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Efficient removal of crystal violet from aqueous solutions with Centaurea stem as a novel biodegradable bioadsorbent using response surface methodology and simulated annealing: Kinetic, isotherm and thermodynamic studies

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ABSTRACT

The novel green bioadsorbent, Centaurea stem, was utilized for crystal violet removal from aqueous solutions. SEM and FT-IR were used for characterization of Centaurea stem. The effects of the pH, time, temperature, bioadsorbent amount, and initial dye concentration were investigated. Response surface methodology was used to depict the experimental design and the optimized data of pH 12.57, time 19.661, temperature 38.94 °C, amount of bioadsorbent 12.218 mg, and initial dye concentration 36.62 mg L^{-1} were achieved. Moreover, artificial neural network (ANN) and simulated annealing (SA) were applied for prediction and optimization of the process respectively. The SA acquired optimum conditions of 10.114, 7.892 min, 25.127 °C, 64.405 mg L^{-1}, 14.54 mg for pH, time, temperature, initial dye concentration, and bioadsorbent amount, respectively which were more close to the experimental results and indicated higher ability of SA-ANN in prediction and optimization of the process. The adsorption isotherms confirm the experimental data were appropriately fitted to the Langmuir model with high adsorption capacity of 476.190 mg g^{-1}. The thermodynamic parameters were evaluated. The positive $\Delta H°$ and $\Delta S°$ values described endothermic nature of adsorption. The adsorption of crystal violet followed the pseudo-second order kinetic model.

1. Introduction

One of the major problems in recent decades is environmental pollution due to the urbanization and different industrial effluent. Water as one of the extremely essential elements to all living beings suffers from the disposal of industrial wastewater (Sharifpour et al., 2017). Dyes i.e. synthetic dyes are definitely toxic and even lethal to human and ecosystem owing to their high stability and high carcinogenic, genotoxic, mutagenic, and teratogenic potential. Interestingly, among all kinds of dyes (i.e. cationic, an ionic, non-ionic), cationic dyes such as crystal violet are more toxic and harmful (Shayesteh et al., 2016). Moreover, the existence of toxic dyes in water sources reduces the sunlight transmission and aquatic plants photosynthetic activity (Farooq et al., 2017). Hence, removal of dyes from polluted water sources has been one of the most important concerns, especially in twentieth century. Different techniques such as ozonation (Hu et al., 2016), photochemical oxidation (Soares et al., 2017), membrane separation (Zhang et al., 2017), coagulation (Jorfi et al., 2016) and flocculation (Othmani et al., 2017), adsorption (Satilmis and Budd, 2017) were used to treat dye-polluted water sources. Since, rapidity, facility, accessibility, and affordability are the main features of any proposed process; adsorption is in center of attention among other dye removal techniques (Hassani et al., 2017; Shirani et al., 2014b). Many synthetic adsorbents such as zeolite (Shirani et al., 2014b), active carbon (Salehi et al., 2016), alumina (Hassani et al., 2017), nanoparticles (Asfaram et al., 2015; Shirani et al., 2015), and bioadsorbents are used for adsorption process. However, due to the sustainable, green and ecofriendly objectives in green chemistry, bioadsorbents are more preferred. In addition, bioadsorbents are more accessible, low cost, and mostly free of charge. According to these reasons application of different bioadsorbents such as peach gum polysaccharide (Li et al., 2017), defatted microalgal biomass (da Fontoura et al., 2017), Grapefruit peelings (Rosales et al., 2016; Saeed et al., 2010), Elaeagnus angustifolia (Rahimdokht et al., 2016), pistachio by-product (Deniz and

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Kepekci, 2016), Yarrowia lipolytica (Asfaram et al., 2016a) have been reported in recent years. Recently, various mathematical and statistical models have been introduced for prediction and optimization of the chemical processes to improve the performance of a process. Response surface methodology (RSM) is one of the most conventional and potent statistical techniques which is widely applied in chemistry. In fact, RSM fits a polynomial equation to the experimental data to depict the statistical behavior of a data set. RSM is applied in many dye removal process (Asfaram et al., 2016a, 2017, 2016b; Shirani et al., 2014b). Artificial neural network (ANN) is one of the most powerful prediction techniques which includes multi-layered perceptron including input, hidden layer, output, and a diverse number of neurons in each layer. However, ANN has high potential in prediction; simulated annealing algorithm as a precise data-based technique is highly capable of optimization. Therefore, the combination of simulated annealing (SA) algorithm with ANN is used for both prediction and optimization. SA as an intelligent optimization algorithm efficiently provides a framework for optimization of complex systems. SA was first proposed by Kirkpatrick and Cerny as a probabilistic meta-heuristic optimization method which imitates the cooling mechanism of metallic atoms in order to gain the minimum energy state (Bahrami and Doulati Ardejani, 2016; Tort et al., 2017). In this study, the removal of crystal violet as a common toxic cationic dye from aqueous solution was considered by the novel green bioadsorbent of Centaurea stem. Response surface methodology and simulated annealing were used to predict and optimize the proposed process. The kinetic, isotherm and thermodynamic of the adsorption of crystal violet onto the Centaurea stem were studied.

2. Materials and method

2.1. Materials

The chemicals used in this study were all in analytical grade and purchased from Merck and Sigma Aldrich. Crystal violet (MW: 407.979 g mol^{-1}, λ_{max} = 589 nm) was the cationic dye removed from the aqueous solution. The standard stock solution of Crystal violet (1000 mg L^{-1}) was prepared by dissolving proper amount of dye. Standard solutions of crystal violet were prepared daily by stock solutions. Sodium hydroxide and hydrochloric acid were used to adjust the pH of the solutions. Deionized water was used for all solutions.

2.2. Apparatus

The pH adjustment in the process was done by 86502-pH/ORP (AZ Instrument, Taiwan) using a combined glass calomel electrode. pH meter (metrohm model 86502-pH/ORP) and oven (Universal model UF 55, Germany) were used for setting pH and drying the bioadsorbent respectively. Ultra spect 3100 UV–visible Spectrophotometer (Amersham Biosciences, USA) was employed for data analyzing. Scanning electron microscopy (SEM) model Mira 3, TESCAN Company, Czech, and FT-IR spectrometer model RT1904C (Perkin Elmer, US) were used for characterization of the bioadsorbent. The mass ratio of 1:100 (bioadsorbent to KBr) was used to make a fine pellet for FT-IR analysis.

2.3. Bioadsorbent preparation

Centaurea is a local flower grows all over shahrekord. The Centaurea stem was collected from Sharekord University Campus. They were washed carefully and then rinsed with deionized water. The stems were put in the shade for 2 days to be completely dried. The dried stems were grinded completely. The prepared Centaurea stem was applied as bioadsorbent for removal of crystal violet.

2.4. Determination of point of zero charge (isoelectric point)

The isoelectric point (pH_{IEP}) i.e. point of zero charge (pH_{pzc}) depicts the type of active centers of the surface and the ability of the surface to adsorb the adsorbate (Hassani et al., 2017). The pH of a series of ten Erlenmeyer flasks containing 15 mL NaCl 0.1 mol L^{-1} as electrolyte solutions were adjusted in the range of 4–13 using NaOH or HCl (0.1 mol L^{-1}) and it was considered as initial pH of the solutions. To reach the equilibrium state the solutions were let for 24 h. Consequently, the final pH of the solutions was determined after the specific time. The pH_{PZC} was obtained from the initial to final pH curve, crossed by y = x line on the graph which was 9 (Ghaedi et al., 2016).

2.5. Adsorption procedure

A 10 mL solution containing crystal violet with certain concentration was added the specified amount of bioadsorbent and was stirred for special time. Then, the solution was centrifuged for 3 min at 5500 rpm to settle down the bioadsorbent. Consequently, the upper phase was taken and the concentration of the remained crystal violet after adsorption process was determined by UV–visible spectrophotometer. The amount of each parameter was obtained by RSM-CCD experimental design based on 32 runs. As reported previously the adsorption capacity and the removal percent can be calculated as follow (Shirani et al., 2014b):

The uptake of adsorbate can be expressed as follows: (Kannan and Veemaraj, 2009)

$$Q_e = (C_i - C_e)V/m \tag{1}$$

Q_e: the adsorbate concentration adsorbed at the equilibrium condition (mg of adsorbate /g of adsorbent)
C_i: The initial dye concentration in the solution (mg L^{-1})
C_e: Equilibrium concentration or final dye concentration (mg L^{-1})

Where m is the adsorbent mass (g) and v is the volume of adsorbate solution (L).

$$\text{Dye removal percentage}(\%) = (C_i - C_e)/C_i \times 100 \tag{2}$$

In which C_i is the initial dye concentration, C_e is the equilibrium concentration or final dye concentration (the concentration of dye in upper phase after adsorption process).

2.6. Modeling

2.6.1. Response surface methodology

RSM as one of the most common factorial designs contains a category of mathematical and statistical techniques based on the determination of the relationships between the independent variables and the obtained response in order to fit the empirical models to the experimental data obtained from experimental design (Bezerra et al., 2008; Prasad and Aikat, 2014). RSM includes two designs of central composite design (CCD) and Box-Behnken design (BBD) which two designs widely used in chemical processes such as dye removal techniques (Khoo et al., 2013; Ong et al., 2011; Sadaf et al., 2015). MINITAB software version 17.0 was used to obtain the experimental design for optimization of the influential factors including their symbols, and the ranges of pH (x_1, [5 − 13]), time (x_2, [5 − 25]), temperature (x_3, [20 − 40]), initial dye concentration (x_4, [20 − 300]) and amount of bioadsorbent (x_5, [3 − 15]).

The precision of the process was assessed by the three replicates at the center of the design. To represent the interaction of the factors, a full quadratic equation was utilized as follows (Shirani et al., 2014a):

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i}^{i<j} \sum_{j} b_{ij} x_i x_j \tag{3}$$