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Research article

Sequencing batch biosorption of micropollutants from aqueous effluents by rapeseed waste: Experimental assessment and statistical modelling

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ABSTRACT

Rapeseed (RS) waste was used for sequential biosorption from aqueous solutions of two target micropollutants: lead ions and Reactive blue 19 (Rb19) dye, through an integrated approach, combining experimental assessment and statistical modeling. In both cases of sequential biosorption, a pseudo-second order kinetic model fitted the biosorption data well. Intraparticle diffusion proved to be the rate-limiting step in the sequential retention of both micropollutants. A selective desorption of metal ions and anionic dye at pH 2.5 and 10.5, respectively was observed. The quadratic models generated by response surface methodology (RSM) adequately described the sequential biosorption process and the desorption process, respectively. XPS and FTIR analysis indicated the mechanisms involved in the retention of target pollutants.

1. Introduction

Water pollution is a major global concern related to environmental and human health, resulting from extensive industrialization and population growth. Heavy (toxic) metals and dyes are micropollutants generated by the textile, pigments, rubber, plastics and paper industries, with significant impacts upon the environment. The major concern about dye-containing effluents is related to wastewater color and turbidity. Reactive blue 19 (Rb19) dye is refractory to biological aerobic treatment and presents high stability in the presence of conventional oxidizing agents (Fathy et al., 2013; Mittal et al., 2010). It negatively affects the liver, skin and appendices in humans and presents a weak mutagenic effect (Leme et al., 2015). Many toxic metals, like lead, cadmium, chromium, copper etc., are considered priority pollutants, due to significant effects of toxicity, mutagenicity and carcinogenicity on human health and ecosystems (He and Chen, 2014; Saravanan et al., 2017). Effluents containing lead (Pb) come from manufacturing of batteries, ammunition, pigments etc. In human organisms, lead bioaccumulates in bones, damages the nervous and reproductive systems and inhibits the activity of enzymes (Largitte and Lodewyckx, 2015; Pawar et al., 2016).

Advanced treatment processes, such as membrane separation, chemical, electrochemical and sorption processes, target the removal of these priority pollutants from wastewaters (Dutta and De, 2017a). Among them, sorption processes have proved to be very efficient for various categories of pollutants (Morosanu et al., 2017a; Paduraru et al., 2015). The utilization of different types of biomaterials (microorganisms, algae, vegetal materials) as sorbents in the biosorption processes has gained particular attention (Hlihor et al., 2017). The valorization of lignocellulosic wastes in treating wastewaters by biosorption considers also the circular economy principles. However, because these materials are not engineered, like activated carbon, the biosorption mechanism can be often difficult to explain. Moreover, an integrative approach of biosorption-desorption is not commonly addressed in the literature. Biosorption, and in general sorption processes, transfer the pollutant from the liquid medium to the solid phase. Hence, it is desirable to reuse the biosorbent in as many cycles as possible and to recover the pollutants in a concentrated form. In order to obtain maximum removal efficiencies with little resources, the operating parameters should be optimized both for the sorption and the desorption processes.

Research has been oriented to biosorption of multiple contaminants from aqueous solutions, primarily with focus on binary systems of toxic metals (Hernández-Hernández et al., 2017; Módenes et al., 2015; Wang et al., 2017) or dyes (Akazdam et al., 2017; Ben Arfi et al., 2017). Studies related to elimination of priority pollutants from heterogeneous binary systems (e.g. metal-dye) are limited (Ding et al., 2014; Garrudo-Guirado et al., 2018; Guler and Sarioglu, 2013; Kyzas et al., 2015a). By

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the sequential biosorption process, the sorbent firstly loaded with one of the pollutants will modify its superficial characteristics and act similar to a new sorptive material, new characterization studies and parameters optimization being thus imposed.

Response surface methodology (RSM) is a mathematical and statistic tool to find the sole and interaction effects of the process parameters (factors) upon the dependent variables (responses) (Torgut et al., 2017; Witek-Krowiak et al., 2014). The data obtained is statistically computed in order to determine an empiric model (mathematical equation) useful for prediction and optimization.

In continuation of our research regarding the application of rapeseed waste as a biosorbent for advanced wastewater treatment, we further investigated the ability of rapeseed to retain multiple micropollutants in a sequential biosorption process. Similar to a sequencing batch reactor operation, the sequential biosorption process consists of contacting the biosorbent with different pollutant solutions one at a time. In this way, a modified biosorbent is obtained and the presence of the pollutant(s) already existing on the solid's surface may influence (compete or augment) the biosorption of the other pollutant(s). In the present study, rapeseed loaded with metal ions (or Reactive blue 19 dye) is used for anionic dye (or lead ions) removal from aqueous solution through a sequential process, as presented in Fig. 1. Sequential biosorption efficiency in relation to several operating parameters, i.e. pH, initial pollutant concentration and biosorbent dose, were evaluated by RSM. Statistical modeling with RSM was used to evaluate the singular and interaction effects of two operating variables (elution pH and RS dose) on desorption process, in order to obtain the optimal operating conditions. Kinetic modeling was applied to determine the rate-controlling step. The biosorbent superficial changes after the sequential deposition of micropollutants were evaluated by Fourier transform infrared and X-ray photoelectron spectroscopies. Water vapor sorption characteristics have been determined. To our best knowledge, this is the first extensive study of sequential elimination of pollutants from aqueous solutions. So far, no study related to mathematical modeling by RSM applied to sequential biosorption, as well as desorption of Pb(II) ions and Rb19 dye has been reported.

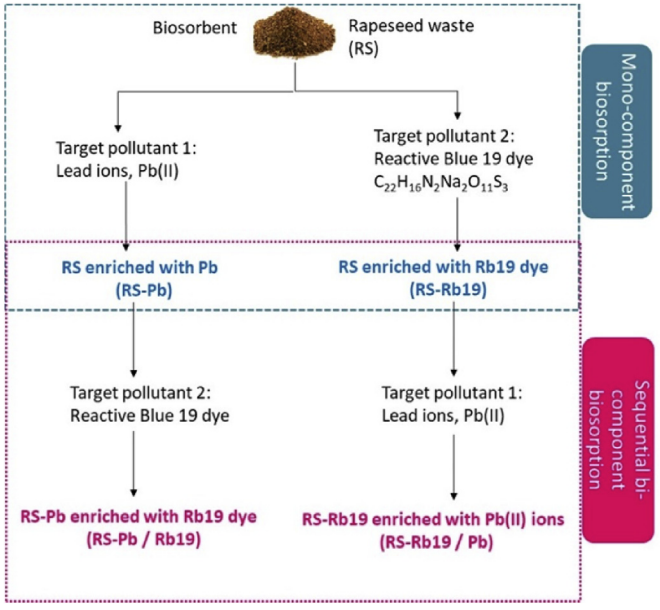

Fig. 1. Sequential biosorption process diagram.

2. Materials and methods

2.1. Materials and instruments

Rapeseed waste (RS) obtained from local biodiesel production units was prepared and used as described in the previous papers of Morosanu et al. (2017a,b). Briefly, after washing and drying (40 °C, 24 h), the material was grounded (0.1–0.2 mm) and kept into a dessicator for further use. Stock solution of 1 g/L Pb(II) or Rb19 dye was prepared from $Pb(NO_3)_2$ or Reactive blue 19 dye (analytical grade) dissolution in deionized water. The working solutions were obtained by dilution of the stock solutions of each target pollutant. Water vapors sorption capacity of the biosorbent has been measured in dynamic regime by using the fully automated gravimetric analyzer IGAsorp (Hiden Analytical, Warrington, UK). Sorption of water vapors was measured at 25 °C in the relative humidity range 0–90%. Brunauer-Emmett-Teller (BET) method was used to evaluate the surface area based on the water vapor sorption data. The Fourier transform infrared spectroscopy (FTIR) measurements of rapeseed before and after sequential biosorption were done over a range of 400–4000 cm^{-1} domain with a resolution of 4 cm^{-1}, in transmission mode using a FTIR spectrometer Vertex 70 model (Bruker-Germany). X-ray photoelectron spectra were collected on a Kratos Analytical Axis NOVA instrument using monochromatic Al Kα X-rays source ($h\nu$ = 1486 eV), 20 mA current and 15 kV voltage (300 W) and base pressure of 10^{-8} to 10^{-9} Torr in the sample chamber. The incident monochromatic X-ray beam was focused on a 0.7 × 0.3 mm^2 area of the surface. The X-ray photoelectron spectroscopy (XPS) instrument was calibrated at the C1s peak (285 eV). The curve deconvolution of the obtained XPS spectra were analyzed using the Vision 2.2.10 software.

2.2. Batch sequential biosorption experiments

The experimental tests of sequential biosorption consisted in contacting RS first with solution containing lead ions (or RB19 dye) and after phase separation, with solution containing the anionic dye (or lead ions), as illustrated in Fig. 1. The first stage was the individual biosorption of each of the model pollutants, under the optimized laboratory conditions described in Morosanu et al. (2017a,b). For this, 0.1 g of RS was added to 100 mL solutions with a 100 mg/L Pb(II) or dye at natural solution pH, 20 ± 1 °C and agitated periodically for 180 min. in the case of metal solutions or 240 min in the case of dye solutions. After equilibration, the biosorbent loaded with pollutant (either metal or dye) was separated from the aqueous phase by centrifugation and dried (30 °C, 2 h), then left at room temperature (20 ± 1 °C) overnight. Thus, two types of biosorbent were obtained: rapeseed with Rb19 dye (RS-Rb19) and rapeseed with lead (RS-Pb) (Fig. 1). The second stage was to contact each of the obtained biosorbents with the other target pollutant, according to the experimental design using RSM. According to parameters in Table 1, a certain amount of RS was added to 100 mL glass flasks containing 50 mL working solutions at room temperature (20 ± 1 °C). The solutions were shaken intermittently and left until equilibration. The pH was adjusted by using 0.01 M HNO_3 or NaOH. Similarly, kinetic measurements were done at different initial concentrations (50 and 100 mg/L) and a biosorbent dose of 10 g/L. The pollutant concentration was determined at different time intervals (20–360 min). All tests were conducted in duplicate and the average value was reported. The concentrations of Pb(II) ions and Rb19 dye, respectively were determined before and after each sorption test. The initial and equilibrium concentrations of the blue dye were determined after centrifugation by using a Jasco UV–Vis spectrophotometer (λ = 590 nm). The initial and equilibrium Pb(II) concentrations were determined using a Buck Scientific atomic absorption spectrometer, at 283.3 nm.

The amount of pollutant retained at equilibrium (q) was calculated with Eq. (1):