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Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge

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Abstract

Experiments were conducted to investigate the adsorption characteristics of dyes by anaerobic sludge in this study. Influence of dye type, sorption time, initial dye concentration, sludge concentration and temperature on dye biosorption was evaluated. Furthermore, the isotherms, kinetics and thermodynamic of biosorption were also explored. Experimental results show that anaerobic sludge had a much higher equilibrium adsorption density on Rhodamine B than on Eosin Y. The adsorption density of Rhodamine B onto sludge decreased with enhancing sludge concentration. At a lower Rhodamine B concentration, adsorption could reach saturation in a lower sludge concentration. Results also indicate that both Langmuir and Freundlich adsorption models were able to adequately describe the biosorption equilibrium of Rhodamine B onto anaerobic sludge. The biosorption followed the pseudo second-order adsorption kinetics.

Keywords: Anaerobic sludge; Biosorption; Dye; Eosin Y; Freundlich model; Kinetics; Langmuir model; Rhodamine B; Thermodynamics

1. Introduction

Dyes are widely used in textile, paper and printing industries today, and the treatment of dye-containing wastewaters is one of the most difficult problems to be solved. Generally dyes are stable to light, heat and oxidizing agents, and are usually biologically non-degradable [1].

Conventionally, chemical coagulation/flocculation, ozonation and adsorption, etc. are all means used for the removal of dyestuffs. Although they can remove dyes partially, their initial investment and operational costs are so high that they can be widely used in dyeing and finishing industries, especially in developing countries [2]. Activated carbon has been extensively studied and might be the most widely used adsorbent for the treatment of color effluents in the past few years. However, due to its high price, activated carbon could not be used in developing countries [3]. Therefore, adsorbents with a high efficiency and a low cost are in greatly desirable. For this purpose, a great amount of materials, such as peat, pith, chitin, soil, silica, activated clay, rice husk, fly ash, wood, pine sawdust, eucalyptus barks, bottom ash from thermal power plants and spent brewery grains have been tested as adsorbents for dyestuffs adsorption [4–6]. In addition, biological treatment also offers a possible alternative to existing methods for dye removal. Recently activated sludge from wastewater treatment plants, thermally treated biological sludge, and purebred fungal biomass have been proved to be efficient biosorbents for dyestuff removal [7,8].

In the past decades, with the invention and development of anaerobic reactors, such as UASB (upflow anaerobic sludge blanket) and EGSB (expanded granular sludge blanket) etc., anaerobic technology has been widely used for wastewater treatment. Meanwhile, some researchers have made great efforts on anaerobic biosorption and found that anaerobic sludge could be resultful biosorbents for the removal of heavy metals and hazardous organic pollutants [9–11]. Aksu and Akpinar [9] reported that, in a batch system, the biosorption yields of phenol and chromium(VI) onto dried anaerobic activated sludge were 44.2 and 51.9%, respectively, when the initial phenol and chromium(VI) ion concentration was about 25.0 mg/l. In dual biosorption, the total biosorption yield could also reach 42.6% when the total initial phenol and chromium(VI) ion concentration was about 50.0 mg/l. This result suggests that dried anaerobic activated sludge could be a promising type of biosorbent for simultaneous removal and separation of phenol and chromium(VI) ions from aqueous effluents.

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Nomenclature

b	constant related to the affinity of the binding sites (l/mg)
C_{eq}	equilibrium concentration (mg/l)
E_a	activation energy of biosorption (kJ/mol)
ΔG°	free energy change (kJ/mol)
ΔH°	enthalpy change (kJ/mol)
$k_{1,ad}$	rate constant of first-order adsorption (min^{-1})
$k_{2,ad}$	rate constant of second-order adsorption (g/(mg min))
K	equilibrium constants
K_F	Freundlich constants
K_0	temperature-independent factor (g/(mg min))
n	Freundlich constants
q	amounts of adsorbed dye onto the biosorbent at time t (mg/g)
q_{eq}	amounts of adsorbed dye onto the biosorbent at equilibrium (mg/g)
$q_{eq,cal}$	the theoretical value of q_{eq} calculated from kinetic models (mg/g)
$q_{eq,exp}$	the experimental data of q_{eq} (mg/g)
Q^0	maximum amount of the dye per unit weight of biomass to form a complete monolayer on the surface bound (mg/g)
R	gas constant (8.314) (J/(mol K))
ΔS°	entropy (kJ/(mol K))
t	biosorption time (min)
T	biosorption temperature (K)

However, at the present time no information concerning the biosorption of dyestuffs onto anaerobic sludge is available in literature. Therefore, the main objective of this study was to evaluate the biosorption characteristics of dye onto anaerobic sludge. A cationic dye, Rhodamine B, and an anionic dye, Eosin Y, which are both used extensively in the printing and dyeing industries in China, were selected as the adsorbates in this study. Both of them have a similar molecule structure except for reverse electric charges. The two dyes are both stable, and moderately soluble in water and organic solvents. They were tested to make a comparison between their biosorption characteristics. The influences of different experimental parameters, such as sorption time, temperature, initial dye concentration and sludge concentration, on biosorption were investigated. Moreover, the biosorption isotherms, kinetics and thermodynamic were also explored. This work could provide useful information for the selection of cost-effective biosorbents as well as the design and operation of biosorption systems for dye wastewater treatment.

2. Materials and methods

2.1. Preparation of the biosorbent

The anaerobic sludge used in this study was collected from a full-scale upflow anaerobic sludge blanket reactor treating citrate-producing wastewater in Bengpu, China. Prior to use, the sludge was first washed with tap water twice, and was then sieved to remove stone, sand and other coarse matters.

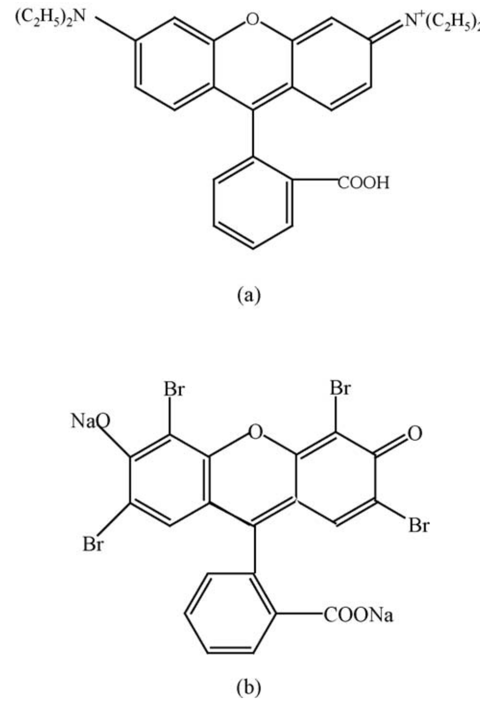

Fig. 1. Molecular structure of: (a) Rhodamine B and (b) Eosin Y.

2.2. Chemicals

The cationic dye, Rhodamine B, and the anionic dye, Eosin Y, used in this study were purchased from Shanghai Chemical Co., China, and were used without further purification. Both dyes were of analytical grade and their molecule structures are shown in Fig. 1.

2.3. Batch experiments

Adsorption experiments were conducted using 250-ml screw-topped flasks to which 150 ml of dye-containing wastewater and biomass were added. One flask with dosage of dye solution but no biomass was used as control. Before shaking, nitrogen was sparged into the flasks and then the flasks were sealed with rubber plugs to ensure the anaerobic condition in the biosorption process. These flasks were then reciprocated in a water-bath shaker with a shaking rate of 150 rpm. Samples were taken at given time intervals and were then centrifuged at 12,000 rpm for 10 min. The supernatant was used for analysis of the residual dye concentration. Each run of the experiments was replicated at least three times.

2.4. Analysis

The concentrations of the two dyes were determined using a UV–vis spectrophotometer (UV751GD, Shanghai) at an absorbance wavelength of 555 nm for Rhodamine B and 516 nm for Eosin Y, respectively. The concentration of volatile suspended solids (VSS) was measured according to the Standard Methods [12].

3. Results and discussion

3.1. Biosorption rates and equilibrium adsorption densities of the two dyes

In order to know the adsorption equilibrium time for each dye, batch experiments were conducted to evaluate the biosorption rate of Rhodamine B and Eosin Y by anaerobic sludge at pH 7.0, 38 °C, VSS of 3.0 g/l and initial dye concentration of 50 μmol/l. Fig. 2 illustrates the extent of dye biosorption as a function of reaction time. Dye biosorption reached equilibrium in 70 min for Rhodamine B, 5 min earlier than for Eosin Y. However, anaerobic sludge had a much lower equilibrium adsorption density on Eosin Y than on Rhodamine B. Since anaerobic sludge has negative charges, the repulsive electrostatic interaction between Eosin Y with negative charges and sludge might be responsible for the lower adsorption density (*q*) than that of Rhodamine B. The latter has attraction force with anaerobic sludge.

Based on the results above, 90 min was taken as the equilibration time for Rhodamine B biosorption in the subsequent experiments, while the Eosin Y biosorption test was not further conducted due to its low adsorption density (2.4 mg/g) onto anaerobic sludge.

3.2. Effects of sludge concentration and initial dye concentration on biosorption

The influences of sludge concentration and initial dye concentration on Rhodamine B biosorption were evaluated at a constant temperature of 38 °C and pH 7.0. Fig. 3a shows the equilibrium adsorption density as a function of VSS concentration. All the curves have the same features, i.e. an initial quick decrease followed by a smoother decline and a final plateau, with the increase of VSS concentration from 1.0 to 15.0 g/l. At a lower dye concentration, Rhodamine B biosorption could reach equilibrium at a lower sludge concentration. At an initial

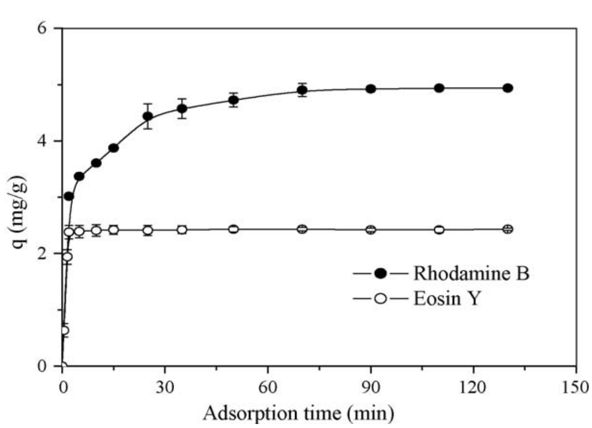

Fig. 2. Adsorption density of Rhodamine B and Eosin Y as a function of time (pH 7.0, sludge concentration 3 g-VSS/l, temperature 38 °C and agitation 150 rpm).

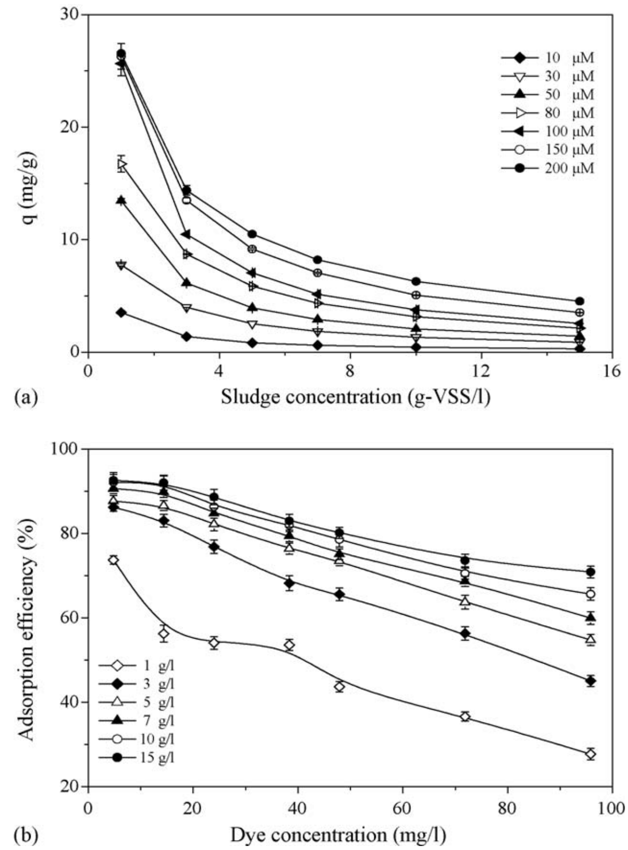

Fig. 3. Effects of sludge concentration and initial dye concentration on: (a) the adsorption density; and (b) the adsorption efficiency of Rhodamine B (pH 7.0, temperature 38 °C and agitation 150 rpm).

dye concentration of 10 μmol/l, for example, at sludge concentration below 5.0 g-VSS/l, the adsorption density significantly decreased with increasing sludge concentration. However, the adsorption density changed slightly at sludge concentration larger than 5.0 g-VSS/l.

On the other hand, the initial dye concentration was an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence, a higher initial dye concentration would enhance the biosorption process. Such an effect could also be seen in Fig. 3a. At a constant sludge concentration, the equilibrium adsorption density of the sludge increased with the increase in initial dye solution concentration from 10 to 200 μmol/l, while the dye adsorption efficiency of showed an opposite trend (Fig. 3b).

3.3. Equilibrium modeling

In this study, two classical adsorption models, i.e. Langmuir and Freundlich isotherms, were employed to describe the Rhodamine B biosorption equilibrium. The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. It is given as Eq. (1):

$$q_{\mathrm{eq}} = \frac{Q^0 b C_{\mathrm{eq}}}{1 + b C_{\mathrm{eq}}} \qquad (1)$$

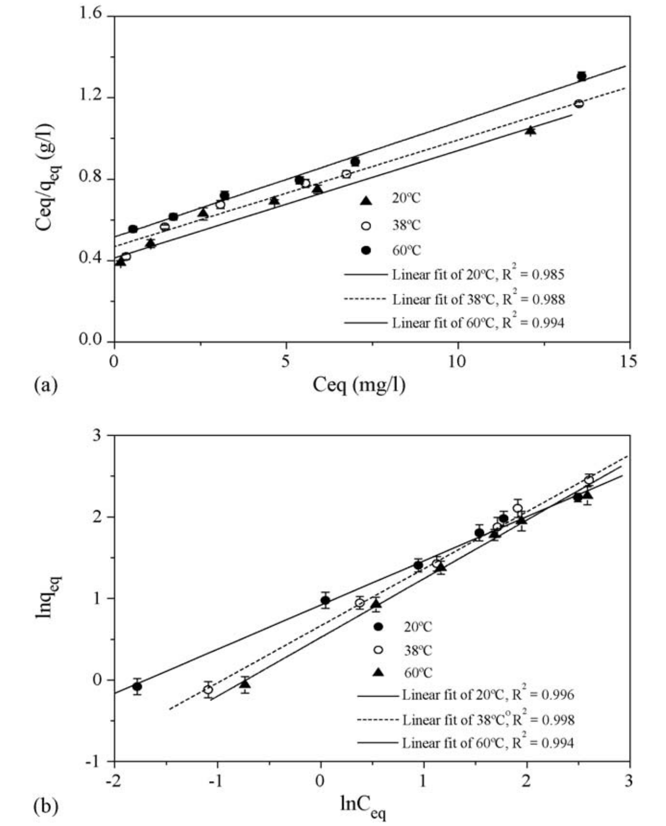

Fig. 4. Linearized adsorption isotherms of (a) Langmuir; and (b) Freundlich at various temperatures (pH 7.0, sludge concentration 5.0 g-VSS/l and agitation 150 rpm).

The linearized form of the Langmuir equation is

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q^0 b} + \frac{C_{eq}}{Q^0} \tag{2}$$

Q^0 and b can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq}. The linearized Langmuir adsorption isotherms of Rhodamine B obtained at 20, 38, and 60 °C are illustrated in Fig. 4a. The values of Q^0 and b estimated from the plots along with the correlation coefficients are listed in Table 1. The high regression correlation coefficients (>0.97) were found for all the temperatures studied, suggesting that Langmuir isotherm model was applicable to describing the Rhodamine B biosorption equilibrium by anaerobic sludge. The Langmuir constant Q^0 decreased with increasing temperature, while the variation of Langmuir constant b was not significant, indicating that biosorption density was higher at a lower temperature. The decrease in Q^0 with increasing temperature was in agreement with the experimental results of temperature effect described later.

Table 1
Langmuir and Freundlich isotherm constants of Rhodamine B adsorption on anaerobic sludge at various temperatures

T (°C)	Langmuir constants			Freundlich constants		
	Q^0 (mg/g)	b (l/mg)	R^2	K_F	n	R^2
20	19.52	0.12	0.985	2.51	1.84	0.996
38	18.74	0.11	0.988	1.95	1.43	0.998
60	17.74	0.11	0.994	1.69	1.39	0.994

The Freundlich equation is given below:

$$q_{eq} = K_F C_{eq}^{1/n} \tag{3}$$

K_F and n are the indicators of adsorption density and adsorption intensity, respectively. Eq. (3) can be linearized as Eq. (4):

$$\ln q_{eq} = \ln K_F + \frac{1}{n} \ln C_{eq} \tag{4}$$

The values of K_F and n can be, respectively, estimated from the intercept and slope of the linear plot of experimental data of $\ln q_{eq}$ versus $\ln C_{eq}$. The Freundlich isotherm provides no information on the monolayer adsorption density in comparison with the Langmuir model [13].

The linearized Freundlich adsorption isotherms obtained at different temperatures are shown in Fig. 4b. The values of K_F and n calculated from the plots are also given in Table 1 along with the regression correlation coefficients.

As seen from Table 1, the parameter K_F related to the adsorption density increased with a decrease in temperature. This was consistent with the experimental observation. Table 1 also shows that n was greater than unity, indicating that Rhodamine B was adsorbed favorably by anaerobic sludge at all the temperatures studied. The regression correlation coefficients of Freundlich model were close to 1.0, suggesting that Freundlich isotherm model was slightly better for describing the biosorption equilibrium than Langmuir model, though the Langmuir model also agreed with the experimental data well.

3.4. Biosorption kinetics

In order to find out the potential rate-controlling steps involved in the process of biosorption of Rhodamine B onto anaerobic sludge, both pseudo first-order and pseudo second-order kinetic models were used to fit the experimental data at various temperatures.

The pseudo first-order rate expression of Lagergren model is generally expressed as follows:

$$\frac{dq}{dt} = k_{1,ad}(q_{eq} - q) \tag{5}$$

The integrated form of Eq. (5) is

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_{1,ad} t}{2.303} \tag{6}$$

However, to fit Eq. (6) to experimental data, the value of q_{eq} (equilibrium adsorption density) must be pre-estimated by extrapolating the experimental data to $t = \infty$. In addition, in most cases the first-order rate equation of Lagergren is usually applicable over the initial 30–50 min of the adsorption process [1].

The plots of $\log(q_{eq} - q)$ as a function of biosorption time are shown in Fig. 5. The linear relationships were observed only for the initial 35 min of biosorption and the experimental data deviated considerably from the theoretical ones (not shown in the figure) after this short period. The rate constants $k_{1,ad}$ and

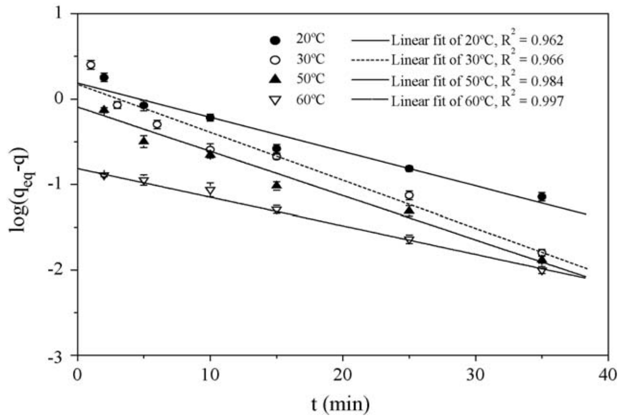

Fig. 5. Linearized pseudo first-order kinetic model for adsorption of Rhodamine B onto anaerobic sludge at various temperatures (initial dye concentration of 50.0 μmol/l).

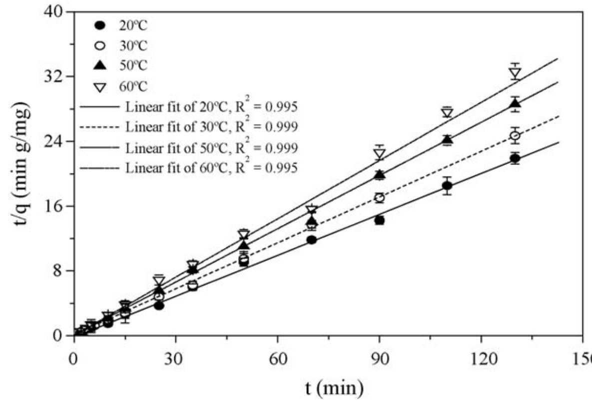

Fig. 6. Linearized pseudo second-order kinetic model for adsorption of Rhodamine B onto anaerobic sludge at various temperatures (initial dye concentration of 50.0 μmol/l).

theoretical values of q_{eq} calculated from the slope and intercept of the linear plots are summarized in Table 2, along with the corresponding correlation coefficients.

The pseudo second-order kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_{2,\text{ad}}(q_{\text{eq}} - q)^2 \quad (7)$$

The integrated form is given as

$$\frac{t}{q} = \frac{1}{k_{2,\text{ad}} q_{\text{eq}}^2} + \frac{t}{q_{\text{eq}}} \quad (8)$$

By plotting t/q against t for the different temperatures, straight lines were obtained as shown in Fig. 6. The second-order rate constants $k_{2,\text{ad}}$ and q_{eq} values presented in Table 2 were determined from the slopes and intercepts of the plots in Fig. 6.

The results of Table 2 show that the second-order rate constant $k_{2,\text{ad}}$ increased with increasing temperature. The correlation coefficients for the second-order kinetic model were close to 1.0 for all cases, and the theoretical values of q_{eq} also agreed well with the experimental data. On the other hand, the correlation coefficients for the pseudo first-order kinetics were lower than those of pseudo second-order one. In addition, the theoretical q_{eq} values calculated from the first-order kinetic model did not give reasonable values with obvious deviation from the experimental ones. Furthermore, the values of $k_{1,\text{ad}}$ obtained from the former had no obvious increasing or decreasing trend with an increase in temperature. These imply that the biosorption of Rhodamine B on anaerobic sludge followed the second-order kinetics rather than the first-order one.

3.5. Thermodynamic analysis

The second-order rate constant can be expressed as a function of temperature by the Arrhenius equation and the activation energy (E_a) can be determined as below:

$$k_{2,\text{ad}} = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

$$\ln k_{2,\text{ad}} = \ln K_0 - \frac{E_a}{RT} \quad (10)$$

Fig. 7 shows a linear plot of $\ln k_{2,\text{ad}}$ as a function of $10^3/T$ for Rhodamine B biosorption at 293–333 K. The apparent activation energy calculated from the slope of the plot was found to be 6.59 kJ/mol. The relatively low positive activation energy indicates that the biosorption of Rhodamine B by anaerobic sludge involved diffusion process.

Thermodynamic parameters for the adsorption such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy (ΔS°) were calculated using the Eq. (11) and van't Hoff equation (Eq. (12)):

$$\Delta G^\circ = -RT \ln K \quad (11)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

The K value can be obtained from the linearized form of Langmuir equation. The values of ΔG° at different temperatures are

Table 2
First-order and second-order adsorption rate constants of Rhodamine B at different temperatures

T (°C)	First-order constants			Second-order constants			Measured
	$K_{1,\text{ad}}$ (min^{-1})	$q_{\text{eq,cal}}$ (mg/g)	R^2	$K_{2,\text{ad}}$ (g/(mg min))	$q_{\text{eq,cal}}$ (mg/g)	R^2	$q_{\text{eq,exp}}$ (mg/g)
20	0.09	0.48	0.962	0.56	6.00	0.999	5.91
30	0.13	0.46	0.966	0.68	5.27	0.999	5.24
50	0.12	0.22	0.984	0.76	4.60	0.999	4.53
60	0.08	0.05	0.997	0.78	4.04	0.998	3.98

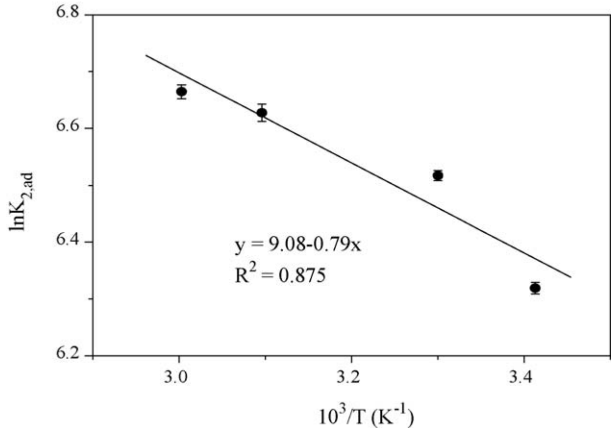

Fig. 7. Arrhenius plot for adsorption of Rhodamine B onto anaerobic sludge.

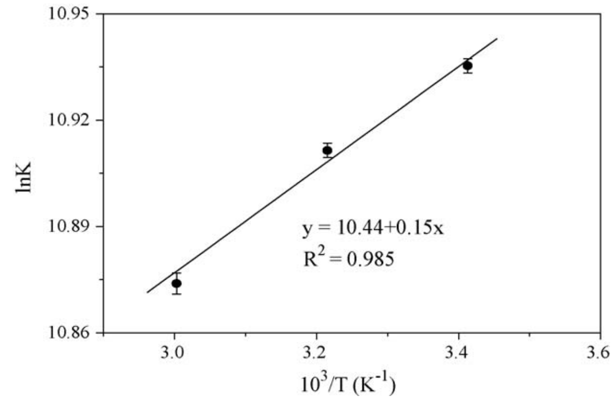

Fig. 8. van't Hoff plot for the adsorption of Rhodamine B onto anaerobic sludge.

Table 3
Thermodynamic parameters of Rhodamine B biosorption

T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/(mol K))	E_a (kJ/mol)
20	−26.64			
38	−28.21	−1.21	0.09	6.59
60	−30.11			

given in Table 3. A plot of $\ln K$ as a function of $10^3/T$ yielded a straight line (Fig. 8). The values of ΔH° and ΔS° obtained from the slope and intercept of the plot are summarized in Table 3.

Generally, the change of free energy for physical adsorption is smaller than that of chemisorption. The former is in the range of nil to −20 kJ/mol, and the later is in the range of −80 to −400 kJ/mol. The values of ΔG° at different temperatures of this study were in the range between those of physical adsorption and chemical adsorption. Thus, the biosorption of Rhodamine B on anaerobic sludge could be considered as a physical adsorption enhanced by the electrostatic effect. The negative values of ΔG° and ΔH° indicate that the adsorption process was exothermic, which agrees well with the experimental observations. The positive value of ΔS° shows the increased randomness at the solid/solution interface during the biosorption of Rhodamine B on anaerobic sludge. An increase in entropy was also reported for adsorption of Cd(II) on Fe(III)/Cr(III) hydroxide [14]. The adsorbed water molecules, which were displaced by the adsorbate species, gained more translational entropy than that which the adsorbate molecules lost, thus allowing the prevalence of randomness in the system. The simplified view of the more ordered arrangement of molecules on the surface may not be applicable to the biosorption of Rhodamine B by anaerobic sludge. The increase in entropy of Rhodamine B biosorption process might be associated with the configuration changes in adsorbate in biosorption process and the changes of sludge surface caused by biosorption.

3.6. Evaluation of anaerobic sludge as a biosorbent

Table 4 shows the comparison of dye adsorption of this work and other relevant studies. The values of Q^0 in Langmuir model, which is an indicator of adsorption capacity, and n in Freundlich model, which is an indicator of adsorption intensity, in this study are larger than those in most of previous works. This suggests that Rhodamine B could readily adsorbed by anaerobic sludge used in this work. Furthermore, anaerobic sludge could be easily obtained from nature and simply pretreated for application. All these showed that anaerobic sludge is a type of cheap and effective biosorbent for dyestuff.

Table 4
Comparison of dye adsorption of this work and previous studies

Dyes	Absorbents	Equilibrium models	Q^0 (mg/g)	n	Reference
Rhodamine B	Anaerobic sludge	Langmuir and Freundlich	19.52[a]	1.84[a]	This study
Procion orange	Orange peel	Langmuir	1.33	–[b]	[15]
Rhodamine B	Orange peel	Langmuir	3.23	–	[15]
Rhodamine B	Sugar cane dust	Langmuir	4.26	–	[16]
Malachite green	Sugar cane dust	Langmuir	4.88	–	[16]
Acid blue 25	Peat	Langmuir	14.40	–	[17]
Congo red	Orange peel	Langmuir	22.40	–	[15]
Reactive blue 2	Dried activated sludge	Freundlich	–	1.16	[1]
Reactive yellow 2	Dried activated sludge	Freundlich	–	1.34	[1]
Methylene blue	Dried activated sludge pretreated by means of coagulation–flocculation	Freundlich	–	1.86	[18]
Methylene blue	Dried anaerobic sludge	Freundlich	–	2.10	[18]

[a] Temperature: 20 °C.
[b] Not available.

4. Conclusions

This study shows that anaerobic sludge had a much higher equilibrium adsorption density on Rhodamine B than on Eosin Y. The adsorption density of Rhodamine B onto sludge decreased with enhancing sludge concentration. At a lower dye concentration, adsorption can reach saturation in a lower VSS concentration. A higher initial concentration of dye can enhance the adsorption process. The Langmuir and Freundlich adsorption models were both able to adequately describe the biosorption equilibrium of Rhodamine B onto sludge. The change of adsorption free energy, calculated with Langmuir isotherms, was a negative value at various temperatures, indicating that the adsorption process was exothermic. Furthermore, the biosorption followed pseudo second-order adsorption kinetics. The second-order kinetic constants increased with increasing temperature and the activation energy of biosorption calculated through the Arrhenius equation was estimated as 6.59 kJ/mol, indicating that the biosorption of Rhodamine B onto anaerobic sludge involved diffusion process.

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