



Isotherm, thermodynamic, kinetics and adsorption mechanism studies of methyl orange by surfactant modified silkworm exuviae

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ABSTRACT

This paper reports on the development of organo-modified silkworm exuviae (MSE) adsorbent prepared by using hexadecyltrimethylammonium bromide (HDTMAB) for removing methyl orange (MO), a model anionic dye, from aqueous solution. The natural and modified samples were characterized by scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and Fourier transform infrared spectroscopy (FT-IR). Batch adsorption experiments were carried out to remove MO from its aqueous solutions using SE and MSE. It was observed that the adsorption capacity of MSE is 5–6 times of SE. The different parameters effecting on the adsorption capacity such as pH of the solution, initial dye concentration, temperature and contact time have been investigated. Analysis of adsorption results obtained at different temperatures showed that the adsorption pattern on the MSE can be described perfectly with Langmuir isotherm model compared with Freundlich and Dubinin–Radushkevich (D–R) isotherm models, and the characteristic parameters for each adsorption isotherm were also determined. The adsorption process has been found exothermic in nature and thermodynamic parameters have been calculated. The adsorption kinetic followed the pseudo-second order kinetic model. The results of FT-IR, EDS and desorption studies all suggest that methyl orange adsorption onto the MSE should be mainly controlled by the hydrophobic interaction mechanism, along with a considerable contribution of the anionic exchange mechanism. The results indicate that HDTMAB-modified silkworm exuviae could be employed as low-cost material for the removal of methyl orange anionic dye from wastewater.

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1. Introduction

Dyes are widely used in many industries such as the textile, leather, food, dyeing, cosmetics and paper [1]. The high level of production and extensive use of dyes generates coloured wastewater which produces toxicological and technical problems and environmental pollution. Most of these dyes are of synthetic origin and toxic in nature with suspected carcinogenic and genotoxic effects [2,3]. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents. Therefore, dye removal has been a very important but challenging area of wastewater treatment [4].

The conventional methods of dye removal have several shortcomings, such as, inefficient removal at low dye concentrations, high needs of chemicals and energy and prohibitively high cost [5]. Therefore, efforts are being made to develop efficient and cost-effective technologies for dye removal from industrial wastewaters. Recently, adsorption is becoming the most popular method for dye wastewater treatment because it is more economical and readily

available [6]. Adsorption process using commercial-activated carbons is very effective for removal of dyes from wastewater, but its high cost limits its commercial application [7,8]. Thus, there is a growing need to find low cost and efficient, locally available materials for the removal of dye. Lately, there has been an increase in the use of agricultural wastes as dyes adsorbents which include: rice husk [9], pineapple stem [10], bagasse pith [11], maize cob [12], wood sawdust [13], hazelnut shell [14], papaya seeds [15], leaves [16,17] and fruit peels [18,19], etc. The advantage of using agricultural waste materials used as dye adsorbent is that it saves disposal costs while alleviating potential environmental problems [20,21]. Moreover, agricultural waste products are usually built up of ligno-cellulosic materials, i.e. contains mainly of cellulose, hemicellulose and lignin, which is considered to be beneficial to adsorption [22,23]. A critical review of low cost adsorbents including agricultural wastes for dye wastewater treatment was just presented extensively by Gupta and Suhas [24]. It can be found in above literatures that adsorption capacity of agricultural waste is commonly high for cationic dyes, whereas a relatively low adsorption capacity was obtained for anionic dyes. This case is likely to be caused by the fact that the plant waste's surface is usually negatively charged in natural water bodies, which is not benefit to adsorb anions. Hence, the surface of the natural plant wastes has to be modified in a man-

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ner to improve their adsorption capacities for anionic dyes. For many plant wastes, there are many negative charges on the surface of them and many kinds of metal ions. So, they can be modified by organic cations such as quaternary ammonium compounds by electrostatic attraction and ion exchange reaction. Recently, some natural plant wastes were modified by surfactant for the removal of anionic dyes and satisfying adsorption capacities were obtained [25–28].

Sericulture is a long history of traditional agriculture project in China. At present, sericulture is widespread in Asia, Africa, Europe, Latin America, Oceania and other countries and regions. Currently, silk annual production is of about 50,000 tons, of which the largest share in China. Silkworm (*Bombyx mori*) belonging to the branch of bombycidae, is created by long-term feeding in ancient China. The silkworm belongs to the insect of complete metamorphosis. In its growth process, a major feature is described as the phenomenon of “sleep”. Exuviation occurred once every sleep time and a lifetime total of four exuviate paper existed, except for the time of from the insect form to pupae form. Sericulture can generate much silkworm exuviae, which is often thrown away as waste. Silkworm exuviae (SE) is not only available in abundant supply as an agricultural waste of sericulture industry, it is also advantageous because of their availability as a renewable resource. SWE is rich in chitin, which is a great potential for its utilization in wastewater treatment. We have tested SE as a good biosorbent for removal of methylene blue dye from aqueous solutions [29]. However, we conducted a preliminary test using SE for anionic dye adsorption and found that the SE was almost no effect for anion dye adsorption. To make the application of the SE adsorbent wider in treatment for different types of dyes wastewaters, the surface of the SE was modified using a cationic surfactant, hexadecyltrimethylammonium bromide (HDTMAB) in the present work.

The main objects of this paper are: (i) to study the feasibility of using surfactant modified silkworm exuviae as an adsorbent for the removal of a model anionic dye, methyl orange, (ii) to determine the various parameters affecting sorption, such as pH, concentration and temperature, (iii) to determine the applicability of various isotherm models (i.e., Langmuir, Freundlich, and Dubinin and Radushkevich) to find out the best-fit isotherm equation, and (iv) to determine thermodynamic and kinetic parameters and explain the nature of adsorption.

2. Experimental

2.1. Adsorbate and chemicals

An anionic dye, methyl orange ($C_{14}H_{14}N_3NaO_3S$, C.I.13025), was purchased from Sigma–Aldrich and used without further purification. A stock solution was prepared by dissolving required amount of dye in double distilled water which was later diluted to desired concentrations. Hexadecyltrimethylammonium bromide was purchased from Shanghai Reagent Co. (Shanghai, China) as high purity (>99%) product. All of chemicals other used were of analytical grade. In all experiments distilled water was employed.

2.2. Preparation and characterization of the adsorbent

SE wastes obtained from sericulture farmers of Linhai City, Zhejiang Province, China, were washed repeatedly with distilled water for several times to remove dirt particles and soluble impurities and were allowed to dry in an air oven at 353 K for 2 days. The sample was grounded in a mechanical grinder and then sieved to obtain particle size of > 100 mesh.

The surfactant modified sample was prepared as follows. 10 g of SE was mixed in 100 mL of aqueous solution containing HDTMAB

(10 wt.% of the system). The suspension was stirred magnetically at room temperature for 24 h. The mixture was filtered and washed several times with distilled water until no bromide ion was detected by $AgNO_3$ solution (0.1 mol L^{-1}). The sample was dried in an air oven at 80°C and ground to 200 mesh size. And then stored in an airtight glass container and labelled as surfactant modified silkworm exuviae (MSE).

The morphological features and energy dispersive spectroscopy (EDS) analyses of SE before and after surfactant modification were performed in a high-performance and ultra high resolution scanning electron microscope (HITACHI S-4800) after coating the sample with a thin layer of gold.

FT-IR spectra measurements of SE, modified SE and dye-loaded MSE were done on a Thermo Nicolet NEXUSTM spectrometer using the KBr pellets. The spectrum was collected 32 times and corrected for the background noise. Dye-loaded MSE used for FT-IR study was obtained by extracting the biosorbent from the liquid phase after centrifugation and drying in an oven at 60°C for 2 h.

Bromine ion in supernatant after adsorption was analyzed by ion chromatography.

2.3. Biosorption studies

Adsorption experiments were evaluated in batch equilibrium mode. All experiments were conducted by mixing 25 mL of aqueous dye solutions with 0.05 g of the adsorbent. The pH values of initial solutions were adjusted with dilute HCl or NaOH solution. The mixtures were shaken in a thermostatic shaker bath (THZ-98A mechanical shaker) at 120 rpm at desired temperature. After a shaking time was completed, the suspension was centrifuged at 5000 rpm for 10 min. The equilibrium concentration of dye solution was measured using UV–vis spectrometer (Specord 200) at the λ_{max} value of 460 nm for MO. The amount of the dye adsorbed onto the adsorbent was determined by the difference between the initial and remaining concentration of dye solution. The adsorption capacity of MO on adsorbent was calculated using the following equation:

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

where q_e is the amount of MO adsorbed on adsorbent (mg g^{-1}), C_0 , the initial concentration of MO solution (mg L^{-1}), C_e , the equilibrium concentration of MO solution (mg L^{-1}), m , the mass of adsorbent used (g) and V , the volume of MO solution (L).

To examine the effect of pH, adsorption experiments were conducted at different pH ranging from 3 to 10 at 350 mg L^{-1} of dye solution.

Adsorption experiments were also carried out to obtain isotherms at different temperatures. This was done at 303.2, 313.2, 323.2 and 333.2 K, respectively. In this group of experiments dye solutions with different initial concentration, in the range of $50\text{--}350 \text{ mg L}^{-1}$, were selected. Adsorption time of 12 h was chosen to allow attainment of equilibrium at constant temperatures.

The procedures of kinetic experiments were similar to those of equilibrium tests. The aqueous samples were taken at different time intervals, and the concentrations of dye were similarly measured. The kinetic experiments were carried out at a temperature of 303.2 K and pH of 7.0. The amount of adsorption at time t , q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_t is the concentration of MO solution at any time t (mg L^{-1}).

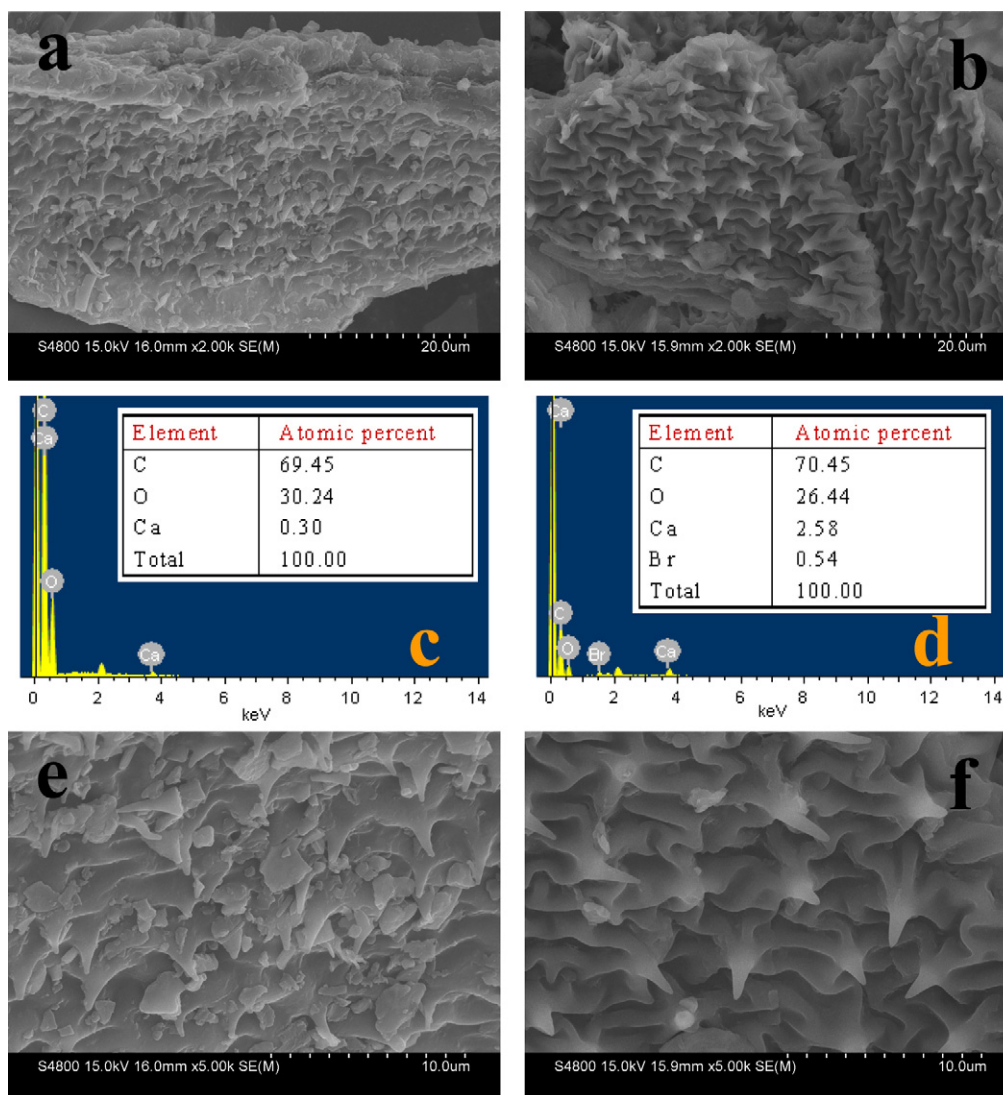


Fig. 1. SEM-EDS analysis of SE (a, c, e) and MSE (b, d, f).

2.4. Desorption studies

For batch desorption study, 50 mg of the adsorbent used for the adsorption of an initial dye concentration of 350 mg L^{-1} was separated from the dye solution by centrifugation. The dye-loaded adsorbent was washed gently with water to remove any unadsorbed dye. Then the spent adsorbent was stirred using a magnetic stirrer with 25 mL of neutral distilled water, 0.1 mol L^{-1} NaOH solution for 12 h, in turn. Desorption efficiency, E_d , was defined in following equation.

$$E_d = \frac{Q_d}{Q_e} \times 100\% \quad (3)$$

where Q_d and Q_e are the amount of dye desorbed (mg) and dye loaded (mg), respectively. All tests were carried out in triplicate and only mean values were presented.

3. Results and discussion

3.1. Characterization of the adsorbent

The results of SEM and EDS analysis for SE and surfactant modified SE are shown in Fig. 1. As shown in Fig. 1, there are obvious morphological differences of the SEM micrographs of SE and MSE.

The micrographs of SE (Fig. 1a and e) represent a compact, uneven and folded surface, mainly containing carbon, oxygen and calcium (Fig. 1c). For MSE, its micrographs show a flexible and porous surface (Fig. 1b and f), which should be benefit for the dye removal [10]. It is important to note that bromine was detected on the surface of the MSE (Fig. 1d). This result indicated that a part of hexadecyltrimethylammonium bromide molecules is most probably arranged through a mode of bimolecular association [30] and/or micelle-type [31,32] except for a popular monolayer coverage mode.

The FT-IR spectra of SE and MSE are shown in Fig. 2. In comparison with spectrum of silkworm exuviae, that of organo-silkworm exuviae shows more intense absorption bands at 2924 and 2853 cm^{-1} attributing to $-\text{CH}_3$ and $-\text{CH}_2$ groups. Furthermore, the peak at 1380 cm^{-1} ascribed to C-H bending vibration also significantly increased. These clearly indicate that natural silkworm exuviae has been successfully modified by surfactant. On the whole, other characteristic peaks of the SE sample do not change after modification, which implies that most likely the surfactant molecules is present on the surface of SE particles through a non-chemical interaction such as cation-exchange and/or electrostatic attraction [29].

It can be clearly seen from Fig. 2 that there are many absorption bands ascribed to characteristic functional groups such as $-\text{OH}$

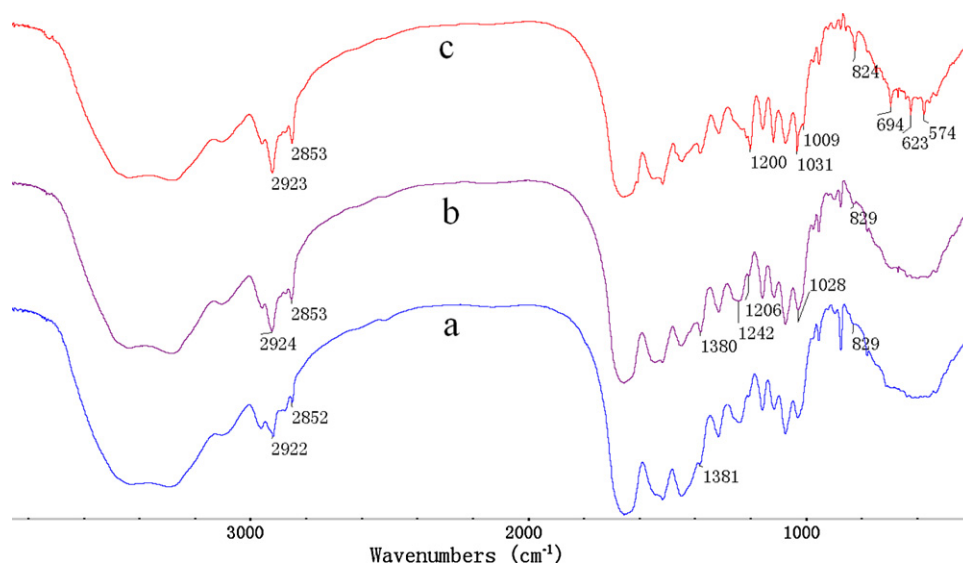


Fig. 2. FT-IR spectra of SE (a), MSE (b) and dye-load MSE (c).

(3431 cm^{-1}), $-\text{NH}_2$ (3294 cm^{-1}), $>\text{C}=\text{N}-$ and $>\text{C}=\text{C}<$ (1655 cm^{-1}), $\equiv\text{C}-\text{C}\equiv$, $\equiv\text{C}-\text{N}<$ and $\equiv\text{C}-\text{O}-$ (1157 cm^{-1}) and $>\text{C}=\text{S}$ (1115 cm^{-1}) [29]. After dye adsorption, both position and intensity of these characteristic peaks almost unchanged, suggesting that these functional groups on the surface of MSE do not participate in the whole adsorption process. The FT-IR spectra of dye-loaded MSE (Fig. 2c), showed the presence of several new bands compared with that of MSE. Also, these new peaks, i.e. 1200 , 1009 , 824 , 694 , 623 , 574 cm^{-1} , are all located in the fingerprint region. The peak observed at 1200 cm^{-1} could be assigned to $-\text{SO}_3$ stretching vibration. The absorbance at 1009 cm^{-1} is due to C–H in-plane bending vibration of benzene rings. The rest of four peaks is the indication of C–H out-plane bending vibration of benzene rings. Take into account the fact that these new peaks mentioned above are also the characteristic peaks for methyl orange dye molecules, it is conceived that the changes of the peaks were very likely caused by the introduction of dye molecules themselves. Based on the above analysis, surfactant should play an important role in this study, which directly affects the mode of interaction between dye and MSE. According to reports in the literature [33–36], it is postulated that adsorption mechanisms of dye onto MSE was distributed into solid organic matter via the hydrogen bond. In addition, there is also anion exchange mechanism in adsorption process considering the existence of bromine as mentioned above. More trials are needed to see how well the two adsorption mechanism play role on adsorption capacity of the adsorbent.

3.2. Effect of pH

The pH of the dye solution is an important parameter controlling the adsorption capacity of dye onto biosorbent [1,15,19,28]. Fig. 3 shows the adsorption capacity for SE and MSE at different pH. It can be observed that the adsorption capacity of the two adsorbents decreases obviously with an increase in pH of the initial solution from 3 to 5, and then decreases at a slower rate until the pH reaches to 8.0. As the pH become more basic, the adsorption capacity obviously decreases again. The trend in pH vs. adsorption capacity is highly dependent on pH of the solution for the two adsorbents, which can be interpreted in terms of electronegative property of adsorbent surface. As pH value is low (3.0), functional groups such as $-\text{OH}$ and $-\text{NH}_2$ on SE are more protonated and form $-\text{OH}_2^+$ and $-\text{NH}_3^+$, hence, they are more available to adsorb MO through the electrostatic attraction. As pH increases to 8.0, the silkworm exu-

viae surface at the moment becomes negatively charged as a whole [29]. A negative charged surface site on the SE does not favor the adsorption of anionic dye due to electrostatic repulsion and causing an evident decrease in the MO adsorption. Although adsorption sites of SE surface are replaced partially by surfactant molecules by cation exchange reaction, there is no difference in the trend in pH vs. adsorption capacity for the two adsorbents. It is worthy to note that still significant amount of dye removal onto MSE was observed as the pH of the solution increases from 8 to 10. This suggests that the other mechanism not electrostatic attraction may be working [37]. To increase the adsorption capacity as possible and keep natural pH value of MO dye solutions, pH of 7.0 was selected for the rest of the batch experiments.

3.3. Adsorption isotherms

The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the adsorption systems. Therefore, the adsorption of MO onto MSE at different temperatures is determined as a function of equilibrium (residual) dye concentration (C_e) and the corresponding adsorption isotherms are plotted in Fig. 4.

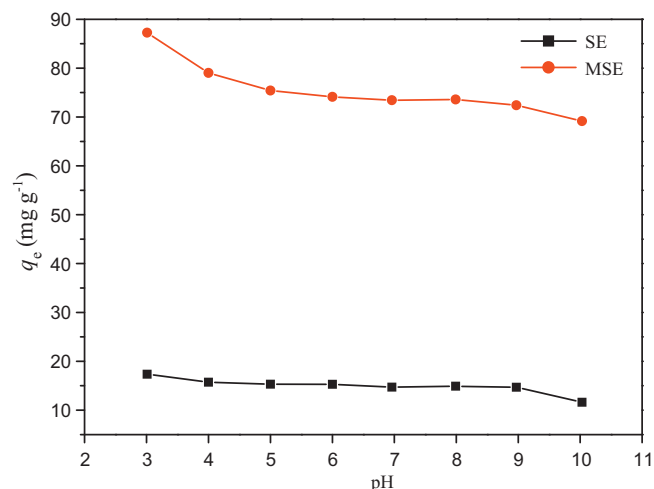


Fig. 3. Effect of pH for the adsorption of MO onto SE and MSE.

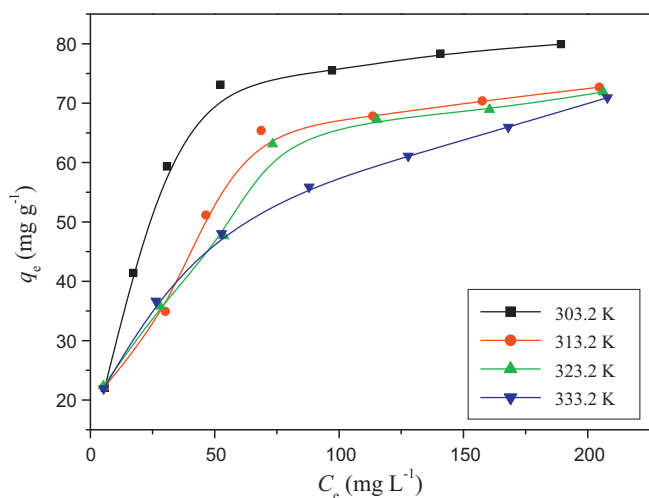


Fig. 4. Adsorption isotherms of MO on MSE at different temperatures.

The adsorption process is normally described by the Langmuir and the Freundlich isotherms. The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogenous sites within the adsorbent and has found successful application in many studies of monolayer adsorption [38]. The linear form of the Langmuir isotherm equation is written as

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

where q_m is the monolayer adsorption capacity of the adsorbent (mg g^{-1}), and b is the Langmuir adsorption constant (L mg^{-1}), which is related to the free energy of adsorption.

The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available [39]. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. Its linearized form can be written as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n (dimensionless) are the Freundlich adsorption isotherm constants, being indicative of the extent of adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

Adsorption equations were obtained from experimental data with Eqs. (4) and (5). The isotherm constants and correlation coefficients were calculated from the linear Langmuir and Freundlich plots by plotting C_e/q_e vs. C_e (Fig. 5) and $\log q_e$ vs. $\log C_e$ (Fig. 6) and are represented in Table 1. By comparing the correlation coefficients r^2 , it can be deduced that the experimental equilibrium adsorption data are well described by the Langmuir equation compared with Freundlich model. This suggests the monolayer coverage of the surface of MSE by MO molecules. The high adsorption capacity in MSE could be due to the large amount of surfactant on the surface of silkworm exuviae particles, which could result in increasing amounts of positively charged sites on the surface of SE and finally facilitates the attraction towards the negatively charged dye molecules [40]. Moreover, the q_{max} decreases with an increase in temperature, which specifies an exothermic nature of the existing process.

Through the discussion about isotherm constants, it can be predicted whether an adsorption system is favorable or unfavorable. The essential characteristics of the Langmuir isotherm can be

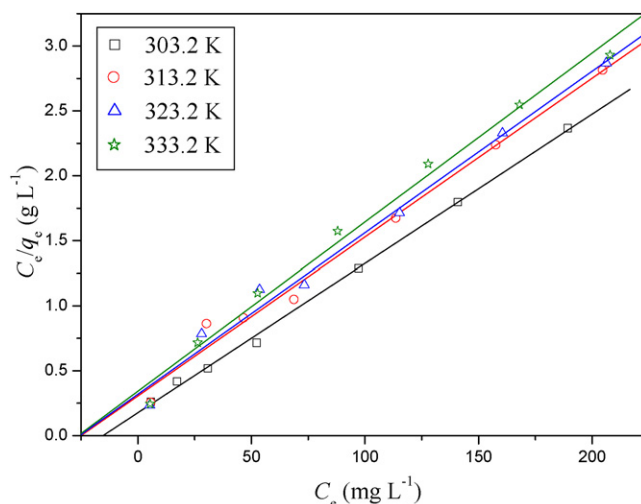


Fig. 5. Langmuir plots for the adsorption of MO on MSE at different temperatures.

expressed by means of ' R_L ', a dimensionless constant referred to as separation factor or equilibrium parameter R_L is defined by

$$R_L = \frac{1}{(1 + bC_0)} \quad (6)$$

where C_0 is the highest initial dye concentration. The parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). As can be seen from Table 1, at all temperatures the R_L values are between 0 and 1.0, indicating that the adsorption of MO onto MSE is favorable.

The n values of Freundlich equation can give an indication on the favorability of sorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor sorption characteristics. The result shows that the values of n are all greater than 2, which implies that dye molecules are favorably adsorbed by MSE. This is in good agreement with the findings regarding to R_L value.

To deepen the understanding of adsorption mechanism, Dubinin–Radushkevich (D–R) isotherm model was chosen to apply on adsorption study. The D–R isotherm can be used to describe adsorption on both homogenous and heterogeneous surfaces [41]. A linear form of D–R isotherm is

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

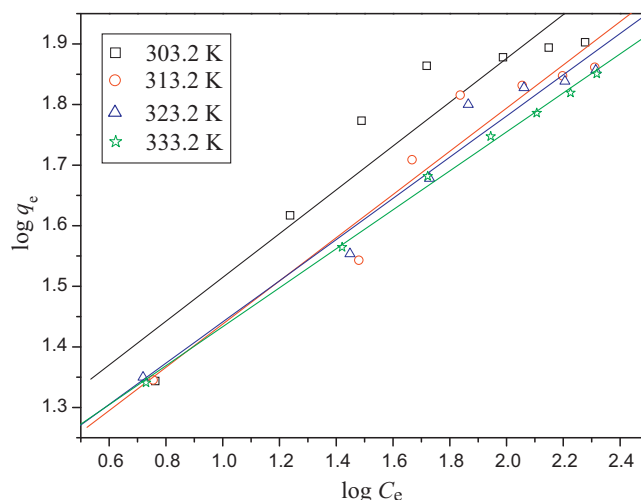


Fig. 6. Freundlich plots for the adsorption of MO on MSE at different temperatures.

Table 1
Isotherm constants and correlation coefficients for the adsorption of MO on MSE at different temperatures.

Model		T (K)			
		303.2	313.2	323.2	333.2
Langmuir isotherm	q_{\max} (mg g ⁻¹)	87.03	81.77	80.45	76.80
	b (L mg ⁻¹)	0.06506	0.03994	0.03898	0.03797
	R_L	0.04207	0.06676	0.06830	0.06998
	r^2	0.9991	0.9936	0.9937	0.9946
Freundlich isotherm	K_f (mg ^{1-1/n} L ^{1/n} g ⁻¹)	14.23	12.05	12.62	12.93
	n	2.767	2.805	2.941	3.110
	r^2	0.9419	0.96824	0.98179	0.99862
Dubinin–Radushkevich isotherm	q_m (mg g ⁻¹)	282.8	224.9	203.6	180.7
	β (mol ² kJ ⁻²)	0.00316	0.00287	0.00255	0.00228
	r^2	0.9589	0.9712	0.98162	0.9989
	E_a (kJ mol ⁻¹)	12.58	13.20	14.00	14.81

β , a constant related to the mean free energy of adsorption (mol² kJ⁻²); q_m , the theoretical saturation capacity; and ε , the Polanyi potential, which is equal to $RT \ln(1 + (1/C_e))$, where R (J mol⁻¹ K⁻¹) is the gas constant and T (K) is the absolute temperature. The plots of specific sorption, $\ln q_e$ against ε^2 for MO is shown in Fig. 7. For D–R isotherm equation, from the β values the mean energy of adsorption, E_a can be calculated using the relation [42].

$$E_a = (2\beta)^{-1/2} \quad (8)$$

Based on Eqs. (7) and (8), the isotherm constants, E_a and correlation coefficients are calculated and presented in Table 1. From the table, the values of E_a at different temperatures are found to lie between 12.58 and 14.81 kJ mol⁻¹ in the whole range of investigated dye concentrations. The mean energy of adsorption is the free energy change when one mole of the ions is transferred from infinity in the solution to the surface of the solid. The value of this parameter can give information about adsorption mechanism. When one mole of ions is transferred, its value in the range of 1–8 kJ mol⁻¹ shows physical adsorption [43], the value of E_a is between 8 and 16 kJ mol⁻¹, which indicates the adsorption process follows by ion-exchange [44], while its value in the range of 20–40 kJ mol⁻¹ is indicative of chemisorption [45]. So, it seems that ion-exchange mechanism is dominating in the adsorption process. However, the above conclusion is not very reliable considering the low correlation coefficient. So, more information about adsorption mechanism is needed to be obtained.

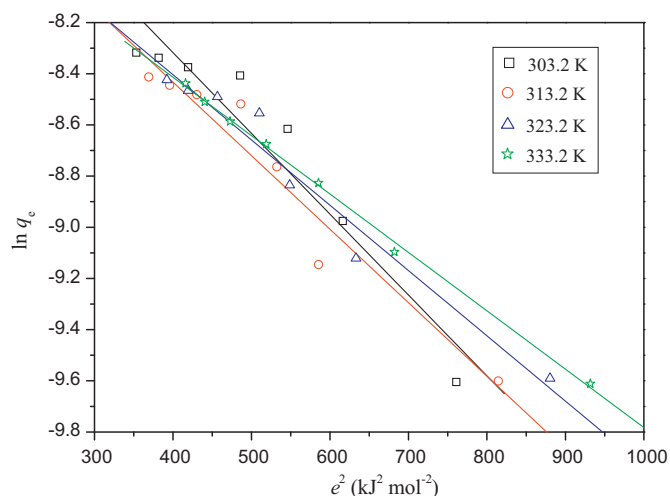


Fig. 7. D–R plots for the adsorption of MO on MSE at different temperatures.

3.4. Thermodynamic studies

In environmental engineering practice, both energy and entropy considerations must be taken into account in order to determine what processes will occur spontaneously. Values of thermodynamic parameters including change in the enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG), are the actual indicators for practical application of a process. In the present work, the effect of temperature on adsorption was studied at four temperatures (303.2, 313.2, 323.2 and 333.2 K) and seven different concentrations of the dye. ΔH and ΔS were calculated from the slope and intercept of the linear plot of $\ln(q_e/C_e)$ vs. $1/T$ according to Eq. (9), i.e. the van't Hoff equation. ΔG can be calculated using Eq. (10)

$$\ln \left(\frac{q_e}{C_e} \right) = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (9)$$

$$\Delta G = -RT \ln \left(\frac{q_e}{C_e} \right) \quad (10)$$

The obtained thermodynamic parameters are given in Table 2. In general, the adsorption process was exothermic with heats of adsorption (ΔH) (mean value -11.38 kJ mol⁻¹) for the concentration range of the dye solution. These values did not indicate strong chemisorptive bond formation between the dye molecules and the adsorbent surface. The values of ΔG were small but most of them were positive, suggesting that the adsorption process led to an increase in the Gibbs energy. Further, the increase in the values of ΔG with the increasing temperature indicates the adsorption is more spontaneous at lower temperatures. The process was accompanied by a decrease in entropy which could be attributed to the higher degree of ordering of the small number of the dye molecules on the solid phase compared with their ordering in the aqueous phase [46]. The results of the measurement of the thermodynamic parameters indicate that the dye–MSE interaction equilibrium could be explored for practical application.

3.5. Adsorption kinetics

Fig. 8 shows the adsorption capacity of the adsorbent as a function of time under the condition of a dye initial concentration of 300 mg L⁻¹. As seen in the figure, the dye adsorption process on the MSE can be rapid in the first ≈ 15 min, then continued with a slower rate during the 15–60 min and nearly reached a plateau after approximately 60 min of the experiment.

In order to investigate dye adsorption rate, the kinetics of methyl orange adsorption by organo-modified silkworm exuviae was modelled using pseudo-first order, pseudo-second order and

Table 2
Thermodynamic parameters for the adsorption of MO onto MSE.

Dye concentration (mg L ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹) at temperature			
			303.2 K	313.2 K	323.2 K	333.2 K
50	2.542	19.55	-3.374	-3.540	-3.901	-3.898
100	-13.27	-38.46	-2.202	-0.3806	-0.6520	-0.9189
150	-20.93	-64.73	-1.649	-0.2510	0.3162	0.2583
200	-20.73	-65.88	-0.843	0.1274	0.4022	1.256
250	-12.45	-43.43	0.6371	1.342	1.4466	2.044
300	-9.184	-35.49	1.478	2.099	2.272	2.590
350	-5.625	-26.07	2.172	2.695	2.833	2.979
Mean	-11.38	-36.36	-0.5399	0.2989	0.3880	0.4256

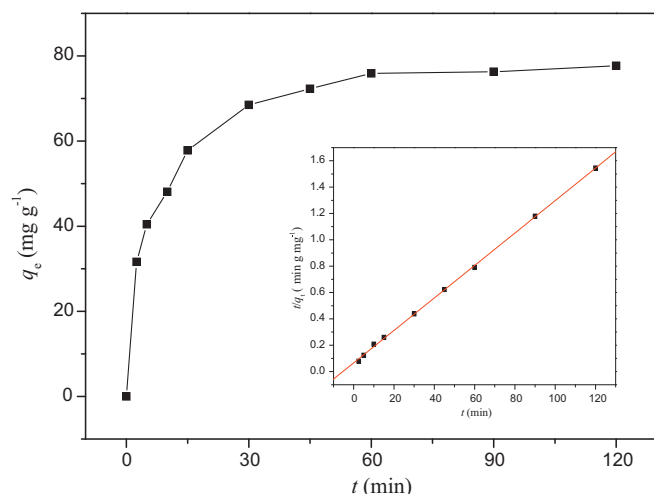


Fig. 8. Adsorption kinetics curve and pseudo-second order plot for the adsorption of MO on MSE.

intra-particle diffusion kinetics equations shown below as Eqs. (11)–(13), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

$$q_t = k_i t^{1/2} + C \quad (13)$$

where k_1 (min⁻¹), k_2 (g mg⁻¹ min⁻¹) and k_i (mg g⁻¹ min^{-1/2}) are the rate constants of the pseudo-first order, pseudo-second order and intra-particle diffusion, respectively. C (mg g⁻¹) is a constant. The models characteristic parameters and regression coefficients (r^2) were determined by linear regression analysis and are listed in Table 3. According to the linear pseudo-second order plot obtained by plotting t/q_t vs. t (inset in Fig. 8) and the r^2 value, it clearly shows that MO adsorption data on the biosorbent were successfully described by pseudo-second order model. Similar phenomena have been observed in the adsorption of anionic dyes on other natural adsorbent materials modified by surfactant [26,27]. Moreover, it is distinctly seen from Table 3 that the value of C in intra-

particle diffusion model is not zero but large value, which reveals that boundary layer diffusion may be the rate-limiting step in the adsorption process for surfactant modified silkworm exuviae [47].

3.6. Desorption of methyl orange

Desorption studies can help enlightening the mechanism of an adsorption process. If the dye adsorbed onto the adsorbent can be desorbed by water, it can be said that the attachment of the dye onto the adsorbent is by weak bonds. If the strong bases, such as NaOH can desorb the dye, it can be said that the attachment of the dye onto the adsorbent is by ion exchange [48]. Hence, neutral distilled water was used in the elution of dyes from the MSE followed by NaOH solution. The percentage of desorption obtained were 15.63% and 17.25% for using neutral distilled water and 0.1 N NaOH solution, respectively. The fact that the low desorption occurred with distilled water and NaOH solution suggests that adsorption of MO onto MSE carries out significantly by another mechanism.

The mode of existence of surfactant molecules on solid surface has been investigated widely. Of many kinds of solid adsorbents, clay minerals were prominent in comparison with other adsorbents. It has been reported that paraffin-type and micelle-type are popular types for HDTMAB on the surface of clay adsorbents [30,32–36]. Besides the uptake of organic cations, the organic molecules could also be adsorbed by the attraction between long chain alkyls, such that the halide ions give the organoclay an anionic exchange capacity [30,32,36,49]. Consequently, it can be conceived from the result of desorption by NaOH that some surfactant molecular arrange in this manner in the research. To verify the reliability of inference above, the supernatant obtained after adsorption under the condition of dye concentration of 350 mg L⁻¹ and 303.2 K was selected for Br⁻ ions detection. It was found that there was 9.35 mg L⁻¹ of bromine ions in the supernatant. Here, the above conclusion related to ion-exchange mechanism is clearly confirms.

Taking all the results that have been discussed above into account, it is proposed that enhanced hydrophobic interaction is the predominant mechanism contributing to the increased MO adsorption on the HDTMAB-modified silkworm exuviae, followed by a certain amount of the anionic exchange. For better illustration of the process of adsorption, a suggested adsorption structure is shown in Fig. 9.

Table 3
Pseudo-first order, pseudo-second order and intra-particle diffusion kinetic parameters for MO adsorption on MSE (C_0 : 300 mg L⁻¹).

q_e (exp) (mg g ⁻¹)	Pseudo-first order model			Pseudo-second order model			Intra-particle diffusion model		
	k_1 (min ⁻¹)	q_e (cal) (mg g ⁻¹)	r^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (cal) (mg g ⁻¹)	r^2	k_i (mg g ⁻¹ min ^{-1/2})	C (mg g ⁻¹)	r^2
77.68	0.04528	46.94	0.96913	0.002296	81.17	0.99975	6.3320	22.429	0.89784

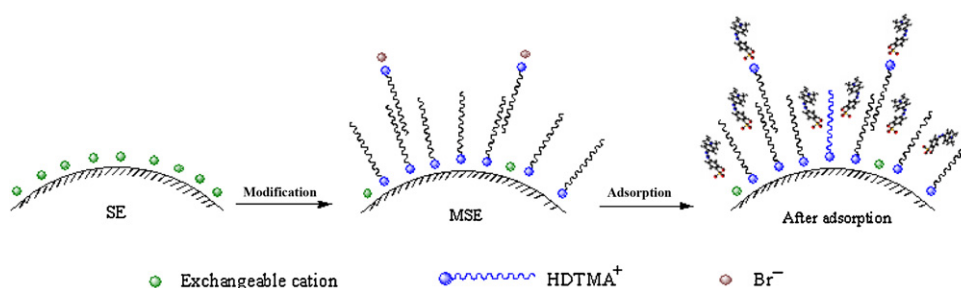


Fig. 9. Schematic illustration of proposed mechanisms for MO adsorption onto MSE.

3.7. Cost evaluation of the adsorbent

Adsorbent cost is important to practicability. Cost of the adsorbent prepared in this work is mainly from use of surfactant. The market price of hexadecyltrimethylammonium bromide is about US \$ 7000 per metric ton. The cost of the prepared adsorbent is around US \$ 630 per metric ton according to the ratio of silkworm exuviae to the surfactant (10:1). The market price of commercial activated carbon is about US \$ 500–800 per metric ton. It is clear that the cost of the two adsorbent is similar. Compared with activated carbon, however, HDTMAB modified silkworm exuviae adsorbent has some advantages, such as simple preparation procedure and low energy consumption, and has good application prospect.

4. Conclusions

The results of this investigation show that HDTMAB modified silkworm exuviae has excellent adsorption capacity for the removal of methyl orange from aqueous solutions. SEM shows that morphological feature of silkworm exuviae changed from compact structure to porous structure after modification. The adsorption isotherm experiment was conducted at different temperatures (303.2, 313.2, 323.2 and 333.2 K), and it was found that the uptake of MO decreased with increasing temperature. The equilibrium data were analyzed by the Langmuir, Freundlich and D–R models and the Langmuir model was found to fit the equilibrium data better. In addition, various thermodynamic parameters such as changes in enthalpy, entropy, and the Gibbs free energy were calculated, showing adsorption to be an exothermic process. The pseudo-second order kinetic model agrees very well with the dynamic behavior for the adsorption of MO onto surfactant modified silkworm exuviae. The desorption studies implied that the hydrophobic interaction and anionic exchange models controlled simultaneously during the adsorption process, but the former is a dominant mechanism.

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