Journal of Environmental Management 152 (2015) 99–108

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Kinetic, isotherm and thermodynamic studies of amaranth dye biosorption from aqueous solution onto water hyacinth leaves

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ARTICLE INFO

Article history:
Received 17 June 2014
Received in revised form
16 November 2014
Accepted 17 January 2015
Available online

Keywords:
Amaranth dye
Biosorption
Isotherm
Kinetics
Thermodynamics
Water hyacinth leaves

ABSTRACT

The present study explored the kinetics, equilibrium and thermodynamics of amaranth (acid red 27) anionic dye (AD) biosorption to water hyacinth leaves (LEC). The effect of LEC particle size, contact time, solution pH, initial AD concentration and temperature on AD biosorption was studied in batch experiments. AD biosorption increased with rising contact time and initial AD concentration, and with decreasing LEC particle size and solution pH. Pseudo-second-order chemical reaction kinetics provided the best correlation for the experimental data. Isotherm studies showed that the biosorption of AD onto LEC closely follows the Langmuir isotherm, with a maximum biosorption capacity of about 70 mg g^{-1}. The thermodynamic parameters confirm that AD biosorption by LEC is non-spontaneous and endothermic in nature. Results indicate that LEC is a strong biosorbent capable of effective detoxification of AD-laden wastewaters.

1. Introduction

Amaranth dye (IUPAC name: trisodium (4E)-3-oxo-4-[(4-sulfonato-1-naphthyl)hydrazono]naphthalene-2,7-disulfonate), also known as FD&C Red No. 2, E123, C.I. Food Red 9, Azorubin S and C.I. 16185, is a synthetic azo dye, extensively used in foods and drinks such as wines, soft drinks, cake mixes, cereals, salad dressings, sweets, caviar and coffee, in order to make them more appealing (Zhang and Ma, 2013). It is also widely used for coloring textiles, leather, paper, wood and phenol-formaldehyde resins and during these processes excess dye enters into the wastewater (Anjaneya et al., 2013; Guerrero-Coronilla, 2013). If discharged into surface waters without prior treatment, the dye-colored wastewaters affect aesthetics and water transparency, and may also block the penetration of sunlight and oxygen, which is harmful to aquatic life (Anjaneya et al., 2013). In addition, amaranth dye (AD) can cause adverse health effects such as tumors, allergy, respiratory problems, birth defects, cytostaticity, citotoxicity, mutagenicity, genotoxicity and carcinogenicity (Gupta et al., 2012; Zhang and Ma, 2013; Zhang et al., 2013).

The amaranth anionic dye (AD) is highly soluble and stable in water and thus difficult to remove from industrial wastewaters by common chemical and physical treatment methods; in addition, these technologies are not significantly effective or economically advantageous (Gong et al., 2005; Gupta et al., 2012). Furthermore, treatment of azo dyes-containing waters with aerobic microbes does not successfully degrade most dyes, and anaerobic microbial degradation produces by-products such as aromatic amines, which are more toxic, mutagenic and carcinogenic than the dyes themselves (Ahmad and Kumar, 2011). In this context, biosorption may be a desirable alternative because its operation is simple, low cost, reliable and effective and does not produce by-products.

The water hyacinth (*Eichhornia crassipes*) is a free-floating aquatic plant of worldwide distribution, which has become an acute, persistent and expensive environmental problem due to its extremely rapid proliferation and congested growth (Ibrahim et al., 2012; Malik, 2007). In addition, water hyacinth rapidly depletes nutrients and oxygen from water bodies, interferes with navigation, fishing, shipping, recreation, irrigation and hydropower generation, favors breeding zones for disease-causing insects, quickens evapotranspiration and reduces biodiversity, which, in turn, lead to adverse effects on the environment, flora, fauna, human health and economic development (Malik, 2007). Nevertheless, the water hyacinth is among the most productive plants on Earth (Ibrahim et al., 2012) and can therefore be used as a valuable biomass resource for

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http://dx.doi.org/10.1016/j.jenvman.2015.01.026
0301-4797/

a variety of useful applications.

A potentially beneficial use for water hyacinth biomass is precisely as biosorbent for the removal of toxic pollutants from aqueous solutions. In this context, a recent study showed that water hyacinth leaves (LEC) have great potential as a simple and inexpensive method to remove AD from aqueous solutions. Particularly, the leaves exhibit much better performance for AD biosorption than any other of the plant's vegetative organs or the entire aquatic plant. Furthermore, certain *E. crassipes* proteins play a dominant role in the AD biosorption process (Guerrero-Coronilla, 2013).

The present work aimed to investigate the influence of several environmental factors such as biosorbent particle size, solution pH, shaking contact time, initial AD concentration and temperature on AD biosorption from aqueous solutions by LEC. Furthermore, the biosorption mechanism of AD onto LEC was evaluated in terms of kinetics, equilibrium and thermodynamics. Additionally, the best AD desorption solutions were determined, and a study of AD desorption kinetics was undertaken.

2. Materials and methods

2.1. Biosorbent preparation

Fresh *E. crassipes* plants were collected from the Xochimilco channels in Mexico City, and thoroughly washed with distilled deionized water to remove dirt. The leaves were cut, separated from the plants and then oven-dried at 60 °C until dry weight was constant. Afterwards, they were milled using a Glen Creston mill, and the resulting particles were screened using ASTM standard sieves to obtain fractions of different particle size. The sieved fractions were stored in airtight plastic containers until used.

2.2. Amaranth anionic dye (AD) solutions for biosorption experiments

AD solutions were obtained by diluting 2 g L^{-1} of stock AD solution, which had been prepared by dissolving a weighed amount of AD (Sigma–Aldrich Chemicals) in distilled deionized water. In this work, initial AD concentrations were varied from 10 to 500 mg L^{-1} and the pH of each AD solution was adjusted to desired value with 0.1 M HCl or NaOH solutions.

2.3. Kinetic and equilibrium AD biosorption studies and analytical method

Batch kinetic studies were performed in order to investigate the effect of LEC particle size, solution pH, initial AD concentration, shaking contact time and temperature on AD biosorption from aqueous solutions by LEC. All experiments were conducted in 500 mL Erlenmeyer flasks containing 120 mL AD solution of known concentration and 1 g (dry weight) L^{-1} of LEC. Care was taken to maintain constant pH in each test solution (±0.1 unit) throughout the course of the experiments by periodic checking and adjusting with 0.1 M HCl or NaOH solutions when necessary. Flasks were agitated in an orbital shaker (Cole Parmer Inc.) at 140 rpm constant shaking speed.

The effect of LEC particle size on AD biosorption was assessed in AD solution at 50 mg L^{-1} initial dye concentration, pH 2.0, with different particle sizes ranging from 0.15–0.18 mm to 1.68–2.0 mm, at 18 °C. In order to explore the influence of solution pH levels on kinetic performance, different pH values ranging from 1.5 to 7.0 were assayed in AD solution at 50 mg L^{-1} initial dye concentration, at 18 °C. The effect of initial AD concentration on dye biosorption was studied by varying the initial dye concentration in the range from 10 to 500 mg L^{-1}. To investigate the influence of temperature

Table 1
Kinetic, isotherm and thermodynamic models.

Kinetic model	Equation	Nomenclature	Reference
Pseudo-first-order	$\ln(q_{e1}-q_t) = \ln q_{e1} - k_1 t$	q_{e1}, biosorption capacity (mg g^{-1}) at equilibrium; q_t, biosorption capacity (mg g^{-1}) at time t (h); k_1, rate constant of the model (h^{-1})	Ho, 2006.
Pseudo-second-order	$q_t = \frac{q_{e2}^2 k_2 t}{1-q_{e2}k_2 t}$	q_{e2}, biosorption capacity (mg g^{-1}) at equilibrium; k_2, rate constant of the model (g mg^{-1} h^{-1})	Ho, 2006.
Elovich	$q_t = \frac{1}{B_E}\ln(A_E B_E) + \frac{1}{B_E}\ln t$	A_E, initial biosorption rate of Elovich model (mg g^{-1} h^{-1}); B_E, desorption constant of Elovich model (g mg^{-1})	Flores-Garnica et al., 2013.
Fractional power	$q_t = K_{FP} t^V$	K_{FP}, fractional power model constant (mg g^{-1}); V, fractional power model constant (h^{-1})	Flores-Garnica et al., 2013.
Isotherm models			
Two-parameter models	$q_e = \frac{q_m b_L c_e}{1+b_L c_e}$		
Langmuir	$R_L = \frac{1}{1+b_L c_0}$; $\theta = \frac{b_L c_O}{1+b_L c_O}$	q_e, biosorption capacity (mg g^{-1}) at equilibrium; c_e, liquid phase concentration of adsorbate at equilibrium (mg L^{-1}); q_m, maximum biosorption capacity (mg g^{-1}); b_L, Langmuir constant (L mg^{-1}); R_L, Hall separation factor; c_o, initial adsorbate concentration (mg L^{-1}); θ, surface coverage	Febrianto et al., 2009.
Freundlich	$q_e = K_F\, c_e^{1/n_F}$	K_F, Freundlich model constant [(mg g^{-1}) (mg L^{-1})$^{-1/nF}$]; n_F, heterogeneity factor	Febrianto et al., 2009.
Temkin	$q_e = \frac{RT}{B_T}\ln(A_T c_e)$	R, ideal gas constant (8.314 J mol^{-1} K^{-1}); T, absolute temperature (K); B_T, constant related to heat of sorption (J mol^{-1}); A_T, Temkin isotherm constant (L mg^{-1})	Febrianto et al., 2009.
Halsey	$q_e = (K_H/c_e)^{\frac{1}{n_H}}$	K_H, Halsey isotherm model constant (L g^{-1})$^{-1/nH}$; n_H, Halsey model exponent	Febrianto et al., 2009.
Dubinin-Radushkevich	$q_e = q_m \exp(-B_{DR}E_{DR}^2)$; $E_{DR} = RT\ln\left(1+\frac{1}{c_e}\right)$	B_{DR}, biosorption energy constant (mol^2 J^{-2}); E_{DR}, Polanyi potential (kJ mol^{-1})	Febrianto et al., 2009.
Three-parameter models			
Sips	$q_e = \frac{q_m K_S c_e^{1/n_S}}{1+K_S c_e^{1/n_S}}$	K_S, affinity coefficient [(mg L^{-1})$^{-1/ns}$] n_s, heterogeneity coefficient	Febrianto et al., 2009.
Redlich-Peterson	$q_e = \frac{K_{RP}c_e}{1+A_{RP}c_e^{\beta_{RP}}}$	K_{RP} (L g^{-1}), A_{RP} [(L mg^{-1})^{BRP}], Redlich-Peterson model isotherm	Febrianto et al., 2009.