SORPTION OF CATIONIC DYES FROM AQUEOUS SOLUTIONS BY MOSS *Rhytidiadelphus squarrosus*: KINETICS AND EQUILIBRIUM STUDIES

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Abstract: With the aim to investigate sorption properties of natural sorbent prepared from moss *Rhytidiadelphus squarrosus* we elucidated biosorption of cationic dyes Malachite green (BG4), Auramine O (BY2) and Thioflavine T (BY1) from aqueous solutions. The removal of dyes by moss biosorbent was found to be rapid at an initial stage and the equilibrium was reached within 1-2 hours. The pseudo-*n*-order kinetic model was successfully applied to the kinetic data and the order of adsorption reaction was calculated in the range from 1.7 to 2.6. The value of rate constant k_n' ranged from 0.001 to 0.039 $[\text{min}^{-1}]/[\mu\text{mol/g}]^{1-n}$. The equilibrium data were fitted to the adsorption isotherms. The Freundlich isotherm was found to represent the measured sorption data of BG4, BY1 and BY2 well. The maximum sorption capacities of moss biomass from single dye solutions calculated by Langmuir equation were 354 μmol/g for BG4, 310 μmol/g for BY1 and 382 μmol/g for BY2. These results showed that the prepared biomass presents low-cost, natural and easy available sorbent which may be potentially used for removal of dyes from environment and also may be an alternative to more costly materials such as activated carbon.

Key words: Malachite green, Thioflavine T*,* Auramine O, *Rhytidiadelphus squarrosus*, sorption kinetics, sorption equilibrium

1. Introduction

Contamination of water sources by many organic pollutants is a major factor of global environmental pollution for the number of years. Dyes represent one of the problematic groups. Two main sources of dye pollution are the textile and dyestuff manufacturing industries. Color is the first contaminant to be recognized in wastewater and the presence of very small amounts of dyes in water is highly visible and undesirable (CRINI and BADOT, 2008; IQBAL and ASHIQ, 2007; AKSU, 2005). The presence of synthetic dyes in the aquatic environment has been of great concern because of their potential health hazards associated with the carcinogenic, mutagenic, allergenic and toxic natures as well as negative effects on the photosynthetic activity in aquatic life.

Adsorption techniques employing solid adsorbents are effective methods for water decontamination. Most commercial systems currently use activated carbon and organic resins as adsorbents to remove dye in wastewater because of their excellent adsorption

abilities. A large variety of non-conventional adsorbent materials have been also proposed and studied for their ability to remove dyes (CRINI, 2006; 2008).

Sorption systems have been investigated to assess their suitability for application in the field of water pollution control. The cost and performance of a product or the mode of application are always of concern to control process efficiency. Therefore the sorption capacity and required contact time are two of the most important parameters to understand (HO *et al.,* 2000).

The aim of this study was to realize biosorption of cationic dyes from aqueous solutions and to consider sorption properties of natural sorbent prepared from moss *Rhytidiadelphus squarrosus*. Experimental kinetics data were analyzed using a pseudo-*n*-order kinetic equation. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms and the characteristics parameters of each isotherm have been determined.

2. Materials and methods

2.1 Chemicals

In sorption experiments cationic dyes Malachite green (BG4, Basic green 4 – malachite green oxalate, M_r 927, C.I. 42 000, Merck, D); Auramine O (BY2, Basic Yellow 2, M_r 304, C.I. 41 000, Aldrich, D) and Thioflavine T (BY1, Basic Yellow 1, M_r 319, C.I. 49 005, Fluka, D) were used. The stock solutions of dyes were prepared in deionized water.

2.2 Biosorbent preparation

Moss *R. squarrosus* was collected from forests in High Tatras Mountains, Slovak Republic. Before using in experiments the biomass was thoroughly washed in deionized water, oven-dried for 72 h at a maximum of 45 °C to avoid degradation of binding sites and pulverized in blade homogenizer. Size analysis showed the following separation of particles size: >600 μm – 5 %; 600-300 μm – 49 %; <300 μm – 46%. Fraction <300 μm was used in sorption experiments.

2.3 Sorption kinetics

Batch sorption experiments were carried out in Erlenmayer flasks containing 20 mL BG4, BY1 and BY2 solutions with defined concentrations. pH value was adjusted to 4.0 with 0.1 M HCl. Biomass (~30 or 40 mg, d.w.) was added and flasks were agitated on a reciprocal shaker (250 rpm) at 25 ºC. Samples were taken from individual flasks in intervals 5, 10, 20, 40, 120, 240 and 1440 min and analyzed using Varian Cary 50 UV-VIS spectrophotometer by measuring the optical densities of dyes at their respective maximum absorbance wavelengths. These are 617, 412 and 435 nm for BG4, BY1 and BY2, respectively. If not otherwise stated, presented data are the arithmetic mean values.

2.4 Sorption equilibrium

All experiments were carried out in Erlenmayer flasks with 20 mL of BG4, BY1 and BY2 solutions with initial concentration from 50 to 400 mg/L. pH value was adjusted to 4.0 with 0.1 M HCl. Biomass (20 mg, d.w.) was added and the flasks were agitated on a reciprocal shaker (250 rpm) for 4 h at 25ºC. At the equilibrium, samples were taken and analyzed spectrophotometrically. If not otherwise stated, presented data are arithmetic mean values.

2.5 Non-linear regression analysis

To calculate parameters of pseudo-*n*-order model, the Q_{max} values and the corresponding parameters of adsorption isotherms non-linear regression analysis was performed by the NLSF (Origin's nonlinear least square fitter) using program MicroCal Origin 8.0 Professional (OriginLab Corporation, Northampton, USA) with automatic initialization of parameters and GraphPad PRISM 5.0 software (GraphPad Software Inc., USA).

3. Results and discussion

3.1 Biosorption kinetics

The time-course studies on the biosorption of cationic dyes BY1, BY2 and BG4 were performed by contacting the dye solutions with moss biosorbent at pH 4.0 and 25 °C. Biosorption of BY1, BY2 and BG4 by *R. squarrosus* is faster at initial stage, during occupation of high affinity sites (Fig. 1.) Maximum uptake, approx. 95% at biosorbent concentration 2.0 g/L and initial BG4 concentration $C_0 = 122$ µmol/L was reached within 60 min. In the case of BY1 ($C_0 = 307$ µmol/L) and BY2 ($C_0 = 339$ µmol/L) uptake reached aprox. 80% within the first 90 min at biosorbent concentration 1.5 g/L. After this time there was no considerable increase during the next 23 hours. CRINI *et al.* (2007) also observed a very fast sorption of BG4 by cyclodextrin-based adsorbent. The largest amount of BG4 was adsorbed to the polymer within the first 90 min. Rapid sorption of BY2 by poly-(γ-glutamic acid) was confirmed by INBARAJN *et al.* (2006). Maximum sorption was accomplished within 12 min indicating a rapid surface adsorption of BY2 on poly-(γ-glutamic acid) occurred.

The mechanism of a short-term dye uptake by biosorbents is generally regarded as an abiotic process. It is known that biomass contains ionogenic groups such as carboxyl, phenolic and alcoholic hydroxyl, and phosphate that generate a negative net charge. Basic dyes can be ionized in solution to form positive charge and chemical reaction through electrostatic interaction may occur between anionic groups of moss biosorbent and cations of dyes molecules (CRINI and PEINDY, 2006).

Biosorption kinetics describing the pollutant uptake rate is one of the important characteristics defining the efficiency of sorption and feasibility of (bio)sorbents for their use in water pollution control. In almost all previous biosorption kinetic studies,

both pseudo-first (1) and pseudo-second (2) order kinetic equations were directly chosen to fit biosorption data without any explanation about the rational behind.

$$\frac{dQ_t}{dt} = k_1^{'}(Q_{eq} - Q_t) \tag{1}$$

$$\frac{dQ_t}{dt} = k_2^{'}(Q_{eq} - Q_t)^2 \tag{2}$$

LIU and LIU (2008) pointed out that, there is no reason and need to preset biosorption kinetics to be the first or the second order unless biosorption mechanisms are known. Considering the complexity of biosorption process and fact that the various mechanisms would be involved ŐZER (2007) and LIU and WANG (2008) the direct calculation of rate constant and order of the biosorption reaction recommended as a more appropriate method. For these reasons the experimental data obtained by non-equilibrium conditions in our work were analyzed using a pseudo-*n*-order (3) model proposed by ŐZER (2007) and LIU and SHEN (2008):

$$\frac{dQ_t}{dt} = k_n^{'}(Q_{eq} - Q_t)^n \tag{3}$$

where *n* is the reaction order determined from biosorption data and k_n is a rate constant. The integrated form of equation (3) has the following form:

$$Q_t = Q_{eq} - \left[(n-1)k_n^{'}t + Q_{eq}^{(1-n)}\right]^{\frac{1}{1-n}} \tag{4}$$

where Q_t is the amount of sorbate sorbed at time *t*, Q_{eq} represents sorbate sorption at equilibrium.
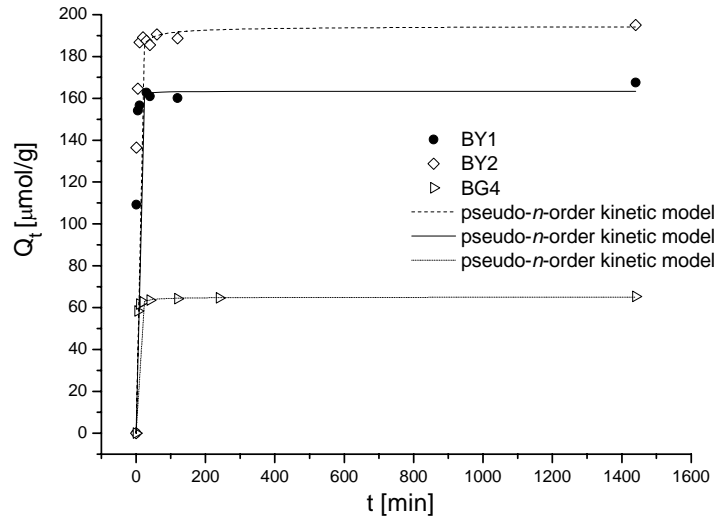

Fig. 1. Kinetics of BY1 (●), BY2 (◇) and BG4 (▷) biosorption by *R. squarrosus* at pH 4 and 25 °C. Experimental data fitted to pseudo-*n*-order kinetic model. Data shown in Table 1.

Plot of pseudo-*n*-order kinetics model (4) for the biosorption of dyes by moss biosorbent is shown in Fig. 1. The model parameters determined by non-linear regression analysis are shown in Table 1. The calculated $Q_{eq\ cal}$ values from the model are in good agreement with experimental $Q_{eq\ exp}$ values and the correlation coefficients for the pseudo-*n*-order kinetic plots are very high. The respective reaction order for BG4, BY1 and BY2 biosorption was estimated as 2.3, 1.7 and 2.6. The values of rate constant k_n' ranged from 0.001 to 0.039 $[min^{-1}]/[\mu mol\ /g]^{1-n}$. From the presented results it is evident that pseudo-*n*-order model provides a satisfactory description of biosorption experimental data compared to prediction by equation (1) and (2) (data not shown).

Table 1. Pseudo-*n*-order kinetics parameters for BG4, BY1 and BY2 sorption by *R. squarrosus* at pH 4 and 25°C from aqueous solutions obtained by using non-linear regression analysis.

Dye	C_0 [μmol/l]	k_n' $[min^{-1}]/[\mu mol/g]^{1-n}$	$Q_{eq\ cal}$ [μmol/g] d.w.	n	R^2	$Q_{eq\ exp}$ [μmol/g] d.w.
BG4 *	122	0.014	65.0 ± 0.3	2.3	1.0	65
BY1 **	307	0.039	163 ± 2	1.7	0.998	168
BY2 **	339	0.001	195 ± 4	2.6	0.996	195

* Biosorbent concentration = 2.0 g/L
** Biosorbent concentration = 1.5 g/L

3.2 Sorption equilibrium in single dye solutions

Two well known adsorption isotherm models, namely Langmuir and Freundlich ones, were applied for the analysis of the experimental data (Table 2).

Table 2. Adsorption isotherm models for single sorption systems in linear and non-linear forms used in this work.

Isotherm	Non-linear form	Linear form
Langmuir	$$Q_{eq} = \frac{bQ_{max}C_{eq}}{1 + bC_{eq}}$$	$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{Q_{max}}C_{eq} + \frac{1}{bQ_{max}}$$
Freundlich	$Q_{eq} = K\,C_{eq}^{(1/n)}$	$log(Q_{eq}) = log\,K + 1/n\ log\,(C_{eq})$

These models use parameters that reflect the nature of the sorbent and can be used to compare biosorption performance. Q_{max} represents the maximum sorption capacity, *b* is a constant related to the energy of adsorption. *k* and *1/n* values are the Freundlich constants referring to adsorption capacity and intensity of adsorption, respectively. Simplicity and easy interpretability are some of the important reasons for the extensive use of these models. Moreover, linear regression has been frequently used to evaluate the model parameters. However, transformations of nonlinear equations into linear

forms usually result in parameter estimation error and distort the fit (KUMAR and SIVANESAN, 2006). For this reason, nonlinear methods for parameters estimation were used in our work.

We have found, that sorption of cationic dyes BY1, BY2 and BG4 by *R. squarrosus* increased with the increasing concentration of dyes in solutions (data not shown) and the equilibrium was reached within 1-2 h. Figure 2 shows the experimental data fitted to the isotherm models for BY1, BY2 and BG4 sorption by *R. squarrosus* at pH 4 from single dye solutions. The obtained adjustable parameters are shown in Table 3 with the corresponding coefficients of determination. Estimated maximum sorption capacity Q_{max} for BY1 biosorption obtained from Langmuir isotherm was 310 ± 10 µmol/g d.w. (Table 3). The Q_{max} 382 ± 11 µmol/g d.w. for BY2 was obtained. The maximum sorption capacity Q_{max} for BG4 biosorption obtained from Langmuir isotherm was 354 ± 33 µmol/g d.w. This indicates a higher sorption capacity of *R. squarrosus* for BY2 in comparison with BY1 and BG4. Freundlich parameter $1/n$ is the heterogeneity factor with the values ranged between 0 - 1. If the value is close to unity this implies that sorption is chemical process. The more heterogenous the surface the closer $1/n$ value is to 0. In fact, for tested dyes the $1/n$ values are close to 0 (Table 3).

The values of R^2 are generally regarded as a measure of the goodness of fit of experimental data on the isotherm models (Al-ASHEH *et al.*, 2000; BASHA *et al.*, 2008). As can be seen from Table 3 higher coefficients of determination R^2 were obtained for the Freundlich model ($R^2 = 0.983$ for BY1, $R^2 = 0.976$ for BY2, $R^2 = 0.945$ for BG4) compared to Langmuir isotherm ($R^2 = 0.906$ for BY1, $R^2 = 0.947$ for BY2, $R^2 = 0.789$ for BG4).
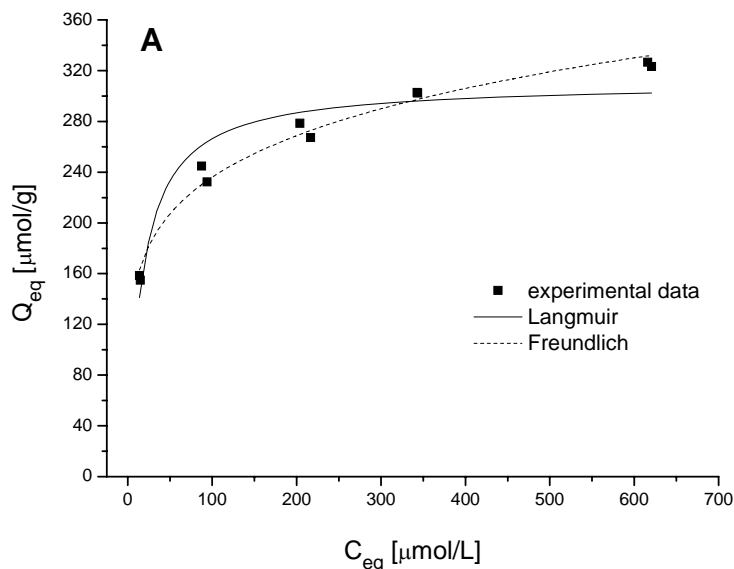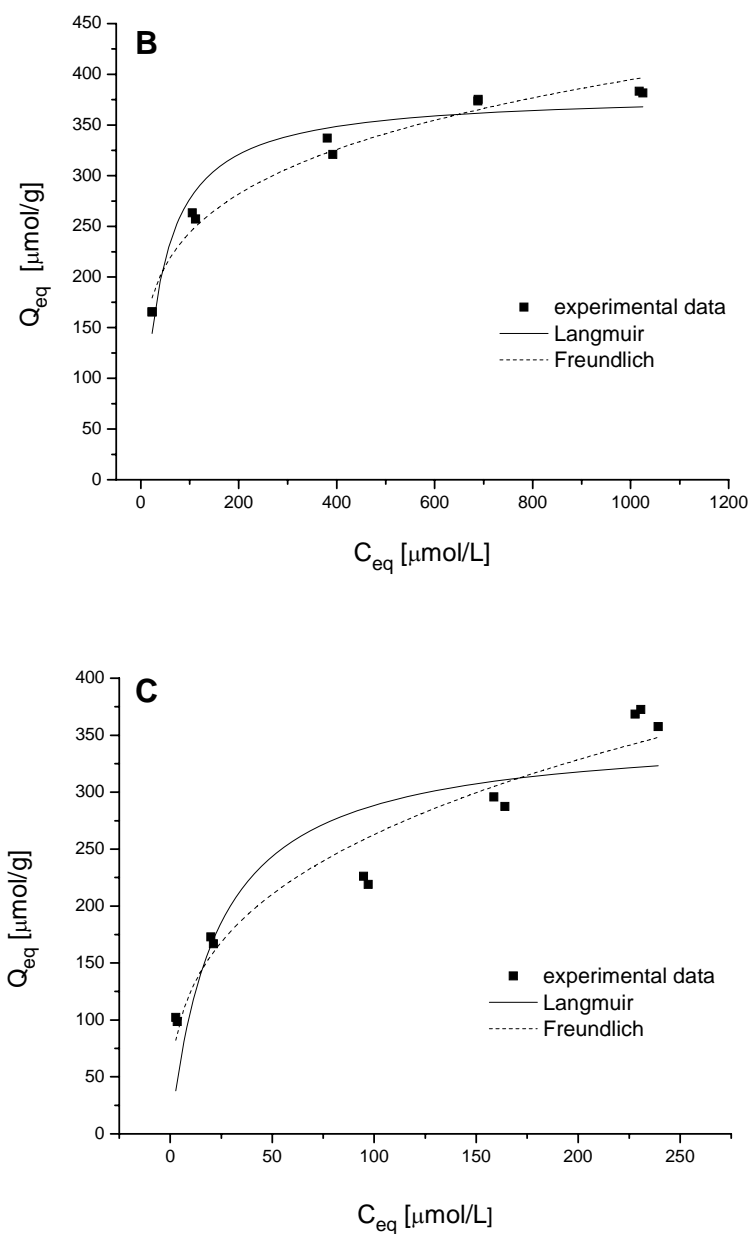
Fig. 2. Fit of the Langmuir and Freundlich adsorption isotherms of BY1 (A), BY2 (B) and BG4 (C) biosorption by *R.. squarrosus* (1.0 g /L, d.w.) from single dye solutions at 25°C and initial pH 4.0. Equilibrium pH 5.4. The corresponding data are shown in Table 3.

Table 3. Adsorption isotherm models and corresponding parameters for BY1, BY2 and BG4 sorption by *R.. squarrosus* from single dye solutions at pH 4 obtained by using non-linear regression analysis.

Model	Dye	Q_{max} [μmol/g] d.w.	b [L/ μmol]	K [L/g]	$1/n$	R^2
Langmuir	BY1	310 ± 10	0.06 ± 0.01	-	-	0.906
	BY2	382 ± 11	0.026 ± 0.004	-	-	0.947
	BG4	354 ± 33	0.04 ± 0.02	-	-	0.789
Freundlich	BY1	-	-	99.7 ± 5.5	0.19 ± 0.01	0.983
	BY2	-	-	93.2 ± 7.7	0.21 ± 0.01	0.976
	BG4	-	-	59.7 ± 10.5	0.32 ± 0.04	0.945

This shows that the Freundlich isotherm is better fitted to the experimental data of BY1, BY2 and BG4 sorption by *R. squarrosus* in the concentration range studied and describes the process well and quantitatively. The Freundlich model provides a more realistic description of dye sorption by organic matter because it accounts for sorption to heterogeneous surfaces or surfaces supporting sites of varied affinity. However, we draw attention to some published papers stressing that the application of adsorption models is not able to explain the biosorption mechanisms of complex biological systems (FRAILE *et al.,* 2005; CORDERO *et al.,* 2004).

4. Conclusions

Sorption capability of biosorbent prepared from moss *R. squarrosus* was tested for cationic dyes BG4, BY1 and BY2 in batch experiments. The removal of dyes by moss biosorbent was found to be rapid at an initial stage and the equilibrium was reached within 1-2 hours. The kinetic analysis showed that biosorption process could be described well with the pseudo-*n*-order kinetic model. The respective reaction order for BG4, BY1 and BY2 biosorption was estimated as 2.3, 1.7 and 2.6. Equilibrium data were analysed using Langmuir and Freundlich isotherm models. The Freundlich isotherm was demonstrated to provide a very good correlation for the biosorption of BG4, BY1 and BY2 onto moss biosorbent.

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