A Three-Stage, Completely Sustainable Process Addressing Industrial Water Waste Treatment Management: The Case of the Sorption of Methylene Blue in Column Experiments

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Abstract: A detailed study regarding the optimization of a complete system for the purification of water waste is presented. Three main concerns are addressed: the nature of the absorbing material, the efficiency dependence on scale and the management of the final waste of the assembly. These three points have to be optimized in the best acceptable way from an environmental point of view. Subsequently, the wet filling material, comprised of the absorbent and the absorbed dye, was buried in dry soil, promoting soil bacterial and fungal growth. The absorbance of CO₂ was determined. The use of natural vegetative material as absorbents of chemical dyes in industrial water waste is an environmentally friendly solution. Combination with the utilization of the final solid waste as fertilizer is an optimum solution, promoting sustainability within an industrial ecology framework. The adsorption column scale-up studied herein, for the removal of basic dyes from wastewaters, using methylene blue as a representative adsorbate and barley straw as a representative waste biomass adsorbent, was successful, as regards consistency and reliability (judged by low absolute and relative standard deviation) of results.

Key words: Waste water treatment, absorbance, bioavailability, industrial ecology.

1. Introduction

The environmental impact of dye effluents in the wastewater streams of many industrial sectors, such as dyes, textiles, paper, tanneries and chemicals, has drawn a lot of attention for the last decades, emphasizing on the necessity of their removal at acceptable cost. The utilization of inexpensive and locally available materials as potential substitutes of commercial activated carbon for the removal of dyes in industrial wastewater is commonly discussed in literature [1-9]. A variety of low cost materials have been proposed [1-9], including cotton waste, rice husk, betonite clay, neem leaf powder, powdered activated sludge, perlite, bamboo dust, coconut shell, groundnut shell, rice husk and straw, sawdust, sewage sludge, gram husk, bagasse fly ash, and blast furnace slag. The suitability of these materials as dye adsorbents is often established using (i) the kinetics of methylene blue adsorption during batch and continuous (column) processes [10, 11] and (ii) the Brunauer-Emmett-Teller (BET) surface area [12]. Not with standing, most of these studies report on bench scale experiments, the literature on scale-up of column adsorption processes is scarce. A column adsorption process represents a complex system with many inherent difficulties in scaling up, especially in predicting performance and in evaluating scale-up factors [13]. From an economic point of view, the column adsorption process should be designed to give a maximum recovery of the desired product from a fluid phase, with an optimum schedule to handle a
certain amount of material. To achieve this goal, extensive laboratory and pilot plant experiments are normally required to find the optimum conditions.

In the present study, the scale up of adsorption column, and the removal of methylene blue by barley straw were studied. The pilot scale (the medium scale between the laboratory scale and the industrial scale) column used herein was 137 cm in length and 19 cm in diameter. The flow rate was determined such as the linear velocity for the pilot scale column to be approximately the same with the linear velocity for the two laboratory scale columns (15 and 25 cm in length, respectively, and 2.5 cm in diameter). The results indicate that barley straw shows high adsorption properties.

2. Materials and Methods

2.1 Material Development

Barley straw used was obtained from Thessaly (Central Greece), as a suitable source for full-scale/industrial applications. Barley straw contains 27% \( w/w \) hemicelluloses, 33% \( w/w \) cellulose, lignin 28% \( w/w \) and 12% \( w/w \) ash. The moisture of the material measured was 8.5% \( w/w \). After grinding in a hummer mill and screening, the fraction with particle sizes between 1 and 2 cm was isolated as “coarse grinded barley straw”. The material was saturated for 24 h prior to adsorption experiments. The absorbance of methylene blue on continuous flow columns of different sizes and absorbent materials was compared. Pine spruce, sea weed, lentil spruce and coffee residues were utilized as absorbents. The column length varied from 15 to 35 cm and flow rates varied from 0.5 to 40 mL/min.

2.2 Experimental Setup

Fixed-bed up-flow adsorption studies were conducted in a 137 cm × 19 cm Plexiglas column, in a 15 cm × 3 cm stainless steel column and in a 25 cm × 3 cm stainless steel column filled with 2,730 g, 14 g and 22 g of coarse grinded barley straw, respectively. The experimental set-up consisted of one column, fed by a peristaltic pump at a constant flow rate, \( Q = 22.5 \text{ mL/min} \) and 16.8 mL/min for the 15 cm and 25 cm laboratory scale columns, respectively, and \( Q = 1.36 \text{ L/min} \) for the pilot scale column. The methylene blue influent concentration was 14 mg/L. Interconnective tubing and fitting were made of Poly Tetra Fluoro Ethylene (PTFE). Effluent samples were analyzed to yield output concentration breakthrough curves. In the case of the laboratory scale stainless steel columns, the cross-section was \( E = 4.91 \text{ cm}^2 \) and the adsorbent (coarse grinded barley straw) was 0.19 g/mL. In the case of the pilot plant Plexiglas column, the cross-section was \( E = 283.39 \text{ cm}^2 \) and the adsorbent was 0.07 g/mL, i.e. the column was filled with 2,730 g of coarse grinded barley straw.

2.3 Analytical Techniques

The lignocellulosic materials were hydrolyzed to glucose and reducing sugars in nearly quantitative yields; the filtrates were analyzed for glucose and xylose. Based on these results the cellulose and hemicelluloses contents of the adsorbents were estimated. Finally, the acid-insoluble lignin (Klason lignin) was determined according to the Tappi T222 om-88 method. The samples were dried under vacuum at 150 °C overnight. The concentration of methylene blue in the solution was obtained by measuring at 663 nm, using a visible spectrophotometer (HACH DR4000U UV).

3. Results and Discussion

It is proposed [15] the use of a bed depth service model for simulating Granular Activated Carbon (GAC) adsorption beds. The model, which name is Bohart and Adams model [16], was based on surface reaction theory and is equivalent to the logistic curve [17-20]. The Bohart-Adams (B-A) equation is as Eq. (1):

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

or
in which $C = \text{effluent concentration (mg/L)}$; $C_i = \text{influent concentration (mg/L)}$; $K = \text{an adsorption rate coefficient (L/(mg·min))}$; $N = \text{an adsorption capacity coefficient (mg/L)}$; $x = \text{bed depth (cm)}$; $u = \text{linear velocity (cm/min)}$; and $t = \text{time (min)}$, $\ln A = K \cdot N \cdot x / u$ and $r = K \cdot C_i$.

The values of $A$ and $r$ can be thus estimated from the column effluent data assuming $C_i = \text{column influent}$ and $C = \text{the column effluent at time } t$. We can calculate $K$, $N$ from the equations $K = r / C_i$ and $N = u \ln A / (xK) = C_i u \ln A / (xr)$. As shown in Fig. 1, the theoretical model expressed by Eq. (1) simulates the experimental data satisfactorily. In addition, the adsorption rate coefficient ($K$) and the adsorption capacity coefficient ($N$), shown for pilot scale column in Table 1, were estimated from the $A$ and $r$ values obtained using the same equation.

The simulation of the 15 cm laboratory scale column gave adsorption capacity coefficient $N = 786 \text{ mg/L}$, adsorption rate coefficient $K = 0.00079 \text{ L/(mg·min)}$ and correlation coefficient $R = -0.9413$. The simulation of the 25 cm laboratory scale column gave $N = 2395 \text{ mg/L}$, $K = 0.00045 \text{ L/(mg·min)}$, $R = -0.96984$. The results of the simulation of the pilot plant column for methylene blue adsorption on Barley Straw according to the B-A bed depth service model are presented in Table 1.

Eq. (1) can be rewritten as:

$$C = \frac{C_i}{1 + Ae^{-rt}}$$
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Fig. 2  (a) Laboratory scale column of 15 cm height with 25 L tank, (b) laboratory scale pump, (c) pilot scale column of 137 cm height (d) 1.000 L tank.

Table 1  Estimated parameter values for methylene blue adsorption on barley straw according to the Bohart-Adams bed depth service model for the case of the pilot scale column.

| Fixed bed height \(x\) (cm) | Adsorption capacity coefficient \(N\) (mg/L) | Adsorption rate coefficient \(K\) (L/(mg·min)) | Flow rate \(Q\) (L/min) | Correlation Coefficient \(R\) | Standard Error of Estimate (SEE) |
|-----------------------------|---------------------------------|---------------------------------|-----------------|-----------------|-----------------|
| 27                          | 50                              | 0.00063                         | 1.32            | -0.9599         | 0.4138          |
| 67                          | 188                             | 0.00076                         | 1.33            | -0.9502         | 0.4559          |
| 107                         | 170                             | 0.00083                         | 1.22            | -0.9333         | 0.2449          |
| 137                         | 161                             | 0.00083                         | 1.58            | -0.9568         | 0.3584          |

This is the well known logistic model, which can be used as an independent phenomenological kinetic expression, since all breakthrough curves exhibit a sigmoid profile. The disadvantage of applying this expression is its symmetry round the inflection point at \(t = (\ln A)/r\), \(C = C_i/2\), as it can be easily proved by replacing \(t\) in the corresponding differential (rate) function with two \(t\)-values, symmetrical round \(t = (\ln A)/r\). Breakthrough curves in the linearized/logarithmic form and in the original/non-linear form (a) for the laboratory scale columns with bed height \(x = 15\) cm and 25 cm, and (b) for the pilot plant column with bed height \(x = 137\) cm (sampling at 27, 67, 107 and 137 cm). Fixed bed: barley straw; methylene blue solution flow rate 22.5 mL/min, 16.8 mL/min and 1.36 L/min for the three columns, respectively; inflow concentration \(C_i = 14\) mg/L (the effect of column scale on the removal efficiency of the dye). When the goodness of fitting of the logistic function is not satisfactory because of its symmetry, we can apply one of the following empirical asymmetrical sigmoid models [21]:

\[
y = \frac{K}{1 + me^{-bt}} \quad \text{(I)}
\]

\[
y = \frac{K}{(1 + me^{-bt})^\gamma} \quad \text{(II)}
\]

\[
y = \frac{K}{(1 + me^{-bt})^\sigma} \quad \text{(III)}
\]
$y = \frac{K}{(1 + me^{-at})}$  \hspace{1cm} (IV)

where: $y = C$, $K = C_i$, $m = A$, $b = r$ and $a =$ exponent. For $a = 1$ we obtain Eq. (2).

4. Conclusions

The adsorption column scale-up studied herein, for the removal of basic dyes from wastewaters, using methylene blue as a representative adsorbate and barley straw as a representative waste biomass adsorbent, was successful, as regards consistency and reliability (judged by low absolute and relative standard deviation) of results. Moreover, the goodness of fitting of the Bohart-Adams model to experimental data was satisfactory, as judged by the corresponding low values of the Standard Error of Estimate (SEE), while the correlation coefficient, estimated on the basis of the corresponding linearized regression equation, was quite acceptable (i.e., negative and close near to -1). By transforming the original B-A model to the well known logistic expression, we suggested a family of empirical alternative models to cope with adsorption kinetic data that do not follow the symmetric pattern, which is the main characteristic of the logistic function. The creation of this family was achieved by introducing a fourth parameter in different modes, which represents a measure of deviation from symmetry.

When the experimental data come close to a symmetrical path, this parameter approaches unit and the empirical model tends to coincide with the logistic function, i.e., the B-A model. This feature enhances the applicability of the B-A model under its modified version, since the lack of symmetrical data does not prevent the use of the most appropriate model of the family while giving the opportunity of coming back from empirical to scientific when the obstacles giving rise to asymmetry have been removed by reconditioning the process.

References

[1] Robinson, T., McMullan, G., Marchant, R., and Nigam, P. 2001. “Remediation of Dyes in Textile Effluent: A Critical Review on Current Treatment Technologies with a Proposed Alternative.” Bioresour. Technol. 77 (3): 247-55.

[2] Sparado, J. T., Gold, M. H., and Renganathan, V. 1992. “Degradation of Azo Dyes by Lignin Degrading Fungus Penicillium chrysosporium.” Appl. Environ. Microbiol. 58 (8): 2397-401.

[3] Mastrangelo, G., Fedeli, U., Fadda, E., Mila, G., and Lange, J. 2002. “Epidemiologic Evidences of Cancer Risk in Textile Industry Workers: A Review and Update.” Toxicol. Industr. Health 18 (4): 171-81.

[4] Song, J., Zou, W., Bian, Y., Su, F., and Han, R. 2011. “Adsorption Characteristics of Methylene Blue by Peanut Husk in Batch and Column Modes.” Desalination 265 (1): 119-25.

[5] Deng, H., Lu, J., Li, G., Zhang, G., and Wang, X. 2011. “Adsorption of Methylene Blue on Adsorbent Materials Produced from Cotton Stalk.” Chem. Eng. J. 172 (1): 326-34.

[6] Sohrabi, M. R., and Ghavami, M. 2008. “Photocatalytic Degradation of Direct Red 23 Dye Using UV/TiO2: Effect of Operational Parameters.” J. Hazard. Mater. 153 (3): 1235-9.

[7] Ciardelli, G., Corsi, L., and Marcucci, M. 2001. “Membrane Separation for Water Reuse in the Textile Industry.” Resour. Conserv. Recycl. 31 (2): 189-97.

[8] Tang, H., Yin, L., and Lu, H. 2012. “Synthesis, Conformations and Cell-Penetrating Properties.” Biomacromolecules 13 (9): 2609-15.

[9] Rafatullah, M., Sulaiman, O., Hashim, R., and Ahmad, A. 2010. “Adsorption of Methylene Blue on Low-cost Adsorbents: A Review.” Journal Hazardous Materials 177 (1): 70-80.

[10] El-Sayed, A. M., Mitchell, V., Manning, L. A., Cole, L., and Suckling, D. M. 2011. “New Sex Pheromone Blend for the Lightbrown Apple Moth, Epiphyas Postvittana.” Journal Chemical Ecology 37 (6): 640-6.

[11] Altenor, S., Ncibi, M. C., Emmanuel, E., and Gaspard, S. 2012. “Textural Characteristics, Physicochemical Properties and Adsorption Efficiencies of Caribbean Alga Turbinaria Turbinata and Its Derived Carbonaceous Materials for Water Treatment Application.” Biochemical Engineering Journal 67: 35-44.

[12] Liu, T., Li, Y., Du, Q., Sun, J., Jiao, Y., Yang, G., et al. 2012. “Adsorption of Methylene Blue from Aqueous Solution by Grapheme, Colloids and Surf.” Biointerfaces 90: 197-203.

[13] Al-Anber, Z. A., Al-Anber, M. A., Matouq, M., Al-Ayed, O., and Omari, N. M. 2011. “Defatted Jojoba for the Removal of Methylene Blue from Aqueous Solution:
Thermodynamic and Kinetic Studies.” *Desalination* 276 (1): 169-74.

[14] Malekbala, M., Hosseini, S., Yazdi, S. K., and Masoudi, S. S. 2013. “The Study of the Potential Capability of Sugar Beet Pulp on the Removal Efficiency of Two Cationic Dyes.” *Chem. Eng. Res. Des.* 90 (5): 704-12.

[15] Theydan, S. K., and Ahmed, M. J. 2012. “Adsorption of Methylene Blue onto Biomass-Based Activated Carbon by FeCl₃ Activation: Equilibrium, Kinetics, and Thermodynamic Studies.” *Journal Analytic Appl. Pyrolysis* 97: 116-22.

[16] Ahmed, M. J., and Dhedanb, S. K. 2012. “Equilibrium Isotherms and Kinetics Modeling of Methylene Blue Adsorption on Agricultural Wastes-Based Activated Carbons.” *Fluid Phase Equilibrium* 317: 9-14.

[17] Oliveira, W. E., Franca, A. S., Oliveira, L. S., and Rocha, S. D. 2008. “Untreated Coffee Husks as Biosorbents for the Removal of Heavy Metals from Aqueous Solutions.” *Journal of Hazardous Materials* 152 (3): 1073-81.

[18] Reffas, A., Bernardet, V., David, B., Reinert, L., Bencheikh, L. M., Dubois, M., Batisse, N., and Duclaux, L. 2010. “Carbons Prepared from Coffee Grounds by H₃PO₄ Activation: Characterization and Adsorption of Methylene Blue and Nylosan Red N-2RBL.” *Journal Hazardous Materials* 175 (1): 779-88.

[19] Baek, M. H., Ijabgemi, C. O., Se-Jin, O., and Kim, D. S. 2010. “Removal of Malachite Green from Aqueous Solution Using Degreased Coffee Bean.” *Journal of Hazardous Materials* 176 (1): 820-8.

[20] Kyzas, G. Z., Lazaridis, N. K., and Mitropoulos, A. C. 2012. “Removal of Dyes from Aqueous Solutions with Untreated Coffee Residues as Potential Low-Cost Adsorbents: Equilibrium, Reuse and Thermodynamic Approach.” *Chemical Engineering Journal* 189-190: 148-59.

[21] Freundlich, H. M. F. 1906. “Über die adsorption in lösungen, Zeitschrift für Physikalische.” *Chemie* 57: 385-471. (in German)