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Biosorption of Methyl Orange from Aqueous Solutions by Silk Maize as an Eco-friendly Biosorbent

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In this study, silk maize activated carbon developed from maize waste material was tested as biosorbent for the removal of methyl orange dye from aqueous solutions. Adsorption of methyl orange onto this low-cost natural adsorbent was studied by batch adsorption at different temperature. The effects of contact time, adsorption dose and initial dye concentration on adsorption capacity were studied. The kinetic of the sorption was analyzed using the pseudo-first-order, pseudo-second-order and Elovich kinetic models. The data showed that the second-order equation was the more appropriate. The equilibrium sorption isotherms have been analyzed by the Langmuir, Freundlich, Tempkin and Harkins-Jura (H-J) models. The Langmuir isotherm has the highest correlation coefficient ($R^2 > 0.99$). The apparent thermodynamic parameters were calculated and the obtained values support the conclusion that the reactive dye molecules sorbs by exothermic process.

Key Words: Biosorption, Silk Maize, Methyl orange, Equilibrium.

INTRODUCTION

The removal of colour from aquatic systems caused by presence of synthetic dyes is extremely important from the environmental view point because most of these dyes are toxic, mutagenic and carcinogenic[1,2]. The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, *i.e.* molecules with one or several azo (N=N) bridges linking substituted aromatic structures. These dyes are designed to be chemically an photolytically stable, they exhibit a high resistance to microbial degradation and are highly persistent in natural environment[3]. Various physicochemical and biological techniques can be employed to remove dyes from wastewaters. They include the membrane filtration[4] coagulation / flocculation[5], adsorption[6], ion exchange[7,8] advanced oxidation (chlorination, ozonation)[9], flotation, chemical reduction[10] and biological treatment[11]. The technical and economic feasibility of each technique is determined by several factors (dye type, wastewater composition, operation costs and generated waste products). Also a number of materials such as natural clay and activated carbon have been used as sorbent for dye removal[12]. Activated carbon is the most popular and widely used adsorbent but it is expensive and it is cost increase with the quality[13]. Many investigations have been done on the feasibility of low cost material as the sorbent for removal of various dye from wastewater including: waste coir pith[14], modified clays[15], giant duck weed, chitosan[16] and powdered peanut hull[17]. The purpose of this work is to investigate the capability of activated carbon developed from silk maize as a biosorbent for removal of methyl orange dye from aqueous solution. Bath studies are carried out involving process parameters such as initial dye concentration, solution temperature, contact time and biosorbent dose. Equilibrium and kinetic analysis were conducted to understanding sorption process.

EXPERIMENTAL

Analytical grade reagent methyl orange was used in all the experiments and used as received without any purification and water purification. Its colour is stable within the pH range of the study. A stock solution of 1000 mgL^{-1} was prepared by dissolving the required amount of dye in double distilled water. Working solutions of the desired concentrations were obtained by successive dilutions of the stock solution. The concentration of the dye was determined at 470 nm, using UV-VIS spectrophotometer (Perkin Elmber Lambda 25).

Adsorbent preparation: The silk maize biomass was washed several times with distilled water and dried in a drier for 2 h at 120 ºC until a constant weight was reached. Then it was cut into small pieces. The sieved raw materials were subject to chemical activation. The sample was soaked in a solution of phosphoric acid (28 %) for 24 h. The sample is then decanted, dried in an oven at 150 ºC then carbonized in a muffle furnace at 350 ºC for 2 h and then sieved to an average particle size and kept in a glass bottle until used.

Batch adsorption experiments: To study the effect of important parameters like the initial dye concentration, biosorbent dose and temperature on the adsorption removal of methyl orange, batch experiments were conducted. For each experimental run, exactly 250 mL of reactive dye solution of known initial concentration, known amount of the biosorbent (50 mg) were taken in a 300 mL stoppered flask, with a constant speed of 400 rpm at 25 ºC. Samples were withdrawn at different time intervals (0-180 min), filtrated and analyzed for remaining dye concentration. The percentage removal of dye was calculated using the following relationship

$$\%\ \text{Colour removal} = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

where, C_0 and C_t (mg L^{-1}) are the initial dye concentration and concentration at time t, respectively. Kinetics of adsorption were determined by analyzing adsorption uptake of the dye from aqueous solution at different time intervals. For adsorption isotherms, dye solutions of different concentrations (20-100 mg L^{-1}) and at different temperatures (25-55 ºC) were agitated with known amounts of adsorbents until the equilibrium was achieved. Equilibrium adsorption capacity was calculated from the relationship.

$$q_e = \frac{(C_0 - C_e)}{W} V \qquad (2)$$

where, q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e is the dye concentration at equilibrium, V(L) is the volume of solution and W(g) is the weight of adsorbent.

RESULTS AND DISCUSSION

Effect of contact Time: The relation between adsorption of methyl orange and contact time were investigated to identify the rate of dye removal. Fig. 1 shows the percentage removal of methyl orange at different initial dye concentrations ranging from (20 to 100 mgL^{-1}) and 25 ºC.

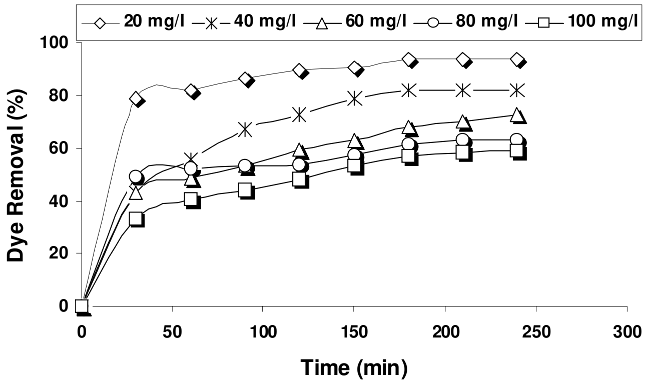

Fig. 1. Effect of contact time on the removal of methyl orange with different initial concentrations using Silk Maize (biosorbent dose = 50 mg) at 25 ºC temperature

The dye was rapidly adsorbed in the first 20-30 min and then the adsorption rate decreased gradually and equilibrium was found to be nearly 3 h when the maximum dye adsorption capacity was reached. At the beginning the adsorption rate was fast as the dye ions were adsorbed by the exterior surface of the activated carbons. When the adsorptions of the exterior surface reached saturation, the dye ions exerted onto the pores of the adsorbent particles and were adsorbed by the interior surface of the particle. This phenomenon takes a relatively long contact time.

Effect of initial dye concentration and temperature on adsorption of methyl orange: The experimental results of the sorption of methyl orange on silk maize activated carbon at various initial dye concentrations are shown in Fig. 2. The experiments were carried out at adsorbent dose (50 mg) in the test solution, room temperature (25 ºC) and at different initial concentrations of methyl orange (20, 40, 60, 80 and 100 mg L^{-1}) for 3 h. The percentage of adsorption efficiency was decreased with the increasing of initial dye concentration in the solution, which reflects adsorption decreasing with increasing in initial dye concentration, although the actual amount of dye adsorbed per unit mass of activated carbon increased with the increase in initial concentration. It is evident from Fig. 2 that the amount of dye adsorbed on the solid phase silk maize activated carbon at a lower initial concentration of dye was smaller than the corresponding amount when higher initial concentrations were used. However, the percentage removal of methyl orange was greater at lower initial concentrations and smaller at higher initial concentrations. In the process of methyl orange adsorption initially dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally, it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time. These results clearly indicate that the adsorption of methyl orange from aqueous solution was dependent on its initial concentration.

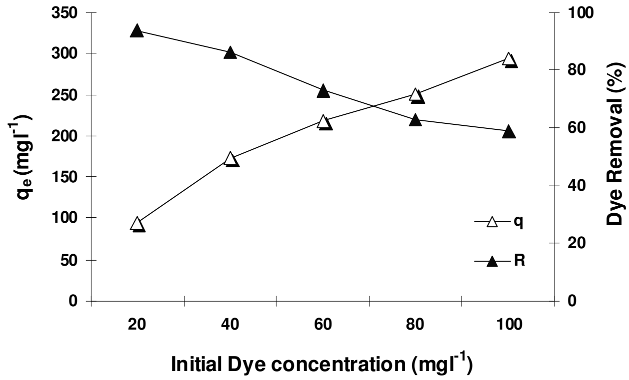

Fig. 2. -▲- R %: relation between initial dye concentrations and the removal of methyl orange (20, 40, 60, 80 and 100 mg L^{-1}), biosorbent dose =50 mg, at room temperature; -Δ- q_e: The relation between amounts of dye adsorbed at equilibrium and its initial concentration using silk maize

Fig. 3 illustrates the effect of temperature on adsorption of methyl orange. It is shown that the adsorption of methyl orange on activated carbon decreases as the solution temperature increases. Similar results were obtained by various authors for the adsorption of dyes on various adsorbents[18-20]. This can be explained by the exothermic spontaneity of the adsorption process and by the weakening of bonds between dye molecules and active sites of adsorbent at high temperatures.

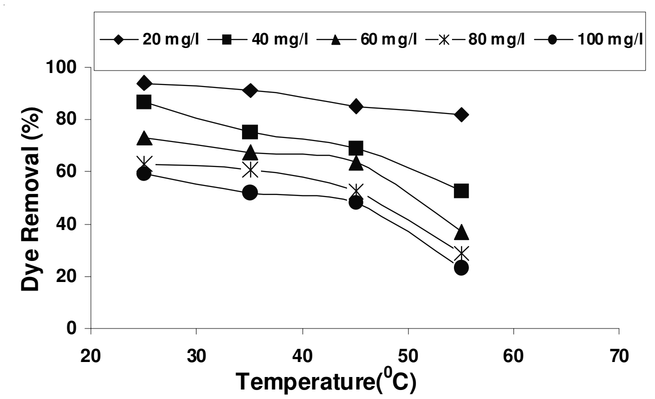

Fig. 3. Effect of temperature on dye removal by Silk Maize (biosorbent dose = 50 mg, dye concentrations = 20, 40, 60, 80 and 100 mg L^{-1}, contact time = 3 h)

Effect of biosorbent dose on methyl orange adsorption: The adsorption of methyl orange on silk maize activated carbon was studied by changing the quantity of biosorbent (20, 40, 60, 80 and 100 mg) in the test solution while keeping the initial methyl orange concentration (100 mg L^{-1}), temperature (25 °C) constant at different contact times for 3 h (Fig. 4.). The per cent adsorption was increased and equilibrium time was decreased with biosorbent dose increased. The adsorption increased from 40 to 100 %, as the biosorbent dose was increased from 20 to 100 mg at equilibrium time (3 h). Increase in the adsorption with biosorbent dose can be attributed to increased activated carbon surface area and availability of more adsorption sites.

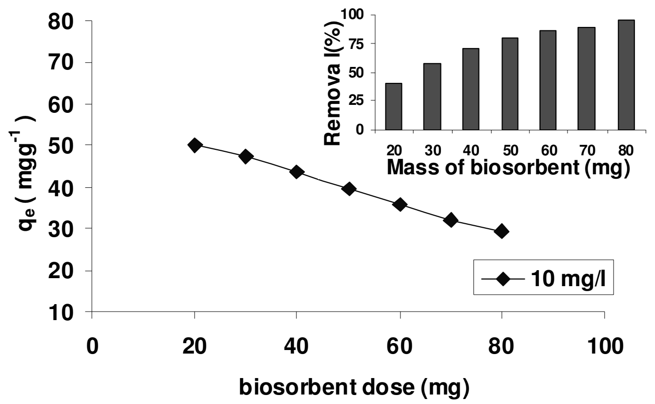

Fig. 4. Effect of biosorbent dose on qe of methyl orange (C_0 = 10 mg L^{-1}), at room temperature; Inside figure: the relation between initial dye concentration and the removal of MO with different biosorbent dose

Adsorption kinetic of methyl orange onto silk maize: Several steps were used to examine the adsorption dynamics controlling of sorption process such as chemical reaction, diffusion control and mass transfer. Kinetic models are used to test experimental data from the adsorption of methyl orange onto silk maize activated carbon. The kinetics of methyl orange adsorption onto silk maize activated carbon is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. Thus, pseudo-first-order,[21] pseudo-second-order,[22] Elovich[23,24] and intraparticle diffusion[25,26] kinetic models were used for the adsorption of methyl orange onto silk maize activated carbon. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1, the relatively higher value is the more applicable model).

Pseudo-first-order model: The pseudo-first-order model was described by Lagergren

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where, q_e and q_t refer to the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). Integration of eqn. (3) for the boundary conditions t = 0 to t and q_t = 0 to q gives:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303}t \tag{4}$$

The values of log (q_e -q) were linearly correlated with t. The plot of log (q_e- q) *versus* t should give a linear relationship from which the values of k_1 were determined from the slope of the plot (Table-1). In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes.[27]

Pseudo-second-order model: The pseudo-second-order model[28] is represented by the following differential equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where, k_2 ($gmg^{-1}min^{-1}$) is the second-order rate constant of adsorption. Integrating eqn. 5 for the boundary conditions q_t = 0 to q_t = q_t at t = 0 to t = t is simplified as can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}(t) \tag{6}$$

The slope and intercept of plot of t/q *versus* t were used to calculate the second-order rate constant k_2. The values of rate constant (k_2) are presented in Table-1. The correlation coefficients of all examined data were found very high (R^2 = 0.99). This shows that the model can be applied for the entire adsorption process and confirms that the sorption of methyl orange on activated carbons prepared from silk maize follows the pseudo-second-order kinetic model. Similar phenomenon was observed for the adsorption of direct dyes onto activated carbon prepared from saw dust,[29] palm ash[27] and Fe(III)/Cr(III) hydroxide. The second-order rate constants were used to calculate the initial sorption rate, given by the following eqn. 7:

$$h = k_2 q_e^{\,2} \tag{7}$$

The values of initial sorption (h, mg g^{-1} min^{-1}) that represents the rate of initial sorption, is practically increased with the increase in initial dye concentrations from (20 to 80 mg L^{-1})

TABLE-1
KINETIC CONSTANT FOR DIFFERENT KINETIC MODELS AT ROOM TEMPERATURE

C_0 (mg/L)	Pseudo-first-order		Pseudo-second-order		Elovich equation				Intraparticle diffusion		
	$k_1 \times 10^3$	R^2	$k_2 \times 10^3$	R^2	h	a	b	R^2	k_{dif}	C	R^2
20	13.8	0.9821	1.03	0.9985	9.93	49.37	8.33	0.9588	1.904	68.0	0.9923
40	17.3	0.9670	0.33	0.9982	11.36	51.29	23.17	0.9891	5.23	103.8	0.9980
60	19.1	0.9257	0.32	0.9976	17.45	85.97	25.32	0.9739	5.75	142.9	0.9945
80	20.0	0.9338	0.31	0.9963	21.74	105.4	27.96	0.9860	6.31	168.8	0.9956

(Table-1). It was observed that the pseudo-second-order rate constant (k^2) decreased with increasing of initial dye concentration from (20 to 80 mg L^{-1}).

Elovich equation: The simple Elovich model equation is generally expressed by the following equation:

$$q_t = a + b \ln t \tag{8}$$

The slope and intercept of plot of q_t *versus* ln (t) were used to calculate the values of the constants a and b as given in Table-1.

Intra-particle diffusion model: Adsorption is a multistep process involving transport of the adsorbate (dye) molecules from the aqueous phase to the surface of the solid (silk maize activated carbon) particles then followed by diffusion of the solute molecules into the pore interiors. If the experiment is a batch system with rapid stirring, there is a possibility that the transport of sorbate from solution into pores (bulk) of the adsorbent is the rate-controlling step[30]. This possibility was tested in terms of a graphical relationship between the amount of dye adsorbed and the square root of time[25]. Since the methyl orange is probably transported from its aqueous solution to the silk maize activated carbon by intraparticle diffusion, so the intraparticle diffusion is another kinetic model should be used to study the rate-limiting step for methyl orange adsorption onto silk maize activated carbon. The intraparticular diffusion is commonly expressed by the following equation:

$$q_t = k_{dif} t^{0.5} + C \tag{9}$$

where, C is the intercept and k_{dif} (mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion rate constant. The values of q_t were found to give two lines part with values of $t^{0.5}$ and the rate constant k_{dif} directly evaluated from the slope of the second regression line and the values of intercept C, which is related to the thickness of the boundary layer was reported in Table-1. The plot confirms that adsorption of the methyl orange onto the silk maize activated carbon is independent of one another, as plot usually shows two intersecting lines depending on the exact mechanism. The first one of these lines representing surface adsorption at the beginning of the reaction and the second one is the intraparticle diffusion at the end of the reaction. There is no sufficient indication about, which of the two steps is the rate-limiting step. Ho[31] has shown that if the intraparticle diffusion is the sole rate-limiting step, it is essential for the q_t *versus* $t^{0.5}$ plots to pass through the origin, which is not the present case. It may be concluded that surface adsorption and intraparticle diffusion were concurrently operating during the methyl orange-silk maize activated interactions.

Adsorption equilibrium study: Equilibrium data, commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. In order to discover the adsorption capacity of activated carbons prepared from silk maize, the experimental data points were fitted to the Langmuir, Freundlich, Tempkin and (H-J) isotherm equations and the constant parameters of the isotherm equations were calculated. For each isotherm, the temperature of solution was varied while the dye concentration and adsorbent weight in each sample were held constant.

Langmuir isotherm: The theoretical Langmuir sorption isotherm[32] is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. The model is based on several basic assumptions: (i) the sorption takes place at specific homogenous sites within the adsorbent; (ii) once a dye molecule occupies a site; (iii) the adsorbent has a finite capacity for the adsorbate (at equilibrium); (iv) all sites are identical and energetically equivalent. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface. The non-linear equation of Langmuir isotherm model can be written as follows:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \tag{10}$$

where C_e and q_e are as defined above in eqn. (10), Q_m is the maximum adsorption capacity reflected a complete monolayer (mg g^{-1}); K_a is adsorption equilibrium constant (L mg^{-1}) that is related to the apparent energy of sorption. The Langmuir isotherm is represented in the linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \tag{11}$$

A plot C_e/q_e *versus* C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_a Q_m)$. The value of Q_m and K_a constants and the correlation coefficients obtained from Langmuir model are presented in Table-2. The isotherm of activated carbon was found to be linear over the whole concentration range studies and the correlation coefficients was extremely high ($R^2 > 0.99$) as shown in Table-2. The values of Q_m decrease with temperature increase, thereby confirming that the process is exothermic[33].

Freundlich isotherm: The Freundlich isotherm model is the earliest known relationship that describing the sorption process[33]. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. This isotherm is an empirical

TABLE-2
COMPARISION OF THE COEFFICIENTS ISOTHERM PARAMETERS FOR MO
ADSORPTION ONTO ACTIVED CARBON AIVELOPED FROM SILK MAIZE

Model	Langmuir			Freundlich			Tempkin			H – J		
T (K)	Q_m	K_a	R^2	K_F	n_F	R^2	A_T	B_T	R^2	$A\times10^{+4}$	B_2	R^2
298	312.5	0.22	0.9965	7.18	3.26	0.9813	4.68	52.98	0.9803	1.6	2.85	0.9831
308	294.1	0.14	0.9981	6.48	3.00	0.9911	2.85	52.31	0.9851	1.2	1.25	0.9738
318	277.7	0.10	0.9921	5.78	2.72	0.9895	1.74	50.49	0.9885	1.0	1.25	0.9666
328	119.0	0.47	0.9998	72.3	8.80	0.9920	513.8	11.11	0.9776	1.6	3.33	0.9823

equation can be employed to describe heterogeneous systems and is expressed as follow:

$$q_e = K_F C_e^{1/n_F} \tag{12}$$

where, K_F is the Freundlich constant (L g^{-1}) related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n_F$ is the heterogeneity factor and n_F is a measure of the deviation from linearity of adsorption[34]. eqn. (12) can be linearized in the logarithmic form eqn. (13) and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n_F}\log C_e \tag{13}$$

The plot of log (q_e) *versus* log (C_e) was employed to generate the intercept value of K_F and the slope of $1/n_F$ (Table-2). The correlation coefficients, ($R^2 > 0.98$), obtained from Freundlich model is comparable to that obtained from Langmuir model linear eqn. (11), while it is lower than that obtained from the Langmuir model. This result indicates that the experimental data fitted well to Langmuir model.

Tempkin isotherm: Tempkin isotherm model contains a factor that explicitly takes into account adsorbing species-adsorbate interactions[35]. This model assumes the following: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Tempkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Tempkin isotherm has commonly been applied in the following form eqn. 14:

$$q_e = \frac{RT}{b_T}\ln\left(A_T C_e\right) \tag{14}$$

The Tempkin isotherm eqn. (14) can be expressed in its linear form as:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{15}$$

where, $B_T = (RT)/b_T$, T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 (J mol^{-1} K^{-1}). The constant b_T is related to the heat of adsorption[36]. The linear isotherm constants and coefficients of determination are presented in Table-2. Examination of the data shows that the Tempkin isotherm is not applicable to the methyl orange adsorption onto silk maize activated judged by low correlation coefficient. The Tempkin constant, B_T, shows that the heat of adsorption decreases with the increase in temperature, indicating exothermic adsorption[37].

Harkin-Jura adsorption isotherm: The Harkins-Jura adsorption isotherm can be expressed as[38]:

$$\frac{1}{q_e^{\,2}} = \left(\frac{B_2}{A}\right) - \left(\frac{1}{A}\right)\log C_e \tag{16}$$

where, B_2 and A are the isotherm constants. The Harkins-Jura adsorption isotherm accounts to multilayer adsorption and can be explained with the existence of a heterogeneous pore distribution. $1/q_e^2$ was plotted *versus* log C_e. Isotherm constants and correlation coefficients are summarized in Table-2.

Thermodynamic study: Thermodynamic parameters were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. Therefore, the thermodynamic constants can be obtained from the following equations:

$$\Delta G^o = -RT \ln K \tag{17}$$

where, ΔG^o is the free energy change (kJ mol^{-1}), R is the universal gas constant (8.314 J^{-1} mol K^{-1}), K the thermodynamic equilibrium constant and T is the absolute temperature (K). Values of K may be calculated from the relation ln q_e/C_e *versus* q_e at different temperatures and extrapolating zero[39,40].

The thermodynamic parameters are listed in Table-3. The negative ΔG^o values confirm the spontaneous nature and feasibility of the adsorption process. The values of other parameters such as enthalpy change (ΔH^o) and entropy change (ΔS^o), may be determined from Van't Hoff equation:

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{18}$$

ΔH^o and ΔS^o can be obtained form the slope and intercept of Van't Hoff plot of ln K *versus* 1/T. The data are presented in Table-3. The negative value of ΔH further confirm the exothermic nature of the adsorption process, while the negative ΔS^o value suggest the decrease in biosorption concentration in solid-liquid interface indicating thereby the increase in biosorption concentration onto the solid phase. It also confirms the decreased randomness at the solid-liquid interface during adsorption. This is the normal consequence of the chemical adsorption phenomenon.

TABLE-3
THERMODYNAMIC PARAMETERS FOR THE
ADSORPTION OF METHYL ORANGE ONTO SILK MIZE

Temperature (K)	ΔG^o(kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1})
298	-13.750	-43.398	-101.27
308	-12.342		
318	-11.077		
328	-10.881		

Conclusion

The present investigation showed that activated carbon prepared from chemically treated silk maize is an effective adsorbent for removal of methyl orange dye from aqueous solution. A small amount (50 mg) of silk maize activated could almost remove over 86 % of 40 mg L^{-1} of methyl orange within 3 h contact time. The experimental results were then compared by checking with the models of Langmuir, Freundlich, Tempkin and (Harkin-Jura). The Langmuir is the adsorption model which allows best to describe the adsorption isotherms and determine the isotherm parameters for adsorption. The equilibrium adsorption is practically achieved in 3 h the kinetic study of methyl orange on silk maize was investigated using pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion equations. The results indicate that the adsorption kinetics follow the pseudo-second-order rate with intraparticle diffusion as one of the rate determining steps. The determination of the thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) indicates the spontaneous and exothermic nature of the adsorption process. The negative sign of ΔS^o indicates that the adsorption process takes place through electrostatic interaction between adsorbent surface and adsorbate species in solution. The present study concludes that the activated carbon prepared from silk maize could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal of acid (methyl orange) dyes from wastewater, in general.

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