

Research Article

Adsorption Thermodynamic and Kinetic Studies of Methyl Orange onto Sugar Scum Powder as a Low-Cost Inorganic Adsorbent

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Received 9 May 2020; Revised 20 May 2020; Accepted 21 May 2020; Published 27 June 2020

Academic Editor: José Morillo

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In the present study, batch adsorption experiments were carried out to investigate the removal of methyl orange (MO) from aqueous solution using sugar scum powder as an effective inorganic adsorbent which is a cheap precursor and abundant. The characteristics of this material were determined using XRD, SEM/EDX, and FTIR. The adsorption performance of sugar scum powder was evaluated using MO as the model adsorbate. Effects of various parameters such as initial dye concentration, contact time, and adsorbent dose were studied. The adsorption process can be best described by the pseudo-second-order kinetic and Langmuir adsorption isotherm models. Maximum monolayer adsorption capacity for MO removal was found to be 15.24 mg/g at temperature 22°C and pH 7.2. Moreover, thermodynamic parameters suggested that the adsorption of MO onto sugar scum powder was a spontaneous and exothermic process. The results demonstrated that sugar scum is a suitable precursor for the preparation of efficient adsorbent for dye removal from wastewater.

1. Introduction

The rapidly growing population, along with improving economic growth, has brought serious problems including the continuous increase in the quantities of the agricultural byproducts and industrial wastes. The resulting wastes represent a significant environmental challenge if they are released to the environment without proper disposal procedure that may cause environmental pollution and harmful effects on human and animal health [1, 2]. Thus, the scientific community has become increasingly interested in the waste management which can be valorized and used for various applications because they are abundant and renewable raw materials. Consequently, the agricultural byproducts and industrial wastes have been used for the production of adsorbents, of energy fuels through fermentation processes, of thermal energy by combustion, and of composts as fertilizer [3–8].

The use of industrial solid wastes as raw materials for the preparation of adsorbents has a positive impact in the protection of the environment by reducing solid wastes and also the production of low-cost adsorbents with high added value which can reduce contaminants in wastewater at a reasonable cost [1, 9, 10]. In fact, numerous studies have shown the possibility of using industrial solid wastes and agricultural byproducts as precursors for the preparation of efficient and inexpensive adsorbents. Thus, adsorbents have been prepared from clay materials [11], zeolites [12], siliceous material [13], marble dust [14], sewage sludge [12], chitosan and its derivatives [15–18], fly ash [19], wood sawdust [20], etc.

In addition to solid wastes, industries produce large volumes of wastewater that contain a wide variety of chemicals which affect, if discharged without any treatment, rivers, seas, lakes, and groundwater and therefore cause degradation of the ecosystem. Often, the chemicals

contained in wastewater are nonbiodegradable, toxic, carcinogenic, and harmful to organisms even at low concentrations. Among these products, the dyes used in several sectors such as textiles, cosmetics, plastics, pigments units, leather, and paper industries have been considered as the primary pollutant due to their stability and low biodegradability [21]. Consequently, the scientific community has contributed to the treatment of industrial effluents by developing effective dye removal techniques. Adsorption is one of the mostly adopted techniques for dye removal from wastewater as it is found to be very effective and economical [22, 23]. Therefore, many researches in recent years have demonstrated the potential use of various low-cost adsorbents for dye removal from wastewater such as magnetic-based materials [16, 24–27], monolithic algal green powder [28], powdered marble [14], sepiashell-based composite [29], chelating resins [30], chitosan and its derivatives [15, 17, 31], and biomass-based activated carbon [1, 20, 32].

Sugar scum is derived from the sugar-refining process through juice carbonation. It is separated from the sugary juices using filtration and disposed of in open fields. The aim of the present work is to study the potential of use of sugar scum for the removal of organic pollutants from aqueous solution. Toward this aim, the effect of various operating conditions on the MO removal was investigated in batch adsorption experiments.

2. Materials and Methods

2.1. Adsorbent. Sugar scum used in this study was coming from a discharge of sugar factory located in Sidi Bennour, Morocco. It was dried at 110°C for 24 h and crushed and sieved to obtain particle size less than 200 µm. Obtained material was used in the experiment without any pretreatment. All the chemicals used in this study were of analytical reagent grade.

2.2. Adsorption Experiments. Adsorption capacity of sugar scum was determined by performing batch mode adsorption. MO was chosen as an adsorbate to evaluate the adsorption characteristics of sugar scum powder and also serves as a model compound for adsorption of organic contaminants from aqueous solution. The effect of various parameters such as initial dye concentration, contact time, adsorbent dose, and temperature on the adsorption capacity of MO was studied. Batch adsorption experiments were performed in 100 cm³ flasks containing a defined amount of adsorbent and 50 cm³ of desired concentration of MO solution. These flasks were kept in a shaker of 180 rpm at 22°C. After adsorption, the residual concentration of MO was determined by spectrophotometric method (UV-3100PC spectrophotometer) at 462 nm.

The amount of adsorption at equilibrium (q_e) was defined as the amount of adsorbate per gram of adsorbent (in mg/g) and was calculated using the following equation:

$$q_e = \frac{C_0 - C_e}{m} \times V. \quad (1)$$

The percentage removal ($R\%$) of the methylene blue at equilibrium was calculated using the following relationship:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)$$

where C_0 and C_e (in mg/L) are the initial and equilibrium concentrations in aqueous solution, respectively, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent.

2.3. Characterization Techniques. X-ray powder diffraction (XRD) analysis of sugar scum powder was carried out in Reminex Managem laboratory in Morocco to identify the various phases present in this material. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX) was used to examine the morphology and the development of porosity of the sugar scum powder as well as to determine its elemental composition using TESCAN VEGA3-EDAX instrument with an accelerating voltage of 20 kV. The surface functional groups of the sugar scum powder were carried out by Fourier transformed infrared (FTIR) spectroscopy on a Nicolet 5700 spectrometer in the scanning range of 4000 to 400 cm⁻¹ (64 scans, at a resolution of 4 cm⁻¹).

3. Results and Discussion

3.1. Characterization of Sugar Scum. The phases present in the sugar scum powder are identified by comparing the XRD pattern of Figure 1 with the JCPDS data (Joint Committee for Powder Diffraction Standards). The XRD pattern shows an intense peak at $2\theta = 29.31^\circ$, which indicates that the calcite (CaCO_3) is the main phase present in sugar scum according to the JCPDS card no. 01-086-2339. This characteristic peak assigned to the calcite (CaCO_3) has also been observed by other authors [33, 34]. In addition, other peaks located at $2\theta = 23.01, 31.31, 35.97, 39.40, 43.13, 47.37, 48.39, 56.59, 57.37, 60.67, 63.01, 64.62$, and 65.37 were matched with the JCPDS card no. 01-086-2339.

The scanning electron microscopy (SEM) was used to observe the surface morphology of sugar scum powder. Figure 2 shows the SEM photograph of this adsorbent. It can be seen that the sugar scum powder is formed of various sizes of agglomerated particles with irregular shapes and has a porous texture. The results of the elemental analysis using EDX (Figure 3) indicate that the major elements present in the sugar scum are oxygen (45.73%), calcium (32.99%), and carbon (16.96%).

Figure 4 corresponds to the FTIR spectra of sugar scum powder. The band located at around 3424 cm⁻¹ is attributed to O-H stretching vibration of the adsorbed water [21]. The peaks at 713, 874, 1078, 1424, and 2511 cm⁻¹ are typically attributed to the calcite (CaCO_3) [21, 35–37]. Finally, the band caused by the bending vibrations of strongly adsorbed water is located at 1630 cm⁻¹.

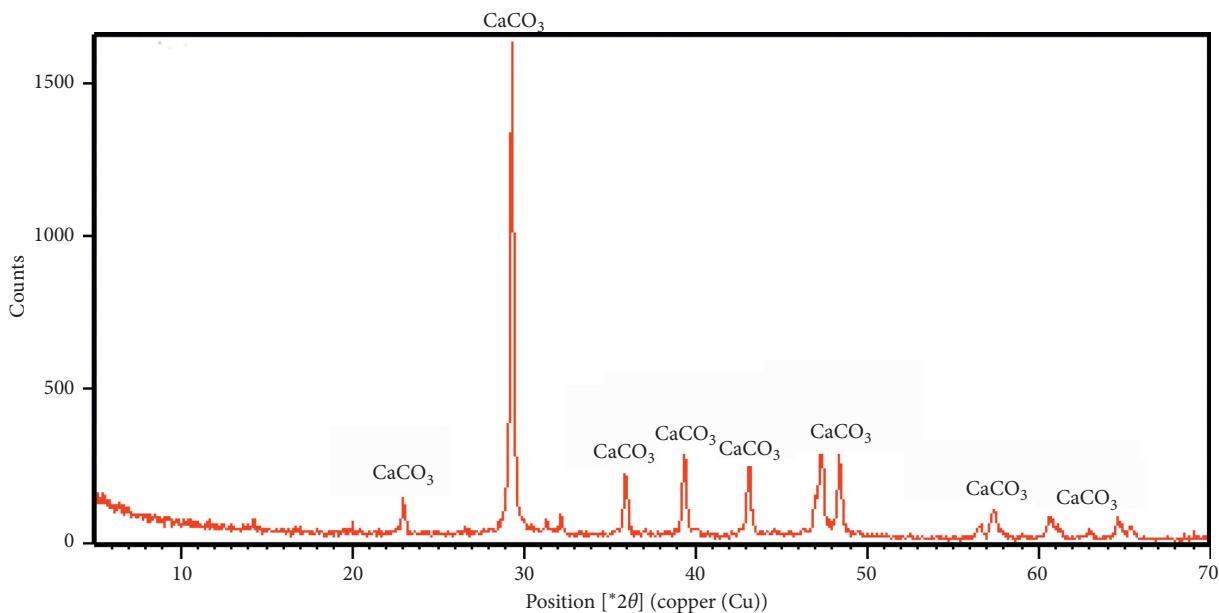


FIGURE 1: XRD patterns of sugar scum powder.

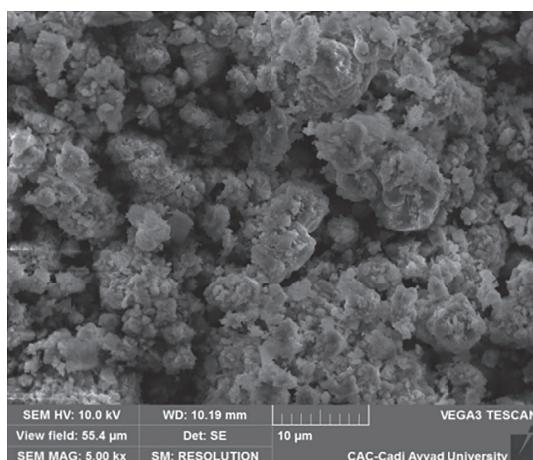


FIGURE 2: SEM of sugar scum powder.

3.2. Study of the Influence of Some Factors on the Removal of MO

3.2.1. Effect of Initial MO Concentration. The effect of increasing initial MO concentration on adsorption capacity of sugar scum is shown in Figure 5. As can be seen, the adsorption capacity increased with an increase in the initial concentration of MO solution if the amount of adsorbent was kept unchanged. This is due to the increase in the diffusion rate of MO with the increase in the concentration gradient between the aqueous solution and the solid phase [21].

3.2.2. Effect of Adsorbent Dose. The effect of the adsorbent dose, ranging from 1 to 16 g/L, on the adsorption of MO is illustrated in Figure 6. The MO removal increases as the amount of the sugar scum powder in solution increases and

reaches a maximum value 80% at 16 g/L. This observation can be explained by the increase in the surface area of the adsorbents and hence the number of available adsorption sites for the adsorption of MO [21]. Therefore, sugar scum dosage of 16 g/L was chosen as maximum removal for 100 mg/L MO dye solution for further studies.

3.2.3. Effect of Contact Time. The adsorption of MO onto sugar scum powder is presented in Figure 7 as a function of contact time from 15 min to 180 min. It is clear from the figure that the adsorption process was fast in the first 20 min and more than 80% of MO was adsorbed in this period. The adsorption process of MO was rapid at the initial stage due to the availability of vacant sites on the exterior surfaces. After the saturation of those active sites, MO entered to the pores of the adsorbent with a slower rate to reach equilibrium time [21]. The equilibrium state was established almost after 30 min. In the subsequent batch experiments, 60 min was taken to ensure the adsorption equilibrium.

3.3. Adsorption Kinetics Models. Adsorption kinetics models provide invaluable information on the controlling mechanisms of adsorption process. The overall adsorption process may be controlled either by external or film diffusion, pore diffusion and adsorption on the pore surface, or a combination of more than one step.

In order to predict the mechanism of the adsorption process of MO onto the sugar scum powder, the experimental data were fitted by the pseudo-first-order [38], pseudo-second-order [39], and intraparticle diffusion [40] models.

The linear pseudo-first-order model is given by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (3)$$

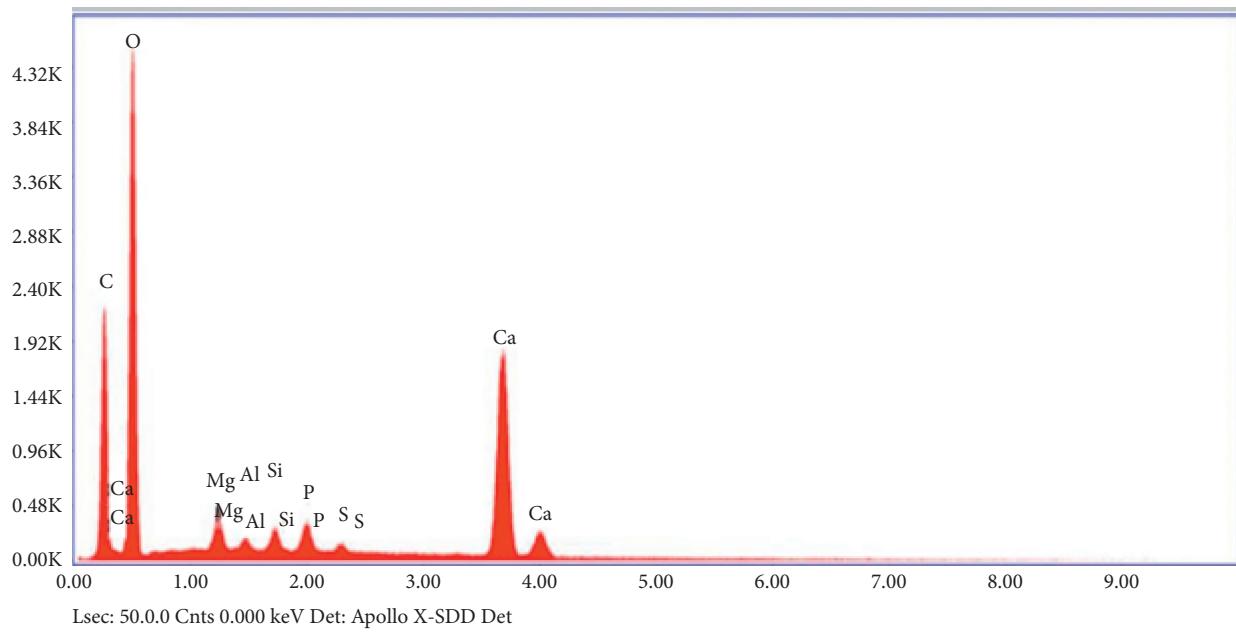


FIGURE 3: EDX of sugar scum powder.

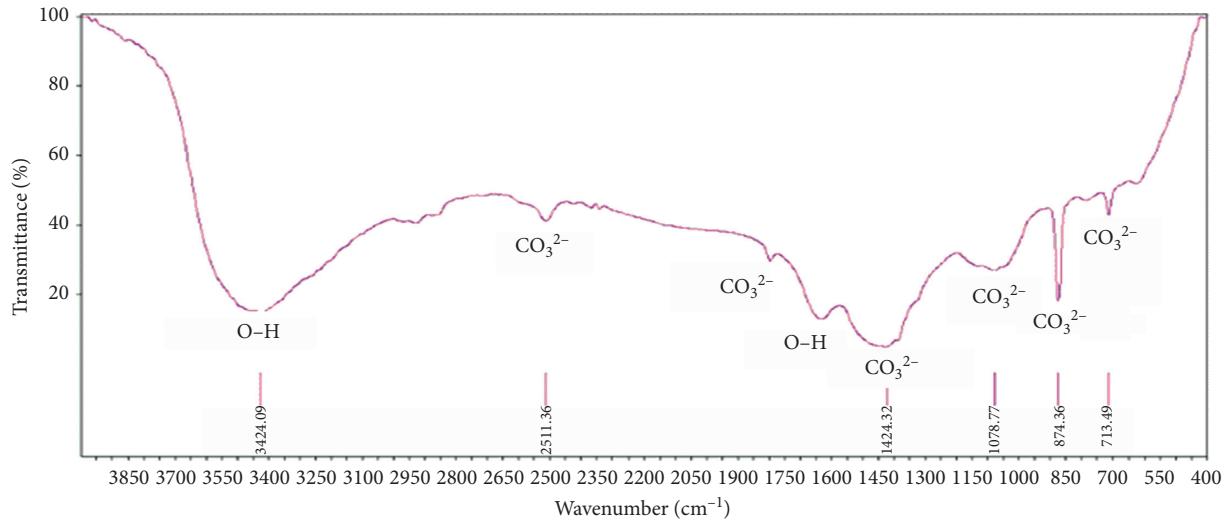


FIGURE 4: FTIR spectra of sugar scum powder.

where q_e (mg/g) is the adsorption amount at equilibrium, q_t (mg/g) is the adsorption amount at time t (min), and k_1 (min^{-1}) is the adsorption rate constant of pseudo-first-order model. Kinetic parameters, q_e and k_1 , can be determined experimentally from the slope and intercept of the plot $\ln(q_e - q_t)$ versus t (Figure 8).

The linear pseudo-second-order equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (4)$$

where q_e (mg/g) is the adsorption amount at equilibrium, q_t (mg/g) is the adsorption amount at time t (min), and k_2 (g/mg min) is the adsorption rate constant of pseudo-

second-order model. Kinetic parameters, q_e and k_2 , can be obtained experimentally by plotting $\ln(q_e - q_t)$ as a function of t (Figure 8).

The intraparticle diffusion model is expressed as follows:

$$q_t = k_{id} t^{1/2} + c, \quad (5)$$

where q_t (mg/g) is the adsorption amount at time t (min), k_{id} (mg/g $\text{min}^{1/2}$) is the adsorption rate constant of intraparticle diffusion model, and c is a constant related to the thickness of the boundary layer.

The calculated kinetic parameters of pseudo-first-order and pseudo-second-order equations are summarized in Table 1. The results showed that the fitting data to the pseudo-second-order model gave a high value of correlation

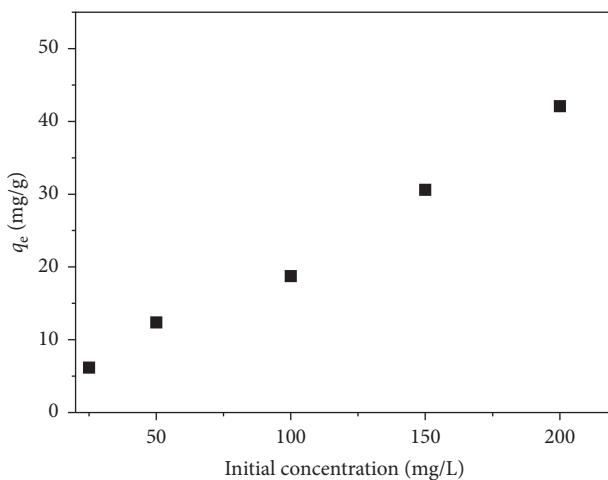


FIGURE 5: Effect of initial MO concentration ($t_{\text{contact}} = 24 \text{ h}$; adsorbent dose = 4 g/L; pH = 7.2; $T = 22^\circ\text{C}$).

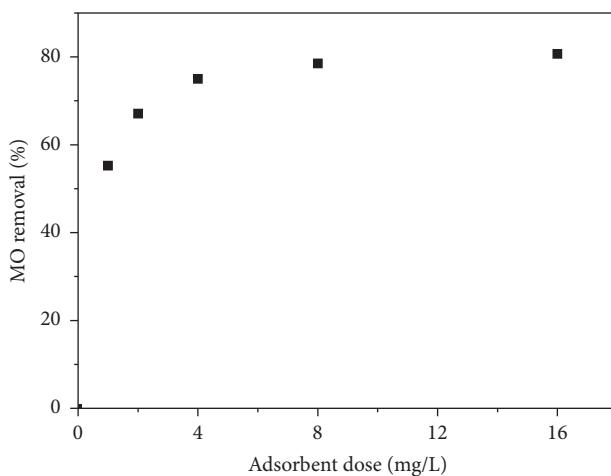


FIGURE 6: Effect of adsorbent dose on the adsorption of MO ($t_{\text{contact}} = 24 \text{ h}$; $C_0 = 100 \text{ mg/L}$; pH = 7.21; $T = 22^\circ\text{C}$).

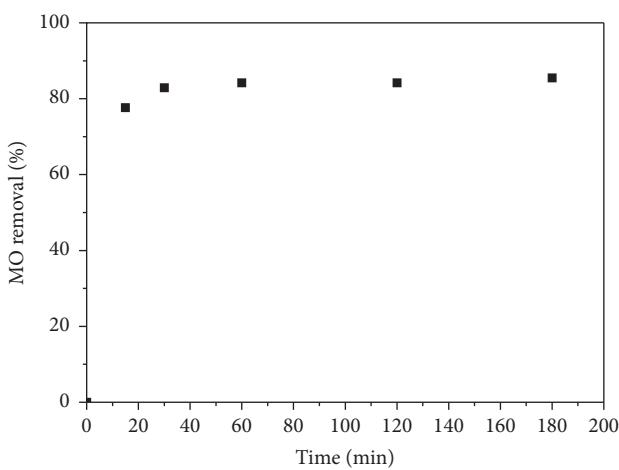


FIGURE 7: Effect of contact time on the adsorption of MO ($C_0 = 100 \text{ mg/L}$; adsorbent dose = 16 g/L; pH = 7.21; $T = 22^\circ\text{C}$).

coefficient R^2 , and its calculated equilibrium adsorption capacity ($q_{e,\text{cal}}$) is closer to the experimental value ($q_{e,\text{exp}} = 5.32 \text{ mg/g}$ which corresponds to 84% of MO

removal). Therefore, the pseudo-second-order model can describe the adsorption process of MO onto sugar scum powder. These results suggest that the boundary layer

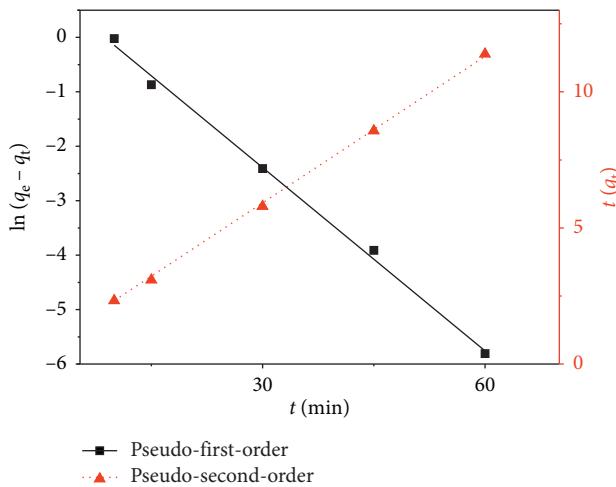


FIGURE 8: Linear fits of pseudo-first-order and pseudo-second-order kinetics for MO adsorption onto sugar scum powder ($C_0 = 100 \text{ mg/L}$; adsorbent dose = 16 g/L; pH = 7.21; $T = 22^\circ\text{C}$).

TABLE 1: Kinetic parameters for the MO adsorption onto sugar scum powder ($C_0 = 100 \text{ mg/L}$; adsorbent dose = 16 g/L; pH = 7.21; $T = 22^\circ\text{C}$).

$q_{e,\text{exp}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
	$q_{e,\text{cal}}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,\text{cal}}$ (mg/g)	k_2 (g/mg min)	R^2
5.32	2.65	0.1118	0.99	5.49	0.0051	0.99

resistance was not the rate-limiting step; it is a process in which a rapid initial stage is followed by a slower second stage limited by the intraparticle diffusion into smaller pores [21, 41].

The plot of the intraparticle diffusion model is shown in Figure 9. It can be observed that the plot is not linear over the whole time range, having three linear segments, which indicated that intraparticle diffusion was not the only rate-limiting step of the adsorption process, but there are other mechanisms which may control the rate of adsorption, all of which may be operating simultaneously [20, 42]. The initial part of the plot is attributed to the diffusion of MO through the solution to the external surface of the adsorbent. Thereafter, the second portion could be attributed to the intraparticle diffusion process. The slope of the linear portion indicates the rate of the adsorption process: the lower slope corresponds to a slower adsorption process [43]. The slope of the first portion was higher than that of the second portion which indicates that the MO molecules are quickly diffused through the boundary layer than through the pores of the adsorbent. Initially, the MO molecules are rapidly adsorbed on the surface of the sugar scum powder, and when saturation is reached, the MO particles are diffused into the internal surface of the particles of adsorbent. The third portion is attributed to the final equilibrium stage for which the intraparticle diffusion starts to slow [20, 44].

3.4. Adsorption Isotherms. The adsorption isotherm describes the interaction between the adsorbate molecules and the adsorbent when the system reaches the equilibrium. It provides the qualitative information on the nature of adsorbate-adsorbent surface interactions and could be used to evaluate the

adsorption capacity. In this study, the experimental data were fitted to the Langmuir and Freundlich models to find which one can be used to describe the adsorption process of MO on the surface of sugar scum powder. Langmuir equation was based on the assumption of monolayer adsorption on a homogeneous surface without interaction between adsorbates, while the Freundlich isotherm assumes the multilayer adsorption on heterogeneous surface [1].

The linear form of Langmuir isotherm equation is given as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \times \frac{1}{C_e}. \quad (6)$$

The linear form of Freundlich isotherm equation is expressed as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (7)$$

where C_e is the equilibrium concentration of adsorbate, q_e is the amount of adsorption at the equilibrium, q_m is the monolayer adsorption capacity, n is the Freundlich intensity constant, and K_L and K_F are the Langmuir and Freundlich constants, respectively.

The adsorption isotherm of MO onto sugar scum powder obtained at temperature 22°C is presented in Figure 10. According to Giles classification [45], this isotherm displayed an H curve pattern, indicating that the MO and sugar scum powder have a high affinity.

Table 2 summarizes the calculated parameters of Langmuir and Freundlich isotherms obtained by linear fitting (Figure 11). The results given in Table 2 show that the adsorption isotherm of MO onto the sugar scum powder is described by the Langmuir model with a correlation

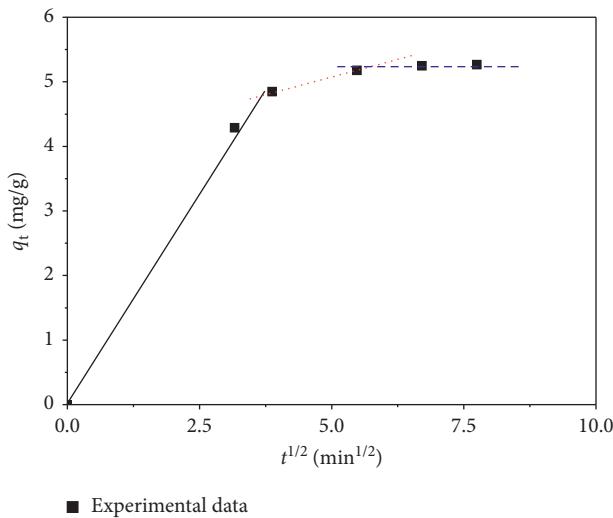


FIGURE 9: Plot of the intraparticle diffusion model for MO adsorption onto sugar scum powder ($C_0 = 100$ mg/L; adsorbent dose = 16 g/L; pH = 7.21; $T = 22^\circ\text{C}$).

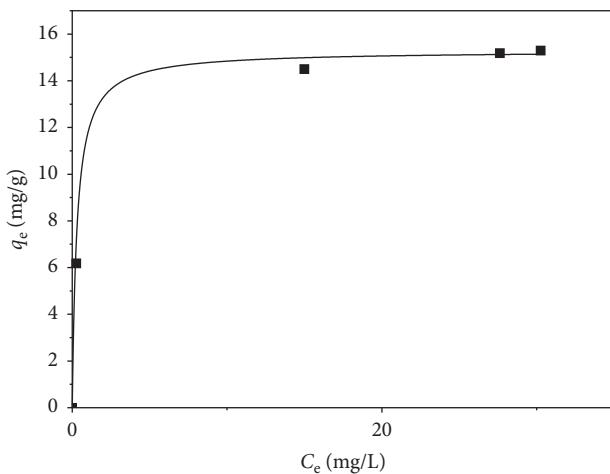


FIGURE 10: Adsorption isotherm of MO onto sugar scum powder (adsorbent dose = 16 g/L; pH = 7.21; $T = 22^\circ\text{C}$).

TABLE 2: Langmuir and Freundlich isotherm parameters (adsorbent dose = 16 g/L; pH = 7.21; $T = 22^\circ\text{C}$).

q_m (mg/g)	Langmuir		Freundlich		R^2
	K_L (L/mg)	R^2	$1/n$	K_F ((mg/g) (L/mg) $^{1/n}$)	
15.24	2.6223	0.99	0.1948	8.0975	0.98

coefficient (R^2) greater than 0.99, suggesting monolayer adsorption on homogeneous surface without interaction between adsorbates. The maximum monolayer capacity for the MO adsorption onto sugar scum powder was found to be 15.24 mg/g at 22°C.

3.5. Thermodynamic Study. The nature and thermodynamic feasibility of MO adsorption onto sugar scum powder were evaluated by calculating the thermodynamic parameters from the experimental data obtained at various

temperatures. The standard free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) are obtained by using the following equations:

$$K_d = \frac{q_e}{C_e},$$

$$\Delta G^\circ = -RT \ln(1000K_d), \quad (8)$$

$$\ln(1000K_d) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R},$$

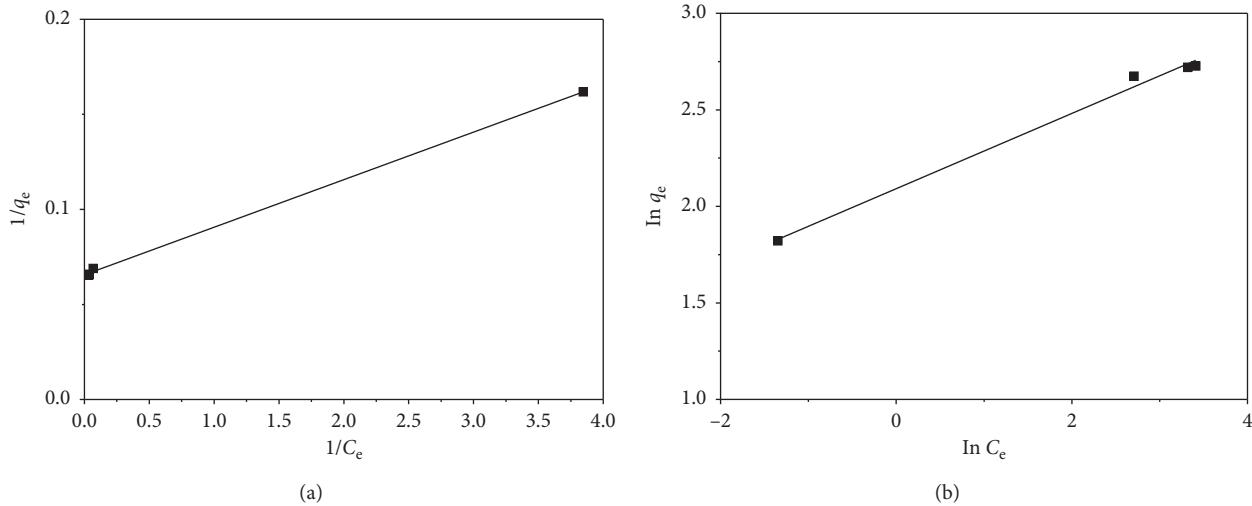


FIGURE 11: Linear modeling of the MO adsorption isotherm onto sugar scum powder (adsorbent dose = 16 g/L; pH = 7.21; T = 22°C): (a) Langmuir; (b) Freundlich.

TABLE 3: Thermodynamic parameters for MB adsorption on optimal activated carbon ($C_0=100$ mg/L; adsorbent dose = 16 g/L; pH = 7.21).

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K mol)
293	-14.63	-14.14	2.03
303	-14.9		
318	-14.73		

where K_d is the thermodynamic distribution coefficient, R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). The values of ΔH° and ΔS° can be determined from the slope and intercept of the plot of $\ln(1000K_d)$ versus $1/T$.

The values of ΔG° , ΔH° , and ΔS° were calculated and are listed in Table 3. The negative values of ΔG° indicate the feasibility and spontaneous of the adsorption processes of MO onto sugar scum powder. The negative value of ΔH° indicates the exothermic and physical nature of the adsorption process involving weak forces of attraction between MO molecules and sugar scum powder [46]. The positive value of ΔS° indicates the increased randomness at the solid-solution interface during the fixation of the MO on the active sites of the studied adsorbent.

4. Conclusion

The present study shows that the sugar scum is a cheap and effective inorganic adsorbent for the removal of anionic dyes such as methyl orange from aqueous solutions. The adsorption kinetics is fast with 60 min needed to reach equilibrium, and more than 80% of MO was adsorbed in the first 20 min. The adsorption of MO can be described by a pseudo-second-order model, and thermodynamic analysis shows that the adsorption is an exothermic process. The equilibrium data were best described by the Langmuir isotherm model, with a maximum adsorption capacity of 15.24 mg/g. As a result of this study, sugar scum powder can be used as

an effective adsorbent for the removal of anionic dyes from wastewater.

Data Availability

All the data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

We are grateful to the Center of Analyses and Characterization (CAC) of University Caddy Ayyad, Morocco. Also, our respectful thanks go to professors of REMATOP, LCOA, and Reminex Managem Laboratories in Marrakech, Morocco.

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