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Biosorption of Acid Blue 15 using fresh water macroalga *Azolla filiculoides*: Batch and column studies

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Abstract

The ability of fresh water macroalga *Azolla filiculoides* to biosorb Acid Blue 15 from aqueous solution was investigated in batch and column studies. Batch experiments were conducted to study the effect of initial solution pH and dye concentration. Langmuir and Freundlich isotherm models were used to fit the equilibrium data. The maximum dye uptake of 116.28 mg/g was observed at pH 7, according to Langmuir model. In column experiments, effects of bed height (15–25 cm), flow rate (5–15 ml/min) and initial dye concentration (50–100 mg/l) on dye removal were studied. An increase in bed height and initial dye concentration favors the dye biosorption, while the minimum flow rate produced maximum dye biosorption. At optimum bed height (25 cm), flow rate (5 ml/min) and initial dye concentration (100 mg/l), *A. filiculoides* exhibited an uptake of 35.98 mg/g of Acid blue 15. The Bed Depth Service Time model and the Thomas model were used to analyze the column experimental data and the model parameters were evaluated.

Keywords: *Azolla filiculoides*; Effluent treatment; Acid dye; Packed column; Thomas model

1. Introduction

Many industries, such as textile, paper, plastics, food, cosmetics, use dyes in order to color the products. The discharge of dye house wastewater into the environment is aesthetically displeasuring, impedes light penetration, damages the quality of the receiving streams and may be toxic to food chain organisms and to aquatic life [1].

A number of processes, like flocculation [2], chemical coagulation [2], precipitation [2], ozonation [3] and adsorption [4] have been employed for the treatment of dye bearing wastewaters. Although the above said physical and/or chemical methods have been widely used, they possess inherent limitations such as high cost, formation of hazardous byproducts and intensive energy requirements [5]. Biological processes such as biosorption [6], bioaccumulation [7,8] and biodegradation [9,10] have been proposed as potential methods for the removal of dyes from textile wastewater. Among these, biosorption is more advantageous for water treatment in that dead organisms are not affected by toxic wastes as they do not require a continuous supply of nutrients and they can be regenerated and reused for many cycles [11].

Several investigators have reported the potential of different biomaterials to biosorb dye from aqueous solutions, including bacteria [12], fungi [13] and microalgae [14]. However, the application of these materials presents few problems when operated in continuous mode; among these the solid–liquid separation is a major constrain. Even though immobilization may solve this problem, chemical costs and mechanical strength should be taken into consideration [15].

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Nomenclature

b	Langmuir model constant
C	Effluent dye concentration (mg/l)
C_0	Initial dye concentration (mg/l)
C_b	Breakthrough dye concentration (mg/l)
C_f	Final or equilibrium dye concentration (mg/l)
dc/dt	Slope of breakthrough curve from t_b to t_e (mg/l h)
F	Flow rate (ml/min)
K_a	BDST model constant (l/mg h)
k_{Th}	Thomas model constant (l/mg h)
M	Biosorbent mass (g)
m_{ad}	Dye mass adsorbed (mg)
m_{total}	Total dye mass sent to the column (mg)
N_0	Sorption capacity of bed (mg/l)
Q	Dye uptake (mg/g)
Q_0	Maximum solid-phase concentration of the solute (mg/g)
Q_{max}	Maximum dye uptake (mg/g)
t	Time (h)
t_b	Breakthrough time (h)
t_e	Exhaustion time (h)
V	Solution volume (l)
V_{eff}	Effluent volume (l)
Z	Bed height (cm)
υ	Linear velocity (cm/h)

Macroalgae, on the other hand, usually possess good mechanical stability and rigidity, and have been widely used for heavy metal biosorption [16]. However, no research attention has been focused on utilization of macroalgae for dye removal. *Azolla filiculoides*, a fresh water blue green alga, has been shown to effectively bind chromium [17], zinc [18] and nickel [19] from aqueous solutions. It is commonly found in ditches, ponds, and slow moving streams and is capable of colonizing rapidly to form dense mats over water surfaces and thus imposing negative effects on the aquatic ecology [18]. Considering this, *A. filiculoides* was employed in the present study for the removal of Acid Blue 15 (AB15) in batch and column modes.

2. Materials and methods

2.1. *A. filiculoides*

A. filiculoides was collected from Milk producers union, Tirunelveli, India. It was then sun dried and crushed to particle sizes in the range of 1–2 mm. The crushed particles were then treated with 0.1 M HCl for 5 h followed by washing with distilled water and then kept for shaded dry. The resultant biomass was subsequently used in sorption experiments.

2.2. Batch experiments

Batch biosorption experiments were performed in a rotary shaker at 150 rpm using 250 ml Erlenmeyer flasks containing 0.2 g *Azolla* biomass in 50 ml of solution containing different AB15 concentration. After 12 h, the reaction mixture was centrifuged at 3000 rpm for 10 min. The dye content in the supernatant was determined using UV-Spectrophotometer (Hitachi, Japan) at λ_{max} 564 nm. The amount of dye biosorbed was calculated from the difference between the dye quantity added to the biomass and the dye content of the supernatant using the following equation:

$$Q=(C_0-C_f)\times\left(\frac{V}{M}\right) \tag{1}$$

where Q is the dye uptake (mg/g); C_0 and C_f are the initial and equilibrium dye concentrations in the solution (mg/l), respectively; V is the solution volume (l); and M is the mass of biosorbent (g).

The Langmuir sorption model was chosen for the estimation of maximum AB15 biosorption by the biosorbent. The Langmuir isotherm can be expressed as:

$$Q=\frac{Q_{max}bC_f}{1+bC_f} \tag{2}$$

where Q_{max} is the maximum dye uptake (mg/g) and b is the Langmuir equilibrium constant (l/mg). For fitting the experimental data, the Langmuir model was linearized as follows:

$$\frac{1}{Q}=\frac{1}{Q_{max}}+\frac{1}{bQ_{max}C_f} \tag{3}$$

The Freundlich model is represented by the equation:

$$Q=KC_f^{1/n} \tag{4}$$

where K and n are constants.

2.3. Column experiments

Continuous flow sorption experiments were conducted in a glass column (2 cm internal diameter and 35 cm height). At the top of the column, an adjustable plunger was attached with a 0.5 mm stainless sieve. At the bottom of the column, a 0.5 mm stainless sieve was attached followed by glass wool. A 2 cm high layer of glass beads (1.5 mm in diameter) was placed at the