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DOI: 10.2225/vol14-issue2-fulltext-8 *RESEARCH ARTICLE*

Biosorption kinetics of a direct azo dye Sirius Blue K-CFN by *Trametes versicolor*

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Abstract In this study, lyophilized *Trametes versicolor* biomass is used as a sorbent for biosorption of a textile dye, Sirius Blue K-CFN, from an aqueous solution. The batch sorption was studied with respect to dye concentration, adsorbent dose and equilibrium time. The effect of pH and temperature on dye uptake was also investigated and kinetic parameters were determined. Optimal initial pH (3.0), equilibrium time (2 hrs), initial dye concentration (100 mg l^{-1}) and biomass concentration (1.2 mg l^{-1}) were determined at 26ºC. The maximum biosorption capacity (q_{max}) of Sirius Blue K-CFN dye on lyophilized *T. versicolor* biomass is 62.62 mg/g. The kinetic and isotherm studies indicated that the biosorption process obeys to a pseudo-second order model and Langmuir isotherm model. In addition, the biosorption capacities of fungal biomass compared to other well known adsorbents such as activated carbon and Amberlite, fungal biomass biosorptions capacities were found to be more efficient.

Keywords: biosorbent, biosorption, direct dye, kinetics, Sirius Blue K-CFN, *Trametes versicolor*

INTRODUCTION

Approximately 700,000 tones and 10,000 different types of dyes and pigments are produced annually across the world and are extensively used in many industries including textile, leather, pulp, paper, food and plastics (Sadettin and Dönmez, 2006; Kiran et al. 2009; Aksakal and Ucun, 2010). Among all the chemical available dye classes, direct azo dyes are water-soluble molecules containing one or more ionic groups (most often sulfonic acid and/or amino groups) and are considered to be recalcitrant, non-biodegradable and persistent (Mohan et al. 2008; Akar et al. 2009). A significant proportion of these dyes is lost in manufacturing and processing units and enter the environment in wastewater. The colored dye effluents are considered to be highly toxic to the aquatic biota and affect the symbiotic process by disturbing the natural equilibrium through reducing photosynthetic activity and primary production due to the coloration of the water in streams (Aksu and Tezer, 2005).

Physico-chemical processes such as electro-coagulation, ozonation, photocatalysis, membrane filtration and adsorption have been employed for the treatment of dye containing wastewater (Patel and Suresh, 2008). Among these technlogies the adsorption method is widely used in the removal of synthetic dyes from the industrial effluent (Calvete et al. 2009; Liang et al. 2010). Through the great variety of adsorbents, activated carbon and ion exchange resins have been investigated for removing the dye from wastewater. Although they have a good adsorption capacity, their high costs limit the commercial application (unit cost of virgin material is about 1 US dolar/kg) as well as activated carbon can not be regenerated easily (thermal regeneration costs are about 1-2 US dolar/kg) (Russo et al. 2010). Therefore, new, low-cost and highly effective sorbents need to be investigated.

Biosorption process employing biopolymers (such as sawdust, wood chips, chitin/chitosan, starch, cyclodextrin and cross linked chitosan/cyclodextrin) and non-viable microbial (fungi, algae and bacteria) biomass has emerged as one of the powerful and attractive option since it is inexpensive,

effective and simple to operate and it also possesses good mechanical properties against abrasion (Crini, 2006; Kumari and Abraham, 2007; Maurya et al. 2006; Renganathan et al. 2006; Batzias and Sidiras, 2007).

Biosorption is becoming a promising alternative to replace or supplement the present dye removal processes from dye wastewaters (Fu and Viraraghavan, 2003). It involves binding of pollutants to the surface of cell membranes and/or cell walls through physical adsorption, electrostatic interaction, ion exchange, chelation and chemical precipitation (Aksu, 2005).

Bhole et al. (2004) studied the effect of different parameters on sorption of methyl violet, basic fuchsin and their mixture in an aqueous solution. They used dead biomass of *Aspergillus niger* and observed that fungal biomass was an efficient biosorbent. Perumal et al. (2007) investigated the rate and efficiency of decolorization of dyes like Blue CA, Black B133, and Corazol Violet SR by white rot fungal strains. They found that *Trametes hirsute* and *Pleurotus florida* showed the greatest extent of decolorization on nutrient salt media.

Although there are several dye biodegradation studies by *Trametes versicolor* (Bayramoglu and Arica, 2007; Yang et al. 2009; Pazarlioglu et al. 2010), in this study, biosorption of a textile dye, Sirius Blue K-CFN, onto lyophilizated *T. versicolor* pellets was investigated in batch system for the first time. Various parameters including effects of pH and temperature on dye uptake was examined and also kinetic and isotherm studies were conducted to evaluate the adsorption capacity of *T. versicolor* biomass.

MATERIALS AND METHODS

Preparation of fungal biomass

The white rot fungus *Trametes versicolor* FPRL 28A IMI (EGHAM SURVEY) was maintained on 2% (w/v) malt extract agar slants at 4ºC and the fungus was activated at 26ºC, for four days. The mycelium were harvested with sterile 0.9% NaCl solution and then inoculated into 100 ml 2% malt extract broth in 250 ml Erlenmeyer flasks at 26ºC and 175 rpm for 4 days. Cultivation was carried out in an orbital shaker. After the growth period of *T. versicolor*, pellets were autoclaved at 121ºC, during 15 min. The biomass separated from broth by filtration and washed with 0.9% NaCl solution. Fungal biomass was lyophilized and pounded in order to increase the surface area and used as adsorbent.

Preparation of dye solution

Sirius Blue K-CFN (synonym; Direct Blue 9, C.I. 24155, (λ_{max} = 583 nm), is a direct dye and its chemical structure is given in Figure 1.

Dye was dissolved in distilled water at a desired concentration. The pH of each solution was adjusted to the required value with 1M HCl and 1M NaOH solutions.

Batch biosorption studies

The biosorption of Sirius Blue K-CFN were investigated in a batch system at different pH values, temperature, biomass concentration and contact time to determinate the rate constant and extent of dye uptake by the biosorbent.

The effect of initial concentrations of the dye on the biosorption rate and capacity was determined in the range 5-500 mg l^{-1} dye concentration. The effects of the initial pH on the biosorption capacity were investigated in the pH range of 2.0-7.0. The effect of temperature on biosorption capacity was studied at five different temperatures, 7, 15, 26, 35 and 45ºC, and at initial pH 3.0. The effect of biosorbent mass on biosorption process was obtained by using different biomass concentrations (*i.e.*, 0.8, 1.0 and 1.2 gl^{-1}).

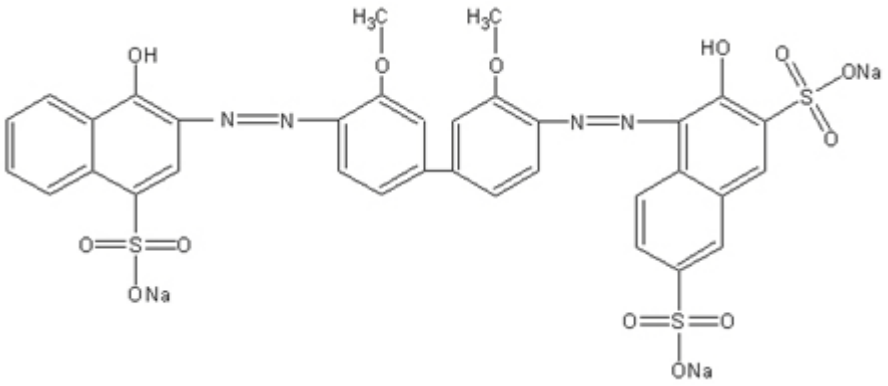

Fig. 1 Chemical structure of Sirius Blue K-CFN.

Typical biosorption experiment was conducted in Erlenmeyer flasks containing 1.2 g l^{-1} of biomass with 100 mg l^{-1} dye solution at 26ºC. The flasks were agitated on an orbital shaker at 150 rpm for 5 hrs to ensure equilibrium.

Before analyzing the remaining dye solution, biomass was removed from solution by centrifugation at 4000 rpm for 15 min and dye concentration of the supernatant was determined.

Analysis of dye

The concentration of unadsorbed Sirius Blue K-CFN was determined spectrophotometrically using a JascoUV/VIS spectrophotometer (λ_{max} = 583 nm).

Comparison with activated carbon and Amberlite XAD-7

In this study, to make a comparison with prepared biomass and the commercial adsorbents such as activated carbon, the most known sorbent, and Amberlite XAD-7, polymeric resin which is moderately polar, were also used for the dye biosorption. This comparative study was conducted by treating 100 mg l^{-1} of final dye solution with 1.2 g l^{-1} of the lyophilized *T. versicolor* biomass at the pH 3.0. All experiments were performed in triplicate and the mean was calculated.

RESULTS AND DISCUSSION

Effect of initial pH on dye biosorption

Textile dyes are complex organic compounds having different aromatic rings and functional groups; the latter have different ionization potentials at different pH and therefore their interaction with microbial biomass depends on the chemistry of a particular dye and the specific chemistry of the biosorbents (Yesilada et al. 2003). The ionic forms of the dye in solution and the surface electrical charge of the biomass depend on the solution pH (Maurya et al. 2006). Therefore, pH significantly influences the dye biosorption. The effect of the pH on dye biosorption is presented in Figure 2. As seen from the figure, the maximum dye biosorption was observed at pH 3.0 and as the pH increased, the biosorption decreased. Since its chemical structure is hidden, the pK_a values of the functional groups of dye molecule cannot be known. Therefore, it's estimated that at lower pH values there may be an electrostatic attractions between charged dye molecules and charged cell surface.

Effect of temperature on dye biosorption

The temperature of the biosorption medium affected the equilibrium uptake of Sirius Blue K-FCN dye on lyophilized *T. versicolor* biomass. The effect of temperature on the equilibrium biosorption capacity

was studied in the temperature range of 7-45ºC at an initial dye concentration of 100 mg l^{-1}. The optimum adsorption temperature was determined as 26ºC. As shown in Figure 3, the biosorption of the dye increased with increasing temperature up to 26ºC. The increase in biosorption could be due to increased surface activity and increased kinetic energy of the dye molecule (Aksu and Çağatay, 2006). The decrease in biosorption capacity of *T. versicolor*. above 26ºC may be attributed to the deactivation of the biosorbent surface or the destruction of some active sites on the biosorbent surface. As a result, the optimum temperature for Sirius Blue K-FCN biosorption was chosen as 26ºC for subsequent experiments.

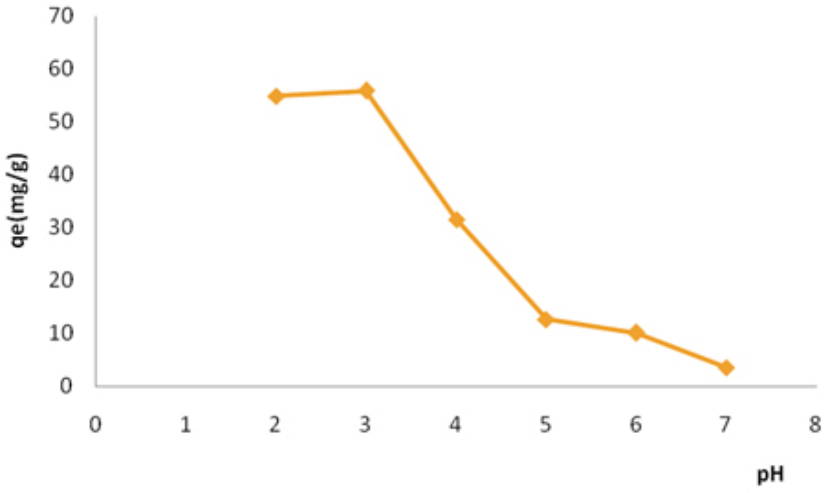

Fig. 2 The effect of initial pH on the equilibrium sorption capacity of *T. versicolor* (C_o 100 mg l^{-1}, *X* 1.2 g l^{-1}, temperature 26ºC, agitation rate 150 rpm).

Biosorption equilibrium time and isoterm models

Adsorption equilibrium is established when the amount of solute being adsorbed on to the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant.

In the present investigation the equilibrium data are analyzed using the Langmuir (Equation 1) and Freundlich isotherm expressions (Equation 2).

$$q_{eq} = \frac{Q^{o} C_{eq}}{1 + b C_{eq}}$$

[Equation 1]

$Q^{o}$and b can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq}.

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

[Equation 2]

Equation 2 can be linearized in logarithmic form and Freundlich constants can be determined. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.

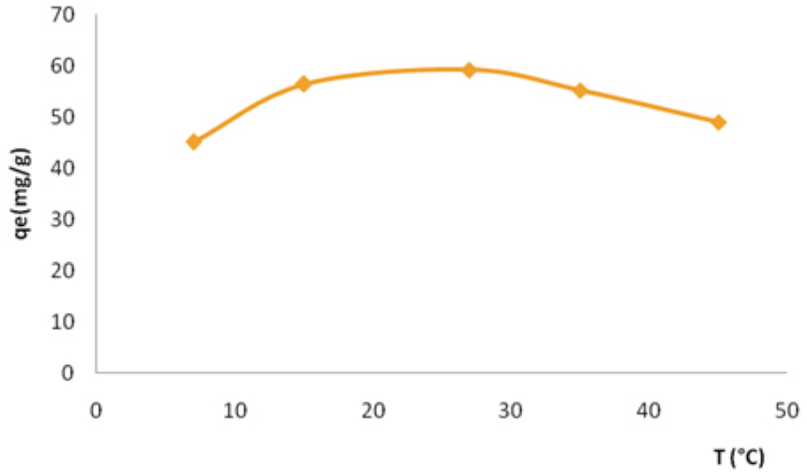

Fig. 3 The effect of temperature on the equilibrium dye sorption capacity of *T. versicolor* (C_o 100 mg l^{-1}, *X* 1.2 g l^{-1}, pH 3.0, agitation rate 150 rpm).

Figure 4 shows the effect of the time contact on Sirius Blue biosorption rate by *T. versicolor* biomass and Figure 5 shows Langmuir isotherms for adsorption of Sirius Blue. Based on the results, 120 min was taken on the equilibration time for Sirius Blue K-CFN in subsequent experiments. The great majority of biosorption was occured in one hour after first contact with dye and biomass. At the residual time biosorption was reached equilibrium within descending acceleration.

The Langmuir constants Q^o and b and the Freundlich constants n, K_f are shown at Table 1. As seen from the Table 1, a linear relation was observed among the plotted parameters with the R^2 value of 0,968 and 0,727 for Langmuir and Freundlich isotherms, respectively. According to these results, Langmuir sorption isotherm more accurately describe the biosorption of Sirius Blue K-CFN onto lyophilized *T. versicolor* biomass since correlation coefficient of Langmuir model is higher than Freundlich model.

Table 1. A comparison of the Freundlich and Langmuir adsorption constants obtained from the Freundlich and Langmuir adsorption isotherms of Sirius Blue K-FCN dye.

Langmuir constants			Freundlich constants		
Q^o(mg g^{-1})	b (1/mg)	R^2	K_F	N	R^2
200	3.6	0.968	3.57 x 10^{-7}	0.2287	0.727

Biosorption kinetics

Biosorption studies indicate that increasing biosorbent dose provides more surface area for binding the dye molecule. In order to find out the rate-controlling steps involved in the process of biosorption of Sirius Blue on to *T. versicolor* biomass, both pseudo first-order (Equation 3) and pseudo second-order kinetic models (Equation 4) were used due to fit the experimental data.

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

[Equation 3]

In most cases the first-order equation does not fit well for the whole range of contact time and is generally applicable over the initial 20-30 min of the sorption process (Liu and Liu, 2008).

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

[Equation 4]

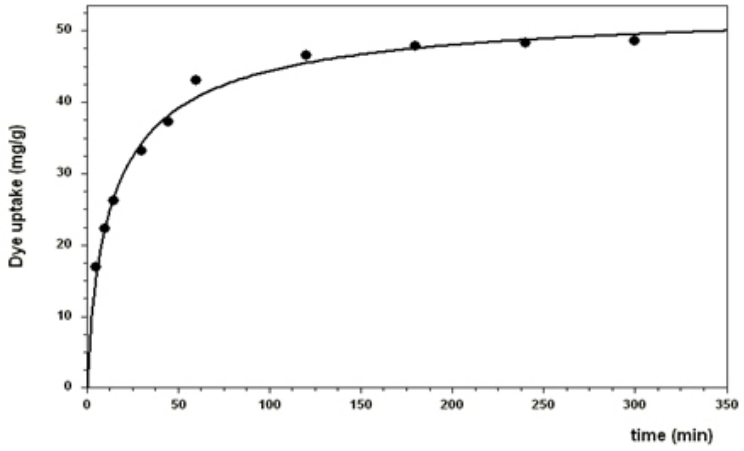

Fig. 4 Effect of the time contact on Sirius Blue (SB) biosorption rate by *T. versicolor* biomass.

The plots of $\log(q_{eq}-q)$ as a function of biosorption time are presented in Figure 6a and the rate constants $k_{1,ad}$, $k_{2,ad}$ and R^2 are presented at Table 2. The plots of (t/q_t) as a function of biosorption time are shown in Figure 6b. As seen from Table 2, the magnitude of the regression coeffcient R^2 for the pseudo-first-order model and pseudo-second-order model are 0.98 and 0.999, respectively. This implies that the Sirius Blue on to *T. versicolor* biomass does not follow first-order kinetic, but follow the pseudo-second-order kinetic models.

Comparison with activated carbon and Amberlite XAD-7

As shown in Figure 7, the biosorption capacity of lyophilized *T. versicolor* biomass for Sirius Blue K-FCN was 62.62 mg/g at the equilibrium time (2 hrs) whereas the biosorption capacity for activated carbon and Amberlite XAD-7 were 31.77 and 4.69 mg/g respectively. This comparative study indicates that lyophilized *T. versicolor* biomass is more effective than Amberlite XAD-7 and activated carbon for removing the dye from an aqueous solution under the same conditions.

Table 2. The rate constants of first order and second order adsorption kinetic models.

Pseudo-First order adsorption		Pseudo-Second order adsorption	
$K_{1,ad}$	R^2	$K_{2,ad}$	R^2
0.01935	0.98	0.00195	0.999

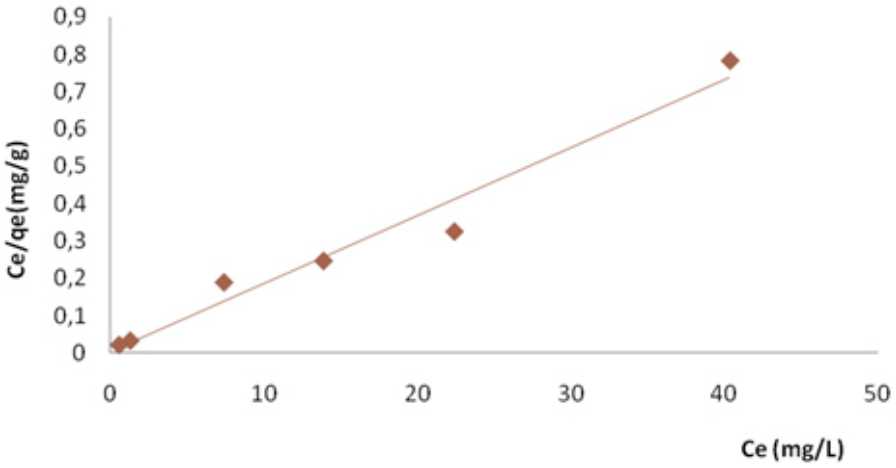

Fig. 5 Langmuir isoterms for adsorption of Sirius Blue K-CFN.

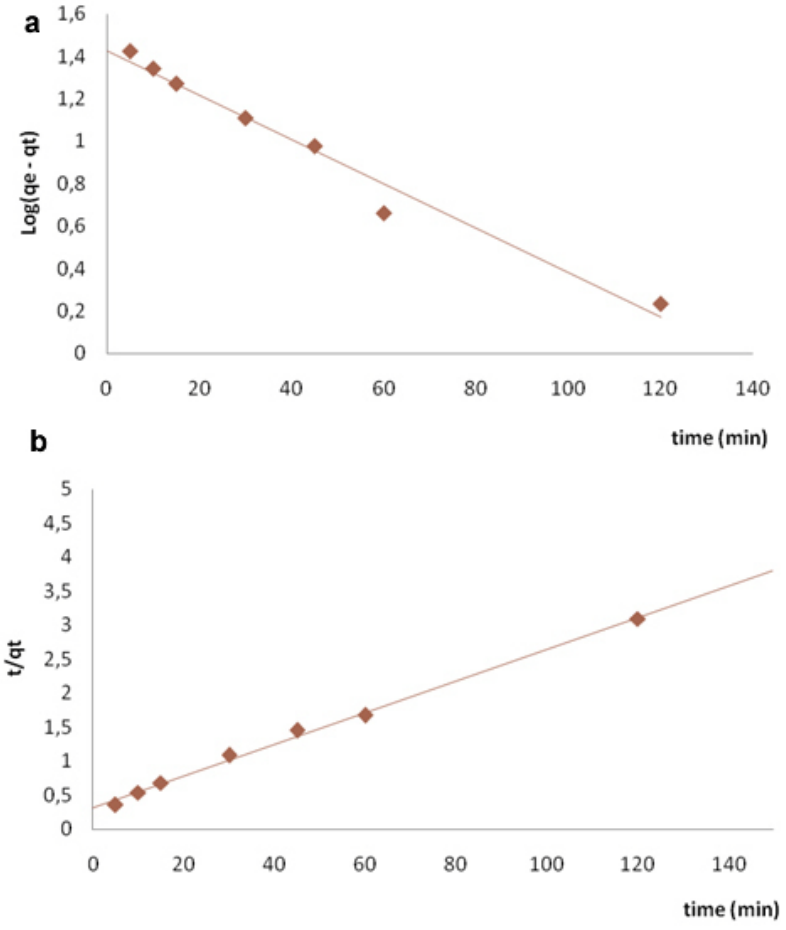

Fig. 6 Plots of sorption kinetic equations for SB sorption by *T. versicolor* biomass. (a) Pseudo first-order kinetic. (b) Pseudo second-order kinetic.

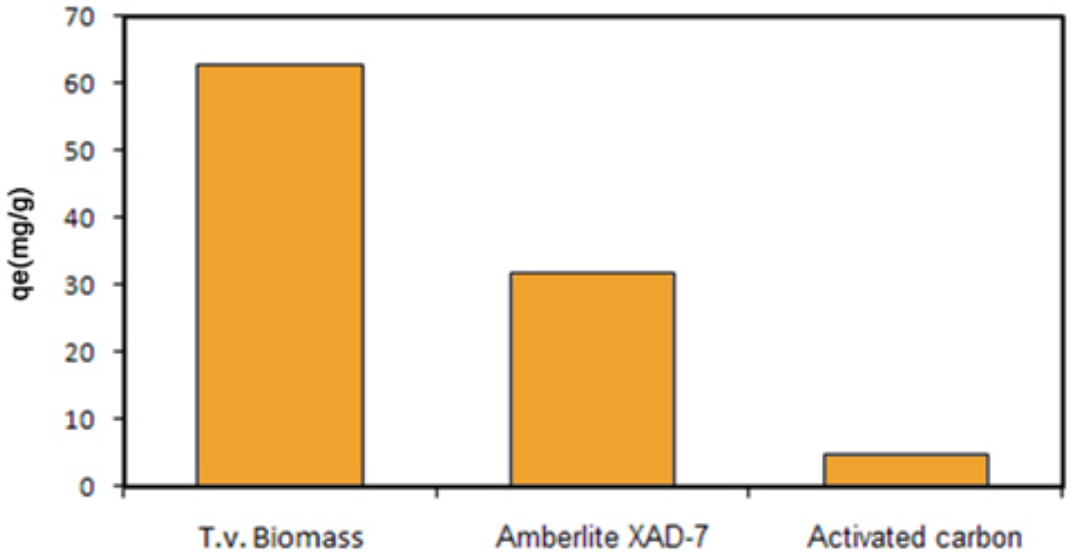

Fig. 7 Comparison of the sorbents via sorption capacity under the same conditions with *T. versicolor* biomass.

CONCLUDING REMARKS

Our previously biodegradation studies have demonstrated that some of the textile dyes could have removed from the effluent by *Trametes versicolor* due to biosorption in the short term (Pazarlioglu et al. 2010). Therefore, in this study, the biosorption of Sirius Blue K-CFN dye was investigated by using a lyophilized *T. versicolor* biomass as a biosorbent. The experimental data indicates that medium pH, temperature and biosorbent concentration play a significant role in biosorption of the dye.

Results obtained from this study showed that lyophilized *T. versicolor* was very effective as a biosorbent material for the removal of Sirius Blue K-CFN dye from aqueous solutions compared with other sorbents such as activated carbon and Amberlite XAD-7.

NOMENCLATURE

B	Langmuir adsorption constant (l mg^{-1})
C_{eq}	Residual dye concentration at equilibrium (mg l^{-1})
C_0	Initial dye concentration (mg l^{-1})
$k_{1,ad}$	First-order adsorption rate constant (min^{-1})
$k_{2,ad}$	Second-order adsorption rate constant (g mg^{-1} min^{-1})
K_F	Freundlich adsorption constant
N	Freundlich adsorption constant
Q	Adsorbed dye quantity per gram of biomass at any time (mg g^{-1})
q_{eq}	Adsorbed dye quantity per gram of biomass at equilibrium (mg g^{-1})
Q^o	Langmuir adsorption constant (mg g^{-1})
R^2	Correlation coefficient
X	Biomass concentration (g l^{-1})

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