Scale Up Of Adsorption Column Packed With Conditioned Waste Lignocellulosics

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Abstract. The present work deals with the scale up of adsorption column for the removal of basic dyes from wastewaters, using methylene blue as a representative adsorbate and barley straw as a representative waste biomass adsorbent. The pilot scale column used herein was 137 cm in height with 19 cm inner diameter. The flow rate was determined so that the linear velocity for the pilot scale column is approximately the same with the linear velocity for the two laboratory scale columns (15 and 25 cm in height, respectively, with 2.5 cm inner diameter). In the case of the pilot scale column the time required for breakthrough (predetermined at C=2 mg/L) was 140 min and the corresponding required influent volume was 220 L (C_i=14 mg/L), where the C, Ci are concentrations for adsorbate output and input, respectively. The results indicate that barley straw exhibits satisfactory adsorption properties. Considering the abundance and the low cost of this lignocellulosic material, barley straw could serve as a cost-effective adsorbent for basic dyes.

Keywords: adsorption; barley straw; packed bed column; methylene blue; scale up.

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, duck weed, 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 BET surface area [12]. Notwithstanding, most of these studies report on bench scale experiments, whereas 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 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. METHODS

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 hours prior to adsorption experiments.

Experimental Setup: Fixed-bed up-flow adsorption studies were conducted in a 137 cm x 19 cm Plexiglas column, in a 15 cm x 3 cm stainless steel column and in a 25 cm x 3 cm stainless steel column filled with 2730 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 mL/min and 16.8 mL/min for the 15 cm and 25 cm laboratory scale columns, respectively, and Q=1.36 L/min for the pilot scale column. The methylene blue influent concentration was 14 $mg.L^{-1}$. Interconnective tubing and fitting were made of polytetrafluoroethylene (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 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 cm^2 and the adsorbent was 0.07 g/mL, i.e. the column was filled with 2730 g of coarse grinded barley straw.

Analytical Techniques: Following the technique proposed by Saeman et al. [14], 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 O.D. at 663 nm, using a HACH DR4000U UV–visible spectrophotometer.

3. RESULTS AND DISCUSSION

Oulman [15] proposed the use of a bed depth service model for simulating GAC (granular activated carbon) adsorption beds. The model, first developed by Bohart and Adams [16], was based on surface reaction theory and is equivalent to the logistic curve [17-20]. The Bohart-Adams equation is as follows:

$$ln\left(\frac{C_i}{C}-1\right)=\frac{K\cdot N\cdot x}{u}-K\cdot C_i\cdot t \quad \text{or} \quad ln\left[\frac{C_i}{C}-1\right]=ln\,A-r\cdot t \tag{1}$$

in which C=effluent concentration ($mg.L^{-1}$); C_i=influent concentration ($mg.L^{-1}$); K=an adsorption rate coefficient ($L.mg^{-1}.min^{-1}$); N=an adsorption capacity coefficient ($mg.L^{-1}$); x=bed depth (cm); u=linear velocity ($cm.min^{-1}$); and t=time (min). $lnA=K.N.x/u$ and $r=K.C_i$.

The values of A and r can be thus estimated from the column effluent data assuming C_i=column influent and C=the column effluent at time t. We can calculate K, N from the equations $K=r/C_i$ and $N=u\cdot lnA/(x\cdot K)= C_i\cdot u\cdot lnA/(x\cdot r)$. 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 parameter -values obtained using the same equation.

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

Equation (1) can be rewritten as:

$$C=\frac{C_i}{1+Ae^{-rt}} \tag{2}$$

This is the well known logistic model, which can be used as an independent phenomenological kinetic expression, since all break through 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 $t=(ln\,A)/r$. 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]:

$$y=\frac{K}{1+me^{-bt^a}}\ \text{(I)},\quad y=\frac{K}{\left(1+me^{-bt}\right)^a}\ \text{(II)},\quad y=\frac{K}{\left(1+me^{-bat}\right)^{1/a}}\ \text{(III)},\quad y=\frac{K}{\left(1+me^{-bat}\right)^a}\ \text{(IV)} \tag{3}$$

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

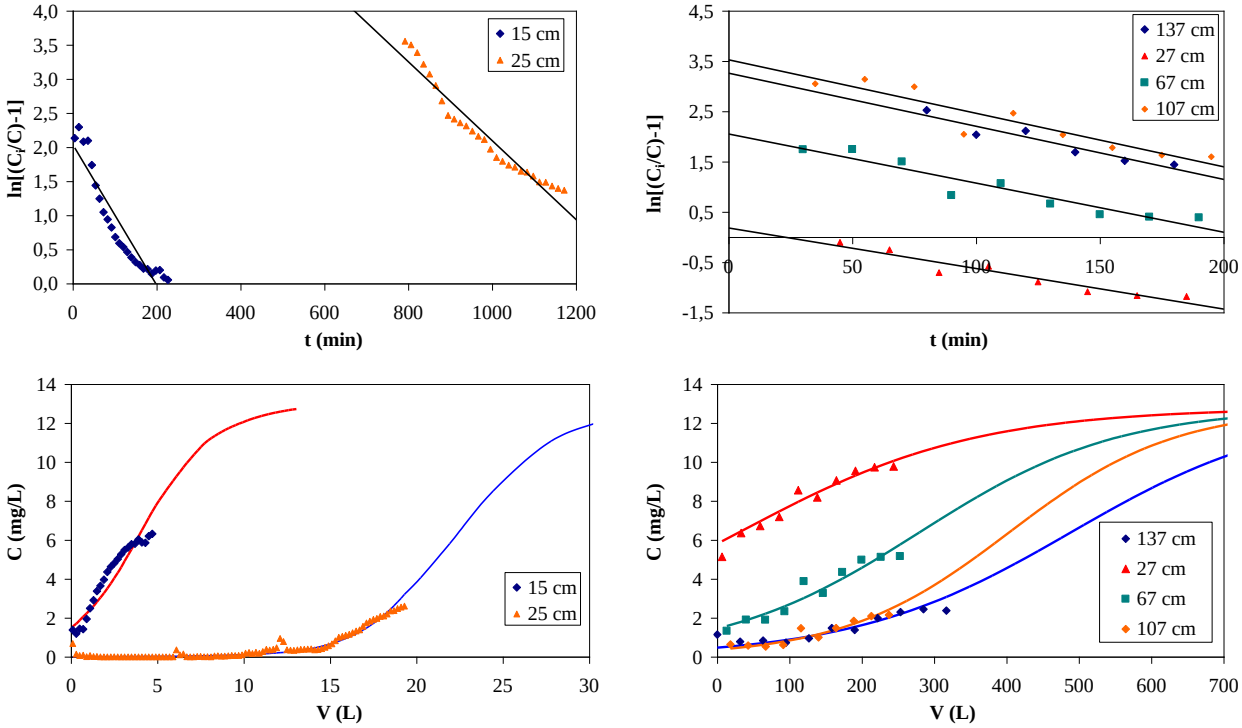

FIGURE 1. Breakthrough curves in the linearized/logarithmic form and in the original/non-linear form (a) for the laboratory scale columns with bed height x=15 cm and 25 cm, and (b) for the pilot plant column with bed height *x*=137 cm (sampling at 27, 67, 107, and 137 cm). Fixed bed: barley straw; Methylene 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.

FIGURE 2. (a) Laboratory scale column of 15 cm height with 25 L tank, (b) laboratory scale pump, and (c) pilot scale column of 137 cm height with 1000 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*** **(Lmg^{-1} min^{-1})**	**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

4. CONCLUDING REMARKS

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 (B-A) 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 -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.

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