Adsorption of Methyl Orange on *Syzygium cumini* Seed Powder: Kinetics, Isotherms, and Thermodynamic Studies

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ABSTRACT

Present research discussed the utilization of *Syzygium cumini* seed powder (SCSP) as an adsorbent for methyl orange (MO) removal from aqueous solution. Batch adsorption experiments were carried out to evaluate the influence of pH, adsorbent dosage, contact time, initial dye concentration, and temperature. Langmuir and Freundlich isotherm models were employed to describe the adsorption of the MO by SCSP. The equilibrium data was better fitted by Langmuir isotherm model than the Freundlich model. The maximum monolayer adsorption capacity of MO onto SCSP was found to be 63.3 mg/g. The pseudo first-order and pseudo second-order model equations were used to analyze the kinetic data of the adsorption process, and the data were fitted well with the pseudo second-order kinetic model. The thermodynamic parameters (ΔG^o, ΔH^o, and ΔS^o) showed that the adsorption of MO onto SCSP was endothermic and spontaneous. Results in this study suggested that SCSP was a suitable material for the removal of MO from aqueous solution.

Key words: Adsorption, Methyl orange, Kinetics, Isotherms, Thermodynamics.

1. INTRODUCTION

Synthetic dyes are widely used in textiles, leather, paper, cosmetics, photoelectron chemical cells, and other similar industries to color their products. Based on the chemical structures and applied methods, synthetic dyes are classified as basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes, and sulfur dyes. Azo derivatives are the major class of dyes used in industries [1]. These types of dyes are characterized by the existence of nitrogen-nitrogen double bonds (azo bonds), and the bright colors are due to the azo bonds and the related chromospheres. Even at low concentrations (lower than 1 mg/L), an azo dye in water is clearly visible and therefore undesirable.

Methyl orange (MO) [Sodium 4-[[4-(dimethyl amino) phenyl] diazenyl] benzene sulfonate] is a typical water soluble anionic azo dye. MO is commonly present in effluent discharges from textile, food, pharmaceutical, printing, and paper manufacturing industries [2]. Due to the toxicity and persistence, these discharges can cause a serious threat to physicochemical properties of fresh water and aquatic life. Therefore, it is necessary to provide suitable technology for the wastewater treatment. To minimize the pollution risks and harmful effects of the dye, effluents should be carefully treated with an appropriate method before discharging the wastewater into the aquatic environment. Several technologies/processes have been employed for the removal of azo dyes from industrial effluents. These include coagulation and flocculation [3], oxidation or ozonation [4,5], membrane separation [6], and adsorption [7]. Among all existing techniques used to remove dye from industrial effluents, adsorption appears to offer the most potential. The major advantages of adsorption over conventional treatment methods include; low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, regeneration of biosorbent, and possibility of sorbate

recovery. In recent years, a number of inexpensive and abundant adsorbents, such as agricultural originating waste biomass [8], woody materials [9], agricultural husk [10], chaff [11,12], rice milling [13], rice husk [14], activated sludge [15], and eucalyptus bark [16] were used in dye removal from wastewaters. In the present study, *Syzygium cumini* seed powder (SCSP) was chosen as an adsorbent for the removal of MO from aqueous solution.

The main objective of the present work is to investigate the potential of SCSP as an adsorbent material for the removal of MO from aqueous solutions. The different parameters such as effect of pH, initial dye concentration, contact time, and temperature were evaluated. The isotherm and kinetics, as well as thermodynamic parameters for the adsorption of MO onto the SCSP, were calculated.

2. MATERIALS AND METHODS

2.1. Adsorbent

Syzygium cumini seeds were collected from a local *S. cumini* tree, Nellore, Andhra Pradesh, washed thoroughly with distilled water to remove surface dirt and adhering impurities, cut into small pieces, crushed, and sieved in a mesh size 150 μm size by standard sieves. The

SCSP dried in an air oven at 105°C for 2 h until a constant weight was reached. After complete drying, the SCSP was stored in air tied bottles for experimental uses.

2.2. Preparation of MO Solution

Stock solution (1000 mg/L) of MO was prepared in deionized and double distilled water and diluted to get the desired concentration of MO. Calibration curve for dye was prepared by measuring the absorbance of different concentrations of the MO.

2.3. Chemicals and Equipment

All chemicals used in this work were of analytical reagent grade and used without further purification. Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. MO dye (formula: $C_{14}H_{14}N_3NaO_3S$, molecular weight: 327.34, λ_{max}: 464 nm) was purchased from Sigma-Aldrich, India. The chemical structure of MO is shown in Figure 1. Working standards were prepared by progressive dilution of the stock MO solution. HCl, NaOH, and buffer solutions were used to adjust the solution pH. A pH meter (Digisun electronics, India) was used for pH measurements. The pH meter was calibrated using buffer standard solutions of pH 4.0, 7.0, and 10.0. The dye concentrations in the samples were determined using UV/Vis spectrophotometer (Shimadzu UV-2450, Japan) at maximum wavelengths of 464 nm. The morphology of adsorbent (before and after MO adsorption) was analyzed by Scanning Electron Microscopy (SEM: Model Evo 15, Carl Zeiss, England). The samples were first sputter-coated with homogeneous gold layer and then loaded onto a copper substrate.

Batch Adsorption Procedure

The adsorption of MO on the SCSP was investigated as an effect of pH, adsorbent dosage, contact time, initial dye concentration, and temperature. 1000 mg/L of MO stock solution was prepared and was used further to obtain a standard solution by appropriate dilution of stock solution. In sorption experiments, 0.03 g of the adsorbent was brought into contact with 30 mL of MO solution in a 50 mL falcon tube. The pH values of the solutions were adjusted using small volumes (1–2 drops) of 0.1 M HCl and 0.1 M NaOH solutions to reach the desired pH. The total added volume to get the desired pH was also considered for calculation of initial concentration. All tubes were agitated in an electrical thermostatic reciprocating shaker at 180 rpm. The adsorbent dosage on MO sorption was performed by varying the amount of adsorbent from 0.01 to 0.09 g/30 mL. The effect of temperature was studied at pH 3.0, and different temperatures in the range of 298–328 K. Sorption kinetic experiments were conducted with an initial concentration of 100 mg/L at 298 K. Samples were collected at various shaking time intervals until the concentration of MO in the dilute phase became constant. The sorption isotherm study was performed using a different concentration of MO solutions, i.e. from 50 to 300 mg/L. A 0.07 g of the adsorbent with 30 mL of MO solutions of various initial concentrations was shaken at 180 rpm for 24 h at 298 K. At the end of adsorption, 1 mL sample was centrifuged at 3000 rpm for 10 min on a centrifuge. The filtrate was diluted in polythene tubes before analysis. The concentration of remaining MO in the adsorption medium was determined using a UV/visible spectrophotometer.

The MO uptake (q) was calculated from the difference between the concentration of MO before and after sorption using the following equation:

$$q = \frac{C_i V_i - C_f V_f}{M} \qquad (1)$$

Where q is the uptake of MO (mg/g), C_i and C_f are the initial and final MO concentrations in the solution (mg/L), V_i and V_f are the initial and final (initial plus added HCl or NaOH solutions) solution volumes, and M is the mass of adsorbent (g) used in MO sorption.

χ^2 Analysis

To identify the suitable isotherm for adsorption of MO onto SCSP, the Chi-square (χ^2) test was carried out using the experimental data, to find the best adsorption isotherm model. The χ^2 value was calculated using Eq. (2) for evaluating the best fit model.

$$\chi^2 = \Sigma \left(\frac{(q_e - q_{e,m})^2}{q_{e,m}} \right) \qquad (2)$$

Where $q_{e,m}$ equilibrium capacity which was obtained by calculating from a model (mg/g) and q_e experimental data of equilibrium capacity (mg/g).

RESULTS AND DISCUSSION

Characterization

To evaluate the textual structure of adsorbent surface, SEM micrographs of before and after MO adsorption were shown in Figure 2. From the surface morphology of before (Figure 2a), it was observed that powder was an assemblage of fine particles, which did not have regular, fixed shape, and size. The particles were of various dimensions, and all of them contained a large number of steps and kinks on the external surface, with broken edges. The size of the voids in the before was increased after MO adsorption, and some distortion of the shape could be seen in the SEM of after adsorption (Figure 2b).

Effect of pH

The pH of dye solution is an important parameter for overall sorption of MO onto SCSP. The effect of pH on the adsorption of MO by SCSP was studied in between pH 3 and 10. Figure 3 shows the effect of pH on the adsorption of MO. The maximum adsorption capacity (39.1 mg/g) was occurred at pH 3.0 followed by a significant decrease in adsorption capacity with increased in pH. At pH 3.0 the H$^+$ ion concentration in the system increased, and the surface of SCSP acquires positive charge by absorbing H$^+$ ions. Therefore, at low pH, high electrostatic attraction exists between the positively charged surface of SCSP and MO (anionic dye molecule) leading to maximum dye adsorption. However, at higher pH, MO anions generally excluded away from the negatively charged surface of adsorbent, thus decreasing the dye adsorption. The maximum adsorption of MO is observed at pH 3.0. Hence, all the succeeding investigations were performed at pH 3.0. A similar type of behavior is also reported for the adsorption of the dye with different adsorbents [17,18].

Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter in adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of dye solution. The effect of adsorbent dosage on the removal efficiency of MO onto SCSP was studied at pH 3.0 employing adsorbent dosage within the range of 0.01–0.09 g/30 mL and the initial dye concentration of 100 mg/L is shown in Figure 4. From the figure, it can be observed that the increasing adsorbent dosage from 0.01 to 0.09 g/30 mL the removal efficiency of MO increased from 25.1% to 48.6%. The maximum removal efficiency reached 49.6% for MO

as adsorbent dosage reached 0.07 g. However, a further increase in adsorbent dosage beyond 0.07 g did not result in sufficient improvement in the removal efficiency of MO by SCSP. The removal efficiency of MO increases in the adsorbent dosage due to the greater availability of the exchangeable sites or surface area at higher concentrations of the adsorbent. Therefore, the optimum adsorbent dosage was taken as 0.07 g/30 mL for further experiments.

Effect of Contact Time

As seen in Figure 5, it is evident that time has a significant influence on the adsorption of dye. It can be observed from the figure that adsorption of MO was quite rapid in the first 60 min, then gradually increased with the prolongation of contact time. After 150 min of contact time equilibrium was observed and with further increase in contact time, there is no additional enhancement in sorption capacity. Based on these results, 150 min was taken as the equilibrium time in batch adsorption experiments.

Adsorption Kinetics

To investigate the mechanism of the adsorption process pseudo first-order and second-order kinetic models were used to fit the kinetic experimental data. The pseudo first-order equation assumes the

adsorption is of one adsorbate molecule onto the active site on the adsorbent surface while in pseudo second-order model one adsorbate molecule is adsorbed onto two active sites. The non-linear form of the pseudo first-order [19] and pseudo second-order [20] kinetic rate equations is given as:

Pseudo first-order model

$$q_t = q_1 (1 - exp(-k_1 t)) \tag{3}$$

Pseudo second-order model

$$q_t = \frac{q_2^2 k_2 t}{1 + q_2 k_2 t} \tag{4}$$

Where q_1 and q_2 are the amount of dye sorbed at equilibrium (mg/g), q_t is the amount of dye sorbed at time t (mg/g), k_1 is the pseudo first-order equilibrium rate constant (1/min), and k_2 is the pseudo second-order equilibrium rate constant (g/mg min). The non-linear kinetic model curves for the adsorption of MO onto SCSP are shown in Figure 6.

The estimated kinetic parameters and coefficient of determination (R^2) from the pseudo first-order and pseudo second-order models are summarized in Table 1. The results indicated that among these two models, the pseudo second-order kinetic model had high R^2 (0.9955) value and experimental q_e value that agree well with the calculated
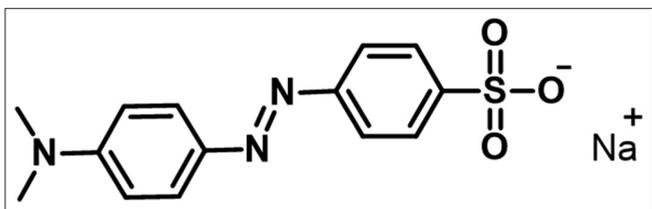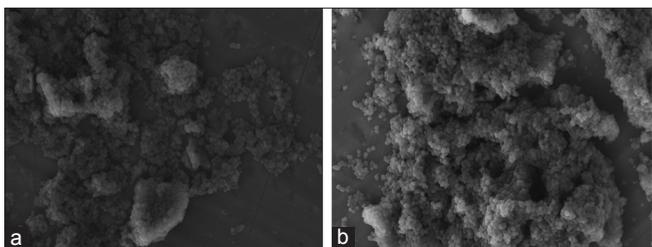

Figure 1: Chemical structure of methyl orange.

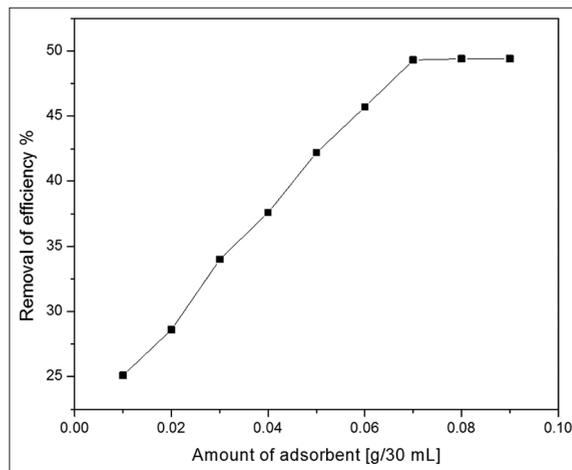**Figure 2:** SEM micrographs of (a) before and (b) after methyl orange adsorption.

Figure 3: Effect of pH for the sorption of methyl orange onto the *Syzygium cumini* seed powder.

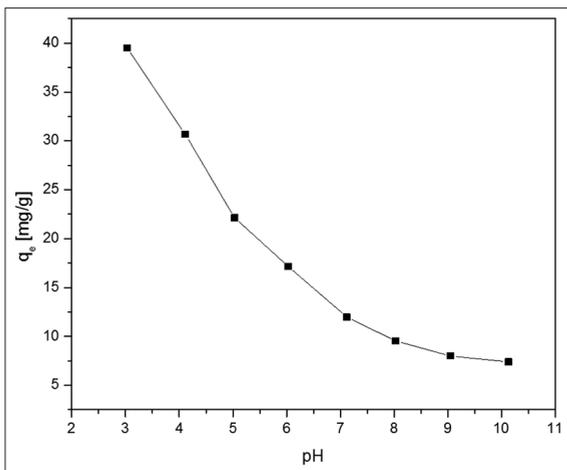**Figure 4:** Effect of adsorbent dosage for the adsorption of methyl orange onto the *Syzygium cumini* seed powder.
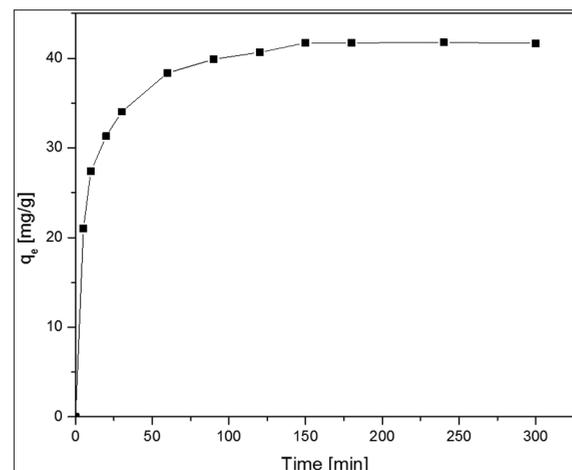

Figure 5: Effect of contact time for the adsorption of methyl orange onto the *Syzygium cumini* seed powder.
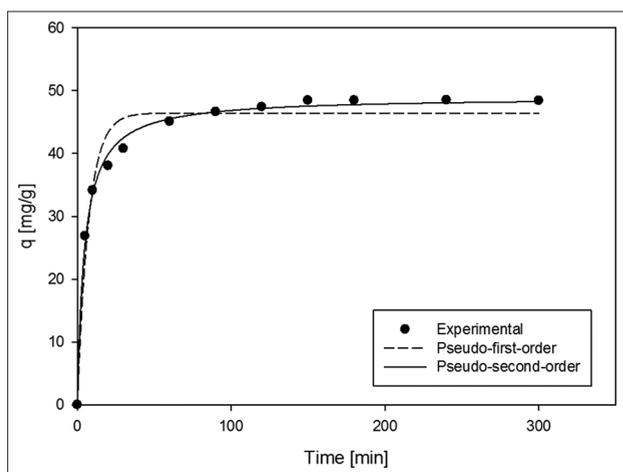
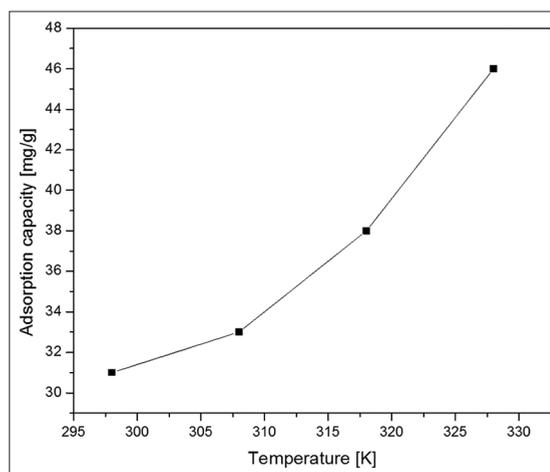**Figure 6:** Kinetic plots for the adsorption of methyl orange onto the *Syzygium cumini* seed powder.

Figure 8: Effect of temperature on methyl orange removal efficiency of the *Syzygium cumini* seed powder.
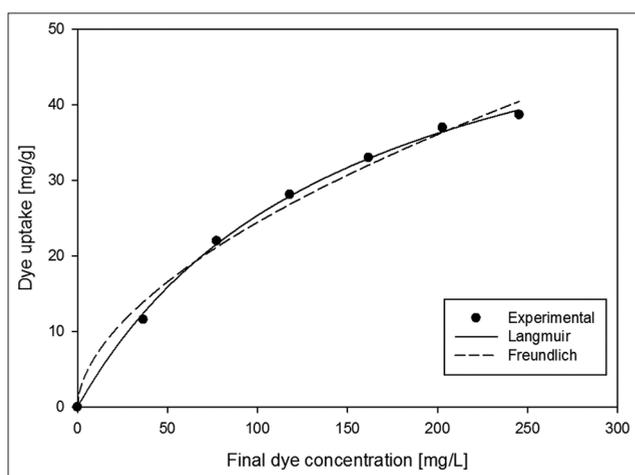

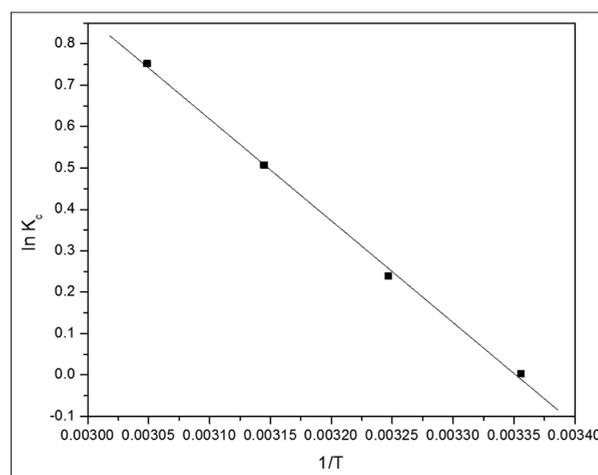**Figure 7:** Adsorption isotherms of methyl orange onto the *Syzygium cumini* seed powder.

Figure 9: Plot of ln K_c versus $1/T$ for the estimation of thermodynamic parameters for adsorption of methyl orange onto *Syzygium cumini* seed powder.

q_2 value. The low R^2 (0.9608) value for the pseudo first-order model indicated that this model did not fit the data well. Furthermore, for the pseudo first-order model, the experimental q_e was not in good agreement with the calculated q_1 value. Thus, these results suggest that the pseudo second-order model provided a good correlation for the adsorption of MO onto SCSP.

Adsorption Isotherms

The successful representation of the dynamic adsorptive separation of solute from a solution onto an adsorbent depends on an appropriate description of the equilibrium separation between two phases. Therefore, the equilibrium data were fitted using Langmuir and Freundlich isotherms models.

Langmuir adsorption isotherm [21] is applicable in many adsorption processes. The basic assumption is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and no further adsorption thereafter. Langmuir isotherm is expressed as the following equation:

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

Where C_e is the equilibrium concentration of dye in solution (mg/L), q_e is the adsorbed value of dye at equilibrium concentration (mg/g), q_m

is the maximum monolayer adsorption capacity (mg/g), and K_L is the Langmuir constant which is related to the energy of adsorption (L/mg).

The type of the Langmuir isotherm could be predicted based on whether the adsorption was favorable or unfavorable in term of equilibrium parameter or dimensionless constant separation factor R_L, which is given by the following equation:

$$R_L = \frac{1}{1 + K_L C_o} \tag{6}$$

Where K_L is the Langmuir constant (L/mg) and C_o is the initial adsorbate concentration (mg/L). The parameter R_L indicates the shape of the isotherm and nature of the adsorption process ($R_L > 1$: Unfavorable; $R_L = 1$: Linear; $0 < R_L < 1$: Favorable; and $R_L = 0$: Irreversible). The values of R_L are all in the range of 0–1, which indicate the favorable adsorption of MO onto SCSP.

A comparison of the Langmuir monolayer adsorption capacity (q_m) for the removal of MO by different adsorbents reported earlier in the literature [22-29] is summarized in Table 2. It is observed that the MO adsorption capacity of the SCSP is significantly higher than most the reported adsorbents. Therefore, SCSP can be considered as a promising adsorbent for the removal of MO from aqueous solution.

Table 1: Pseudo first-order and pseudo second-order model constants for the adsorption of MO on SCSP.

Sorbent	q_e (mg/g)	Pseudo first-order			Pseudo second-order		
		q_1 (mg/g)	k_1 (L/min)	R^2	q_2 (mg/g)	k_2 (g/mg min)	R^2
SCSP	48.6	44.35	0.1352	0.9608	48.9	0.0045	0.9955

MO: Methyl orange, SCSP: *Syzygium cumini* seed powder

Table 2: Comparison of the maximum adsorption capacity of MO onto SCSP with other reported literature.

Adsorbent	q_m (mg/g)	Reference
Bottom ash	3.618	[22]
De-Oiled Soya	16.664	[22]
Banana peel	21.0	[23]
Orange peel	20.5	[23]
Chitosan	34.83	[24]
Algerian cork	16.66	[25]
Activated clay	15.85	[26]
Skin almonds	20.02	[27]
Activated alumina	9.8	[28]
Calcium alginate MWNTs	12.5	[29]
SCSP	63.3	Present study

MO: Methyl orange, SCSP: *Syzygium cumini* seed powder

Table 3: Isotherm model parameters for the adsorption of MO onto SCSP.

Isotherm	Parameters	Values
Langmuir	q_m (mg/g)	63.3
	K_L (L/mg)	0.0067
	R_L	0.36
	R^2	0.9986
	χ^2	1.01
Freundlich	K_f (mg/g)	1.8484
	n	1.7832
	$1/n$	0.561
	R^2	0.9798
	χ^2	3.37

MO: Methyl orange, SCSP: *Syzygium cumini* seed powder

Table 4: Thermodynamics parameters for the adsorption of MO onto SCSP.

Temp. (K)	ΔG^o (kJ/mol)	ΔS^o (kJ/mol K)	ΔH^o (kJ/mol)
298	−0.0131		
308	−0.5735	0.071	17.4
318	−1.3392		
328	−1.8687		

MO: Methyl orange, SCSP: *Syzygium cumini* seed powder

Freundlich isotherm [30] is an empirical equation describing that the adsorption surface becomes heterogeneous during the adsorption process. The Freundlich isotherm is commonly presented as the following equation.

$$q_e = K_f C_e^{1/n} \tag{7}$$

Where C_e is the equilibrium concentration of dye in solution (mg/L), q_e is the adsorbed value of dye at equilibrium concentration (mg/g), and K_f and n are the Freundlich constants characteristics of the system, respectively, indicating the adsorption capacity and the adsorption intensity. The non-linear isotherm model curves for the adsorption of MO onto SCSP are shown in Figure 7.

The parameters of isotherms models, R^2 values χ^2 values are summarized in Table 3. On the basis of higher R^2 and lower χ^2 values for the Langmuir isotherm model indicate that the adsorption of MO onto SCSP follows the Langmuir model. The excellent fit of the Langmuir isotherm to the experimental adsorption data confirms that the adsorption is monolayer; adsorption of each molecule has equal activation energy, and that sorbate-sorbate interaction is negligible.

Effect of Temperature

The effect of temperature on the adsorption capacity of adsorbent under optimized conditions was studied. It has been observed that adsorption of MO increases from 31.3 to 45.7 mg/g with temperature from 298 to 328 K (Figure 8). The increase in adsorption capacity of the adsorbent was attributed to the enlargement of pore size and activation of the adsorbent surface with temperature [31]. Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. The adsorption is an endothermic process if the adsorption capacity increases with increase in temperature.

Adsorption Thermodynamics

Thermodynamically, in an isolated system, energy cannot be gained or lost; the entropy change is the driving force. In the practice of environmental engineering, both energy and entropy factors ought to be considered to determine the processes that occur spontaneously. The thermodynamic parameters including the Gibbs free energy change of adsorption (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) for the adsorption of MO onto SCSP were calculated using the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{8}$$

$$\Delta G = -RT\ln K_c \tag{9}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{10}$$

$$\ln K_c = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{11}$$

Where C_{Ae} and C_e are the equilibrium concentration in solution (mg/L) and the solid phase concentration at equilibrium (mg/L), respectively. K_c is the distribution constant of each temperature. R is the universal

gas constant (8.314×10^{-3} kJ/mol K) and T is the absolute temperature (K). From the slope and intercept of the linear plot of $ln\ K_c$ against $1/T$ (Figure 9), the values of enthalpy and entropy changes could be obtained. The negative values of ΔG^o imply that the adsorption of MO onto SCSP was spontaneous. The magnitude of ΔG^o also increased with increase in the temperature indicating that the adsorption was more favorable at higher temperatures. The positive values of ΔH^o indicate the endothermic nature of the adsorith of MO onto SCSP in the temperature range of 298–328 K. The positive values of ΔS^o suggested an increase in randomness at the solid/liquid interface during the biosorption of MO onto SCSP. The values of ΔG^o, ΔH^o, and ΔS^o for the adsorption of MO onto SCSP are given in Table 4.

CONCLUSIONS

The following conclusions were drawn from the present study:
1. SCSP is a potential and prominent adsorbent for the removal of MO from aqueous solution.
2. Adsorption performance was strongly affected by the parameters such as pH of solution, adsorbent dosage, contact time, initial dye concentration, and temperature.
3. Equilibrium kinetic results revealed that the pseudo second-order model was the best kinetic model for the description of the adsorption mechanism.
4. Adsorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The maximum monolayer adsorption capacity of MO was 63.3 mg/g at an optimum pH 3.0.
5. Thermodynamic studies on the MO adsorption revealed that the process was feasible, spontaneous, and endothermic.
6. Finally, it can be also concluded that SCSP has a potential as an adsorbent for the removal of MO from aqueous solutions due to its low cost, reasonable high adsorption capacity.

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