Silkworm exuviae—A new non-conventional and low-cost adsorbent for removal of methylene blue from aqueous solutions

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ABSTRACT

In this paper, silkworm exuviae (SE) waste, an agricultural waste available in large quantity in China, was utilized as low-cost adsorbent to remove basic dye (methylene blue, MB) from aqueous solution by adsorption. Kinetic data and sorption equilibrium isotherms were carried out in batch process. The adsorption kinetic experiments revealed that MB adsorption onto SE for different initial dye concentrations all followed pseudo-second order kinetics and were mainly controlled by the film diffusion mechanism. Batch equilibrium results at different temperatures suggest that MB adsorption onto SE can be described perfectly with Freundlich isotherm model compared with Langmuir and D–R isotherm models, and the characteristic parameters for each adsorption isotherm were also determined. Thermodynamic parameters calculated show the adsorption process has been found to be endothermic in nature. The analysis for the values of the mean free energies of adsorption (E_a), the Gibbs free energy (ΔG^0) and the effect of ionic strength all demonstrate that the whole adsorption process is mainly dominated by ion-exchange mechanism, which has also been verified by variations in FT-IR spectra and pH value before and after adsorption and desorption studies. The results reveal that SE can be employed as a low-cost alternative to other adsorbents for MB adsorption.

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1. Introduction

Dyes are colour organic compounds which can colorize the other substances. About 700,000 tons and 10,000 different types of dyes and pigments are being produced annually across the world [1]. These substances are widely used in many industries such as the textile, leather, food, dyeing, cosmetics and paper [2], which can generate a large amount of coloured wastewaters. Therefore, removal of dyes from polluted effluent is an essential task for environmental protection [3,4].

Adsorption has been found to be an efficient and economic technology to remove dyes, pigments and other colorants [5]. It is superior to other technique for wastewater treatment, such as oxidation–ozonation, coagulation, coagulation–flocculation and biological methods in terms of initial costs, simplicity of design, ease of operation and insensitivity to toxic substances [6]. As we know, activated carbon is the most promising adsorbent for adsorption because of its high surface area, but a relatively high price limits the use of activated carbon [7,8]. Hence, there is a need for an equally effective but cheaper material as an alternative adsorbent. In recent years, numerous non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from

industry and agriculture, have been proposed as sorbents for the removal of dyes from solution by many workers [1,9]. Among these sorbents, agricultural wastes show greater potential for the treatment of dye wasterwaters due to very large quantities, easy to get and very low costs, which is more realistic for most developing countries. Moreover, there are usually many types of functional groups in agricultural wastes such as carboxyl, hydroxyl, amino, aldehyde, ketone and anhydride, which are benefit for the dye adsorption. For above reasons, a wide range of agricultural wastes including bagasse pith [10], rice husk [11], hazelnut shell [12], pineapple stem [13], maize cob [14], papaya seeds [15], fruit peels [16,17], plant leaves [18,19] and wheat shells [20], etc., is attracting interests of environmental scientists for the removal of dyes.

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 from the wild after people in ancient China created by the long-term feeding species. 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 give a large amount of silkworm exuviae, which is often thrown away as waste. Silkworm

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Nomenclature

SE	silkworm exuviae
MB	methylene blue
C_0	the initial concentration of the adsorbate in solution ($mg\,L^{-1}$)
C_e	the equilibrium concentration of the adsorbate in solution ($mg\,L^{-1}$)
C_t	the concentration of the adsorbate in solution at any time t ($mg\,L^{-1}$)
V	the volume of the solution added (L)
m	the mass of the biosorbent used (g)
pH_i	The initial pH value of solution
pH_f	The final pH value of solution
E_d	desorption efficiency of the biosorbent
Q_d	amount of dye desorbed (mg)
Q_e	amount of dye loaded (mg)
t	adsorption time (min)
k_1	pseudo-first order rate constant of adsorption (min^{-1})
k_2	pseudo-second order rate constant of adsorption ($g\,mg^{-1}\,min^{-1}$)
k_i	intra-particle diffusion rate constant ($mg\,g^{-1}\,min^{-1/2}$)
z	the number of data points
q_e	adsorption capacity of the biosorbent at equilibrium ($mg\,g^{-1}$)
q_t	adsorption capacity at any time t ($mg\,g^{-1}$)
q_{max}	the monolayer capacity of the biosorbent ($mg\,g^{-1}$)
b	the Langmuir constant ($L\,mg^{-1}$)
K_f	the Freundlich constant ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$)
n	experimental constant indicative of the adsorption intensity of the biosorbent
β	a constant related to the mean free energy of adsorption ($mol^2\,kJ^{-2}$)
q_m	the theoretical saturation capacity ($mg\,g^{-1}$)
ε	the Polanyi potential, which is equal to $RT\ln(1+(1/C_e))$
T	the absolute temperature (K)
ΔG^0	change in the Gibbs free energy ($kJ\,mol^{-1}$)
ΔH^0	change in the enthalpy ($kJ\,mol^{-1}$)
ΔS^0	change in the entropy ($kJ\,mol^{-1}\,K^{-1}$)

exuviae (SE) is rich in chitin, which applies to its adsorption possible.

This study presents the first outcomes of the possible use of silkworm exuviae wastes as methylene blue dye adsorbents. MB is a thiazine (cationic) dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools, etc. Its chemical structure is as follows:
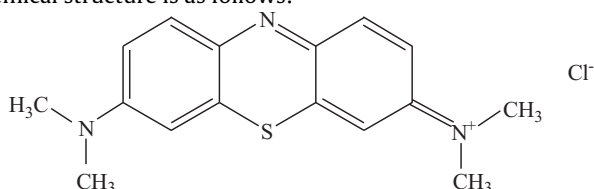
The adsorption kinetics, isotherm and thermodynamics under various experimental conditions (i.e., pH, ionic strength of the solution, contact time, concentration and temperature) were investigated and the adsorption mechanism is discussed comprehensively based on the results.

2. Experimental

2.1. Adsorbate and chemicals

A cationic basic dye, methylene blue (MB), was obtained 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 needed concentrations. All the solutions were prepared in double distilled water. All reagents used were of analytical grade.

2.2. Preparation of the adsorbent

SE wastes kindly 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 80 °C for 2 days. The sample was grounded in a mechanical grinder and then sieved to obtain particle size of >100 mesh.

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 and contact time. After a shaking time was completed, the suspension was centrifuged at 5000 rpm for 10 min. Concentrations of the dye solutions were determined by measuring the absorbance of the solution at the characteristic wavelength ($\lambda_{max} = 668$ nm) of MB using a UV–Vis spectrophotometer (Specord 200). The amount of the dye adsorbed onto SE was determined by the difference between the initial and remaining concentration of dye solution. The adsorption capacity of MB on adsorbent was calculated using the following equation:

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

To examine the effect of pH, adsorption experiments were conducted at different pH ranging from 3 to 9 at $100\,mg\,L^{-1}$ of dye solution.

For kinetic studies three different initial concentrations (25, 50, $100\,mg\,L^{-1}$) of dye solution with adjusting pH of 7.0 were chosen as the initial concentration of dye solution. The adsorption capacity of the biosorbent at any time was calculated by:

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

Adsorption experiments were also carried out to obtain isotherms at different temperatures. This was done at 303.2, 313.2 and 323.2 K, respectively. In this group of experiments dye solutions with different initial concentration, in the range of $12.5–100\,mg\,L^{-1}$, were selected. Adsorption time of 12 h was chosen to allow attainment of equilibrium at constant temperatures.

The effect of ionic strength was studied using NaCl as the ionic medium. The concentration of this salt was varied within the range $0.001–0.1\,mol\,L^{-1}$. The final pH values of solutions at equilibrium were measured in order to more in-depth understanding of adsorption mechanism.

Normally, pH 7.0; ionic strength of 0 and 303.2 K were selected as adsorption conditions unless otherwise stated in the whole study. Each experiment was triplicated under identical conditions and only mean values were presented.

In order to reveal the agreement of the kinetic and equilibrium models with experimental results, the average relative error (ARE)

Table 1
Physical and chemical properties of SE.

Moisture content (%)	8.175
Volatile matter (%)	88.27
Ash (%)	2.684
Fixed carbon (%)	0.875
Bulk density (kg m^{-3})	275.6
pH$_{PZC}$	8.0
Iodine number (mg g^{-1})	183
Methylene blue index (mg g^{-1})	26.6

was selected and computed as follows [21]:

$$ARE(\%) = \frac{100}{z} \sum_{i=1}^{z} \left| \frac{(q_{e,\text{meas}} - q_{e,\text{calc}})}{q_{e,\text{meas}}} \right|_i \tag{3}$$

2.4. Desorption studies

For batch desorption study, 50 mg of the adsorbent utilized for the adsorption of an initial dye concentration of 100 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 double distilled water, 0.1 mol L^{-1} HCl solution for 12 h, in turn. Desorption efficiency was defined in following equation.

$$E_d = \frac{Q_d}{Q_e} \times 100\% \tag{4}$$

2.5. Characterization of the adsorbent

The pH at point zero charge (pH$_{PZC}$) of the adsorbent was determined by the solid addition method described by Balistrieri and Murray [22]. To a series of 100 ml conical flasks, 45 ml 0.01 mol L^{-1} of KNO$_3$ solution of known concentration was transferred. The pH$_i$ values of the solution were roughly adjusted from pH 2 to 12 by adding ether 0.1 mol L^{-1} HCl or NaOH by using a Mettler Toledo 320 pH meter. The total volume of the solution in each flask was made up to 50 ml by adding the KNO$_3$ solution of the same strength. The pH$_i$ of the solution was accurately noted, and 0.1 g of the adsorbent was added to the flask, which was securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquids were noted. The difference between the initial and final pH values (ΔpH = pH$_f$ − pH$_i$) was plotted against the pH$_i$. The point of intersection of the resulting curve at which pH 0 gave the pH$_{PZC}$.

Moisture content, fixed carbon, volatile matter and ash content of the adsorbent were determined by proximate analysis [23]. About 1 g of SE sample weighed accurately and taken in a crucible was dried in hot air oven at 105 ± 5 °C for 1 h. The loss of weight on drying was reported as percentage moisture content. The remaining sample was placed (covered with lid) in a muffle furnace and heated at 925 ± 20 °C for 7 min. The loss in weight was reported as volatile matter. The residue was again heated (without lid) at 700 ± 50 °C for 30 min. The loss in weight was reported as ash. The fixed carbon was then determined by calculating the difference. Bulk density was calculated by weighing 100 cm^3 (untapped) of sample. Proximate analysis and density measurement was carried out thrice and the average values had been reported in Table 1.

The iodine number defined as the quantity of iodine adsorbed per gram of the biosorbent at an equilibrium concentration of 0.02 N was calculated according to D-4607 standard test method [24]. The methylene blue index was calculated by the difference between the initial and remaining concentration of dye solution in the condition of 500 mg L^{-1} of an initial dye concentration.
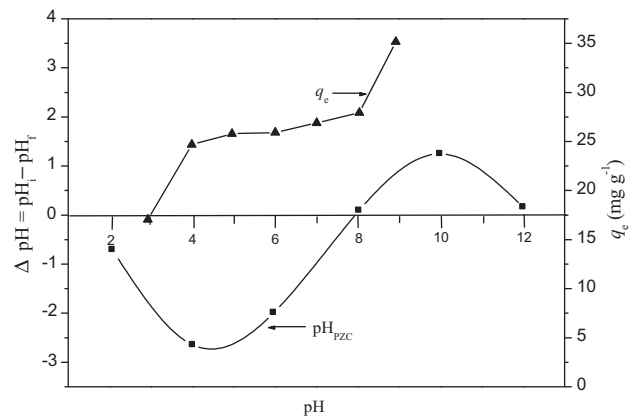

Fig. 1. Point of zero charge of SE and effect of pH on the adsorption capacity for MB (C_0 = 100 mg L^{-1}, contact time 12 h, T = 303.2 K).

Table 1 shows that the SE consists of mainly volatile matter, and small amounts of ash and fixed carbon. The biosorbent possesses certain moisture content and bulk density. Parameters of the iodine number and methylene blue index can reflect micropores and mesopores of the adsorbent, respectively [25]. Therefore, in Table 1 it can be inferred that the SE has some porosity.

FT-IR spectra measurements of SE and dye-loaded SE were done on a Thermo Nicolet NEXUS TM spectrophotometer using the KBr pellets. The spectrum was collected 32 times in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and corrected for the background noise. Dye-loaded SE 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.

3. Results and discussion

3.1. Effect of pH

The pH of the aqueous solution is an important variable in the adsorption of dyes on the biosorbents. So the influence of the initial pH of solution on the adsorption of MB onto SE was examined in the pH range of 3–9 (Fig. 1). As can be seen, the adsorption capacity of dye tended to increase with increasing pH value. The q_e increases rapidly with increasing pH from 3 to 4, and then increases slowly with further increase in pH. At value of pH exceeded 8, an obvious increase in q_e occurred. Similar variations of q_e vs. pH have been earlier recorded in study on methylene blue adsorption onto some biosorbents [13,20].

The influence of the solution pH on the dye uptake can be explained on the basis of the pH at point zero charge (pH$_{PZC}$) of the biosorbent [26]. This is a convenient index when the surface of biosorbent becomes either positively or negatively charged as a function of pH. When pH of mixture of the biosorbent and solution is lower than pH$_{PZC}$, it means surface of the biosorbent is positively charged. Otherwise it would show negatively charged. The pH$_{PZC}$ of SE determined by the solid addition method was about 8.0 (Fig. 1). For the adsorption experiments, pH values after solid–liquid interactions are both significantly lower than the pH at point zero charge (pH$_{PZC}$) of the biosorbent (see details in second paragraph of Section 3.6). So, it is clear that the surface of the biosorbent is positively charged as a whole in this study. Accordingly, electrostatic attraction mechanism can be easily excluded. In fact, the variation in q_e vs. pH can be interpreted by following facts. In a highly acidic solution (pH of 3), a high concentration of H$^+$ ions compete with MB$^+$ ions for exchangeable cations on the surface of biosorbent, resulting in the suppression of MB$^+$ adsorption on SE surface and a low q_e was observed. So, a rapid increase in adsorption capacity occurred at
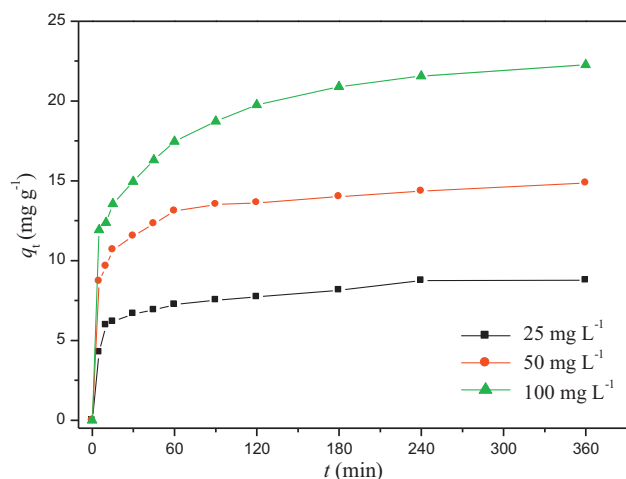
Fig. 2. Effect of contact time on the adsorption of MB onto SE at different dye concentrations (initial pH 7.0, $T = 303.2$ K).

Fig. 3. B_t vs. t plots for MB adsorption onto SE at different dye concentrations.

pH range of 3–4. As pH value is higher, more exchangeable cations contained in the biosorbent can be exchanged with MB$^+$ due to weak competitive adsorption of H$^+$ ions, resulting in the increase of adsorption capacity. This increased trend at a slower rate continues until the pH reaches to 8.0. Considering pH$_{PZC}$ of SE about 8.0, it can be concluded that the SE surface at the moment become negatively charged as a whole and more MB can be adsorbed on it so that the q_e increases obviously as pH was higher than 8. To increase the adsorption capacity as possible and keep natural pH value of MB dye solutions, pH of 7.0 was selected for the rest of the batch experiments.

3.2. Adsorption kinetics

Fig. 2 represents the effect of contact time on the adsorption capacity of SE for dye at different initial concentrations. As can be seen in Fig. 2, the adsorption of MB is rapid from the beginning of the experiment and thereafter it proceeds at a slower rate and finally reaches to equilibrium. With the increase in concentration, the trend becomes more obvious. Similar findings for dye adsorption onto bio-waste materials have been reported by other investigators [2,10,12,13,15].

To explore the adsorption kinetics of MB on SE, three different kinetic models, pseudo-first order, pseudo-second order, and intra-particle diffusion, have been used to fit experimental data obtained from batch MB removal experiments. Table 2 lists the results of the rate constant studies for different initial dye concentrations by the three kinetic models. At all studied initial MB concentrations, the extremely high correlation coefficients (>0.999) and the lowest average relative error (ARE) were gained by calculating with pseudo-second order kinetic equation. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second order kinetics. These suggest that the adsorption data are well represented by pseudo-second order kinetics in comparison to the other two kinetics models. It is also observed from Table 2 that the value of the rate constant k_2 decreases with increasing initial dye concentration for SE. The reason for this behaviour can be attributed to the lower competition for the sorption surface sites at lower concentration. At higher concentrations, the competition for the surface active sites will be high and thus lower sorption rates are obtained. Similar phenomena have been observed in the adsorption of methylene blue on other natural adsorbent materials [12,13,15].

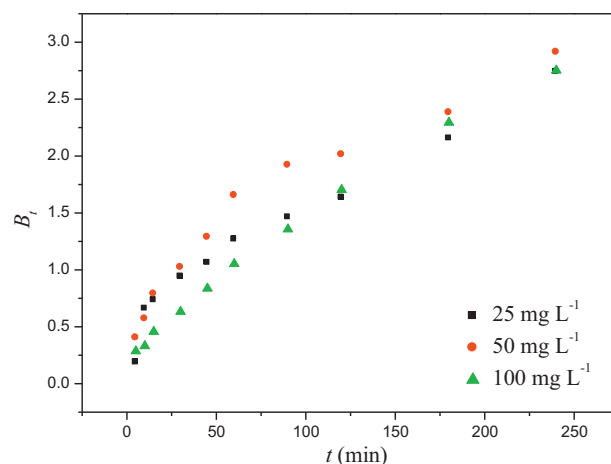Adsorption kinetics is generally controlled by different mechanism, of which the most limiting are the diffusion mechanisms, including film diffusion and intra-particle diffusion. To determine the actual process involved in the present adsorption, Eq. (5) of the adsorption dynamics can be employed [27].

$$F = 1 - \frac{6}{\pi^2} \sum_1^\infty \left(\frac{1}{n^2} \right) \exp(-n^2 B_t) \tag{5}$$

where F is the fractional attainment of equilibrium at time t and is obtained by using Eq. (6), n is Freundlich constant of the adsorbate and B_t is a calculated mathematical function of F (and vice versa) derived from the Reichenberg's table [27].

$$F = \frac{Q_t}{Q_\infty} \tag{6}$$

where Q_t and Q_∞ are amounts adsorbed after time t and after infinite time, respectively.

Rearranging the above equation gives:

$$B_t = -\ln(1 - F) - 0.4799 \tag{7}$$

Thus the value of B_t can be calculated for each value of F using Eq. (7). The B_t values were plotted against t as shown in Fig. 3. The linearity of this plot can be used to distinguish between film diffusion and intra-particle diffusion mechanism. If this plot is a straight line passing through origin, adsorption will be governed by an intra-particle diffusion mechanism, otherwise governed by film diffusion [28]. It can be clearly seen from Fig. 3 that all origin cannot form a straight line. This implies that MB adsorption onto silkworm exuviae was mainly controlled by the film diffusion mechanism. Moreover, the relative values of intercept C for intra-particle diffusion model, which give an idea about the boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect [29]. It is observed from Table 2 that the intercept C increases with increasing initial dye concentrations, which implies that film diffusion (boundary layer diffusion) mechanism should become more significant when the initial dye concentration becomes higher.

3.3. Adsorption isotherms

The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the adsorption systems. Hence, the adsorption of MB on SE 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. The parameters and correlation coefficients obtained from the plots of Langmuir, Freundlich (figures not shown) and D–R (shown in Fig. 5) are listed in Table 3. The values of r and ARE suggest that the Freundlich model gave closer fittings than those of

Table 2
A comparison of pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models rate constants calculated from experimental data.

| Model		C_0 (mg L^{-1})		
		25	50	100
Pseudo-first order	$q_{e,meas}$ (mg g^{-1})	8.78	14.86	22.28
	k_1 (min^{-1})	0.01607	0.01135	0.01218
	$q_{e,calc}$ (mg g^{-1})	4.6816	5.6104	11.7647
	r	0.93206	0.91109	0.97277
	ARE (%)	61.175	48.117	73.517
Pseudo-second order	k_2 (g mg^{-1} min^{-1})	0.010068	0.008218	0.003172
	$q_{e,calc}$ (mg g^{-1})	8.969	14.975	22.805
	r	0.99873	0.9996	0.99899
	ARE (%)	9.809	6.6216	10.318
Intra-particle diffusion	k_i (mg g^{-1} min$^{-1/2}$)	0.33636	0.55232	0.92034
	C (mg g^{-1})	3.75888	6.87704	8.33859
	r	0.80741	0.78053	0.86459
	ARE (%)	10.654	10.737	9.4905

Table 3
Isotherm constants and correlation coefficients for the adsorption of MB on SE at different temperatures.

Model		T (K)		
		303.2	313.2	323.2
Langmuir isotherm	q_{max} (mg g^{-1})	25.530	27.338	29.539
	b (L mg^{-1})	0.05474	0.08517	0.12846
	R_L	0.15447	0.10508	0.07222
	r	0.99161	0.98629	0.98481
	ARE (%)	5.3793	9.9760	14.2930
Freundlich isotherm	K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	2.8870	4.6441	6.9140
	$1/n$	0.5370	0.4340	0.3516
	r	0.99402	0.99684	0.99378
	ARE (%)	4.9075	3.4291	4.3041
Dubinin–Radushkevich isotherm	q_m (mg g^{-1})	181.9424	121.2325	88.98608
	ε (mol^2 kJ^{-2})	0.00414	0.003	0.00216
	E_a (kJ mol^{-1})	10.990	12.910	15.215
	r	0.99631	0.99414	0.9863
	ARE (%)	3.6073	4.4321	6.7849

Langmuir and D–R models. This suggests that the adsorption data are well represented by Freundlich isotherm model and support the assumption that adsorption takes place on heterogeneous surfaces [30]. Since the parameter $1/n$ is related to the degree of surface heterogeneity (smaller value indicates more heterogeneous surface whereas value closer to or even 1.0 indicates a material with relatively homogenous binding sites) [31], the values of 0.3516–0.5370 obtained for SE at three different temperatures suggest that there are a heterogenous distribution of active sites on the surface of SE. Different types of sites (–OH, –NH$_2$, etc., see Section 3.7) possess

different adsorption energy on the surface of SE, it is most likely that exchangeable cations of SE are located in different surroundings. This is responsible for the heterogeneous adsorption of MB onto silkworm exuviae. In addition, the adsorption capacity (q_{max} and K_f) increases with an increase in temperature while the opposite behaviour is presented for q_m. Seen overall, the information thus obtained specifies an endothermic nature of the existing process.

Through the discussion for isotherm constants, it can predict whether an adsorption system is favorable or unfavorable. The essential characteristics of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation
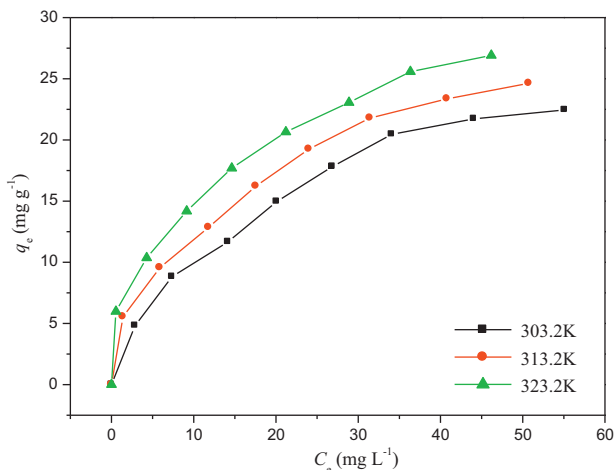
Fig. 4. Adsorption isotherms of MB on SE at different temperatures.
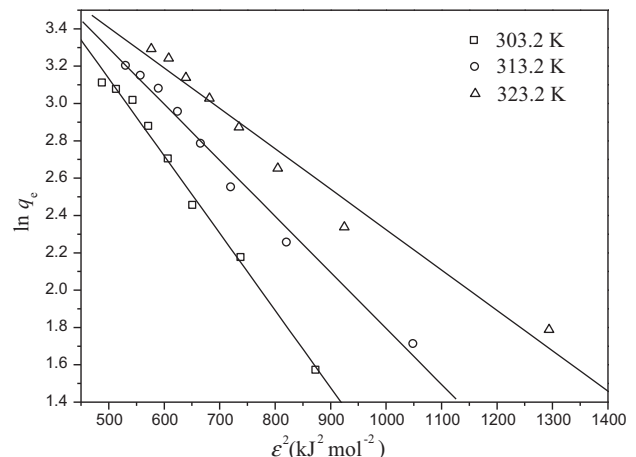
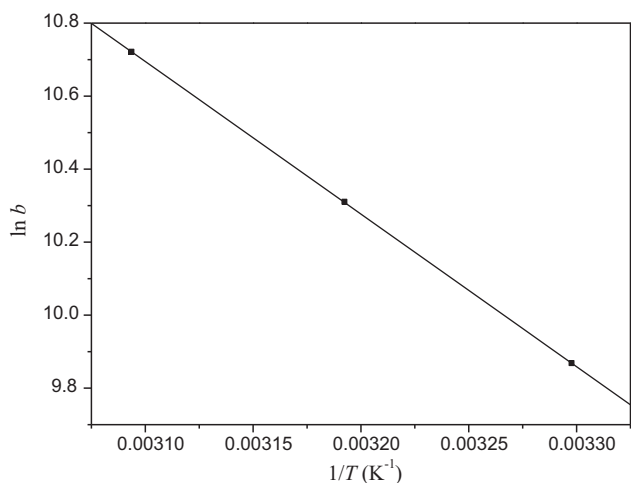**Fig. 5.** D–R plots for the adsorption of MB on SE at different temperatures.

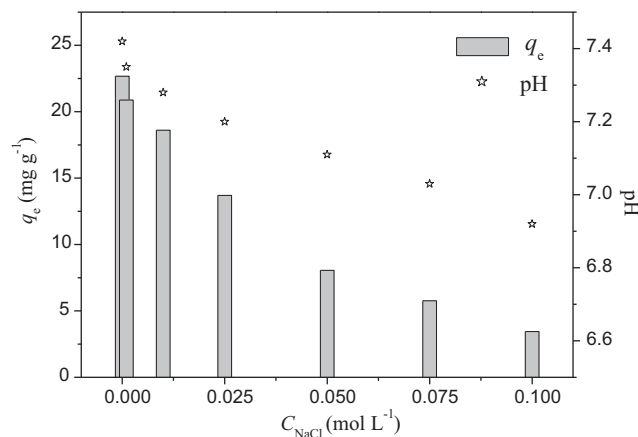**Fig. 6.** Van't Hoff plot for the adsorption of MB by SE.

Fig. 7. Effect of ionic strength on the adsorption of MB onto SE ($C_0 = 100$ mg L^{-1}, initial pH 7.0, contact time 12 h, $T = 303.2$ K).

factor or equilibrium parameter, which is defined by [32]

$$R_L = \frac{1}{1 + bC_0} \qquad (8)$$

where C_0 is the highest initial metal concentration. The parameter indicates 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 seen from Table 3, at all temperatures the R_L values were between 0 and 1.0, indicating that adsorption of MB onto SE is all favorable.

Based on D–R isotherm equation, E_a can be calculated using the equation, $E_a = (2\beta)^{-1/2}$ [33]. The isotherm constants, E_a and correlation coefficients are calculated and presented in Table 3. As seen in the table, the values of E_a at different temperatures are between 10.99 and 15.22 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 ion is transferred to the surface of the solid from infinity in the solution. 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} suggests physical adsorption [34], the value of E_a is between 8 and 16 kJ mol^{-1}, which indicates the adsorption process follows by ion-exchange [35], while its value in the range of 20–40 kJ mol^{-1} is indicative of chemisorption [36]. So, it is likely that the whole adsorption process was predominated by ion-exchange mechanism.

3.4. Thermodynamic parameters

According to values of thermodynamic parameters, what process will occur spontaneously can be determined. ΔG^0 can be calculated using the relation:

$$\Delta G^0 = -RT \ln b \qquad (9)$$

ΔH^0 and ΔS^0 were calculated from the slope and intercept of the linear plot of $\ln b$ vs. $1/T$ (Fig. 6) according to the Van't Hoff equation. Obtained thermodynamic parameters are given in Table 4. As seen in the table, ΔH^0 was positive value, indicating endothermic reaction. The positive value of ΔS^0 suggests the increased random-

ness at the solid and solution interface during the adsorption of MB onto SE. The negative values of ΔG^0 imply the spontaneous nature of the adsorption process. Further, the decrease in the values of ΔG^0 with the increasing temperature reveals the adsorption was more spontaneous at higher temperatures [37]. Generally, the change in free energy for physisorption is between -20 and 0 kJ mol^{-1}, but chemisorption is a range of -80 to -400 kJ mol^{-1} [38]. The values of ΔG^0 obtained in this study are within the ranges of neither the physisorption nor chemisorption, indicating that the other adsorption such as ion-exchange is likely the main mechanism.

3.5. Effect of ionic strength

Dye wastewaters from many industries contain various types of suspended solids and salts. The presence of ions leads to high ionic strength, which may significantly affect the performance of the adsorption process. Fig. 7 presents the effect of ionic strength on the removal of MB. It was observed that the adsorption capacity decreased significantly with the increase in ionic strength. The decline in MB removal by NaCl could be explained by the following fact. As the NaCl concentration increased, the competitive effect of Na$^+$ on binding sites increased. In addition, the presence of NaCl causes an increase or expansion of the electrical diffused double layer [39]. The two aspects mentioned above both are not benefit for the increase of adsorption capacity. The result reveals that the presence of external electrolyte, such as sodium chloride, has an obvious effect on the adsorption capacity between SE and MB.

The pH value of final dye solution is indicative of the property of liquid system because it is the result of interaction between biosorbent and dye solution. Hence, the variation of the pH of the dye solution before and after adsorption in the conditions of different ionic strengths was investigated. As seen in Fig. 7, pH of final solution decreases sharply from 7.4 to 6.9 with the increase of NaCl concentration. Based on the previous isothermal and thermodynamic studies, it is considered that the ion-exchange is most likely adsorption mechanism. Ion-exchange would induce the decrease in pH value of solution due to the lower hydrolyse constants of released cations such as Ca^{2+}, Mg^{2+}, etc., from surface of adsorbent to aqueous solution. According to the results of pH values above, it can be concluded that the whole adsorption process is mainly dominated by ion-exchange mechanism. The result well corroborates the previous speculation in Sections 3.4 and 3.5.
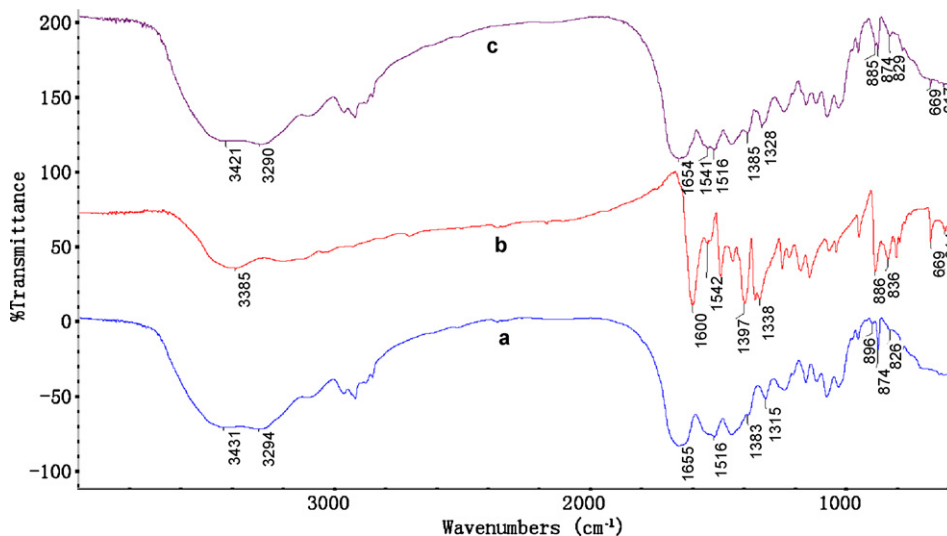
Table 4
Thermodynamic parameters for the adsorption of MB on SE.

T (K)	b (L mol^{-1})	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K^{-1})
303.2	19263.55	−24.870	34.751	0.19664
313.2	29972.17	−26.842		
323.2	45206.36	−28.803		

**Fig. 8.** FT-IR spectra of SE (a) and dye loaded-SE (b).

3.6. Desorption studies

Desorption studies can help clarifying the mechanism of an adsorption process [40,41]. 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 acid, such as HCl can desorb the dye, it can be said that the attachment of the dye onto the adsorbent is by ion exchange [42]. Hence, neutral distilled water was used in the elution of dyes from the silkworm exuviae followed by HCl solution. To explore effect of pH on adsorption mechanism, three different pH of dye solution, i.e., 5.0, 7.0 and 9.0, were selected to represent acid, neutral and base conditions, respectively. Desorption results show that the percentage of desorption with neutral distilled water for the adsorbent in acid, neutral and basic conditions were 3.75, 3.28 and 18.52%, respectively. While in the case of 0.1 N HCl solution, 95.16, 95.61 and 81.05% were obtained. Compared with acid and neutral condition, the desorption efficiency with neutral distilled water in basic condition has a higher value, which implies existence of electrostatic attraction under basic condition. However, whether pH is acidic, neutral or basic, most of desorption occurs in the second step of desorption. The fact suggests that adsorption of MB onto SE carries out significantly via an ion-exchange mechanism. This result supports the mechanism of adsorption mentioned in above studies again.

3.7. FT-IR study of dye adsorption

The chemical structure of the adsorbent is of vital importance in understanding the adsorption mechanism [13,40]. In this study, FT-IR technique is used to probe the change after adsorption in the characteristic functional groups of SE. The FT-IR spectrum of SE and dye loaded-SE are displayed in Fig. 8. The resolution of the apparatus used was $4\,cm^{-1}$, which means any shift of equal to or less than $4\,cm^{-1}$ may be caused by the instrument itself. So the shifts of more than $4\,cm^{-1}$ were mainly focused in this study. FT-IR measurements showed the presence of a large number of functional groups, notably –OH ($3431\,cm^{-1}$), –NH_2 ($3294\,cm^{-1}$), $>$C=N– and $>$C=C$<$ ($1655\,cm^{-1}$), $\equiv$C–C$\equiv$, $\equiv$C–N$<$ and $\equiv$C–O– ($1157\,cm^{-1}$) and $>$C=S ($1115\,cm^{-1}$). After MB loading, the most of characteristic peaks corresponding to these groups unchanged. However, there are also different changes in some peaks. The wavenumber of –OH group blueshifted from 3431 to $3421\,cm^{-1}$ compared with that of SE. The

peak at $1315\,cm^{-1}$ attributed to N–H bending redshifted of $13\,cm^{-1}$ and the peak at $1383\,cm^{-1}$, was almost no changed, but intensity of the peak dramatically enhanced. A new peak at $1352\,cm^{-1}$, which can be attributed to N–C bending, appeared. The absorption at $896\,cm^{-1}$ related to C–H rocking vibrations also changed obviously. The result seems to be the fact that –OH and –NH_2 participate in the adsorption process. Nevertheless, it must be noted that the changed peaks mentioned above are also location for the characteristic peaks of MB dye molecules in FT-IR spectra. This implied that the changes of some peaks were very likely caused by the introduction of dye molecules themselves. There were no complex chemical interactions between MB molecules and the groups on the surface of SE, which has been verified by the results of desorption experiment [13,40]. Hence, the changes of infrared spectra further verified that MB on silkworm exuviae is held by ion-exchange, which can be represented by Eq. (10).

$$SE-M^{n+}+MB^+ \rightleftarrows SE-MB^+ + M^{n+}(M = \text{Na, K, Ca, Mg, etc.}) \quad (10)$$
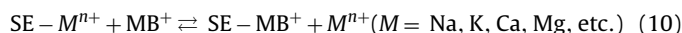
4. Conclusions

The aim of this work was to find the possible use of silkworm exuviae as a biosorbent for the removal of methylene blue from aqueous solutions. In kinetic study, the pseudo-second order kinetic model was found to be well suited for the entire adsorption process of MB on SE. Adsorption kinetic studies reveal that film diffusion mechanism should be a main rate control mechanism. All equilibrium data obtained at different temperatures fit perfectly with Freundlich isotherm model compared to Langmuir and D–R isotherm models. The Langmuir model coefficients implied that the adsorption of MB onto SE is favorable. According to variations in FT-IR spectra and pH values before and after adsorption, it is considered that ion-exchange was the major removal mechanism. High rate of dyes desorption suggest an efficient recovery of the adsorbate and adsorbent which can be reused in desired process. The overall results show that the silkworm exuviae is an effective and low-cost biosorbent for the removal of methylene blue from aqueous solutions.

anonymous reviewers for their valuable comments, which greatly improved the presentation of this paper.

Appendix A.

Model	Equation
Pseudo-first order kinetics	$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$
Pseudo-second order kinetics	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
Intra-particle diffusion kinetics	$q_t = k_i t^{1/2} + C$
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}$
Freundlich isotherm	$\log q_e = \log K_f + \frac{1}{n} \log C_e$
Dubinin–Radushkevich isotherm	$\ln q_e = \ln q_m - \beta \varepsilon^2$
Van't Hoff	$\ln b = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$

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