Ecotoxicology and Environmental Safety 139 (2017) 219–227

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Application of experimental design and derivative spectrophotometry methods in optimization and analysis of biosorption of binary mixtures of basic dyes from aqueous solutions

Arash Asfaram[a], Mehrorang Ghaedi[a,*], Gholam Reza Ghezelbash[b,*], Francesco Pepe[c]

[a] Chemistry Department, Yasouj University, Yasouj 75918-74831, Iran
[b] Biology Department, Faculty of Science, Shahid Chamran University of Ahvaz, 61357-831351, Iran
[c] Dipartimento di Ingegneria, Università del Sannio, Piazza Roma 21, 82100 Benevento, Italy

ARTICLE INFO

Keywords:
Biosorption
Binary solutions
Crystal violet
Malachite green
Response surface methodology
Yarrowia lipolytica ISF7

ABSTRACT

Simultaneous biosorption of malachite green (MG) and crystal violet (CV) on biosorbent *Yarrowia lipolytica* ISF7 was studied. An appropriate derivative spectrophotometry technique was used to evaluate the concentration of each dye in binary solutions, despite significant interferences in visible light absorbances. The effects of pH, temperature, growth time, initial MG and CV concentration in batch experiments were assessed using Design of Experiment (DOE) according to central composite second order response surface methodology (RSM). The analysis showed that the greatest biosorption efficiency (> 99% for both dyes) can be obtained at pH 7.0, $T = 28$ °C, 24 h mixing and 20 mg L^{-1} initial concentrations for both MG and CV dyes. The quadratic constructed equation ability for fitting experimental data is judged based on criterions like R^2 values, significant *p* and lack-of-fit *value* strongly confirm its high adequacy and applicability for prediction of revel behavior of the system under study. The proposed model showed very high correlation coefficients ($R^2 = 0.9997$ for CV and $R^2 = 0.9989$ for MG), while supported by closeness of predicted and experimental value. A kinetic analysis was carried out, showing that for both dyes a pseudo-second order kinetic model adequately describes the available data. The Langmuir isotherm model in single and binary components has better performance for description of dyes biosorption with maximum monolayer biosorption capacity of 59.4 and 62.7 mg g^{-1} in single component and 46.4 and 50.0 mg g^{-1} for CV and MB in binary components, respectively. The surface structure of biosorbents and the possible biosorbents–dyes interactions between were also evaluated by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The values of thermodynamic parameters including ΔG° and ΔH° strongly confirm which method is spontaneous and endothermic.

1. Introduction

Water quality remarkably affects the quality of human life and environment and worldwide more and more attention is paid to hazardous pollutants released to rivers, lakes and oceans (Liu et al., 2015). Among pollutants, a significant source of concern derives from synthetic dyes, which are used in many industrial applications, among which paper making and textile industries, and are sometimes toxic to living organisms (Wang et al., 2008; Kousha et al., 2013). In particular, cationic dyes are known to have both a higher toxicity and a greater resistance to degradation, thus encouraging the researchers to look for efficient removal techniques in order to reduce their concentrations in effluent water to very low values (Witek-Krowiak, 2011).

Malachite green (MG) and crystal violet (CV), because of their extensive applications, are released into the environment in very high volumes (Bekçi et al., 2009). On the other hand, CV is known to be toxic toward mammalian cells, since it has mutagenic properties, is a mitotic poison and is candidate as a carcinogenic agent (Ali and Muhammad, 2008); similarly, MG has highly cytotoxic properties against mammalian cells (Godbole and Sawant, 2006), for these reasons, the removal of both dyes is important in treatment of contaminated wastewater.

Various methods such as biosorption, adsorption, coagulation/flocculation, chemical oxidation, membrane filtration, ozone treatment and photocatalysis have been considered for the removal of these pollutants. Among these, biosorption appears quite interesting both from an economical and an environmental point of view, in light of its performances and reduced environmental impact (El Haddad et al., 2012; Deniz, 2013). This method is based on the use of microorganisms

* Corresponding authors.
E-mail addresses: m_ghaedi@mail.yu.ac.ir, m_ghaedi@yahoo.com (M. Ghaedi), gh.r.ghezelbash@gmail.com (G.R. Ghezelbash).

http://dx.doi.org/10.1016/j.ecoenv.2017.01.043
Received 17 September 2016; Received in revised form 21 January 2017; Accepted 24 January 2017
Available online 31 January 2017
0147-6513/

or other biomass (bone (El Haddad et al., 2012, 2013), persea species (Regti et al., 2017), neem sawdust (Khattri and Singh, 2009), orange peel (Annadurai et al., 2002), *brown macroalga Stoechospermum* (Daneshvar et al., 2012), algae, eggshell (Slimani et al., 2014), mussel shells (El Haddad et al., 2014), hazelnut shell (Dogan et al., 2008) and some agricultural wastes (Reddy et al., 2012; Senthil Kumar et al., 2014), etc.) as adsorbents. However, the adsorption capacities of the above-mentioned adsorbents are not very high. In order to improve the efficiency of the adsorption processes, it is necessary to develop cheaper and easily available adsorbents with high adsorption capacities and has the advantages of allowing high removal efficiencies even when diluted solutions have to be treated, and of having a reduced environmental impact, since the active biomass can usually be easily disposed of. *Yarrowia lipolytica*, belonging to dimorphic, non-pathogenic, ascomycetous yeast category, has distinct physiological and biochemical properties that makes it a suitable candidate for biosorption in environmental applications (Zinjarde et al., 2014) and absence of any application of under study biosorbent for dyes removal especially on binary mixture encourage us to apply this material for simultaneous dyes biosorption.

In the present paper simultaneous biosorption of MG and CV by *Yarrowia lipolytica* was investigated. In particular the role by a number of experimental parameters, viz. pH, temperature, growth time, initial MG and CV concentration was assessed by central composite design (CCD), using response surface methodology (RSM), and the optimal conditions for removal of these pollutants were individuated. Furthermore, a kinetic, isotherm and thermodynamic analysis of the process is presented, allowing a significant insight into the mechanisms of biosorption.

2. Materials, instrumentation and methods

2.1. Biosorbent preparation

Yarrowia lipolytica ISF7 isolated from wastewater and registered at NCBI Genebank with accession number JX010454.1 was used. The selected biosorbent was streaked on Yeast–Peptone–Glucose (YPG: 1% yeast extract, 2% peptone, 1% glucose) agar and incubated overnight at 30 °C. Then, a single colony was inoculated into a 100 mL Erlenmeyer flask containing 25 mL of YPG broth (pH: 7.0) and incubated in a shaker (160 rpm) for 24 h at 30 °C, and then centrifuged for 10 min (Asfaram et al., 2016).

2.2. Dyes and chemicals

MG (CAS number: 569-64-2, color index number: 42000, molecular weight: 364.91 g mol^{-1}, empirical formula: $C_{23}H_{25}ClN_2$, λ_{max}: 616 nm) and CV (CAS number: 548-62-9, color index number: 42555, molecular weight: 407.98 g mol^{-1}, empirical formula: $C_{25}H_{30}N_3Cl$, λ_{max}: 580 nm) were obtained from Sigma Aldrich Company (St. Louis, MO, USA, www.sigmaaldrich.com). Prior to use, 50 mg of each dye was dissolved in 500 mL of water to obtain a 100 mg L^{-1} stock solution of each dye). Yeast extract, peptone, glucose, and agar were similarly obtained from Sigma-Aldrich. NaOH and HCl solutions, which were used to adjust pH were necessary, were obtained from Merck (Darmstadt, Germany).

2.3. Instrumentation

The pH measurements were carried out by a digital pH meter (Ino Lab pH 730, Germany). The absorbance spectra for dyes were recorded in the range of 300–800 nm using a Perkin Elmer Lambda 25 spectrophotometer. A bench centrifuge (HERMLE 2206 A, Germany) was used to accelerate the phase separation. The samples were agitated in an incubator shaker (Labcon, FSIM-SPO16, United States) at 160 rpm. The morphology of *Y. lipolytica* ISF7 was observed by scanning electron microscopy (Hitachi S-4160, Japan). The FT-IR spectra of *Y. lipolytica* ISF7 before and after biosorption of dyes were obtained between 400 and 4000 cm^{-1} using a Perkin-Elmer RX-IFTIR Series FT-IR system. Response surface analysis was performed with the Design-Expert® Software (Version 7.0, Stat-Ease). The significances of all terms in the polynomial equation were analyzed statistically by computing the *F*-value at (p) of 0.05.

2.4. Batch mode biosorption experiments

Batch biosorption experiments were carried out by mixing 0.04g of biomass deriving from centrifugation (see 2.1 above) with 25 mL of solution containing 5–25 mg L^{-1} of MG and/or CV. The mixture was stirred with shaking rate of 160 rpm at various temperature (15–35 °C) and contact times (0–24 h: the maximum contact time was chosen since preliminary experiments showed that it was largely sufficient to attain equilibrium: see Section 3.1 below). After each experiment, the material was centrifuged at 3000 rpm for 10 min, and the supernatant was analyzed by UV/visible spectrophotometer for non-biosorbed MG and CV. The sediment phase (yeast) was centrifuged again, and the remaining biomass was dried at 65 °C for 24 h.

In binary solutions, the first-order derivative of absorbance with respect to wavelength was used to find the optimal wavelength for each dye without significant interference correspond to other species (see Section 3.1), and the concentration of each dye at time t was calculated from the calibration graphs obtained at similar concentrations. The following equation has been utilized for determining the removal efficiency of dye "*D*" (R_D, with $D = MD$ or CV):

$$R_D\% = \frac{C_{0,D} - C_{t,D}}{C_{0,D}} \times 100\% \qquad D:\ MG\ or\ CV \tag{1}$$

where $C_{O,D}$ (mg L^{-1}) and $C_{t,D}$ (mg L^{-1}) are the initial concentration of dye "*D*" and its concentration at time t, respectively.

The biosorbed amount of dye "*D*" at equilibrium $q_{eq,D}$ (mg g^{-1}) was computed as follows:

$$q_{eq,D} = \frac{C_{0,D} - C_{eq,D}}{X_{0,D}} \qquad D: MG\ or\ CV \tag{2}$$

where $C_{eq,D}$ (mg L^{-1}) is the concentration at equilibrium of dye "*D*" and X_O is the biosorbent concentration (g L^{-1}).

2.5. Design of experiments study of operational parameters

Response surface methodology (RSM) is a technique often used for simultaneous optimization of variables and estimation of their interaction, with a synthetic approach which requires a reduced number of experiments (Basiri Parsa et al., 2013). The most popular way of designing experiments in RSM is central composite design (CCD). In the present study, CCD was used to find quadratic equation and model based on testing lack of fit (Dasgupta et al., 2015).

CCD was applied to evaluate the role that five variables, viz. pH (5.0–9.0, X_1), temperature (15–35 °C, X_2), growth time (0–24 h, X_3), initial MG and CV concentrations (5–25 mg L^{-1}, X_4 and X_5 respectively) play on MG and CV removal efficiency (R_D, with $D = MD$ or CV). Five coded levels, denominated -2, -1, 0, $+1$ and $+2$ respectively, were considered for each variable (see Table 1), and accordingly 32 experiments were carried out. Following RSM, a second order polynomial relationship was assumed to exist between the removal efficiency (R) and the five variables mentioned above (Dil et al., 2016), *i.e.*:

$$R = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j \tag{3}$$

where k is the number of variables (here $k = 5$), X_i represents each variable, and β_O, β_i, β_{ii} and β_{ij} are zero–, first– and second–order coefficients of the polynomial equation.

Analysis of variance (ANOVA) and the subsequent results viz.