Bioresource Technology 160 (2014) 161–165

Contents lists available at ScienceDirect

Bioresource Technology

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

Biosorption of malachite green by eggshells: Mechanism identification and process optimization

Daria Podstawczyk [a], Anna Witek-Krowiak [a], Katarzyna Chojnacka [b,*], Zygmunt Sadowski [a]

[a] *Wroclaw University of Technology, Department of Chemistry, Wroclaw, Poland*
[b] *Institute of Inorganic Technology and Mineral Fertilizers, Department of Chemistry, Wrocław University of Technology, Smoluchowskiego 25, 50-372 Wrocław, Poland*

HIGHLIGHTS

- Removal of malachite green by eggshells via biosorption was investigated.
- Response Surface Methodology was employed to model and optimize the process.
- The investigation was focused on proposing and describing the removal mechanism of the dye.
- Eggshells appeared to be promising biosorbent for dyes-containing wastewater treatment.

ARTICLE INFO

Article history:
Available online 24 January 2014

Keywords:
Alkaline fading
Eggshells
Malachite green
Biosorption
Response Surface Methodology

ABSTRACT

In the present work, eggshells were used to remove a dye (malachite green) from wastewater. The study was focused on identification and describing the binding mechanism of the dye by eggshells in a biosorption process optimized by Response Surface Methodology based on the Box–Behnken Design. The mechanism of biosorption was determined by characterization of the biosorbent before and after biosorption using scanning electron microscopy, X-ray diffraction analysis, the Brunauer–Emmett–Teller isotherm method, Fourier transform infrared spectroscopy. The second-order polynomial equation and 3D response surface plots were used to quantitatively determine the relationships between dependent and independent variables. The obtained results suggested the mechanism of wastewater treatment that included physical adsorption, alkaline fading phenomenon and microprecipitation. The results of the present study showed that waste eggshells have the potential to be used as an inexpensive but effective biosorbent useful in wastewater treatment.

1. Introduction

Wastewater generation and the need of treatment and recycling associated with it is an essential part of human activity in the industrialized countries. One of the most hazardous substances discharged with wastewater are dyes, especially industrial dyes. Due to the high efficiency, one of the most popular methods of dyes removal from industrial effluents is adsorption. It is activated carbon that is the most frequently used type of sorbents, however its application is economically unviable, and thus it has been recently replaced by cheaper waste sorbents of organic origin, such as: soybean meal (Witek-Krowiak and Reddy, 2013), beech sawdust (Witek-Krowiak et al., 2010a,b), green microalgae (Chojnacka et al., 2005).

Malachite green (MG) is a basic dye, commonly used for dyeing textiles and paper, as well as an antiparasitic and antifungal agent in aquaristics. Both malachite green and its major metabolite, leucomalachite green (LMG), have mutagenic, carcinogenic and teratogenic effects (Srivastava et al., 2004). Due to its complex chemical structure stabilized by the aromatic character, MG is characterized by a high stability and resistance to chemical and biological degradation. Moreover, the form in which the dye is present in the solution depends on the conditions such as pH. Malachite green exists in aqueous solution in two pH-dependent forms. At alkaline pH, the dye undergoes the alkaline fading phenomenon, which involves changing of the structure of the dye from cationic chromatic MG to precipitate carbinol base and the simultaneous loss of color (Samey and Toosi, 2009).

Lee et al. (2011) investigated the contribution of alkaline fading phenomenon to the effective removal of malachite green, and for this purpose they used aminopropyl functionalized magnesium phyllosilicate (AMP clay). The mechanism that the researchers proposed for the dye removal included adsorption of MG onto AMP clay, alkaline fading of MG by AMP clay and induced precipitation of MG and AMP sheets at alkaline pH. Eggshell (ES) waste due to its

* Corresponding author. Tel.: +48 71 3202435; fax: +48 71 3203469.
E-mail address: katarzyna.chojnacka@pwr.wroc.pl (K. Chojnacka).

0960-8524/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2014.01.015

good sorption properties could be a cheaper alternative to AMP clay prepared by sol–gel technique, because it does not require additional processing or modification.

Food industry generates thousands of tons of eggshell waste annually. In Poland, egg production reached 0.6 m tons (about 10 billion eggs) in 2011. It would be advantageous to find a method of cost-effective utilization of this waste, e.g. as adsorbent. Eggshells were evaluated as an efficient biosorbent for heavy metal ions (Chojnacka, 2005). The application of this waste material for the removal of dyes has not been sufficiently described in scientific literature (Kobiraj et al., 2012; Tsai et al., 2008), especially in the case of sorption of malachite green (Chowdhury and Das, 2011). In most cases, when the effect of pH on the removal of malachite green by biosorption was investigated (Sun et al., 2008), the optimum pH was about 8–9, and the degree of removal under these conditions was close to 100%. Researchers assumed that sorption on a biomaterial surface was responsible for such a high percentage of removal, however they did not take into account the alkaline fading phenomenon and the precipitation of the dye. The phenomenon contributes significantly to the removal of the dye and cannot be ignored. Utilization of ES provides satisfactory approach for removal of MG without using any additional chemicals.

The novelty of study presented in this paper was to propose an effective method for the removal of malachite green from dye-containing wastewater by means of waste eggshells material. Research was focused on identifying and describing the removal mechanism of the dye by eggshells in the biosorption process optimized by the Response Surface Methodology (RSM) based on the Box–Behnken Design (BBD).

2. Methods

2.1. Biosorbent preparation

Eggshells were obtained from a local store. The first step of the biosorbent preparation process was size fractionation. For further study 2 mm size fractions were chosen. The biosorbent was washed three times with double distilled water and dried at room temperature for 24 h. The prepared material was used in biosorption experiments.

2.2. Analytical measurements

The surface structure of biomass was visualized and analyzed by scanning electron microscopy (SEM). The mineralogy of the biosorbent before and after the adsorption process was characterized by X-ray diffraction (XRD) System Ultima IV. Fourier transform infrared spectroscopy (FT-IR) studies (Spectrometer 2000 FT-IR) with a range of 4000–400 cm^{-1} were carried out to identify the functional groups present on the eggshell surface, which make adsorption process possible. The sorption properties such as porosity and surface area of eggshells were determined via low-temperature N_2 adsorption isotherms (BET) with the aid of ASAP 2020 gas sorption analyzer (Micromeritics, USA).

The dye concentration was measured spectrophotometrically at a maximum wavelength of 619 nm. The absorbance calibration curve was prepared for dye solutions in a concentration range of 0–10 mg L^{-1}. The solution of malachite green before and after biosorption by eggshells was analyzed for the exchanged ions, using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry, Varian Vista MPX, Australia at the laboratory certified by Polish Centre for Accreditation and ICAC-MRA according to PN-EN ISO 17025) method.

2.3. Preparation of aqueous dye solutions

Stock solution of malachite green was prepared by dissolving a weighed amount of the dye (PoCh, Poland) in 1 L of distilled water to obtain a concentration of 1000 mg L^{-1}. Samples of various concentrations were prepared by diluting the stock solution. 0.1 M NaOH and HCl solutions were used to adjust pH to the required value.

2.4. Optimization by Response Surface Methodology

Experiments were conducted in batch mode with the application of 100 mL of dye solution with an appropriate concentration and pH in a range of 100–500 mg L^{-1} and 2–6, respectively. The input levels of the biosorbent dosage were established as 1, 2, and 3 g L^{-1}.Time required to reach the equilibrium was 3 h.

All further biosorption experiments were performed in the optimal conditions determined by the RSM method coupled with BBD.

The Box–Behnken factorial design (BBD) consisting of 15 experiments coupled with Response Surface Methodology (RSM) was effectively applied in the optimization of the biosorption process. The maximum uptake was designated as a dependent response and optimized. Three independent factors such as pH (X_1), biosorbent dosage (X_2) and the initial dye concentration (X_3) were selected as the parameters mostly affecting the biosorption process. The highest, lowest and center values of the independent variables were coded as 1, −1, and 0, respectively. A non-linear regression method was assumed to fit the quadratic polynomial model to the experimental data points (Eq. (1)):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (1)$$

where β_0 is the model constant coefficient, while β_1, β_2, β_3 and β_{11}, β_{22}, β_{33}, and β_{12}, β_{13}, β_{23} are linear, quadratic and interaction effects regression coefficients, respectively. The analysis of the variance (ANOVA) of the quadratic model was performed in order to check if experimental values fit the model. The second-order polynomial equation was also used to determine the optimal conditions of malachite green removal via biosorption. All calculations were performed in Matlab 7.14.0.739.

2.5. Equilibrium experiments

Batch biosorption experiments were carried out in 250 mL Erlenmeyer flasks containing 100 mL of malachite green solution with various initial dye concentrations (20–1000 mg L^{-1}) and with the pH adjusted with 0.1 M HCl or NaOH to optimal value determined by RSM. The biosorbent dosage added to the solutions was also optimized by the statistical tool, already mentioned in this article. After 24 h agitation, all samples were centrifuged and the dye concentrations were measured. Two two-parameter (Langmuir, 1916; Freundlich, 1906) models were chosen to correlate the experimental sorption of malachite green by eggshells data to predicted values. Mathematical models were fitted by non-linear regression with Matlab 7.14.0.739 software.

3. Results and discussion

3.1. Sorbent characterization

The scanning electron microscopy images of internal and external surfaces of eggshells showed that both outer and inner layers of ES are porous, which makes the biosorbent attractive as a potential