Equilibrium and kinetic modelling of methylene blue biosorption by pretreated dead *streptomyces rimosus*: Effect of temperature

Yeddou Nacèra[*], Bensmaili Aicha

Laboratoire de Génie de la réaction, Faculté de Génie Mécanique et Génie des procédés,
Université des sciences et de la technologie Houari Boumediène, BP 32 El Alia Bab Ezzouar, Alger, Algeria

Abstract

This paper aims to investigate the biosorption of basic dye, methylene blue onto dead *Streptomyces rimosus*. In our experiments the batch sorption is studied with respect to solute concentration, contact time, adsorbent dose and temperature. The results show that as the amount of the dead bacterial increases, the percentage of dye sorption increases accordingly. The bacterial biomass exhibits the highest methylene blue uptake capacity at 20 °C. Biosorption capacity decreased from 9.86 to 6.93 mg g^{-1} with an increase in temperature from 20 to 50 °C at the initial methylene blue concentration of 50 mg l^{-1}. Intraparticle diffusion, pseudo-first order and pseudo-second order models can be used to describe the kinetics of basic dye sorption for different initial temperature values. In our study, we have used the Freundlich and Langmuir isotherm models to represent the equilibrium data of methylene blue biosorption at several temperature values. In addition, an activation energy of sorption has also been determined based on the pseudo-second order rate constants.
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1. Introduction

Dyeing industry wastewater is one of the major environmental problems. Color is one of the characteristics of an effluent which is easily detected. Most of the dyes are stable to biological degradation. Color affects the nature of the water and inhibits sunlight penetration into the stream and reduces photosynthetic action. Some of dyes are carcinogenic and mutagenic [1]. Adsorption processes have been investigated as an efficient and effective method to remove dyes from wastewater. Recent research work has been focused towards alternative adsorbents namely low cost adsorbents including the utilization of waste materials capable of removing significant quantities of dyes from aqueous solutions [2,3].The sorption of various dyes onto peat [4] onto pith [5,6], wood [7,8], orange peel [1] bagasse fly ash [9] and fungal biomass [10] have been studied. Over the last decade, efforts have been made towards the development of biosorption for the uptake of inorganic ionic species [11–13]. Biosorptive uptake of dyes has not received adequate attention so far. Biosorption using dead cells has many advantages over

the live cell systems [14,15]. The aim of this study is to determine the adsorption capacity of bacterial dead *Streptomyces rimosus* biomass which is produced during oxytetracyclin antibiotic production.

2. Adsorption dynamics

The study of adsorption dynamics describes the solute uptake rate. This rate controls the residence time of adsorbate uptake at the solid–solution interface. The kinetics of methylene blue biosorption on dead biomass were analysed using pseudo-first order [16,17], pseudo-second order [18] and intraparticle diffusion [19] kinetic models. The model predicted values are validated by the correlation coefficient r^2 that should be close or equal to 1.

2.1. The pseudo-first order model

The sorption kinetics are described by pseudo-first order as follows:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{K_1 t}{2303} \tag{1}$$

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[*] Corresponding author.
E-mail addresses: yeddouna@yahoo.fr, mezennerna@yahoo.fr (Y. Nacèra).

where q_e is the amount of dye sorbed at equilibrium, $mg\,g^{-1}$; q_t the amount of dye sorbed at time t, $mg\,g^{-1}$ and K_1 is the rate constant of pseudo-first sorption, min^{-1}.

2.2. The pseudo-second order model

The pseudo-second order kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

where k_2 is the rate constant of pseudo-second order adsorption ($g\,mg^{-1}\,min^{-1}$). Taking into account, the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (2) can be rearranged to obtain Eq. (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

The initial adsorption rate, h ($mg\,g^{-1}\,min^{-1}$) is expressed as

$$h = k_2 q_e^2 \tag{4}$$

The plot of (t/q_t) versus t of Eq. (3) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

2.3. Intraparticle diffusion model

The intraparticle diffusion model presented here refers to the theory proposed by Weber and Morris [19] who concluded that the uptake is proportional to the square root of contact time during the course of adsorption. Accordingly

$$q_t = k_i t^{0.5} \tag{5}$$

where k_i is the intraparticle diffusion rate constant, $mg\,g^{-1}\,min^{-0.5}$.

2.4. Equilibrium modelling

Equilibrium data, commonly known as adsorption isotherms, are the basic requirement for the design of adsorption systems. Classical adsorption models, such as Langmuir and Freundlich models were used to describe the equilibrium between adsorbed dye on the biomass and dye in solution (C_e) at a constant temperature.

The Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites, is given by

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \tag{6}$$

where q_o ($mg\,g^{-1}$) is the maximum amount of dye per unit weight of biomass, to form a complete monolayer on the surface bound at high C_e, and b ($l\,mg^{-1}$) is a constant related to the affinity of the binding sites. q_o and b can be determined from the linear plot of C_e/q_e versus C_e [20]. The essential characteristics of the Langmuir isotherm can be expressed in terms of dimension-less

Table 1
Constant parameter R_L

R_L-value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable

constant separation factor for equilibrium parameter, R_L [21] which is defined by

$$R_L = \frac{1}{1 + bC_o} \tag{7}$$

Hall and Vermeylem [21] show, using mathematical calculation, that the parameter R_L indicates the shape of isotherm as follows (Table 1).

Freundlich [22] model was also used. The empirical Freundlich equation that corresponds to the sorption on heterogeneous surface is given below:

$$q_e = K_f C_e^{1/n} \tag{8}$$

where K_f and n are the Freundlich constants characteristics of the system (n, dimensionless; K_f, $mg^{1-1/n}\,g^{-1}\,l^{1/n}$). Eq. (8) can be linearized in logarithmic form and the Freundlich constants can then be determined.

3. Materials and methods

Dead *S. rimosus* biomass was obtained from oxytetracyclin antibiotic production after fermentation. The biomass was washed with deionised water, dried at $50\,°C$ for $24\,h$ in a drying oven, then the biomass pigments were oxidized using 1% NaOCl, and once again washed, dried and then screened through a set of sieves to get geometrical size $80–315\,\mu m$. The dye used in the experiments was the methylene blue which is used as commercial salt. Several sets of experiments were conducted to determine the effect of biosorbent dose, initial dye concentration and initial solution temperature on the biosorption of methylene blue onto biomass. Samples were withdrawn at suitable time intervals and were separated from the sorbent by centrifugation at 10,000 rpm for 30 min and their concentrations determined by spectrophotometer UV–vis, $\lambda = 660\,nm$.

The removal efficiency of dye was calculated from:

$$\%\text{removal} = \frac{C_0 - C_f}{C_0} \times 100 \tag{9}$$

The sorption capacity of dye is the concentration of dye on the bacterial biomass and can be calculated based on the balance principle where

$$q = \frac{V(C_0 - C_f)}{m} \tag{10}$$

where q represents the amount of dye uptaken per unit mass of the biomass ($mg\,g^{-1}$); V the volume of the solution (l); m the dry mass of the biosorbent (g); C_0 and C_f are the initial and final concentrations ($mg\,l^{-1}$), respectively.

3.1. Effect of initial dye concentration

The effect of initial concentration of dye solution on the sorption was studied in conical flasks at fixed temperature, 20 °C.

A 450 mg sample of dead *S. rimosus* was added to each 100 ml volume of methylene blue solution. The initial tested concentrations of methylene blue dye solution were 50, 100 and 150 mg l^{-1}.

3.2. Effect of biosorbent dose

Samples of dead biomass (0.25, 0.30, 0.35, 0.40, 0.45, and 0.5 g) were added to dye solution (100 ml). The initial dye concentration ranges from 50 to 150 mg l^{-1} at constant temperature (20 °C).

3.3. Effect of temperature

A sample of dead *S. rimosus* (450 mg) was added to dye solution (100 ml, 50 mg l^{-1}). The experiments were carried out at 20, 30 and 50 °C in a constant temperature shaker bath.

3.4. Sorption isotherm

Batch sorption experiments were carried out at 20, 30 and 50 °C. A 250 mg sample of dead biomass is added to each 100 ml of methylene blue solution. The initial tested concentration of dye solution were 10, 30, 50, 100 and 150 mg l^{-1}.

4. Results and discussion

4.1. Effect of initial dye concentration

Fig. 1 shows the adsorption kinetics of dye removal at 50, 100 and 150 mg l^{-1} by plotting the methylene blue uptake capacity, q, versus time. An increase in initial dye concentration leads to an increase in the adsorption capacity of methylene blue on biomass. The removal of dye increases rapidly in the beginning (first 5 min) and then more slowly until the equilibrium. The removal of methylene blue decreases from 86 to 75% with the increase of initial concentration from 50 to 150 mg l^{-1}. The kinetic of dye biosorption onto *S. rimosus* were analysed using pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models. The kinetics of methylene blue sorption onto biomass follow the pseudo-second order rate expression. The parameters of Eq. (3) were obtained from the slope and intercept of straight line plots of t/q_t versus t. The equilibrium sorption capacity, q_e, increases from 9.86 to 30.48 mg g^{-1} when the initial concentration of methylene blue increases from 50 to
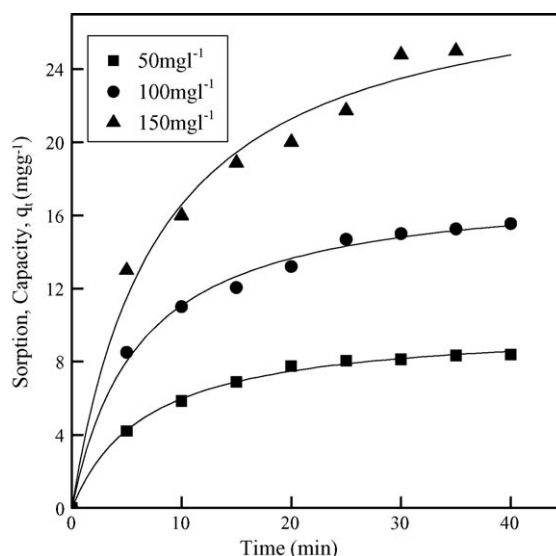

Fig. 1. Kinetics of methylene blue uptake by dead biomass at various initial concentrations.

150 mg l^{-1}. Plotting the amount of dye sorbed per unit mass of dead biomass versus the square root of time generates the best fit straight lines for the initial 20 min. The pseudo-second order rate parameters, k_2, are compared with r_i^2 and k_i values for the intraparticle diffusion based model in Table 2.

4.2. Effect of biosorbent mass

According to Fig. 2, the removal increases with the increase sorbent doses from 250 to 500 mg (100 ml of methylene blue solution) for a given initial dye concentration. This indicates that with an increase of sorbent mass, more surface area is made available, and therefore an increase of the total number of sites.

4.3. Effect of temperature

Fig. 3 shows the adsorption kinetics of methylene blue at 20, 30 and 50 °C by plotting the methylene blue uptake capacity, q_t, versus time at the initial methylene blue concentration of 50 mg l^{-1}. A larger amount of methylene blue was removed by *S. rimosus* in the first 15 min of contact time. Increasing the temperature reduces the biosorption capacity of biomass. When the temperature is raised from 20 to 50 °C, the removal percentage of methylene blue decreases from 86 to 54%.

The pseudo-second order rate parameters are compared with r_1^2 and k_1 values for the pseudo-first model. The temperature dependence of dye sorption by dead biomass, shows a

Table 2
Effect of initial concentration on parameters for the methylene blue/biomass system

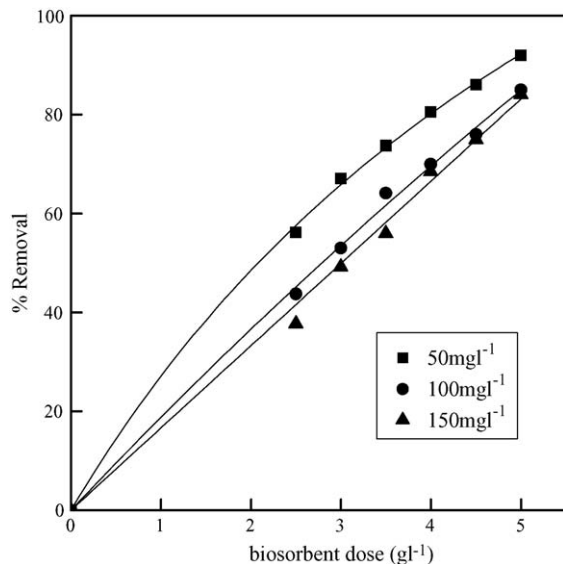| C_0 (mg l^{-1})	K_1 (min^{-1})	r_1^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	r_2^2	k_i (mg g^{-1} min$^{-0.5}$)	r_i^2
50	7.2×10^{-2}	0.929	1.59×10^{-2}	9.86	0.998	1.78	0.997
100	8.49×10^{-2}	0.983	8.67×10^{-3}	18.04	0.997	3.19	0.971
150	11.67×10^{-2}	0.880	3.8×10^{-3}	30.48	0.987	4.84	0.975

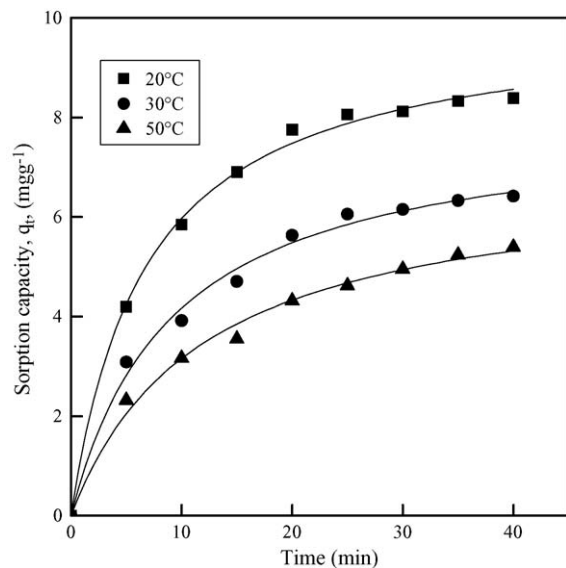Fig. 2. Effect of biosorbent dosage on methylene blue removal by dead biomass at various concentrations.

Fig. 3. Kinetics of methylene blue uptake by dead biomass at several initial temperatures.
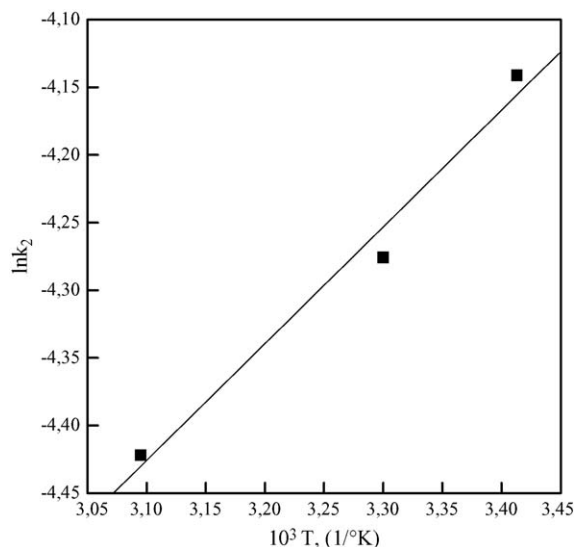

Fig. 4. Plot of $\ln k_2$ against reciprocal temperature for methylene blue sorption onto biomass.

order rate constant is expressed as a function of temperature using the Arrhenius Eq. (11):

$$k_2 = k_0 \exp(-E/RT) \tag{11}$$

where k_0 is the temperature independent factor ($\text{g mg}^{-1}\,\text{min}^{-1}$); E the activation energy of sorption (kJ mol^{-1}); R the gas constant ($8.314\,\text{J mol}^{-1}\,\text{K}^{-1}$), and T is the solution temperature (K). From this equation, the rate constant of sorption, k_0, is $8.23 \times 10^{-4}\,\text{g mg}^{-1}\,\text{min}^{-1}$ and the activation energy of sorption E is $-7.18\,\text{kJ mol}^{-1}$.

These results show that methylene blue biosorption process by *S. rimosus* is exothermic. The low value of the energy of activation suggests the existence of a physical biosorption. Therefore, the affinity of methylene blue for the biomass may be ascribed to Van Der Walls forces or hydrogen bonds between the dye and the surface of the particles biosorbantes (the wall). However, the real process is much more complex.

4.4. Equilibrium modelling

The Freundlich and Langmuir adsorption constants, evaluated from the isotherms at different temperatures with the correlation coefficients are presented in Table 4. According to Table 4, high regression correlation coefficients (>0.970) were found at all the studied temperatures. The higher correlation coefficients show that both the Freundlich and Langmuir models are suitable, for describing the biosorption equilibrium of dye by the pretreated dead bacterial, in the studied concentration range.

good compliance with the pseudo-second order equation, which are reflected by high coefficients of correlation (Table 3).The values of the initial sorption rate, h, vary from 1.545 to $0.589\,\text{mg g}^{-1}\,\text{min}^{-1}$ as the solution temperature increases from 20 to 50 °C.

Fig. 4 shows a linear relationship between the logarithm of the rate constant and the reciprocal of temperature. The second

Table 3
Effect of temperature on parameters for the methylene blue/biomass system

T (°C)	K_1 (min^{-1})	r_1^2	k_2 (g mg^{-1} min^{-1})	r_2^2	q_e (mg g^{-1})	h (mg g^{-1} min^{-1})
20	7.2×10^{-2}	0.929	1.59×10^{-2}	0.998	9.86	1.545
30	4.99×10^{-2}	0.933	1.39×10^{-2}	0.993	7.95	0.878
50	5.84×10^{-2}	0.991	1.2×10^{-2}	0.990	6.93	0.589

Table 4
Parameters for Langmuir and Freundlich isotherms

T (°C)	q_o (mg g^{-1})	b (l mg^{-1})	C_0 (mg l^{-1})	R_L	$r^2 = r_l^2 = 0.9752$[a]	n	K_f	$r^2 = r_f^2 = 0.9970$[b]
20	34.34	0.0194	10	0.837	0.9752	1.50	1.164	0.997
			30	0.632				
			50	0.507				
			100	0.340				
			150	0.255				
30	32.98	0.0173	10	0.852	0.984	1.40	0.919	0.997
			30	0.658				
			50	0.536				
			100	0.366				
			150	0.278				
50	24.35	0.0171	10	0.854	0.992	1.42	0.658	0.977
			30	0.661				
			50	0.539				
			100	0.369				
			150	0.280				

[a] Correlation coefficient for langmuir model by linear regression analysis.
[b] Correlation coefficient for freundlich model by linear regression analysis.

The highest K_f and n values were found as 1.164 mg$^{1-1/n}$ g^{-1} l$^{1/n}$ and 1.50, respectively at 20 °C. According to Treybal [23], it has been shown, using mathematical calculations that values of n between 1 and 10 represent beneficial adsorption.

5. Conclusion

The kinetics of methylene blue sorption by pre-treated dead *S. rimosus* were fast, reaching 86% ($C_0 = 50$ mg l^{-1}) of the total adsorption capacity in 5 min. The mechanism follows a pseudo-second order reaction model. The activation energy of sorption was evaluated as -7.18 kJ mol^{-1}. These results show that dye adsorption process by biomass is exothermic.

Langmuir and Freundlich models present good fits of the experimental data. The application of these models to complex biological system may not be able to explain the biosorption behaviour. Hence, conclusions derived only from good fit of the models should be avoided.

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