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ScienceDirect
Journal of Hazardous Materials 153 (2008) 478–486
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Competition of Reactive red 4, Reactive orange 16 and Basic blue 3 during biosorption of Reactive blue 4 by polysulfone-immobilized *Corynebacterium glutamicum*

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Received 3 June 2007; received in revised form 28 August 2007; accepted 28 August 2007
Available online 1 September 2007

Abstract

Competition of Reactive red 4 (RR4), Reactive orange 16 (RO16) and Basic blue 3 (BB3) during biosorption of Reactive blue 4 (RB4) by polysulfone-immobilized protonated *Corynebacterium glutamicum* (PIPC) was investigated in batch and column mode of operations. Through potentiometric titrations, and with the aid of proton-binding model, carboxyl, phosphonate and amine were identified as functional groups of PIPC, with apparent pK_a values of 3.47 ± 0.05, 7.08 ± 0.07 and 9.90 ± 0.05 mmol/g, respectively. Since reactive dyes release dye anions ($ROSO_3^-$) in solutions, the positively charged amine groups were responsible for biosorption. PIPC favored biosorption at pH 3 when RB4 was studied/used as single-solute; while the presence of RR4 and RO16 severely affected the RB4 biosorption. When present as a single-solute, PIPC recorded 184.5 mg RB4/g; while PIPC exhibited 126.9, 120.9 and 169.6 mg RB4/g in the presence of RR4, RO16 and BB3, respectively. In general, the accessibility of amine group depends on the molecular size, number of sulfonate groups and reactivity of each reactive dye. Single and multicomponent Freundlich equations successfully described the biosorption isotherms. With 0.1 M NaOH, it is possible to reuse PIPC for RB4 biosorption in 10 repeated cycles. Column experiments in an up-flow packed column coincided with batch results, that is PIPC showed strong preference towards highly reactive and relatively small RB4 anions; however, the presence of competing dyes hinder the RB4 column biosorption performance.

Keywords: Multicomponent; Isotherm; Kinetics; Immobilization; Packed column

1. Introduction

In recent years, fermentation wastes are portrayed as potential sorbents for dye molecules [1,2]. One such waste is *Corynebacterium glutamicum*, generated in lysine fermentation industries. *C. glutamicum*, a Gram-positive organism, belonging to the order of Actinomycetales, is widely used for the biotechnological production of amino acids. Currently, the production of amino acids in fermentation processes with *C. glutamicum* amounts to 1,500,000 t of L-glutamate and 550,000 t of L-lysine per year [3]. Hence, the wastes generated after the process are high; however, they are not often recycled as animal feed or as organic manure but are incinerated or dumped at sea [1].

Our previous studies identified *C. glutamicum* as an excellent biosorbent for reactive dyes [4–6]. However, the free biomass posed problems when biosorbent reuse was attempted. It is well known that microorganisms such as bacteria and fungi have poor mechanical strength and little rigidity [5,7]. These factors limit their application in real conditions despite their high dye binding abilities. Immobilization is the possible and practical method for successful reuse of biosorbent in multiple cycles. The choice of immobilization matrix is a key factor in environmental application of immobilized biomass and it determines the mechanical strength and chemical resistance of the final biosorbent particle [8].

Although most industrial effluents contain several dye components; little attention has been given to multicomponent adsorption systems [9]. Many problems are to be solved for multicomponent biosorption, the important being the evaluation of competition between solutes in occupying the limited binding sites. Multicomponent dye adsorption has been the subject of

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doi:10.1016/j.jhazmat.2007.08.079

Nomenclature

b	Langmuir equilibrium constant (L/mg)
b_j	moles of functional group per gram of biomass (mmol/g)
BB3	Basic blue 3
C_1	equilibrium or final concentration of component 1 (mg/L)
C_2	equilibrium or final concentration of component 2 (mg/L)
C_A	concentration of component A
C_B	concentration of component B
C_f	equilibrium or final dye concentration (mg/L)
d_1	optical density or absorbance at λ_1
d_2	optical density or absorbance at λ_2
dc/dt	slope of the breakthrough curve from breakthrough to exhaustion time (mg/(L h))
k_i	intraparticle diffusion constant (mg/(g min$^{0.5}$))
K_{A1}	calibration constant for component A at wavelength λ_1
K_{A2}	calibration constant for component A at wavelength λ_2
K_{B1}	calibration constant for component B at wavelength λ_1
K_{B2}	calibration constant for component B at wavelength λ_2
K_F	Freundlich constant ((mg/g)(L/mg)$^{-1/n}$)
K_j	equilibrium constant (mol/L)
M	biosorbent mass (g)
n	Freundlich model exponent
N	number of data points
p	number of parameters
PIPC	polysulfone-immobilized protonated *Corynebacterium glutamicum*
q_{eq}	equilibrium dye uptake (mg/g)
$q_{eq,cal}$	calculated equilibrium dye uptake (mg/g)
$q_{eq,meas}$	measured equilibrium dye uptake (mg/g)
$(q_{eq})_i^j$	amount of solute (i) sorbed per unit weight in the presence of solute, j (mg/g)
q_{max}	maximum monolayer coverage capacity of the biosorbent (mg/g)
q_t	uptake at any time (mg/g)
Q	column uptake capacity (mg/g)
R^2	correlation coefficient
RB4	Reactive blue 4
RO16	Reactive orange 16
RR4	Reactive red 4
t	time (h)
t_b	breakthrough time (h)
t_e	exhaustion time (h)
X	biomass dosage (g/L)

Greek symbols

β	selectivity factor
ε	average error (%)
η_1	interaction factor for first dye
η_2	interaction factor for second dye
θ_{ij}	competitive coefficient
λ_1	wavelength at which maximum absorbance of component A obtained (nm)
λ_2	wavelength at which maximum absorbance of component B obtained (nm)

few studies [10,11]; however, the mechanism and competition effect has hardly been understood. The evaluation and predication of multicomponent sorption equilibrium are tedious and they are still most challenging problems in adsorption field.

As studies on multi-dye biosorption in batch mode are relatively limited in number [9], the behavior of multi-dye in column biosorption has not even been attempted. In columns, treating multi-dye mixtures may result in irregular concentration profile and overshoot of particular toxicant; this is because of dye molecules competition over the biosorbent.

Motivated by all these aspects, this study employed polysulfone-immobilized protonated *C. glutamicum* biomass for the biosorption of Reactive blue 4. Multicomponent biosorption has been attempted by selecting three possible binary mixtures (RB4 + RR4, RB4 + RO16 and RB4 + BB3). In addition, the interference of other reactive dyes and basic dye on RB4 biosorption in an up-flow packed column was also attempted.

2. Experimental

2.1. Preparation of biosorbent

The fermentation wastes (*C. glutamicum* biomass) were obtained in the form of dried powder from a lysine fermentation industry (BASF-Korea, Kunsan, Korea). The biomass were grounded and sieved to obtain particle sizes in the range of 0.1–0.25 mm. The biomass (10 g/L) was then protonated with 0.1 M HNO_3 for 1 h at constant temperature (25 °C). After this pretreatment, the biomass was washed with deionized water, and dried in an oven at 60 °C for 12 h.

A 9% (w/v) solution of polysulfone was prepared in *N*,*N*-dimethyl formamide (DMF) solution. After stirring the above mixture for 10 h, the protonated biomass (14%) were mixed with the polysulfone slurry and the resulted slurry was dripped in deionized water, where beads were formed by phase inversion process. Beads were then washed with deionized water, put into a water bath for 18 h in order to remove all residual DMF. The resultant polysulfone-immobilized protonated *C. glutamicum* (PIPC) beads (1–3 mm diameter) were then stored at 4 °C.

2.2. Dyes and analysis

All dyes, used in this study, were purchased from Sigma–Aldrich Korea Ltd. (Yongin, Korea). Dye concentrations were analyzed using a spectrophotometer (UV-2450, Shimadzu,