Evaluation and modeling of methyl green adsorption from aqueous solutions using loofah fibers

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Abstract−Loofah fiber, an economical adsorbent material, was first developed for the methyl green (MG) removal from aqueous solutions. The loofah fibers were characterized by SEM, FTIR, N_2-BET and the potentiometric titration. The pH, contact time and temperature were examined extensively. The adsorption of MG on loofah fiber increased very quickly in the pH range 3.0 to 7.0, remaining a high level at pH>7.0. The kinetics of adsorption of MG on the loofah fiber was proved to coincide with pseudo-second-order kinetic models (r^2>0.99) very well. Langmuir isotherm was demonstrated to fit the experimental data better than Freundlich isotherm model. Monolayer adsorption capacity increased with the increase of temperature. Thermodynamic constants were evaluated, and the results indicated that MG adsorption onto loofah fiber was feasible, spontaneous and endothermic. The high removal efficiency of MG on loofah fiber suggested that the loofah fiber was suitable material in MG pollution cleanup.

Keywords: Loofah, Economical, Methyl Green, Adsorption, Wastewater

INTRODUCTION

Dyes are widely used in the textile industry, pulp mills and dye manufacturing. The carcinogenicity and toxicity of the dyes cause serious environmental pollution [1], even if at very low concentration [2,3]. Removal of hazardous dyes from industrial effluents becomes a highly demanded and challenging project currently. Many methods have been developed for the removal of dyes, which include microbial degradation, electrolysis, photocatalysis [4], flocculation [5], membrane separation process [6], and adsorption [7]. Generally, adsorption is regarded as a conventional and economical method [8].

Various materials have been used for adsorption, such as commercial active carbon [9], clay minerals [10,11], bioadsorbents, polymeric adsorbents [12-16] and wastes from agriculture [17]. Loofah, which grows in tropical and subtropical zones, is mainly composed of cellulose, hemicellulose and lignin [18]. The fruits of loofah have a cylindrical fibrous vascular system. The dried fibrous network structure of the loofah serves like an open cell foam material. Loofah fiber is considered to be a promising adsorption material due to not only the fibrous mesh structure for adsorbing organic compounds from effluents, but also the low cost, biodegradability, good selectivity and favorable physicochemical stability [19,20]. In recent years, significant effort has been made to investigate the use of loofah fibers as reinforcement in thermoplastic composites, catalytic reactor and packing materials [21-24].

Herein, we present the results of loofah fibers in the adsorption of cationic triphenylmethane dye methyl green (MG). MG, is widely used in medicine and biology [25] and identifying DNA [26] as staining solutions. The same with most of the dyes, MG is not only chemically and photolytically stable but also has a complex aromatic structure, which hinder bio-degradation process in the natural thereby pose a threat to aquatic life [27,28]. A number of adsorbents have been applied to remove MG from aqueous solutions, such as graphene sheets [29], sepiolite [30] and polymeric resins [31]. Among these materials, graphene is quite an efficient material for wastewater treatment; however, the high cost and complex operation limits its application, which leads us to develop a more economical, easily available and highly effective adsorbents. Loofah fibers, which are promising absorbents due to the unique mesh structure, came into our sight.

The objectives of this study were to investigate the removal of MG on loofah fibers as a function of shaking time, pH, and temperature, to gain the thermodynamic data of the MG adsorption on loofah fibers, and to discuss the kinetic models and adsorption models of MG adsorption on loofah fibers.

EXPERIMENTAL SECTION

1. Chemicals

All the chemicals were analytically pure and used without further purification. Methyl green stock solution was prepared by dissolving an accurately weighed amount of methyl green in double distilled water. Solutions for all the experiments were prepared from the stock solution.

The molecular weight of methyl green is 474.4. The systematic name of methyl green is 4,4-(dimethy-lamino)phenyl-4-(dimethyli-minio)-2,5-cyclohexa-dien-1-ylidene methyl-N,N,N-trimethylben-zenaminium ion. The structural formula of methyl green is shown in Fig. 1. The color index name and number is basic blue 20, 42585 [32].

2. Preparation of Loofah Fibers

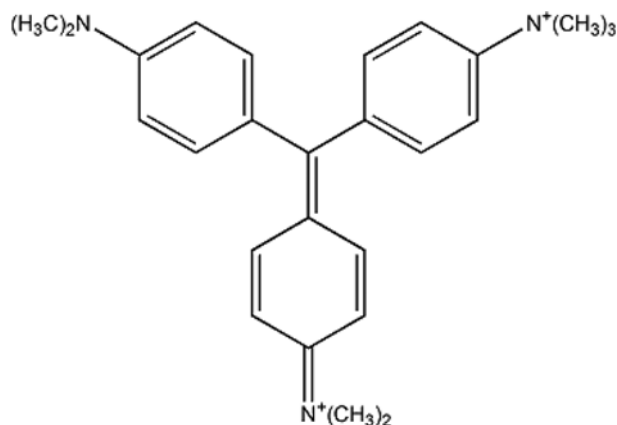Loofah fibers, which were obtained from a local farmer, were

Fig. 1. Structural formula of methyl green.

washed with distilled water and then dried in an oven at about 343.15 K. The dried fibers were cut into pieces (length 2-3 mm), followed by pretreatment with 30% NaOH solution in anhydrous ethanol at 298.15 K for 48 h. After the delignification of the fibers [33] in the presence of sodium hydroxide catalyzed by anhydrous ethanol, the loofah fibers were washed to a neutral pH with distilled water and then dried in oven at 343.15 K. The sample was characterized by the scanning electron microscopy (SEM), N_2-BET surface area, Fourier transform infrared spectroscopy (FTIR) and the potentiometric titration. All the samples that used to characterize were in piece (length 2-3 mm) form.

3. Bath Adsorption Experiments

The adsorption of methyl green on loofah fibers was conducted by using batch equilibrium technique. Loofah fibers (0.01 g) were added to methyl green solutions (25.0 mL) with different initial concentrations in polyethylene centrifuge tubes, which were shaken in a thermostatted bath at different temperatures. The effect of pH on adsorption was investigated by adjusting the pH of the dyes solution from 3.0 to 11.0 using minimum HCl (1.0 M or 0.1 M) and NaOH solution (1.0 M or 0.1 M). After adsorption equilibrium, the solution was separated by centrifugation (*TG1850-WS Shanghai China*) at 9000 r for 30 min. Subsequently, the residual dye con-

centration was analyzed with ultraviolet spectrophotometer (*UNICO, WEJ7200*) at 630 nm. Sorption percentage (%) and the amount of dye adsorbed q_e were calculated from the following equations:

$$\text{adsorption } (\%) = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{2}$$

where m (g) is the mass of sorbent and V (mL) is the volume of the solution.

For desorption experiments, Loofah fibers (0.01 g) were added to methyl green solutions (5 mg L^{-1}, 25.0 mL). Then the sample was shaken and centrifuged through the same procedure with adsorption experiments. The amount of MG was analyzed by UV spectrophotometer. To remove the remaining MG, then the loofah fibers were washed several times with distilled water until the absorbancy of the solution was extremely close to the reference solution. All results were the averages of triplicate determinations.

4. Characterization of Loofah Fibers

4-1. Scanning Electron Microscopy

The treated loofah fiber is characterized by scanning electron microscopy (SEM), (*Sirion 200, FEI America*). The SEM of loofah, which reveals the surface of loofah, is shown in Fig. 2. The fibers present an irregular structure and a harsher surface [34], which leads to the high surface area. From (a) the structure of loofah is complete and has not been destroyed. From (b), the cavities and tubular channels indicate a good capacity for the adsorption of MG on loofah. The N_2-BET (*ASAP 2020 system, Micromeritics, USA*) surface area is 1.2359 m^2/g.

4-2. FTIR Spectroscopy

The spectra of the treated and untreated loofah fibers are presented in Fig. 3(A); as seen from Fig. 3(A), the spectrum peaks of treated loofah fibers are evidently less than the untreated loofah fibers in 500 to 1,500 cm^{-1}. Peaks ranging from 500 to 1,500 cm^{-1} suggest the presence of lignin. This change is due to removal of the ligneous and hemicellulose constituents present in the fiber by alkali treatment, which is similar to the study of AlMaadeed et al. [35].
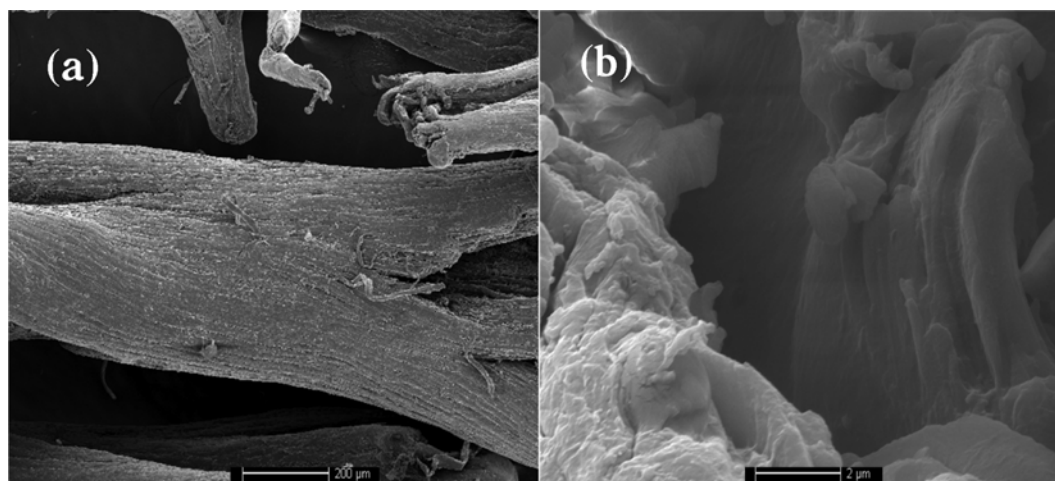

Fig. 2. SEM micrographs of the treated loofah fibers at (a) 200 m (b) 2 μm.
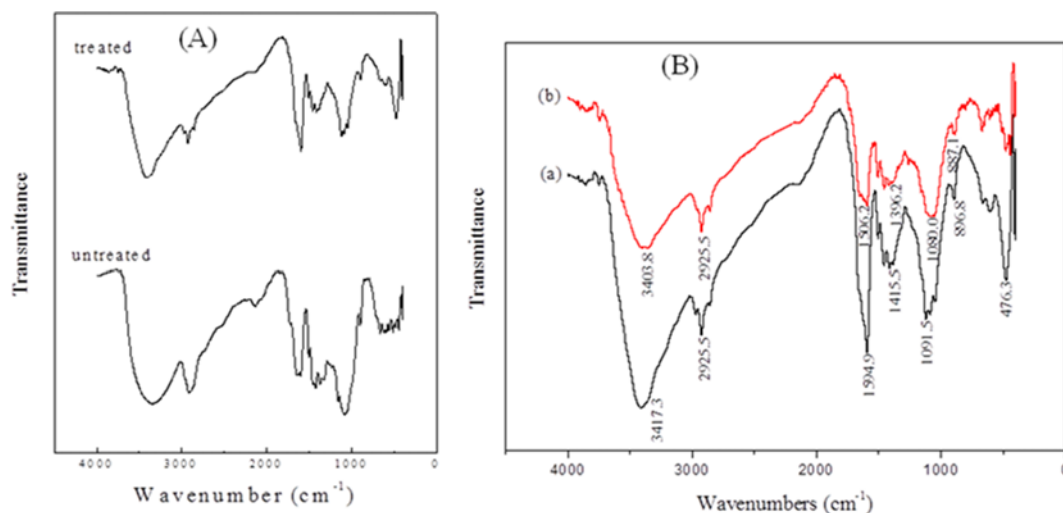
Fig. 3. (A) FTIR spectrum of treated loofah fibers and untreated loofah fibers. (B) FTIR spectrum of loofah (a) before adsorption (b) after adsorption.

FTIR spectra (*Nicolet 5700, Thermo Electron America*) of loofah before adsorption and after adsorption are shown in Fig. 3(B) (a and b) in the wavenumbers ranging from 0 to 4,000 cm^{-1}. The peak at 3,417.3 cm^{-1} may be attributed to the presence of -OH group on the surface of adsorbent, shifting to 3,403.8 cm^{-1} after MG are adsorbed onto the surface of adsorbent. The decrease in wavenumber of the peak is due to the adsorption of MG on -OH groups. The peak at 2,925.5 cm^{-1} is typical deformation vibration of the CH$_2$ and CH. Therefore, the wavenumber is not changed after adsorption. There C=O stretching of acetyl or carboxylic acid is a shift from 1,594.9 cm^{-1} to 1,506.2 cm^{-1}. And peaks at 500-1,500 cm^{-1} are the aromatic region related to the ligneous constituents [18]. The peaks at 897 cm^{-1} and 1,056 cm^{-1} may be due to β-glucosidic linkage and C-O stretching vibrations. Observed from Fig. 3(B), there is an increase in the intensity of the functional group, which shows that the MG dye molecules are attached to the loofah fibers that absorbed at these frequencies.

RESULTS AND DISCUSSION

1. Effect of pH

The initial pH plays an important role in separation systems since it may control the adsorption mechanism as well as influence the adsorption sites. For dye adsorption, the pH determines the surface charge of the adsorbent and color stabilities as well as degree of ionization [36]. The dye molecule became protonated and the chemical form of the dye modified in the acid medium. The protonation of the dyes makes the formation of the ionic-pair more difficult because of the increase of the total charge of the dyes. The effect of pH on the adsorption of MG dyes onto loofah fibers is shown in Fig. 4, which displays a gradual increase with the removal for MG in the pH range of 3.0-7.0. The maximum adsorption is reached at approximate pH value of 7.0 and maintains in a high level at pH> 7.0.

The low adsorption at low pH is due to adsorption competition for the active sites between the excess hydrogen ions (H$^+$) and MG
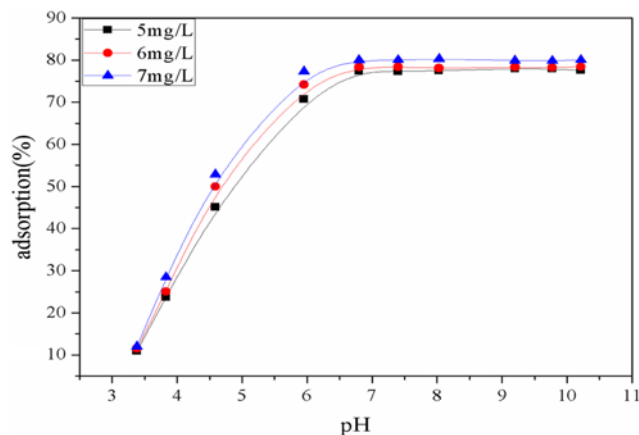

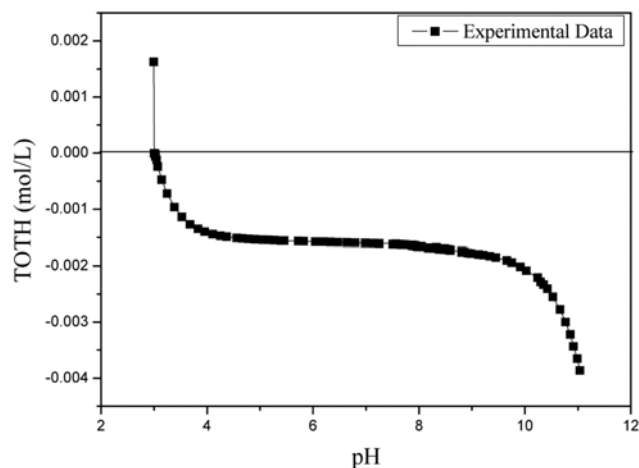Fig. 4. Effect of pH on MG by loofah fiber (m=0.4 g/L, T=298.15 K).

Fig. 5. TOTH curves of loofah fibers.

molecules. Moreover, the protonated groups on loofah fibers create a repulsive force between cationic dye molecules and proton-

ated adsorption sites [37]. When pH is increased above 7.0, the number of negatively charged adsorbent sites increases, and the concentration of H^+ ions decreases [38]; therefore, the surface of the adsorbent occupies negatively charged OH^- ions and facilitates the adsorption of MG molecules to equilibrium.

The points of zero charge (PZC) are shown in Fig. 5, where TOTH is the total concentration of protons consumed in the titration process. As shown, the pH_{ZPC} of the loofah is 3.0. The point of zero charge governs the electrophoretic mobility in the sample where surface exhibits a net neutral charge. Potentiometric titration provides a measure of the sequential binding of the proton by the surface functional groups of materials [39]. Based on Tan [39], the added titrant first reacts with extra acid in solution, then reacts with the functional groups of the loofah, and finally results in the increase in total pH. When the pH is lower than 3.0, the loofah would be in favor of retaining anionic dye. On the other hand, when the pH is higher than 3.0, the loofah surface is negatively charged, which is easy to adsorb cationic dye MG. This further indicates that the adsorption of MG onto loofah fibers is enhanced due to electrostatic interaction within the pH range studied. The result is similar to the research of Douissa et al. [40].

2. Adsorption Kinetics

The kinetics of adsorption provides information about efficiency and the overall rate of dye uptake of a process [41,42]. Two of classic kinetic models are chosen to study the adsorption process: pseudo-first-order and pseudo-second-order. The pseudo-first and pseudo-second order equations are based on sorption capacity between solid and liquid phases [43].

The pseudo-first-order equation can be expressed as the following equation:

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

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order, and q_e and q_t (mg/g) are the amounts of MG adsorbed at equilibrium and at time t (min), respectively.

Through the slopes and intercepts of the plots of $\log(q_e - q_t)$ versus t, the values of k_1 and q_e could be gained, which are given in Table 1. The parameters r^2 for the pseudo-first-order model changed less than 0.99. This suggests that the adsorption of MG onto loo-
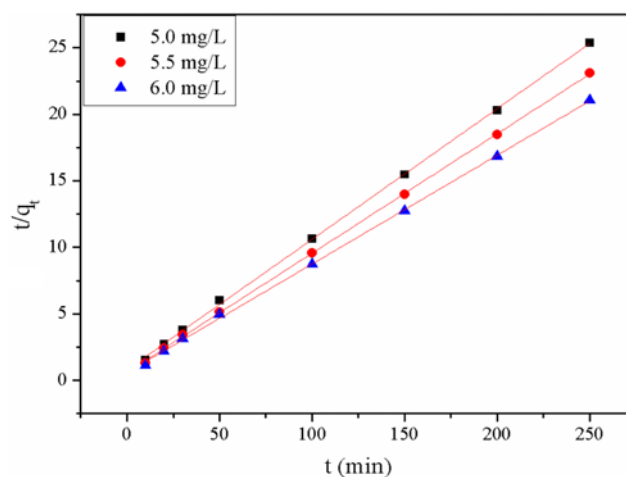
Table 1. Kinetic parameters of the MG adsorption by the loofah fiber

Kinetic models	Dye concentration (mg/L)		
	5.0	5.5	6.0
Pseudo-first-order			
$q_{e,exp}$ (mg/g)	9.85	10.83	11.87
$q_{e,cal}$ (mg/g)	9.71	10.73	11.56
k_1 (min-1)	5.26	4.57	3.88
r^2	0.9283	0.9291	0.9279
Pseudo-second-order			
$q_{e,cal}$ (mg/g)	10.19	11.15	12.25
k_2 (g/mg min)	0.0120	0.0134	0.0113
r^2	0.9996	0.9998	0.9995

Fig. 6. Pseudo-second-order kinetic plot for adsorption of MG onto loofah fiber (pH=6.5, m=0.4 g/L, T=298.15 K).

fah fibers was not appropriate for the pseudo-first-order kinetic model.

The pseudo-second-order kinetic model can be expressed as the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{4}$$

where k_2 (g/mg min) is the rate constant of the pseudo-second-order. From the slopes and intercepts of plots of t/q_t versus t, the values of q_e and k_2 could be determined as shown in Fig. 6. The parameters are listed in Table 1. As shown there, the correlation coefficients r^2 at different concentrations were higher than 0.999.

This indicates that the adsorption process follows a pseudo-second order model which is based on the assumption that adsorption may be the rate-limiting step [44]. Adsorption of MG by other adsorbents also followed the second order kinetic model [31,45].

3. Adsorption Isotherm Models and Thermodynamic Study
3-1. Adsorption Isotherms

Adsorption isotherms are important for the description of how molecules or ions of adsorbate interact with adsorbent surface sites [46]. For the adsorption system, isotherm equations usually use the Langmuir model and the Freundlich model.

The Langmuir equation can be expressed as [47]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{5}$$

where q_e (mg/g) and C_e (mg/L) is the metal concentration in solution at equilibrium; q_m is the maximum amount of the metal per unit mass of loofah to form a complete monolayer on the surface bound at high C_e and b is a constant related to the affinity of the binding sites (L/mg).

The Freundlich equation is expressed as [48]:

$$q_e = K_f C_e^{1/n} \tag{6}$$

where q_e is the adsorbed equilibrium amount (mg/g); C_e is the equilibrium concentration of the adsorbate (mg/L). K_f and $1/n$ are the Freundlich constants related to adsorption capacity and inten-
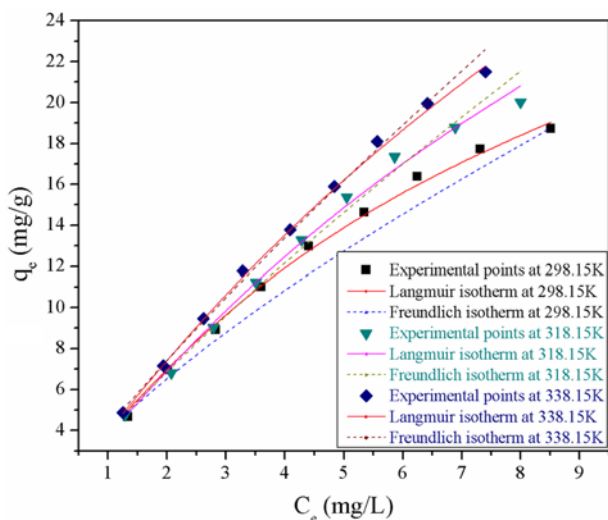
Fig. 7. Adsorption isotherms for the adsorption of MG onto loofah fiber (pH=6.5, m=0.4 g/L).

Table 2. Langmuir and Freundlich isotherm parameters for MG adsorption into loofah fiber

Adsorption isotherm models	Temperature (K)		
	298.15	318.15	338.15
Langmuir			
q_{max} (mg/g)	18.16	20.11	22.33
b (L/mg)	0.106	0.063	0.054
r^2	0.9947	0.9937	0.9974
Freundlich			
K_f (mg/g)(L/mg)$^{1/n}$	3.97	3.89	4.13
n	1.379	1.215	1.178
r^2	0.9850	0.9309	0.9775

sity of adsorption, respectively.

Both Langmuir and Freundlich isotherms of MG onto loofah fibers are compared in Fig. 7. As can be seen, the Langmuir model could fit the experimental data better than the Freundlich model under different concentrations. Table 2 summarizes the obtained results including the correlation coefficients and the other constants of the mentioned isotherm models for adsorption of methyl green onto loofah fibers. The data are in accord with the adsorption isotherms.

3-2. Thermodynamic Study

The thermodynamic parameters have an important role to affect the adsorption process [49]. The adsorption enthalpy (ΔH^o), Gibbs free energy (ΔG^o) and entropy (ΔS^o) were calculated using the following thermodynamic equations:

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{7}$$

$$K_d = \frac{q_e}{C_e} \tag{8}$$
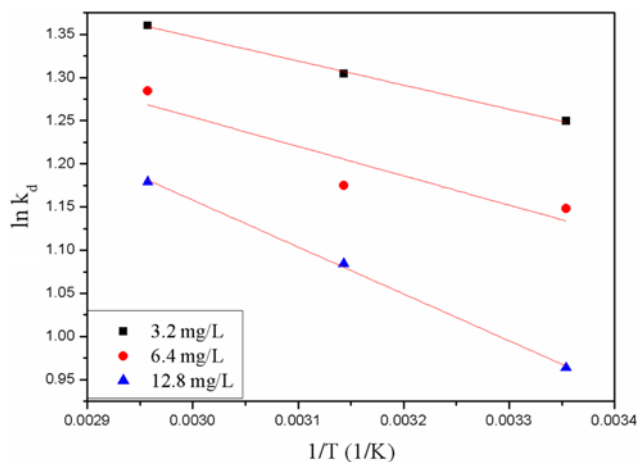
$$\Delta G^o = -RT\ln K_d \tag{9}$$

Fig. 8. Plot of $\ln K_d$ versus 1/T for the estimation of thermodynamic parameters (pH=6.5, m=0.4 g/L).

Table 3. Thermodynamic parameters for MG adsorption into loofah fiber

C_0 (mg/L)	ΔH^o (kJ mol^{-1})	ΔS^o (Jmol^{-1} K^{-1})	ΔG^o (kJ mol^{-1})		
			298.15 K	318.15 K	338.15 K
3.2	2.343	18.228	−3.091	−3.456	−4.611
6.4	2.855	18.990	−2.807	−3.187	−3.566
12.8	4.555	23.291	−2.389	−2.860	−3.326

where K_d is the equilibrium constant of the adsorption. q_e (mg/g) is the amount of the MG per unit weight of the loofah fibers, C_e (mg/L) is the equilibrium concentration of the adsorbate, T is the temperature (K) and R is the universal gas constant (8.314 J/mol K). Values of ΔH^o (kJ mol^{-1}) and ΔS^o (kJ mol^{-1} K^{-1}) can be obtained from the slope and intercept of the plot of $\ln K_d$ versus 1/T (Fig. 8).

Table 3 showed the values of the thermodynamic parameters at three different temperatures. The negative values of ΔG^o at 298.15 K, 318.15 K and 338.15 K indicated that the adsorption process was feasible and spontaneous. The positive values of enthalpy indicated that the adsorption process was endothermic. When $\Delta H^o < 25$ kJ·mol^{-1}, the adsorption process was generally considered physical. Furthermore, the positive values of ΔS^o indicated an irregular increase of the randomness at the solid-liquid interface during the adsorption. A similar result was reported Kumar in the adsorption of aniline blue dye onto Prosopis Juliflora carbon/Ca/alginate polymer composite beads [50].

The Arrhenius activation energy can be determined by the following Arrhenius type relationship:

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \tag{10}$$

where E_a (kJ/mol) is the Arrhenius activation energy, k_0 is the Arrhenius factor, k_2 (g/mg min) is a pseudo-second-order rate constant of adsorption, T (K) is the absolute solution temperature and R is the universal gas constant (R=8.314 J/mol K). E_a can be calculated from the slope of the plot of $\ln k_2$ versus 1/T (Fig. 9).

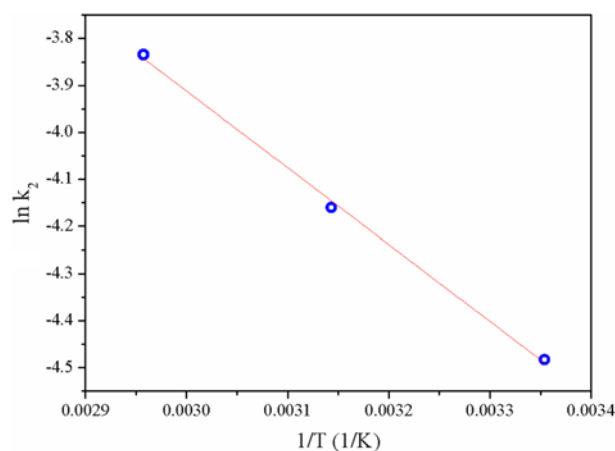The value of activation energy gives an idea about the type of

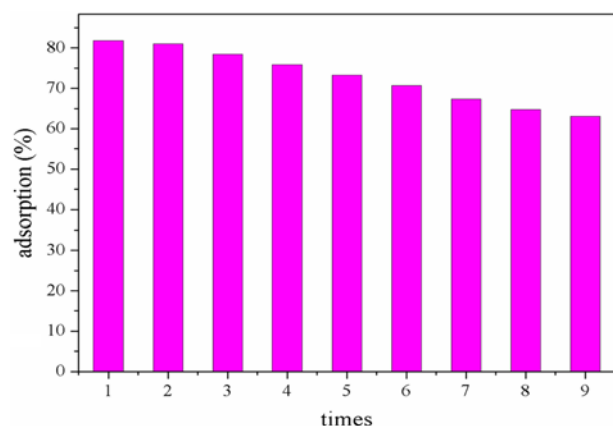**Fig. 9. ln k$_2$ versus 1/T according to Arrhenius equation (pH=6.5, m=0.4 g/L).**

Fig. 10. Recycling of loofah fibers in the adsorption of MG from aqueous solutions (m=0.4 g/L, T=298.15 K).

adsorption. The adsorption process is classified to physisorption when activation energies are low (5-40 kJ mol^{-1}), and chemisorption when activation energies are high (40-800 kJ mol^{-1}) [51]. Moreover, the activation energy (E$_a$) is 13.558 kJ mol^{-1} for the adsorption, which implies a physisorption process. Lower activation energies (below 16 kJ mol^{-1}) are characteristic for film-diffusion controlled [52].

4. Recycling of Loofah

The regeneration capacity of loofah fibers was investigated for the application potential of loofah fibers in the removal of MG from wastewater. As can be seen from Fig. 10, the adsorption capacity of loofah fibers decreased slightly from 81% to 71% after nine cycles. The excellent repeated availability suggested that loofah fibers were an effective adsorbent for the adsorption of MG from large volumes of aqueous solutions.

5. Comparison of Loofah Fibers with other Adsorbents

In the present study, the methyl green adsorption capacities (q$_m$, a parameter that has been calculated from the Langmuir isotherm model) of different materials were compared in Table 4. It could be concluded that loofah fiber has a relatively higher adsorption capacity than the other kinds of adsorbents.

Table 4. Comparison of adsorption capacity of MG by various adsorbents

Adsorbent	q$_m$ (mg/g)	Reference
Graphene sheets	292.39 mg/g	[29]
Sepiolite	0.2 mole$_c$/kg	[30]
Amberlite XAD-4 resin	0.002440 mol/g	[31]
Loofah fiber	18.16 mg/g	In this work

CONCLUSIONS

The adsorption of MG on loofah fibers was examined at various pH, contact time and temperature. The results showed that alkaline condition benefited MG adsorption. The percentage removal increased sharply from 11.4% to 75.8% with increasing pH from 3.5 to 6.5. The kinetic adsorption process tends to fit very well in the pseudo-second-order model. Adsorption isotherm model can be described by Langmuir isotherm equations well, and the maximum adsorption capacity of MG onto loofah fibers was. 22.33 mg/g. Thermodynamic calculations for MG dye indicate that the adsorption reaction is endothermic and spontaneous. The adsorption capacity of loofah fibers decreased slightly from 81% to 71% after nine cycles, which shows excellent repeated availability of loofah fibers. This investigation will be beneficial to the development of loofah fibers in the removal of MG from wastewater. More applications of loofah fibers in the absorption field will be reported in due course.

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