.357	-0.319
1100	74	66	64	-3.172	-3.222	-3.235	-0.585	-0.469	-0.444
1200	83	82	76	-3.16	-3.165	-3.198	-0.769	-0.745	-0.62
1300	94	92	86	-3.141	-3.15	-3.179	-1.222	-1.097	-0.854
1400	100	100	100	-3.146	-3.146	-3.146	-	-	-

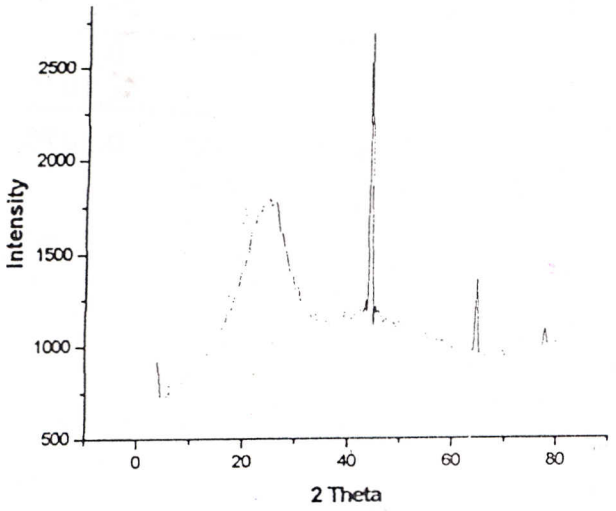


Figure 2. *X-ray diffraction pattern for KHAC*

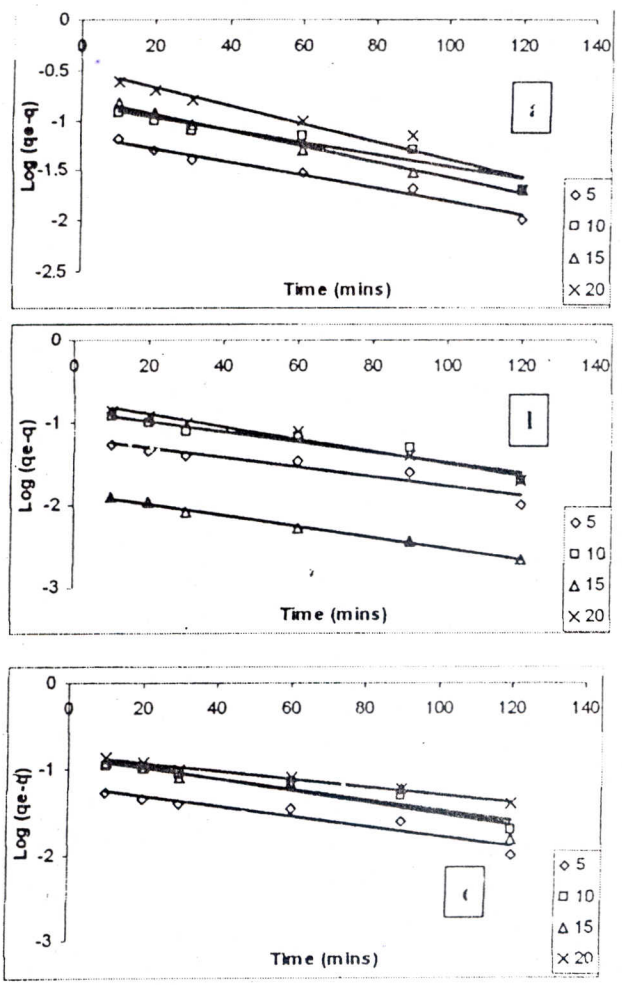


Figure 3. *Lagergren plot for malachite green removal of (a) 100 (b) 150 (c) 250 BSS particle size at 300K*

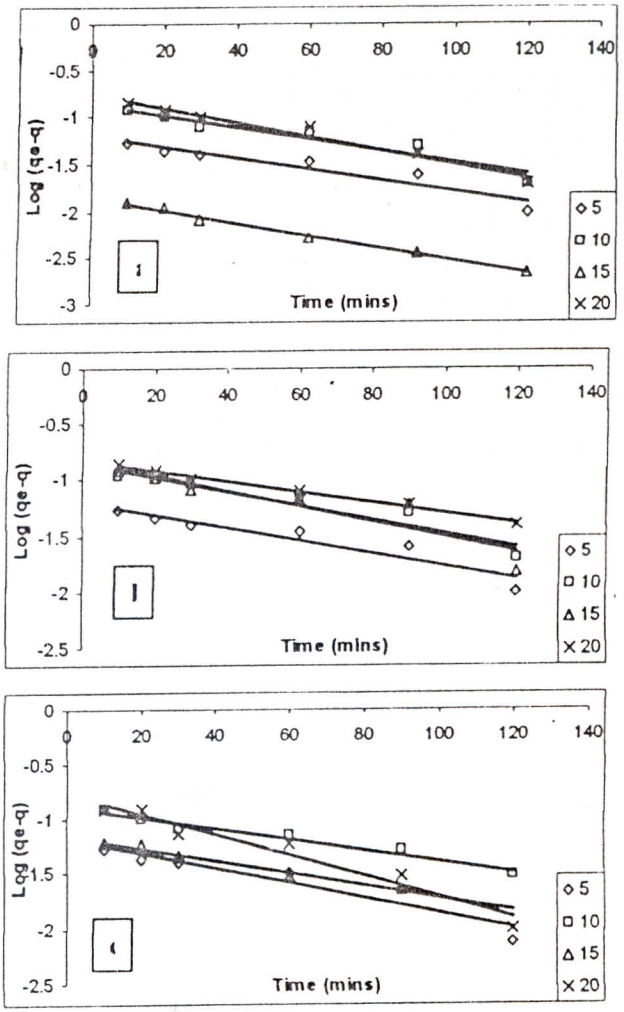


Figure 4. *Lagergren plot for malachite green removal of (a) 100 (b) 150 (c) 250 BSS particle size at 318K*

Table 3. *Freundlich constants for the adsorption of malachite green at various particle sizes at various temperatures*

Temp., K	Particle size, BSS mesh	nx10	$K_F x10^2$	R^2
300	250	0.8647	2.8727	0.5280
	150	1.1105	2.8464	0.6646
	100	1.3737	2.8325	0.7146
318	250	0.9093	2.9255	0.4625
	150	1.2653	2.8639	0.6094
	100	1.4375	2.8679	0.6874
330	250	0.9093	2.9255	0.4625
	150	1.2653	2.8639	0.6094
	100	1.4375	2.8679	0.6874

Table 4. *Adsorption kinetic data for dye removal with various particle sizes, equilibrium time for 150min*

Particle size, BSS mesh no.	Temp., K	Dye conc., mg/100mL	q_e	γ x 10^{-5}	K_{ad}	K_P	D_P x 10^{-10}
100	300	5	0.42	5.53	0.0067	0.022	0.1075
		10	0.77	5.13	0.0062	0.040	
		15	1.20	5.33	0.0080	0.062	
		20	1.52	5.07	0.0089	0.080	
	318	5	0.43	5.73	0.0058	0.022	0.1075
		10	0.79	5.27	0.0062	0.041	
		15	1.24	5.51	0.0068	0.062	
		20	1.54	5.13	0.0074	0.077	
	330	5	0.43	5.73	0.0058	0.022	0.1075
		10	0.79	5.27	0.0062	0.041	
		15	1.24	5.51	0.0068	0.062	
		20	1.54	5.13	0.0074	0.077	
150	300	5	0.43	5.73	0.006	0.022	4.7789
		10	0.79	5.27	0.006	0.041	
		15	1.24	5.50	0.007	0.062	
		20	1.54	5.13	0.008	0.077	
	318	5	0.44	5.87	0.006	0.022	4.7789
		10	0.81	5.40	0.006	0.042	
		15	1.25	5.53	0.007	0.062	
		20	1.56	5.20	0.008	0.077	
	330	5	0.44	5.87	0.006	0.022	4.7789
		10	0.81	5.40	0.006	0.042	
		15	1.25	5.53	0.007	0.062	
		20	1.56	5.20	0.008	0.077	
250	300	5	0.44	5.87	0.006	0.023	1.72
		10	0.81	5.40	0.006	0.042	
		15	1.25	5.53	0.007	0.062	
		20	1.56	5.20	0.005	0.077	
	318	5	0.45	6.0	0.007	0.023	1.72
		10	0.84	5.6	0.005	0.043	
		15	1.26	5.6	0.006	0.061	
		20	1.61	5.37	0.009	0.082	
	330	5	0.45	6.0	0.007	0.023	1.72
		10	0.84	5.6	0.005	0.043	
		15	1.26	5.6	0.006	0.061	
		20	1.61	5.37	0.009	0.082	

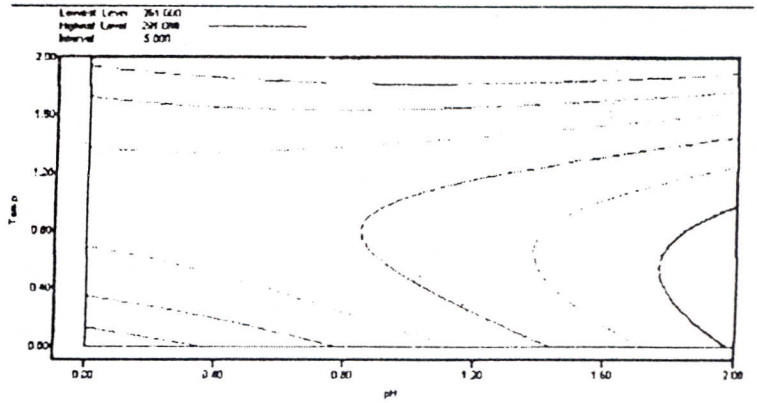
of sludge disposal. In this connection, the present study is envisaged to develop a cost effective method of treatment of textile dye. The color removal from textile effluent was attempted (McKay, 1979) and the wastewater management studies were planned and executed (Jorgensen, 1979). Industrial wastewater treatment from manufacturing chemical industries was analysed (Kiff, 1987) and the chemical properties of synthetic process (Judkins, 1982) and methodologies were formulated (Datya Keshav and Vaidya, 1984). Decolorizing dye with chlorine and ozone was developed (Ince and Gonene, 1957; Liakon *et al.*, 1997; Namboodri *et al.*, 1994;

Model : Quadratic

Response : R1

Variables
X – pH
Y – Temperature

Constants : P. Size



Model : Quadratic

Response : R1

Variables
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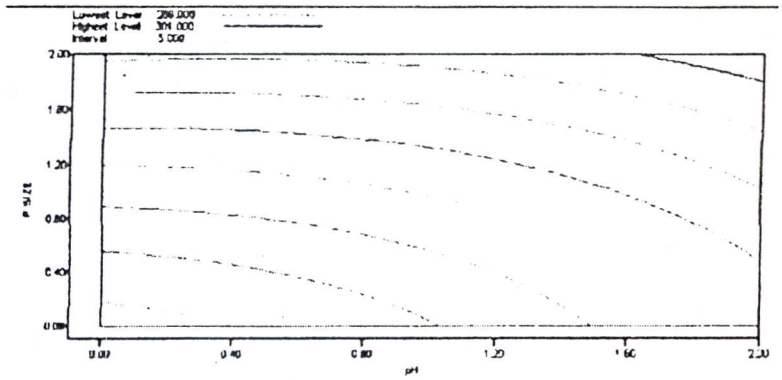
Y – P. Size

Constants : Temp.



Mcdel : Quadratic

Response : R1

Variables
X – Temperature
Y – P. Size

Constants : pH

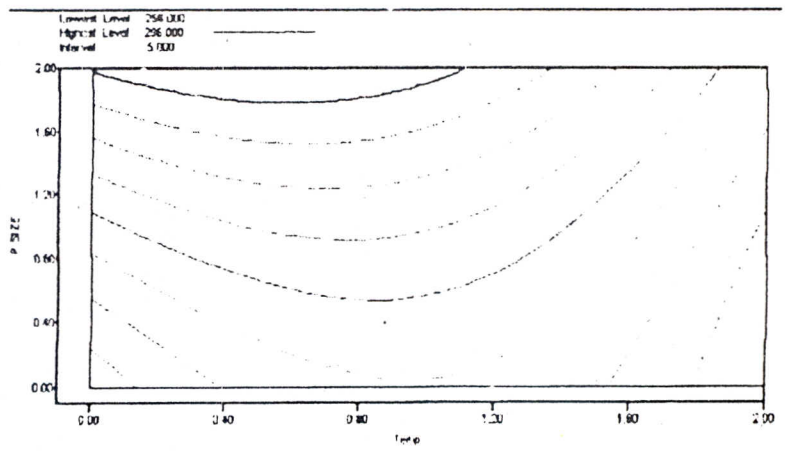


Figure 5. *Response surface plot for the adsorption of malachite green*

Uygur and Kok, 1999).

The conventional method for the removal of dyes using alum, ferric chloride, activated carbon, lime, etc., is not economical in the Indian context. The low cost conventional adsorbent for the treatment of industrial wastewater had been reviewed by Polard *et*

Table 5. *Langmuir constants and thermodynamic parameters for malachite green adsorption with different temperatures and particle size*

Particle size	Temp., K	Slope	Intercept	b, 1/mg	$Q_o x 10^2$ mg/g	R_L	ΔH^0	ΔG^0	ΔS^0
100	300	2.2931	0.3233	7.0920	0.4360	0.0802	1439	-156.9	88.66
	318	2.3292	0.2867	8.1240	0.4290	0.0790			
	330	2.3292	0.2867	8.1240	0.4290	0.0790			
150	300	1.4458	0.0449	32.200	0.6916	0.1215	1640	-863.2	139.07
	318	2.3878	0.3505	6.8125	0.4187	0.0772			
	330	2.3878	0.3505	6.8125	0.4187	0.0772			
250	300	3.3153	0.4934	6.7124	0.3016	0.0569	4242	-323	253.61
	318	2.5100	0.2506	10.010	0.3984	0.0738			
	330	2.5100	0.2506	10.010	0.3984	0.0738			

Table 6. *Box-Behnken design for three independent variables*

Trial no.	pH	Particle size, BSS mesh no.	Temp., K
1	-1	-1	0
2	+1	-1	0
3	-1	+1	0
4	+1	+1	0
5	-1	0	-1
6	+1	0	-1
7	-1	0	+1
8	+1	0	+1
9	0	-1	-1
10	0	+1	-1
11	0	-1	+1
12	0	+1	+1
13	0	0	0
14	0	0	0
15	0	0	0

al. (1992). Some works of low cost, non-conventional adsorbents has been carried out. Adsorbents used include agricultural solid wastes, such as saw dust (Asfour *et al.,* 1985), peat mass and rice hulls (Nawar and Doma, 1989), coconut husk (Low and Lee, 1990), industrial solid wastes, such as flyash from coal-burning industries (Gupta *et al.,* 1990) and Fe(III)/Cr(III) hydroxide (Namasivayam and Chandrasekaran, 1991). A study on the use of wastes of biogas residual slurry and waste banana pith which is the effective removal of Congo red, malachite green and acid violet (Namasivayam and Kanchana, 1992; Namasivayam and Yamuna, 1994), bagasse and paddy straw (Deo and Ali, 1993), coir pith (Namasivayam and Kadirvelu, 1994). Non-conventional material, like chitosan (Juang *et al.,* 1997), chitosan fibre, thermal power waste (Malik, 1994), red mud (Namasivayam and Arasi, 1997), Silica fomes (Venkatamohan *et al.,* 1998), Eucalyptus bark (Morais *et al.,* 2000), carbon from cassava peels (Rajeswari *et al.,* 2001). Activated carbon from Jackfruit peel (Stephan Inbaraj and Sulochana, 2002), activated Parthenium (Rajeswari and Subburam, 2002), palm nut shells, cashew nut shells and Broom sticks (Rajavel *et al.,* 2003), Flyash (Janos *et al.,* 2003), saw dust (Malik, 2004), Coffee grounds (Namane *et al.,* 2005), and pine saw dust (Ozacar and Sengil, 2005).

The objective of the present study is to prepare and characterize quality and evaluate the efficiency of using Kapok hull carbon as an adsorbent for the removal of dye like malachite green. However in the present study malachite green has been subjected for color removal using KHAC. 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 agitation time, initial concentration, adsorbent dose, desorption, pH and temperature. The Box-Behnken design study model was adopted. The data generated over this study have been tabulated and

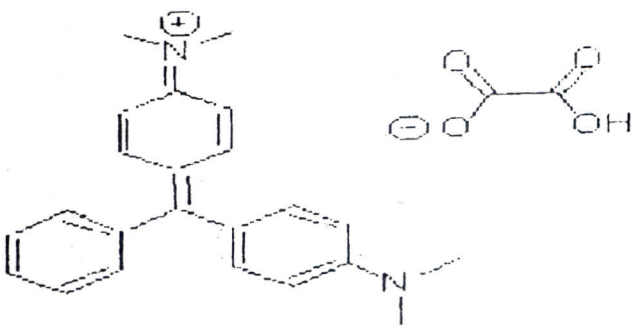
Table 7. *ANOVA for Box-Behnken model for the adsorption of malachite green*

Source	Sum of squares	Degrees of freedom	Mean square	F value
Model	5914	6	739.3	2.024
Error	2188	8	364.66	
Cor. Total	8102	14		
Root MSE	19.07		R-squared	0.928
C.V.	0.110		Adj R-squared	0.909

discussed.

MATERIAL AND METHOD

The kapok hull was cut into small pieces, dried in sunlight, then 333K for 24 hr in hot air oven. The dried material is digested in sulphuric acid (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 383K for 12 hr. Then it was taken in an iron vessel in muffle furnace and the temperature was gradually raised to 823K for an hour, ground well by using ball mill and then sieved into particle size of 250,150 and 100 BSS mesh numbers. The preparation of stock solution of dye for 1000 ppm by using double distilled water. These dye solutions were taken for adsorption studies with KHAC. The characterization of KHAC was carried out and the results were tabulated in table 1. Malachite green is a basic dye and water soluble. It dissociate into anion and coloured cations. The electrostatic attraction builds up between the coloured cations and acidic groups of acrylic fibres lead to form salt and develop the colour fade upon the fabrics. The structural studies will open the door to know about the adsorption mechanism involved with these dyes. It belongs to triphenyl methane class and it contains two amino groups. The structure of malachite green is given.



Structure of malachite green (λmax : 616.5nm)

The adsorbent KHAC sieved particle size of 250BSS mesh number was magnified by scanning electron microscope (SEM) studies by using JOEL JSM 8404 scanning microscope as shown in the figure 1. The X-ray diffraction studies of KHAC were carried out using Rotoflux X-ray Diffractometer 20KW/20A, Model 10.61 with a microprocessor recorder. The XRD pattern of the KHAC is shown in the figure 2. The morphological and XRD studies clearly revealed that the adsorbent is amorphous and highly porous in nature. From the SEM analysis it was found that there were holes and cave type openings on the surface of the adsorbent, which would have more surface area available for adsorption (Khattri and Singh, 1999). The Freundlich and Langmuir isotherm studies and Lagergran kinetic studies at various temperatures, dye solution of various concentrations was agitated with 1g of the adsorbent of 250, 150 and 100BSS mesh number particle size over a period of time with constant stirring at various pH (4, 6, 7 and 9.2). The carbon dosage (mg/L) of 100 to 1400 was agitated with a known concentration of dye solution.

The exhausted activated carbon was used for desorption studies. The carbon loaded with dye was separated and gently washed with distilled water to remove any unadsorbed dyes. The dye-laden carbons were agitated with 100ml of neutral pH

water, 1M sulpuric acid, 1M sodium hydroxide, 10% acetic acid (v/v) and 50% acetic acid (v/v) separately for 1 hr. The response surface method using the Box-Behnken design (Box and Behnken, 1960) of experiments gives a mathematical model for the adsorption of dyestuff. In this study the effect of several factors influencing the dye adsorption, such as pH, particle size and temperature have been considered as the critical variables designated as X_1, X_2 and X_3, respectively and statistical design was used to determine the optimal levels of adsorption studies. The low, middle and high level of each variable pH (4, 6, 5 and 9), particle size (250, 150 and 100BSS mesh number) and temperature (300,318, and 330K were designated as -1, 0 and +1, respectively. For the three significant independent variables X_1, X_2 and X_3, the mathematical relationship of the predicted response on these variable can be approximated by the quadratic model equation :

$$M = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_{11}X_1 + A_{22}X_2^2 + A_{33}X_3^2 + A_{12}X_1X_2 + A_{13}X_1X_3 + A_{23}X_2X_3$$

Where M is the predicted response, A_0 is constant, X_1 is pH, X_2 is particle size and X_3 is temperature, A_1, A_2, A_3 are linear coefficients, A_{12}, A_{13} and A_{23} are cross product quadratic coefficients. The degree of experiments chosen for this study was Box-Behnken (Box and Hunter, 1957), a fractional design for the three independent variables. It is applicable once the critical variables have been identified (Kapat *et al.*, 1996). The design is preferred only because relatively few experimental combinations of the variables are adequate to estimate potentially complex response functions. For the Box-Behnken design of three independent variables, a total of 15 experiments were necessary to estimate the 10 coefficients of the model (Myers, 1971). The present study models were presented and used for surface plot study.

RESULT AND DISCUSSION

Langmuir adsorption isotherm

Langmuir adsorption isotherm is based on the assumption that, ''adsorption is a type of chemical combination in which adsorbate is adsorbed on the adsorbent surface and the adsorbed layer is unimolecular''. Langmuir represented the following equation :

$$qe = (Q_o \times b \times C_e) / (1 + (b \times C_e))$$

Where, qe is equal to the quantity of dye adsorbed in mg/g of the adsorbent, Q_o is the maximum quantity of dye adsorbed in mg/gram of the adsorbent, b and C_e is the constant of Langmuir adsorption and the dye concentration at equilibrium in mg/L, respectively.

Langmuir adsorption parameters are determined by transforming the equation, which is in linear form. The Linear plot of C_e/q_e vs. C_e showed that the adsorption followed Langmuir isotherm model. The values of monolayer capacity 'Q_0' and Langmuir constant 'b' had been evaluated from the intercept and slope of these plots by using graphical techniques. The effect of isotherm shape has been taken into consideration with a view to predict whether the studied adsorption system is favorable or unfavorable. The essential features of the Langmuir isothem may be expressed in terms of equilibrium parameter R_L, which is dimension less constant referred to as separation factor or equilibrium parameter (Weber and Chakravarti, 1974) :

$$R_L = 1/(1 + bC_o)$$

Where C_o is the initial concentration and 'b' is the constant related to the energy of adsorption (Langmuir constant). The values of R_L indicate the nature of the isotherm, if the conditions are $R_L > 1$, $R_L = 1$, $0 < R_L < 1$ and $R_L = 0$ are unfavorable, linear, favorable and irreversible, respectively. The value of R_L was less than one which showed that the adsorption process was favorable.

Effect of temperature

The adsorption study was carried out for malachite green at various temperatures, like

300, 318 and 330K. This was mainly due to the increase in pore volume. It may be due to the adsorption increases with increase in temperature and pores volume. Further, the results were analysed and found that the adsorption process was endothermic and best fitted to Langmuir adsorption isotherm model. By employing graphical and mathematical methodologies, the Q_0 b and R_L values for different particle size for the dye was evolved and it was revealed that R_L values lay between 0 and 1. It was inferred that the adsorption process followed Langmuir model and favorable for adsorption. The free energy change (ΔG^0), enthalpy change or total energy change (ΔH^0) and entropy change (ΔS^0) values were evolved by utilizing mathematical tools and adopting the following thermodynamic formulae :

Free energy change, $\Delta G^0 = -RT \ln b$

Enthalpy change or total energy change (ΔH^0) can be calculated by using the thermodynamics formula :

$\ln [b_1/b_2] = \Delta H^0/RT$

The Gibbs free energy is :

$\Delta G^0 = [\Delta H^0 - \Delta S^0]/T$

The results of ΔG^0, ΔH^0 and ΔS^0 were summarized in the table 5. The positive values of ΔH^0 indicate that the adsorption is involved with weak forces of attraction. It was observed that the ΔH^0 values increased with decrease of particle size. The adsorption was found to be endothermic in nature. The positive and increased ΔS^0 values for smaller particle size indicated that the KHAC showed greater affinity towards the dye. Further, the negative ΔG^0 value indicated the spontaneous nature of the adsorption model. For unimolecular reactions, the energy of activation was evolved by using the following equation :

$E_a = \Delta H^0 + RT$

If the energy of activation of adsorption system was less than 42KJ/mol, then the process was confirmed to be diffusion controlled. Suppose if it is in between 5 to 20 KJ/mol, the sorption process was due to activated sorption. It was observed that, the value of energy of activation for malachite green by KHAC was in between 5 to 20 KJ/mol in our study that confirms the activated adsorption. The carbon follows Langmuir adsorption isotherm, it had greater affinity towards the dye then the process was spontaneous. Similar pattern of results were inferred (Gupta *et al.*, 2003; Ho *et al.*, 2002).

Freundlich adsorption isotherm

The livear plot of log X/m vs. log C_e showed that the adsorption followed Freundlich adsorption isotherm model. The values of X/m and C_e observed from the adsorption experiments carried over by using KHAC of different particle sizes, namely 100, 150 and 250BSS mesh numbers of constant mass was agitated with malachite green of known concentration at various temperatures to the respective equilibrium periods are presented in table 4. Based upon these experiments Freundlich adsorption isotherm plot was formed by plotting log X/m vs. log C_e and the slope and intercept of this linear portion of isotherm plots were determined by adopting graphical methodology. These slope values had indicated adsorption intensity 'n' and the intercept values indicated an idea about adsorption capacity K_F. These values were tabulated in table 3. It was observed that the adsorption capacity of the KHAC had increased with decrease of particle size at 300, 318K of the dye selected for the present study and there is no change for adsorption at the elevated temperatures namely 330K. The adsorption process, the surface energy q_e is a fuction of heat for adsorption. The term K_F and n are adsorption constants are used to explain adsorption process (Albanis *et al.*, 2000). The Freundlich adsorption isotherm is as follows :

$q_e = X/m = K_F C_e^{1/n}$

$\ln X/m = \ln q_e = \ln K_F + 1/n \ln C_e$

Where q_e, C_e, X and M are adsorbed amount on the adsrobent at equilibrium concentration of dye in solution (mg/L), amount of dye adsorbed (mg) and weight of the adsorbent used (g). The constant K_F represents the quantity of dye adsorbed in mg/g adsorbent for a unit equilibrium concentration which is an approximate indicator of adsorption capacity. These constants can be evolved by linearising the above equation by adopting mathematical techniques (Vondrias *et al.*, 2002). The 1/n is a measure of adsorption intensity. It was learnt that, If n = 1 then that the partition between the two phases was independent of the concentration. If the 1/n value is below one it indicates a normal adsorption. On the other hand 1/n being above one indicates cooperative adsorption (Atkins, 1970; Mohan and Karthikeyan, 1997). It is generally stated that the value of 'n' that is in the range of 2 to 10, represents good adsorption isotherm. It was also observed that the 'n' values of the adsorbent for the dye at various temperature and particle sizes were found out and this value is from 2 to 10, which confirmed that the activated carbon underwent a favourable for Freundlich isotherm. The experimental data were attempted to fit into Freundlich adsorption isotherms, and it was efficiently and most effectively fitted. It clearly indicated that the system followed Freundlich adsorption isotherm model and the adsorbent's surface under study were heterogeneous. The correlation coefficient was evolved with graphical techniques and it was tabulated (Table 3).

These values exhibited some deviation from linearity and tried to form curves. It was clearly indicated in the graphs under observations. The reason for this behaviour was that the initial curve portion represented the formation of monolayer followed by intraparticle diffusion at later stages and final plateau portion indicate the saturation of adsorption process. It was summarized that the KHAC followed Freundlich adsorption isotherm model, the derived 'n' value for almost all dyes being in the value from 1 to 10. The graphical studies showed that the small deviation from linearity, the mechanism of adsorption followed the formation of monolayer, intraparticle diffusion and saturation in a favorable pattern.

Kinetics of adsorption

The adsorption kinetic study is quite significant in wastewater treatment as it describes the solute uptake rate, which in turn controls the residence time of adsorbate uptake at the solid-solution interface. Dosage study is an important parameter because it determines the capacity of adsorbent for a given initial concentration of the dye solution (Atkins, 1970). In this present investigation, the kinetics of the adsorption systems were studied by plotting the amount of dye adsorbed on the adsorbent with time for different adsorbent dosages at a constant initial concentration (100 mg/L), at different temperatures and particle size 250, 150, 100BSS mesh numbers. In all the experiments, it was observed that with increase in adsorbent loading, the fraction of dye removal increases and it was graphically plotted. From the nature of the curves, the amount of dye adsorbed on the adsorbent more or less remained constant. Moreover, the smoothness of the curves for dye adsorption showed that the process of adsorption was continuous and involved either monolayer formation of the adsobent surface or monolayer coupled with other mechanism predominantly with intra particle diffusion. Since the increase in active adsorption sites increased with adsorbent dosage, the amount of dye adsorbed increased with sorbent dosage. The large availability of adsorption sites with higher adsorption dosage has a positive effect on the initial rate of dye uptake. Similar type of trend in adsorption of dyes on different types of low cost adsorbents were reported (Lakshminarayan *et al.*, 1994; McKay *et al.*, 1980; Deo and Al; 1993).

Adsorption rate constant

Determination of efficiency of adsorption process requires a thorough understanding of kinetics of uptake of adsorbate by adsorbent or the time dependence of the concentration distribution of the solute in both bulk solution and solid adsorbent and identification of rate determining step. In order to investigate the mechanism of sorption and potential rate controlling steps, such as mass transport and chemical reaction processes, the Lagergren kinetic model (Figure 4) known as pseudo-first order equation, has been used to test the experimental data.

Pseudo–first order equation

The pseudo-first order equation of Lagergren is generally expressed as follows :

$$dq/dt = K_{ad} (q_e - q_t)$$

Where q_e and q_t are the sorption capacity at equilibrium and sorptin capacity at time and K_{ad} is the rate constant of pseudo = first order sorption (1/min). After integration and applying boundary condition t = 0 to t = t and q = 0 to q = q_t, the integrated form becomes :

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

Data for Lagergren plots of dyes were presented in figure 4. The linear plots of log (q_e-q_t) vs. t showed that adsorption followed the pseudo first order rate expression given by Lagergren. The K_{ad} value for malachite green was calculated from the slope of linear plots. The rate constants for adsorption (1/min) of dye at ambient temperature of different particle size are presented in the figures. From these observations, the KHAC follows Lagergren pseudo first order kinetics. Similar patterns of results were reported earlier (Bhatnagar and Jain, 2005; Webber, 1967).

Pore diffusion coefficient (D_P)

The pore diffusion coefficient values fall between 10^{-11} to 10^{-13} and the process is said to be controlled due to intraparticle diffusion coefficient (stephen Inbaraj and Sulochana, 2002). Similarly, if the external diffusion coefficient value falls between 10^{-5} to 10^{-8}, then the process is said to follow external mass transfer (Furusuwa and Smith, 1974; Khare *et al.,* 1987). The geometry of the adsorbent particles is spherical in nature, based upon the Helfferich (Helfferich, 1962) assumption. The studies of Webber proves that the adsorption kinetics with pore diffusion coefficient are inter related and the rate determining step is based upon pore diffusion coefficient (Gupta *et al.,* 2003; Lee *et al.,* 2003).

Pore diffusion coefficient, $D_P = 0.03 (r_o^2)/t_{1/2}$

Where, $t_{1/2}$- Time for half-change (min), r_0- Radius of adsorbent (cm). The values of pore diffusion coefficients were calculated on the particles size for the dye and these inferences were compared with the results and it was inferred that pore diffusion was not the rate limiting step (Wu, *et al.,* 1999). Based upon different ideas available in literature, it is possible to determine the nature of adsorption process with reference to the pore diffusion coefficient. If the values fall between 10^{-11} to 10^{-13} (cm^2/sec) and the process is said to be controlled due to intraparticle diffusion coefficient (Stephen Inbaraj and Sulochana, 2002), but the dye system under the study showed the value within the limit (10^{-11} cm^2/sec). It confirms that the process is controlled due to intraparticle diffusion. These values were presented in the table 4.

Intraparticle diffusion (q)

The intraparticle diffusion rate constant can be given as follows :

$$q = K_P T^{1/2}$$

K_P values for the adsorption of the dye are presented in the table 4. The rate constant for intraparticle diffusion K_P was calculated from the slope of the linear equation by q (mg/g) vs. $T^{1/2}$ (sec). From the plots it was found that the initial sharp portion with

subsequent linearity indicated that more than one mode of sorption mechanism was in operation. The first sharp portion may be due to final equilibrium stage (McKay *et al.,* 1980). The values of K_p generally increased with the increase in dye concentration and it can be related to concentration diffusion. Similar results were reported for metal ion adsorption onto activated carbon cloths (Deo and Ali, 1993; Kadirvelu *et al.,* 2005).

Initial adsorption coefficient (γ)

The initial adsorption coefficient equation can be given as :

$\gamma = (dC/dt)t_o \times V/M\ C_o$

Where, $dC = C_e$ at equilibrium time, dt = Equilibrium time, V = Volume of solution, M = Mass of carbon, C_o = Initial concentration (mg/L).

The values for the adsorption coefficient of the dyes are presented in the table 4. The initial adsorption coefficients increased with increase in initial dye concentration and therefore it is concentration dependent. From the results, an overall examination of effect of dye concentration on rate constant K_{ad} describe the mechanism of adsorption takes place. In the cases of strict surface adsorption, a variation of rate should be proportional to the concentration. The relationship between initial solute concentration and the rate of adsorption was not linear This was due to the limitation caused by pore diffusion of the adsorption. It is clearly indicated in the table 4. It was concluded that pore diffusion also limited the overall rate of adsorption.

Effect of pH

The experiments carried out at different pH show that there was no change in the percent removal of dye over the entire pH range. The neutral dye malachite green did not have any impact to pH change. From this it is clear that due to the dye is not having any ionic character therefore the adsorption is not influence by pH variation. The adsorption is only based upon activated carbon adsorbent. In other words, the adsorption of malachite green dye on KHAC does not involve ion exchange mechanism. If the adsorption would have occured through ion exchange mechanism there should have been an influence on the dye adsorption while varying the pH.

Box-Behnken model

Response surface methodology is an empirical modelization technique devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. In the present investigation the adsorption of malachite green by KHAC from aqueous solution is optimized by Box-Behnken method. The influence of the three factors, such as temperature, pH and adsorbent particle size on adsorption was investigated and the results for the linear coefficients and quadratic cross product coefficients A_0, A_1, A_2, A_3, A_{11}, A_{22}, A_{33}, A_{12}, A_{13} and A_{23} were 242.83, 11.833, 16.833, 35.333, 2.8333, 2.833, -14.167, -3, -8 and -6, respectively. The summary of the analysis of variance (ANOVA) is listed in table 7. From the table 7, it was found that quadratic regression and quadratic square regression was significant at the confidence level of >98%. This indicates that the selected variance (Temperature, pH and particle size) have a combined effect on the adsorption of malachite green by KHAC. The theoretical values of dye adsorption on adsorbents by the Box-Behnken model at each experimental point and experimentally observed values were compared and found that a close agreement between the experimental values and the theoretical values for 15 trials. The experimental values are 210.3, 239.1, 248.8, 265.9, 171, 209.5, 255.1, 262.5, 168.1, 212.4, 248.3, 269.3, 235.5, 235.5 and 235.5. The predicted values are 216.8, 246.5, 256.5, 274.2, 176.3, 216, 263, 270.7, 173.3, 219, 256, 277.6, 242.8, 242.8 and 242.8.

Effect of contour plot

The effect of variables was analyzed and plots were obtained to assess the effect of each factor graphically. The effect of certain factors is function that describes how the response moves as the level of those factor changes, when the other factors are fixed at their optimum levels. From the figure 5, it can be observed that each of the three variables used in the present study has its individual effect on adsorption. From the contour plots, it has been found that there is a gradual increase in adsorption of dyes with increase in temperature from the lower level 300K (coded value -1) to the middle level 318K (coded value -0) and there is no further increase to adsorption even if the temperature is increased to 330K (coded value +1). Similarly, the adsorption increases with respect to the particle size of KHAC from 100, 150 and 250BSS mesh numbers (coded value -1, 0 and +1). It is also revealed that the malachite green dye would have no marked change to adsorption with respect to pH change. The pH level selected for this study was 4, 6.7 and 9 (coded value -1, 0, +1).

The results obtained by adapting Box-Behnken model in the study of absorption of various dyes on KHAC proves, absorption of dye depends only upon the particle size of absorbent and it was not influenced by pH or temperature. The experimental values and the predicted values of Box-Behnken design model are in close agreement with quadratic regression >98%. From the contour plots figure 5, it is revealed that the carbon particle of 250BSS mesh number highest level of absorption. Similar type of results was reported by Annadurai *et al.* (1999).

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dye can be desorbed using neutral pH water, then the attachment of the dye on the adsorbent is by weak bonds. If sulphuric acid or alkaline water can desrobs the dye, then the adsorption is by ion exchange. If an organic acid, like acetic acid can desorbs the dye, then the dye is held by the adsorbent through chemisorp-tion. Neutral pH water, 1M sulphuric acid and 1M sodium hydroxide did not show any desorption of the dye. However, 10% acetic acid (v/v) and 50% acetic acid (v/v) solubilized 9 and 37% of malachite green, respectively, from the dye adsorbed carbon. The non-reversibility of adsorbed dye in mineral acid or base is in agreement with the pH independent results obtained. Desorption of dye in acetic acid (organic medium) indicates that the malachite green are adsorbed onto KHAC carbon through activated adsorption mechanism.

CONCLUSION

Carbon prepared from waste Kapok hull was found effective in removing malachite green dye from aqueous solution. The adsorption is faster and the rate is mainly controlled by intraparticle diffusion based on sorption phenomenon. The structure of the dye is also influenced on adsorption.

The surface morphology studies using SEM proves that, it contains more pores that leads to develop more adsorption sites. The XRD pattern confirms the amorphous nature of the adsorbent.

The adsorption is controlled only by particle size because small particles will have more surface area for adsorption it is proved in the above studies. The adsorption in independent of pH of the medium. The adsorption increases from 300 to 318K and further the increase in temperature do not have any influence upon adsorption therefore this adsorbent can be effectively utilized from 300 to 318K and even elevated temperatures. It is revealed that the adsorbent is effectively utilized in all temperatures. The above said results were confirmed by the kinetic studies and supported by Box-Behnken design of experiments and surface plots.

It is evident from the studies that the use of chemically modified Kapok hull activated carbon for the removal of malachite green dye is technically feasible, ecofriendly and economically attractive for the treatment of dye house wastewater before subjecting it to reverse osmosis by this the life of costly resin could be effectively be increased.

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