Fixed-bed-column Studies for Methylene Blue Removal and Recovery by Untreated Coffee Residues

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Abstract: This paper contributes to the Industrial Ecology Concept by using a common urban solid waste, i.e., coffee residues, to clean industrial wastewaters polluted by basic dyes, e.g., Methylene Blue. For the data from the continuous fixed-bed column system, two common models, namely (a) Bohart and Adams and (b) Clark were implemented. The Bohart and Adams capacity was up to N = 46,166 mg·L⁻¹ or q₀ = 104.5 mg·g⁻¹ for bed-depth 15 cm, initial dye concentration 800 mg·L⁻¹ and flow rate 20 mL·min⁻¹. The results revealed that the Methylene Blue is fairly adsorbed on coffee residues. Consequently, this process can be applied as a low cost technique for cleaning basic dyes from the aquatic environment.

Key words: Adsorption, desorption, column, methylene blue, coffee residues.

1. Introduction

Many industries, such as paper, plastics, food, printing, leather, cosmetics and textile, use dyes in order to color their products [1]. In textile industries, about 10-15% of the dyes get lost in the effluent during the dyeing process which are harmful products and may cause cancer epidemics [2, 3]. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade [1-4]. The industrial runoffs are usually discarded into rivers and lakes, altering the biological stability of surrounding ecosystems [5]. Therefore, removal of dyestuffs from wastewater has received considerable attention over the past decades. In wastewater treatment, various methods applied to remove dyes include photocatalytic degradation [6], membrane separation [7], chemical oxidations [8] and electrochemical process. Among the above mentioned techniques of dye removal, the process of adsorption gives the best results as it can be used to remove different types of coloring materials [9].

Adsorption onto activated carbon is the most widespread technology for the removal of pollutants from water and wastewaters. The disadvantage of activated carbon is its high cost [10]. Hence, it is of pivotal importance thence of low-cost substitute absorbents to replace activated carbons. Various types of untreated biomass have been reported to have a use in dye removal: peanut husk [11], palm kernel fibre [11], Turbinaria turbinate alga [12], graphene [13], defatted jojoba [14] and sugar bet pulp [15]. Further, numerous pretreated lignocellulosic materials are used to remove dyes in water and wastewater. Pyrolyzed date pits [16], date stones [17] and Turbinaria turbinate alga [12] have proved to be effective adsorbents.

Coffee residues and others similar byproducts like coffee husks and coffee grounds have been investigated to remove various dyes and heavy metals from aqueous solutions. Coffee husks have been used for the removal of Cu(II), Cr(VI), Cd(II) and Zn(II) [18], coffee grounds for Nylosan Red N-2RBL [19] and degreased coffee bean for Malachite Green [20]. Kyzas et al. [21] reported the removal of Remazol Brilliant Blue RN and Basic Blue 3G using coffee residues, focusing on batch processes and not on continuous systems.
In the current study, the adsorption capacities of coffee residues to remove Methylene Blue (MB) from aqueous solutions were investigated. Continuous fixed-bed-column systems were investigated. As regards the fixed-bed-column systems filled with coffee residues, various bed-depths, flow rates and initial dye concentrations were examined for the first time.

2. Materials and Methods

Coffee residues, a low-cost material acquired from different cafeterias in the city of Piraeus (Greece) were used as adsorbent. This adsorbent was washed with distilled water and dried at 110 °C for 24 hrs to remove the humidity.

The dye used herein in batch and column experiments was Methylene Blue (C₁₆H₁₄C₁₂N₃S·3H₂O, molecular weight = 373.90·10⁻³ kg·mol⁻¹) supplied by Sigma-Aldrich. A stock solution was prepared by dissolving a specific amount of MB (humidity 22%) in distilled water. Working solutions were 3-140 mg·L⁻¹. MB concentrations were determined by measuring the absorbent values in each experiment with HACH DR4000U UV-VIS spectrophotometer at λ = 664 nm.

Continue-flow experiments were carried out on Stainless steel columns with dimensions 15 × 2.5 and 25 × 2.5 cm. The bed height was x = 15 cm and 25 cm, respectively. The adsorbent weight was m = 32 g and 54 g, respectively. The pH was 8.0. The flow rates were fixed at approximately 10, 20, 40, 70 and 80 mL·min⁻¹ using a preparative HPLC pump, LaPrep P110-VWR-VWR International. The initial concentrations of MB were 165, 800 and 1,600 mg·L⁻¹. To determine the concentration of MB in the effluent, samples of outflow were peaked at 100 mL intervals. At the end of each one of the above mentioned sorption experiments, desorption tests were performed using distilled water as influent. The flow rate was fixed at about 20 mL·min⁻¹. To determine the concentration of MB in the effluent, samples of outflow were collected at 100 mL intervals. The concentration of output solution was measurement at λ = 664 nm and using HACH DR4000U UV-vis spectrophotometer. Finally, pH measurements were made using a digital pH meter, MultiLab model 540.

3. Results and Discussion

A widely used continuous fixed-bed-column model was established by Bohart and Adams [22-27], who assumed that the rate of adsorption is controlled by the surface binding (through chemical reaction or physical interaction) between adsorbate and unused capacity of the solid, i.e., adsorption rate = K·C·Cu, where K is the adsorption rate coefficient, C is the adsorbate concentration at the solid phase at distance x, and Cu is the unused surface adsorptive capacity at time t, expressed as mass per volume of bed. The material balance for adsorbate is given by the partial differential equation:

\[
\frac{\partial C_a}{\partial t} = -K \cdot C \cdot C_u
\]  (1)

while the corresponding partial differential equation for the Cu decrease is

\[
\frac{\partial C}{\partial x} = -\frac{K}{u} \cdot C \cdot C_u
\]  (2)

where \( u \) is the superficial liquid velocity. These equations are obtained neglecting diffusion and accumulation terms, assumptions that are valid in chemical engineering practice, provided that strict scale up specifications are kept in the design stage and successful operation conditions are kept in the industrial operation stage.

The differential equations can be integrated over the total length x of the bed to give:

\[
\ln\left(\frac{C_i}{C} - 1\right) = \ln[\exp\left(\frac{K \cdot N \cdot x}{u}\right) - 1] - K \cdot C_i \cdot t
\]  (3)

where \( N \) (mg·L⁻¹); is the initial or total adsorption capacity coefficient, also quoted as \( C_{a0} \) [28]; \( C = \) effluent concentration (mg·L⁻¹); \( C_i = \) influent concentration (mg·L⁻¹); \( K = \) adsorption rate coefficient.
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\[ \ln \left( \frac{C_i}{C} - 1 \right) = \frac{K \cdot N \cdot x}{u} - K \cdot C_i \cdot t \]  

(4)

which is commonly used by researchers, because of its convenience in estimating the values of parameters K and N through linear regression either of \( \ln[(C_0/C_i - 1)] \) vs t or t vs x when the following rearrangement is adopted:

\[ t = \frac{N \cdot x}{C_i \cdot u} - \frac{1}{K \cdot C_i} \cdot \left( \ln \frac{C_i}{C} - 1 \right) \]  

(5)

In this rearrangement, t is the time to breakthrough, i.e., the time period required for concentration to reach a predetermined value. For using the last expression as a linear regression model, wastewater is passed through beds of varying depths, keeping constant \( C_i \) and u, preferably at values similar to those expected to prevail under real conditions at full scale. Alternatively, it can be performed by the aid of at least three columns arranged in series. In such a case, sampling takes place at the bottom of each column and measured for adsorbate concentration, making more frequent measurements when approaching the breakthrough concentration C. Finally, the time at which the effluent reaches this concentration is used as the dependent variable while x plays the role of the independent one. Evidently, the use of such a regression model implies the additional error of measuring the independent variable with less precision in comparison with the dependent. The common error in both models comes from the estimation of concentration from measuring absorbance although the reference relation/curve has been structured/drawn in the inverse mode, i.e., for predetermined concentrations, the corresponding absorbances have been measured. In the present work, the model of Eq. (3) has been used for parameter values estimation through linear regression to obtain numerical results comparable with corresponding data found for other fixed bed adsorption studies in literature. The non-linear form of this model is:

\[ C = \frac{C_i}{1 + Ae^{-nt}} \]  

(6)

where \( A = e^{K \cdot N \cdot x/u} \); \( r = K \cdot C_i \). The model of Eq. (6) has been used for parameter values estimation through NLRA to obtain more reliable numerical results, i.e., with a lower total standard error of estimate (SEE). In the last care, the regression model is written under the form for parameter identification through \( C_i \) value estimation (a) endogenously and (b) exogenously.

On the other hand, Clark [29] has advanced the Bohart and Adams model [28] by incorporating the parameter n of the Freundlich adsorption isotherm:

\[ n = \frac{1}{\ln \left( \ln \frac{C_i}{C} \right)} \]  

(7)

where n = inverse of the slope of the Freundlich isotherm [22]. Finally, the Bohart and Adams model [28] can be reduced for n = 2 from Clark model [29]. In this study, continuous fixed-bed-column systems were investigated. The column systems were filled with coffee residues at various initial dye concentrations, flow rates and bed-depths.

The effects of initial MB concentration have been investigated at 165-1600 g·L\(^{-1}\), respectively. The bed height was 15 cm and the temperature was 23 °C. The flow rate was fixed at 20 mL·min\(^{-1}\) and the pH of MB solution was 8. The breakthrough curves were plotted in Fig. 1 according to the Bohart and Adams model. It was illustrated from the breakthrough time decreased with increasing MB concentration. In order to find the effect of bed height on the breakthrough curve, the adsorbate MB solution (initial MB concentration 165 mg·L\(^{-1}\), pH 8) was passed through the adsorption column at a flow rate 70 mL·min\(^{-1}\) by varying the bed height. The breakthrough curves at bed heights of 15 and 25 cm are shown at Fig. 3. The results showed that
the shape and gradient of the breakthrough curve was slightly different with the variation in the bed depth. The concentration of MB in the effluent rapidly increased after the breakthrough point. The lower bed depth (15 cm) gets saturated earlier than the higher bed depth (25 cm) (Fig. 3).

The values of parameters A and r according to (i) the Bohart and Adams model [28] and (ii) the Clark model [29] were estimated by NLRA from the column effluent data for all the cases presented in Figs. 1-3, respectively. The expressions used to calculate the parameter K and N values after having performed NLRA are $K = r/C_i$ and $N = u\cdot\ln A/(x\cdot K) = C_i\cdot u\cdot\ln A/(x\cdot r)$. The effluent dye solution volume $V$ (in L) is $V = Q\cdot t$, where $Q$ is the dye solution flow rate.

The theoretical estimations, according to the Bohart and Adams model [28]. The N and K values are estimated. The SEE-values are estimated too. According to them, the fitting of the Bohart and Adams model to experimental data was found to be better than the fitting of the Clark model.

The kinetic equation used for desorption is the following:

$$C = C_0' e^{-k't'}$$

where $C_0'$ is the initial MB concentration of desorption.
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Fig. 3  Column experimental data and theoretical curves of MB adsorption on coffee residues; the effluent concentration is presented vs. the effluent volume for $x = 15$ and 25 cm, $Q = 70 \text{ mL·min}^{-1}$, $C_i = 165 \text{ mg·L}^{-1}$ (the theoretical curves are according to the Bohart and Adams model).

Fig. 4  Column experimental data and theoretical curves of MB adsorption and desorption on coffee residues; the effluent concentration is presented vs. the effluent volume for $x = 15$, $Q = 20 \text{ mL·min}^{-1}$, $C_i = 1,600 \text{ mg·L}^{-1}$ (the adsorption theoretical curve is according to the Bohart and Adams model).

effluent, $k'$ is desorption rate constant assuming first order desorption kinetics and $t'$ is desorption time. According to the experimental adsorption/desorption data shown in Fig. 4, desorption was approximately 17% of the maximum adsorbed MB quantity which was $q_0 = 83.0 \text{ mg·g}^{-1}$. In this case, the bed depth was $x = 15$, the flow rate was $Q = 20 \text{ mL·min}^{-1}$, the MB initial concentration was $C_i = 1,600 \text{ mg·L}^{-1}$ for adsorption and equal to zero for desorption (i.e., pure water was used for desorption).

Our study is a research on the adsorption capacity of the coffee residue and its application to industrial scale. There is an object for further research to determine the coffee residues quantity by region distribution and corresponding exploitation by industrial scale unit. The Methylene Blue adsorption capacity for various lignocellulosic materials found in the literature was compared to the coffee residues adsorption capacity estimated in the present work (see Table 1). The adsorption capacity of the coffee residue was better than the adsorption capacity of other waste biomass such as peanut husk [14], turbinaria turbinate alga [12], and wheat straw. The coffee residues adsorption capacity found in the present work was close to the
Table 1  Column models parameters of Methylene Blue adsorption on coffee residues.

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<th>C_i (mg/L)</th>
<th>Q (mL/min)</th>
<th>n</th>
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<th>K</th>
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average of the Freundlich and Langmuir capacities, i.e., KF and qm respectively, reported in the literature.

4. Conclusions

The use of coffee residues is an innovative technique using waste biomass from urban and rural areas in and Industrial Ecology Framework. Also, that is an index of the sensitivity of citizens for the rational management of waste and their contribution to sustainable development. The present work proves the viability of using coffee residues to remove basic dyes like MB from wastewaters. The effect of different system parameters on (a) batch and (b) continuous fixed-bed column systems were studied. The experimental systems data were simulated using the most commonly used isotherm and kinetic models. The continuous fixed-bed column results proved that the MB is practically adsorbed on coffee residues giving maximum Bohart and Adams capacity N = 46,166 mg·L⁻¹ or q0 = 104.5 mg·g⁻¹ for bed-depth 15 cm, initial dye concentration 800 mg·L⁻¹ and flow rate 20 mL·min⁻¹. These results provide evidence for suggesting this low cost residue for the removal of basic dyes in industrial scale applications.

References


