

Adsorption of Anionic and Cationic Dyes onto Granular Activated Carbon

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Abstract: Granular coconut shell activated carbon was used for the adsorption of methylene blue and methyl orange from aqueous effluent. Effect of initial dye concentration (10, 25, 50, 75, 100 mg/L), pH (2 to 10), Temperature (30 to 50°C), adsorbent dosage (1, 1.5, 2 and 2.5 g/L) and adsorbent size (0.088, 0.707 and 1.68 mm) were studied. The process followed pseudo second order kinetics (for MB) and intra particle diffusion (MeO). Equilibrium data was examined using Langmuir and Freundlich, Tempkin and Dubinin - Radushkevich adsorption isotherm models. Langmuir adsorption isotherm model was found to be the best fit model with high R^2 value for both MB and MeO adsorption. Langmuir monolayer adsorption capacity of coconut shell GAC was found to be 90.55 mg of MB/g of GAC and 57.30 mg of MeO/g of GAC. Thermodynamic study carried out to find Gibbs free energy, Enthalpy and Entropy values. The positive and low values of ΔH° , ΔS° confirms the adsorption of MB and MeO are endothermic physisorption.

Key words: Granular activated carbon • Isotherm • Kinetics • Methylene blue • Methylene orange • Thermodynamics

INTRODUCTION

Dyes are basically chemical compounds that can connect themselves to surface of fabrics to impart colour. Synthetic dyes are widely used in many fields of advanced technology, e.g. textile, paper, leather tanning, food processing, plastics, cosmetics, rubber, printing and dye manufacturing industries [1]. Over 10,000 dyes with a total yearly production over 7×10^5 MT are commercially available [2-4]. Several research reports revealed that even small quantities of dyes are highly toxic which causes acute disorders in aquatic organisms.

Methylene blue (MB) is one of the most commonly used dyes for industrial applications. Methyl orange (MeO) is a commonly used monoazodye in laboratory assays, textiles and other commercial products [5]. These dyes are considered as highly toxic, methylene blue has various dangerous effects on human and animals. It can cause heart rate increasing, nausea and vomiting [6].

Adsorption has been found to be superior to other techniques for waste water treatment in terms of initial cost, flexibility and simplicity of design, ease of operation

and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances [7,8]. Activated carbon is the most widely used adsorbent with great success because of its high adsorption capacity [9].

The adsorption of anionic MO or cationic MB from MO/MB mixture using polyacrylonitrile fiber hydrothermally treated with hyper branched polyethylenimine [10], date - pits activated carbon [11] and variety of adsorbents used for multicomponent adsorption process was listed in ref [12].

In this study we reported the adsorption kinetics, isotherm and thermodynamics of cationic MB and anionic MeO onto coconut shell granular activated carbon in batch mode.

MATERIALS AND METHODS

Adsorbent: Coconut shell granular activated carbon (GAC) supplied by Adsorbents carbon private limited, Tuticorin was used as an adsorbent and was not purified prior to use. The physiochemical properties of adsorbent are shown in Table 1.

Table 1: Physiochemical properties of GAC

Adsorbent Material	Coconut Shell AC
Physical state	Granules
Size	8 x 30 mesh
pH	9 to 11
Surface Area(min)	1000 m ² /g
Iodine Value (min)	1100 mg/g
Ash Content (max)	5%

Table 2: Physical and Chemical properties of dyes

Adsorbate	Methylene Blue	Methyl Orange
Chemical Formula	C ₁₆ H ₁₈ N ₃ S	C ₁₄ H ₁₄ N ₃ NaO ₃ S
λ _{max} (nm)	665	475
Molecular Weight (g/mol)	319.85	327.34
Color	Blue or Dark green	Bright orange
Physical state	Powder	Powder

Adsorbate - Methylene Blue and Methyl Orange:

Methylene Blue and Methyl Orange supplied by Sigma-Aldrich (Trichy) was used as adsorbate. Double distilled water was employed for preparing all the solutions. Stock solution of 1000 mg/L of both MB and MeO dye was prepared. The properties and molecular formula of MB and MeO is given in Table 2.

Experimental Details - Batch Mode: To investigate the influence of pH, Initial dye concentration, Adsorbent dosage, Adsorbent size and Temperature of dye solution experiments were conducted in 250ml conical flasks. 100ml of dye sample with initial dye concentration of 100 mg/L (MB and MeO) was taken and placed in a shaker at 30°C, constant pH (3.5 for MeO, 8.5 for MB). An adsorbent dose of 1g/L of 1.698 mm GAC was added. The size distribution of GAC was analyzed using sieve analysis. The volume surface mean diameter of GAC was obtained as 1.693mm. The shaker speed maintained constantly at 130rpm for all runs except effect of temperature study for that 250rpm is maintained. At regular interval of time sample was collected using micropipette and analyzed using colorimeter (λ_{max} 665 nm for MB and λ_{max} 475nm for MeO). The experiments were carried out till the equilibrium reached. Standard calibration curve for concentration versus optical density prepared initially for both the dyes. To study effect of concentration C^o varied from 25 to 100mg/L (for MB) and 10 to 100mg/L (for MeO), for effect of amount of adsorbent 1g/L to 2g/L, for effect of adsorbent size varied from 0.088mm to 1.68 mm. pH 2 to 10 and temperature 30°C to 50°C used to study the effect of pH and temperature over dye adsorption process. By comparing with the

standard curve equilibrium dye concentration was measured. Experiments are repeated three times and all the calculations are made for the average value. The equilibrium amount of dye adsorbed as calculated using the formula given below,

$$q_e = \frac{v}{m}(C_o - C_e) \tag{1}$$

$$q_t = \frac{v}{m}(C_o - C_t) \tag{2}$$

Where, q_e and q_t are Equilibrium amount of adsorbate adsorbed and amount of adsorbate adsorbed per gram of adsorbent at time t(mg/g), V is volume of dye solution(L), m is mass of an adsorbent (mg), C_e and C^o residual dye concentration at equilibrium time and at t=0 (mg/L).

Adsorption Isotherm: There are several equations for analyzing experimental adsorption equilibrium data. The Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (Two parameter model) is the most accepted surface adsorption model for single solute systems. The equations and parameters of such isotherms are given below [12],

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \tag{3}$$

Where, q_e and q_{max} are Equilibrium amount of adsorbate adsorbed and Maximum amount of adsorbate adsorbed per gram of adsorbent(mg/g), K_L Langmuir adsorption equilibrium constant (L/mg), C_e residual dye concentration (mg/L) [13].

Separation factor is given by,

$$R_L = \frac{1}{1 + K_L C_o} \tag{3.a}$$

If R_L > 1, Unfavorable; R_L = 1, Linear; 0 < R_L < 1, Favorable; R_L = 0, Irreversible.

The Freundlich adsorption isotherm is given as:

$$q_e = K_F C_e^{1/n} \tag{4}$$

Where, q_e is Equilibrium amount of adsorbate adsorbed per gram of adsorbent (mg/g), K_F Freundlich adsorption equilibrium constant (mg /g.(L/mg)^{1/n}), C_e residual dye concentration (mg/L) and n is intensity of adsorption (n>1, Heterogeneous adsorption).

Tempkin Isotherm is given by,

$$q_e = \frac{RT}{b} \ln AC_e \quad (5)$$

Where, q_e is Equilibrium amount of adsorbate adsorbed per gram of adsorbent (mg/g), R gas constant (kJ/mol.K), T is temperature in Kelvin, A and b are tempkin isotherm constants, C_e residual dye concentration (mg/L).

Dubinini - Radushkevich Isotherm is given by,

$$q_e = (q_D) \exp(-B_{DR} \varepsilon^2) \quad (6)$$

$$\varepsilon = RT \ln(1 + C_e^{-1}) \quad (6.a)$$

$$E = \sqrt{\frac{1}{2B_{DR}}} \quad (6.b)$$

Where, q_e and q_D are Equilibrium and isotherm constant amount of adsorbate adsorbed per gram of adsorbent (mg/g), R gas constant (kJ/mol.K), T is temperature in Kelvin, ε is polanyi potential(-), B_{DR} DR isotherm constant, C_e residual dye concentration (mg/L) and E is sorption energy (kJ/mol).

Kinetics Models: Adsorption kinetics like pseudo first and second order kinetics and intra particle diffusion model was studied. The pseudo first order model equation as follows [13, 14].

$$q_t = q_e (1 - e^{-K_1 t}) \quad (7)$$

Where, q_t and q_e are Amount of MB adsorbed at time t and Equilibrium amount of MB adsorbed per gram of adsorbent (mg/g), K_1 pseudo first order constant (minute⁻¹).

The pseudo second order model equation is given as follows:

$$q_t = \frac{K_2 q_e^2}{1 + K_2 q_e t} \quad (8)$$

Initial Sorption rate given by,

$$h = K_2 q_e^2 \quad (8.a)$$

Where, q_t and q_e are Amount of MB adsorbed at time t and Equilibrium amount of MB adsorbed per gram of adsorbent (mg/g), K_2 pseudo second order constant (g/mg.minute).

The intra particle diffusion model is given by:

$$q_t = K_{id} \sqrt{t + I} \quad (9)$$

Where, q_t is Amount of methylene blue adsorbed at time (t) per gram of adsorbent (mg/g), K_{id} Morris - Weber model constant g / (mg. minute)^{1/2}, I is intercept.

Thermodynamics: The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°) were calculated using the following equations

$$K_d = \frac{q_e}{C_e} \quad (10)$$

$$G^0 = -RT \ln K_d \quad (11)$$

$$\Delta G^0 = \Delta H^0 - \Delta S^0 \quad (12)$$

Where K_d is the distribution coefficient, q_e is Equilibrium amount of adsorbate adsorbed per gram of adsorbent (mg/g), R gas constant (kJ/mol K), T is temperature in Kelvin, C_e residual dye concentration (mg/L), ΔG° is Gibbs free energy (kJ/mol), ΔH° is enthalpy (kJ/mol) and ΔS° is entropy (J/mol). The values of ΔH° and ΔS° are determined by Van,t Hoff's plot between $\ln K_d$ vs 1/T.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH was investigated on the adsorption of MB and MeO on coconut shell GAC at a pH of 2 to 10 for 24h. The efficiency of adsorption is depends on solution pH. Variation in solution pH leads to the variation in degree of ionization of adsorptive molecule. The results shows maximum amount of MB which is the cationic dye adsorbed per gram of adsorbent occurs at pH 8 to 9 and for the anionic MeO dye pH 3 to 4 was optimum. The graphs are shown in Fig.1.a and b respectively.

Effect of Initial Dye Concentration on Adsorption: To determine the proper MB and MeO adsorption and equilibrium time, the effect of dye solution concentration was studied by varying the initial concentration 25 to 100 mg/L for MB and 10 to 100 mg/L for MeO until no adsorption of dye onto GAC took place. The adsorption data for amount of dye adsorbed versus time at different concentrations plot given in Fig.2.a and b respectively.

The results indicate that the amount of dye adsorbed per unit mass of GAC increased with increase in dye concentration. This is due to increase in the driving force of the concentration gradient with increase in initial dye

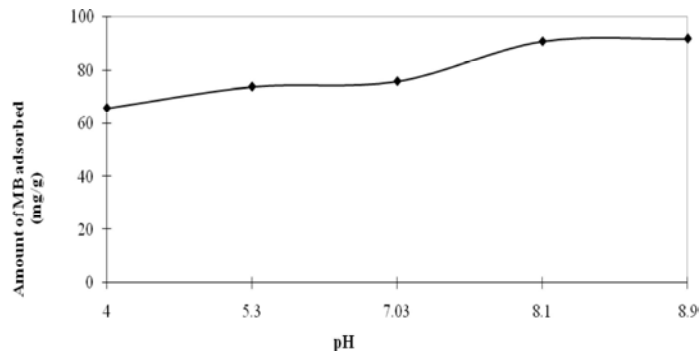


Fig. 1: a. Effect of pH on MB adsorption
 Conditions: 100 mL of 100 mg/L MB solution, 1g/L of 1.693 mm GAC, 130rpm shaker speed at 30°C

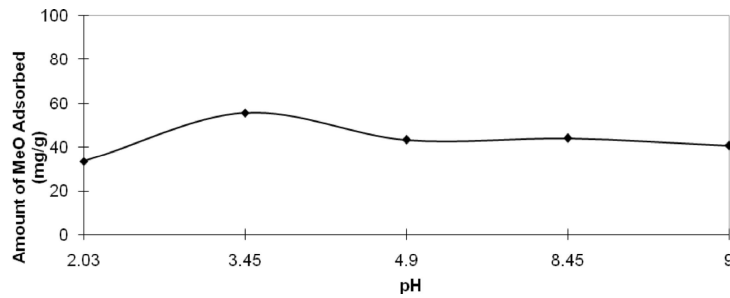


Fig. 1: b Effect of pH on MeO adsorption
 Conditions: 100 mL of 100 mg/L MeO solution, 1g/L of 14 mesh GAC, 130rpm shaker speed at 30°C

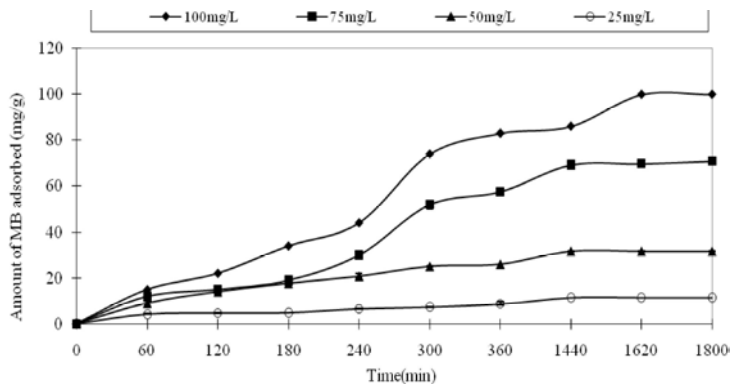


Fig. 2: a Effect of initial dye concentration on MB adsorption
 Conditions: 100mL of MB solution at pH 8.5, 1g/L of 1.698 mm GAC, 130rpm shaker speed at 30°C

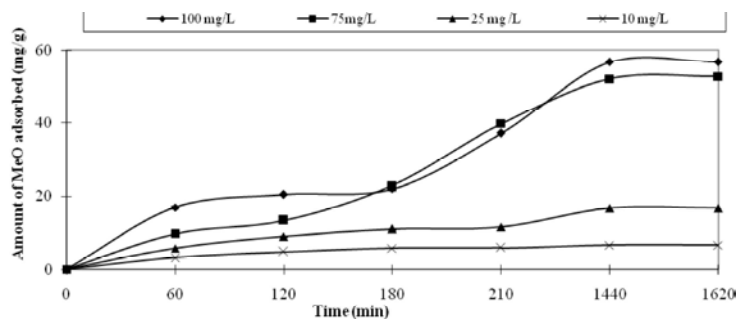


Fig. 2: b Effect of initial dye concentration on MeO adsorption
 Conditions: 100mL of MeO solution at pH 3.5, 1g/L of 14 mesh GAC, 130rpm shaker speed at 30°C

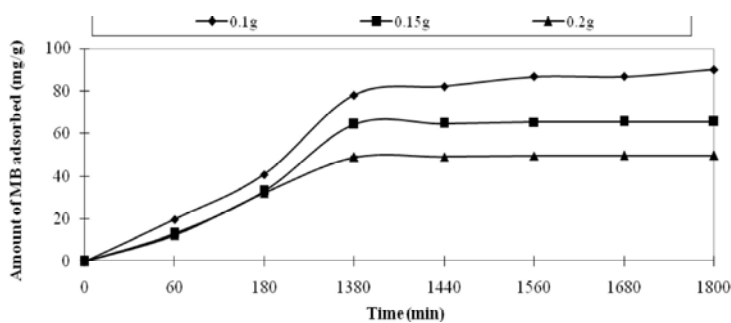


Fig. 3: a Effect of amount of adsorbent on MB adsorption
 Conditions: 100mL of 100 mg/L MB solution at pH 8.5, 1.698mm GAC, 130rpm shaker speed at 30°C

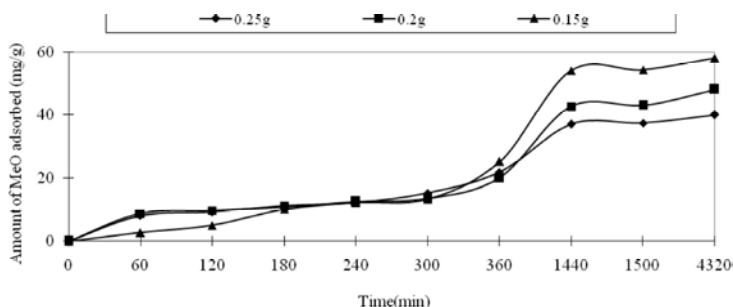


Fig. 3: b Effect of amount of adsorbent on Moe adsorption
 Conditions: 100mL of 100mg/L Moe solution at pH 3.5, 1g/L of 14 meshes GAC, 130rpm shaker speed at 30°C

concentration and also the available sites of on an adsorbent. The amount of MB adsorption increased from 11.5 to 100 mg/g by increasing initial concentration from 25 to 100 mg/L and for MeO 6.67 to 56.67mg/L. The contact time needed for dye adsorption at high initial concentration 100 mg/L of both MB and MeO took 24 h to reach equilibrium.

Effect of Adsorbent Amount on Mb Adsorption: The effect of adsorbent dosage was studied by varying the mass of GAC from 1g /L to 2.5g/L. The initial concentration of MB solution was 100mg/L and pH 8.5, Temp 30°C and for MeO initial concentration 100mg/L and pH 4 at 30°C. In both the cases the shaker speed 130 rpm and volume of dye solution 100mL was taken. The amount of dye adsorbed versus time at different mass of GAC shown in Fig.3.a and b respectively. The adsorption Capacity decreases with increases in mass of adsorbent. The capacity decreased with increase in mass of adsorbent added due to the increasing in number of available adsorption sites and the adsorption sites remain unsaturated by increasing mass of adsorbent.

Effect of Adsorbent Particle Size: The batch experiments were carried out using adsorbent with different particle size (0.088, 0.707 and 1.68mm) at pH 8.5, 30°C and

100 mg/L for MB and pH 4 for MeO. The rate of adsorption increased for decreased particle size is shown in Fig.4.a and b. This is due to the increase in surface area per unit volume of adsorbent (i.e. smaller particles yield larger surface area for adsorption) [15].

Effect of Temperature: The Effect of temperature over adsorption of dyes was studied by varying the temperature between 30 to 50°C ($\pm 2^\circ\text{C}$) shown in Fig 5.a and 5.b. 100mL of 100mg/L MB and MeO solutions at pH 8.5 and 4 with 1g/L and 1.5g/L of GAC respectively kept in temperature controlled shaker at 250rpm. The results showed for an endothermic process of adsorption the amount of adsorbent adsorbed increased with increase in temperature. This is due to increasing the mobility of the dye molecules and increasing the number of active sites with increase in temperature [16].

Adsorption Isotherms: Adsorption isotherm constants obtained from linear regression are given in Table 3. The maximum adsorption capacity of MB onto GAC based on Langmuir isotherm is obtained as 90.33mg/g. Langmuir isotherm is perfectly fits to the experimental value and its R^2 value is calculated as 0.9989 and for MeO q_{max} is 57.035 mg/g with R^2 0.999. The separation factor (R_L) shows adsorption is favorable for both dyes. The intensity of

Table 3: Adsorption isotherm constants of MB onto GAC

	Isotherm Constants	MB	MeO
Langmuir	q_{max} ($g\ g^{-1}$)	90.33	57.3015
	K_L ($L\cdot mg^{-1}$)	0.9373	5.3756
	R_L	0.01055	0.0019
	R^2	0.9989	0.9990
Freundlich	n	5.7893	3.6506
	K_F ($mg^{-1+1/n}\cdot L^{1/n}$), g^{-1}	47.8863	4.6867
	R^2	0.9488	0.8810
Tempkin	$B(-)$	10.9077	6.9108
	$A(-)$	87.4754	406.3775
	R^2	0.958	0.963
Dubinin-Radushkevich	a_m ($g\ g^{-1}$)	86.4735	3.9373
	β ($mol^2\cdot kJ^{-2}$)	0.4781	0.0138
	E ($kJ\cdot mol^{-1}$)	1.0226	6.0067
	R^2	0.9730	0.958

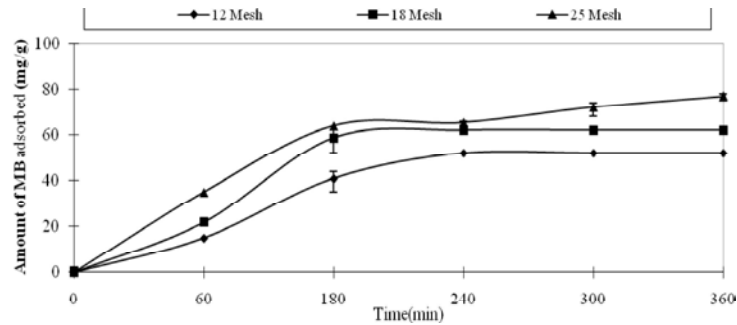


Fig. 4 a: Effect of size of adsorbent on MB adsorption
 Conditions: 100mL of MB solution at pH 8.5, 1g/L GAC, 130rpm shaker speed at 30°C

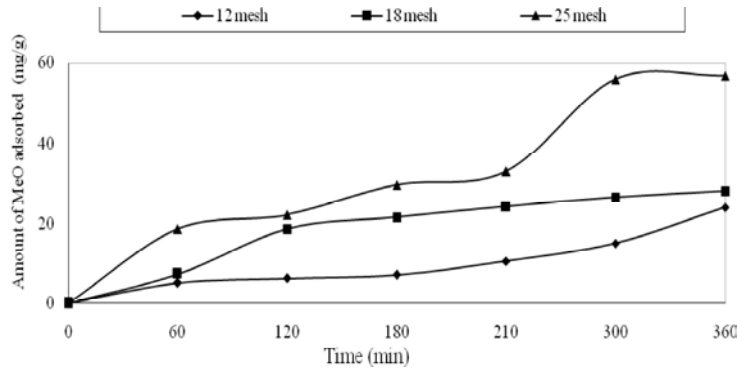


Fig. 4 b: Effect of amount of adsorbent on Moe adsorption
 Conditions: 100mL of 100mg/L Moe solution at pH 3.5, 1.5 g/L of 0.99mm GAC, 130rpm shaker speed at 30°C

adsorption (n) shows heterogeneity of MB, MeO adsorption on GAC. Non linear plots of adsorption isotherm of MB and MeO onto GAC given in Fig.6.a and b.

Adsorption Kinetics: Kinetic constants are tabulated in Table 4 for $C^{\circ}100$ mg/L and amount of adsorbent added is 0.1 g of GAC per 100mL of dye solution. The best fit model was reported using R^2 value. Pseudo

second order and intra particle diffusion models are fitted with experimental data. Iodine value of GAC is high which indicates the volume of micro pores so intra particle diffusion plays role in adsorption of dyes on GAC.

Non linear plot of pseudo first order, pseudo second order and intra particle diffusion models of adsorption kinetics for MB and MeO onto GAC given in Fig 7.a and 7.b.

Table 4: Kinetic constants for C^o- 100 mg/L, 1 g/L of GAC

Kinetic Constants		MB	MeO
Pseudo first order	K_1 (minute ⁻¹)	0.0012	0.00137
	$q_{e,1}$ (mg.g ⁻¹)	98.8667	51.1713
	R^2	0.955	0.908
Pseudo second order	K_2 (g.(mg.minute) ⁻¹)	2.77504E-05	1.3493E-05
	$q_{e,2}$ (mg.g ⁻¹)	105.3856	85.0076
	R^2	0.9967	0.9303
Intra particle diffusion	K_{id} (g.(mg. minute) ^{-1/2})	1.4308	1.5661
	I	21.8653	-6.369
	R^2	0.8739	0.9912

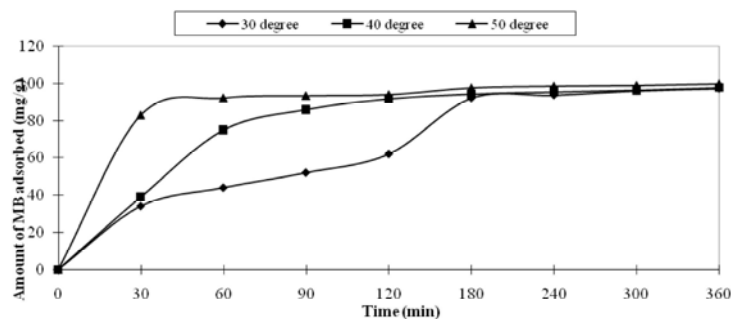


Fig. 5: a Effect of Temperature on MB adsorption
 Conditions: 100mL of 100mg/L MB solution at pH 8.5, 1.5 g/L of 0.088mm GAC, 250rpm shaker speed

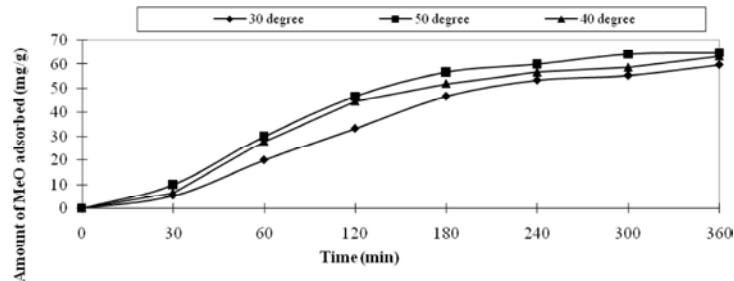


Fig. 5: b Effect of Temperature on Moe adsorption
 Conditions: 100mL of 100mg/L Moe solution at pH 3.5, 1.5 g/L of 0.088mm GAC, 250rpm shaker speed

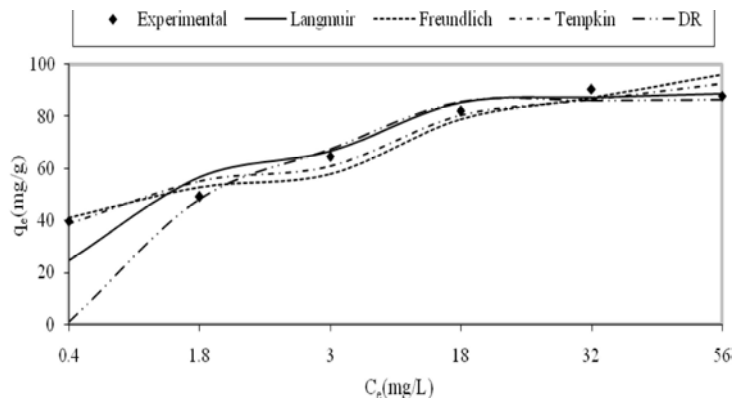


Fig. 6: a Non Linear plot of MB adsorption isotherm

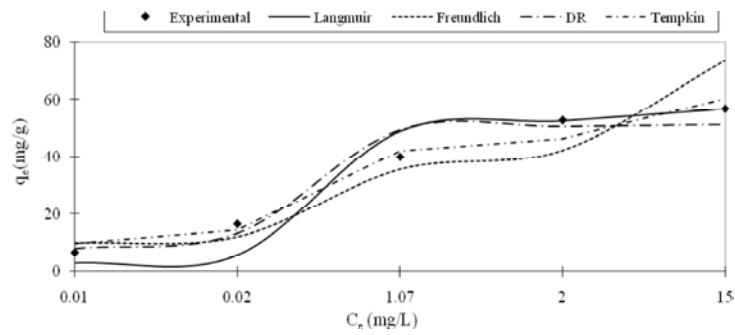


Fig. 6: b Non Linear plot of MB adsorption isotherm

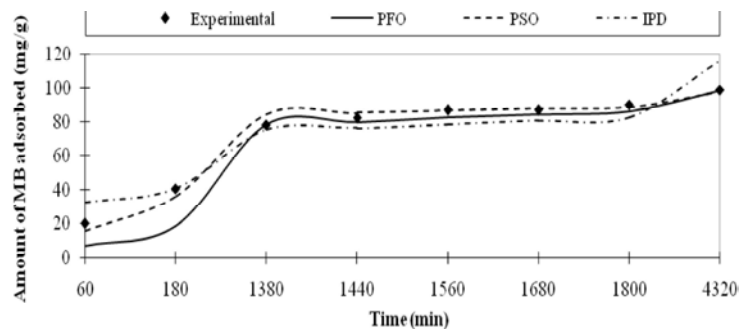


Fig. 7: a Non Linear plot of MB adsorption kinetics

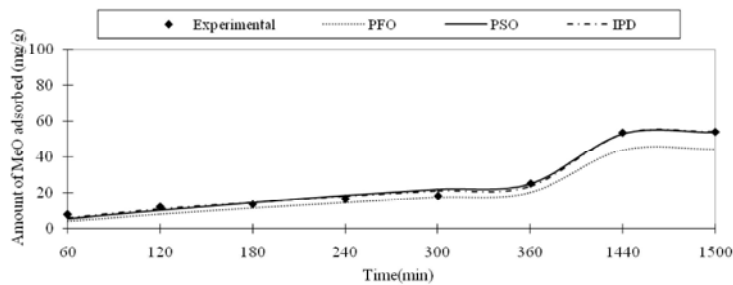


Fig. 7: b Non Linear plot of MeO adsorption kinetics

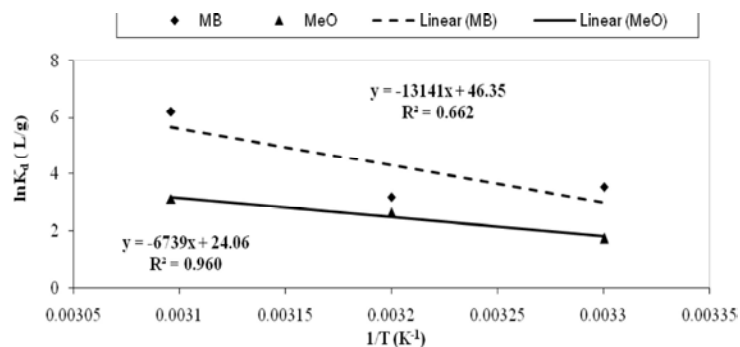


Fig. 8: Thermodynamic analysis of MB and MeO

Thermodynamic Parameters: The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°) were calculated and listed in Table 5. The Values of ΔH° and ΔS° were determined by

plotting linear graph between $\ln K_d$ vs. $1/T$ shown in Fig. 8 The negative value of ΔG° at all the temperatures for both the dye indicates the feasibility of process. The positive value of ΔH° confirms the adsorption reaction is

Table 5: Thermodynamic parameters for the adsorption of MB and MeO onto GAC

Thermodynamic Constants	MB			MeO		
	303	313	323	303	313	323
T(K)	303	313	323	303	313	323
ΔG° (kJ/mol)	-8.9363	-8.3190	-16.6845	-4.377	-6.9156	-8.3722
ΔH° (kJ/mol)	109.2618	56.3305				
ΔS° (J/mol.K)	385.4119	200.9124				
R ²	0.662	0.97				

endothermic for both dyes. The low value of sorption energy from DR isotherm ($E < 8$ kJ/mol) [17] confirms that the nature of adsorption process is physisorption for both MB and MeO.

CONCLUSION

Adsorption of textile dyes (methylene blue and methyl orange) on to granular coconut shell activated carbon was studied. Effect of initial dye concentration, adsorbent dosage and adsorbent size, pH and temperature were studied in batch mode. By increasing the adsorbate concentration, adsorbent size and operating temperature the amount of adsorbate adsorbed per gram of adsorbent gets increased. The optimum pH for MB and MeO is found to be 8.5 and 3.5 respectively. Langmuir, Freundlich, Tempkin and D-R isotherms were calculated. Langmuir adsorption isotherm model was found to be the best fit model with high R² value. Langmuir monolayer adsorption capacity of coconut shell GAC is 90.33 mg/g for MB and 57.30 mg/g for MeO. Adsorption kinetics was fitted with pseudo second order kinetics and intra particle diffusion for MB and MeO respectively. Based on the thermodynamic study results both MB and MeO adsorption process is endothermic. The ΔH° (kJ/mol), ΔS° (J/mol.K) value is 109.262, 385.41(for MB) and 56.33, 200.91 (for MeO).The nature of adsorption is physical adsorption. From the results, it could be concluded that the coconut shell GAC is used to remove textile dyes from aqueous solution (multicomponent adsorption). Further the study is continued simulation and validation of this batch study in industrial type adsorption column.

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