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Application of Model Molecule and Alternative Adsorbents for Mathematical Modeling of the Fluidized Bed Adsorption Process

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Abstract

The issue of textile dyes and other emerging contaminants present in industrial effluents can be addressed by adsorption in a continuous system, such as a fluidized bed column. In the present study, a fluidized bed adsorption system using alternative adsorbents (NaZC and HZC) was employed to study the removal of the model molecule methylene blue (MB). The experiments were conducted in a column with an effective height of 22 cm and an internal diameter of 0.5 cm, coupled to a peristaltic pump, where 0.25 g of the adsorbent (NaZC or HZC) was added to the column. The MB solution (50 mg L^{-1}) was introduced into the column in an upward flow at flow rates of 10, 15, and 20 mL min^{-1}. The experimental data were fitted to non-linear forms of the Thomas, Yan, Clark, and Empty Bed Contact Time (EBCT) models. S-shaped breakthrough curves were obtained with a breakthrough time of around 5 minutes for the studied flow rates, with the Yan model providing the best fit to the experimental data, suggesting that the adsorption mechanism is governed by intraparticle diffusion phenomena. In this context, laboratory studies of fixed-bed column adsorption demonstrate potential in elucidating parameters and kinetic modeling for real-world application.

Keywords: Continuous system adsorption, textile dyes, modeling, intraparticle diffusion.

1. Introduction

The treatment of effluents generated in the textile production and dyeing industries is extremely necessary and urgent, as approximately 15% of synthetic dyes are lost during manufacturing and processing stages annually [1]. Additionally, these dyes are associated with the reduction of parameters such as BOD and COD, and many of them exhibit carcinogenic, teratogenic, and mutagenic potential for human health and aquatic life [2] [3].

Various methods are applied in treatment plants, such as adsorption, coagulation/flocculation, ion exchange, photocatalysis, advanced oxidation processes, biological treatment, etc. [4]. Among these, adsorption can be applied in batch operations or continuous systems, with the latter being the most used industrially. This model enables process automation and allows for greater efficiency, which is associated with the treatment of larger volumes of effluent in a shorter time. [5].

Some research groups have studied the adsorption of textile dyes in continuous systems [6], [7], [8], [9], [10], [11]. In these studies, various mathematical models of mass transfer are typically applied to elucidate the column's performance, with some parameters previously determined in batch kinetic and equilibrium studies, such as adsorption capacity, equilibrium time, heat of reaction, initial adsorbate concentration, etc., as well as appropriate correlations. The use of previously determined parameters facilitates the development of mass transfer models since the concentration profiles in the solid phases do not operate in a steady state, i.e., they vary with space and time.

In continuous system adsorption studies, the most evaluated models are those developed by Thomas, Clark, Yan, and Adams-Bohart, also known as Bed Depth Service Time. The Thomas model has been used to predict column performance. In this model, some assumptions are made, such as constant physical properties between adsorbate and adsorbent, negligible external mass transfer resistance and intraparticle diffusion, adsorption equilibrium described by Langmuir, and constant temperature and pressure throughout the process. However, since adsorption is controlled by mass diffusion and not limited by reaction kinetics, there is an associated error with this model. Nevertheless, it continues to be used, mainly for determining the maximum adsorption capacity and the kinetic constant [15].

The Clark model was developed by combining the Freundlich equation with the concept of mass transfer. The Yan model minimizes the error of the Thomas model, particularly at the operational extremes (short and long periods of operation). Finally, the BDST (Bed Depth Service Time) model is a simple model that correlates column height with operation time, assuming that the adsorption rate is controlled by the surface reaction between the adsorbate and the unused capacity of the adsorbent. Although this model is typically applied to variations in column height, in this study, it was correlated with fluid flow rate and adsorbent utilization rate [15].

In addition to understanding and mathematical modeling, an efficient fluidized bed adsorption process requires the use of adsorbents with high adsorption capacity, stability against process variables, low cost, and the ability to be regenerated and reused [12]. In the present study, alternative adsorbents (NaZC and HZC) produced from residual diatomaceous earth from the brewing process [13] were applied for the removal of methylene blue (MB) dye as a model molecule in a fluidized bed system. The Thomas, Clark, Yan, and Empty Bed Contact Time (EBCT) models were fitted to the experimental data to better elucidate the parameters for process scale-up.

2. Materials and Methods

Adsorption tests in a fluidized bed were conducted using a column with a useful height of 22 cm and an internal diameter of 0.5 cm, coupled with a peristaltic pump (TCP LDP-201-3). The column was charged with 0.25 g of each adsorbent (NaZC and HZC). A model molecule solution (50 mg L^{-1}) was introduced into the column in an upward flow at flow rates of 10, 15, and 20 mL min^{-1}. The fluid flow rate was determined by the ratio of the flow rate to the cross-sectional area. The pH of the solution was maintained near neutrality using NaOH and HCl solutions (0.1 M). Samples were collected from the top of the column over time, in triplicate, and analyzed using UV-Vis spectroscopy (Spectrophotometer Drawell, Du-8800d) at a wavelength of 664 nm to determine the corresponding AM concentrations.

Non-linear models of Thomas, Yan, Clark, and EBCT were fitted to the experimental data according to equations (1), (2), (3) and (4), respectively.

$$\frac{C_t}{C_o} = \frac{1}{1 + e^{\left[\frac{K_T q_T m}{\dot{Q}} - K_T C_o t\right]}} \quad (1)$$

In equation (1), C_t represents the concentration at time (mg L^{-1}) in time t (min), C_0 is the initial concentration (mg L^{-1}), k_t is the Thomas rate constant, q_t denotes the adsorption capacity (mg g^{-1}), m is the mass of the adsorbent (g), $\dot{Q}$ is the fluid flow rate (ml min^{-1}).

$$\frac{C_t}{C_o} = \frac{1}{1 + \left(\frac{\dot{Q} q_{YAN} m t}{C_o}\right)^{a}} \quad (2)$$

In equation (2), q_{YAN} is the adsorption capacity (mg g^{-1}), and a is the parameter of the Yan model.

$$\frac{C_t}{C_o} = \left(\frac{1}{1+\left(\frac{C_0^{n-1}}{C_{break}^{n-1}}-1\right)\exp\left((n-1)\frac{k_{CL}v}{U_0}t_{break}\right).\exp\left(-(n-1)\frac{k_{CL}v}{U_0}\mathrm{t}\right)}\right)^{\frac{1}{n-1}} \quad (3)$$

In equation (3), n is the Freundlich constant (2.9 for NaZC and 4.5 for HZC [13]), C_{break} is the breakthrough concentration (mg mL^{-1}), t_{break} is the breakthrough time (min), k_{CL} is the Clark kinetic constant (min^{-1}), U_0 is the superficial velocity, and v is the migration rate.

$$\text{EBCT (min)} = \frac{V_T}{\mathrm{H}.A_{sec}} \quad (4)$$

In equation (4), V_T is the internal volume of the empty column (mL), H is the hydraulic load (mL $min^{-1}cm^{-2}$) and A_{sec} is the cross-sectional area (cm^2).

The adsorbent utilization rate (U_R) was determined using equation (5). V_B is the volume of solution treated at the breaking point (L).

$$U_R(\mathrm{g}.L^{-1}) = \frac{m}{V_B} \quad (5)$$

3. Results and Discussion

The figure 1 illustrates the breakthrough curves for the adsorption of AM on NaZC and HZC in a fluidized bed column with varying fluid flow rates. The data were fitted to the non-linear models of Thomas, Clark, and Yan. It can be observed that all the breakthrough curves exhibit an S-shaped trend, with a steeper slope for the data corresponding to the highest flow rate (20 mL min^{-1}).

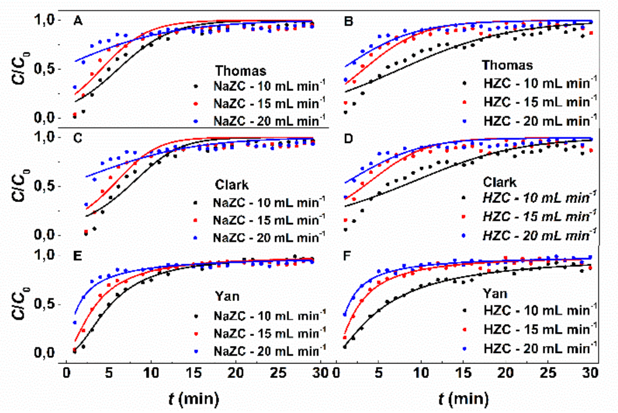

Fig. 1- Breakthrough curves and the Thomas, Clark, and Yan models for the adsorption of AM (50 mg L^{-1}) on NaZC and HZC at flow rates of 10, 15, and 20 mL min^{-1}.

As observed in Figure 1, the breakthrough point (C/C_0 = 5%) was reached within 5 minutes of operation, showing an inverse relationship with the flow rate. The exhaustion point (C/C_0 = 95%) varied slightly among the adsorbents and flow rates. For NaZC, exhaustion was reached approximately 15 minutes for all three flow rates. Although the exhaustion time was the same, the flow rate influenced the slope of the curve. For HZC, exhaustion occurred around 10 minutes for flow rates of 15 and 20 mL min^{-1}, and approximately 25 minutes for flow rate of 10 mL min^{-1}. This behavior is attributed to the fact that a lower flow rate allows for a longer contact time between the adsorbent and adsorbate within the column.

Among the models studied, Yan model provided the best fit to the data (Figure 1 (E) and (F)) for all three flow rates investigated. In contrast, the Thomas model appears to have provided a poor fit. This behavior may be correlated with the fact that the equilibrium mechanism between the adsorbents studied, and AM is described by the Freundlich isotherm [13], whereas the Thomas model is based on the Langmuir isotherm.

Figure 2 presents the adsorbent utilization rate curves as a function of the Empty Bed Contact Time (EBCT), which measures the duration that a portion of the AM solution remains in the column, given that there is no adsorbent material in the column [14].

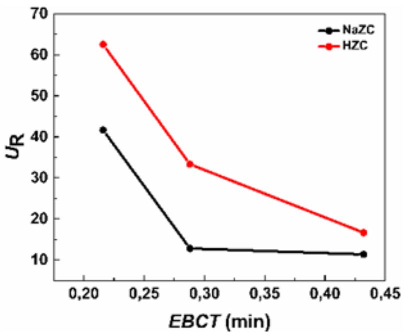

Fig. 2 – Adsorbent utilization rate with EBCT.

Figure 2 demonstrates that as the EBCT decreases, the adsorbent utilization rate (UR) increases for both adsorbents, indicating that larger quantities of adsorbent are required for the treatment of a unit volume. It is also noted that the UR is lower for NaZC, indirectly supporting the superior adsorption capacity for the pollutant studied, as previously reported in earlier studies [13].

The parameters obtained from the fittings of the models for adsorption in a fluidized bed are presented in Table 1.

Table 1 – Kinetic parameters obtained from fitting the models to the experimental data.

	NaZC			HZC		
$\dot{Q}\left(\frac{ml}{min^{-1}}\right)$	10	15	20	10	15	20
Thomas						
k_T	0.006	0.007	0.003	0.003	0.006	0.005
q_T	1.21x 10^4	1.23x 10^4	4.47x 10^3	1.47x 10^4	9.28x 10^3	1.83x 10^3
R^2_{adj}	0.936	0.853	0.645	0.883	0.825	0.834
χ^2	0.005	0.008	0.006	0.006	0.006	0.003
Clark						
t_{break}	15.69	13.80	1.832	22.34	5.631	1.178
k_{CL}	0.053	0.058	0.041	0.036	0.051	0.004
C_{break}	48.30	49.00	31.18	45.69	33.41	21.87
υ	5.357	5.885	4.053	3.628	5.122	4.485
R^2_{adj}	0.911	0.815	0.638	0.846	0.787	0.801
χ^2	0.007	0.010	0.007	0.008	0.007	0.003
Yan						
q_{Yan}	3.799	3.784	6.671	3.318	4.874	6.760
α	1.697	1.576	1.000	1.382	1.353	1.105
R^2_{adj}	0.992	0.975	0.934	0.986	0.970	0.973
χ^2	0.001	0.001	0.001	0.001	0.001	0.001

Through the statistical parameters R^2_{adj} and χ^2, as well as the analysis of Figure 1 (E) and (F), it is evident that the Yan model best describes the experimental data, whereas the R^2_{adj} e χ^2, values for the Thomas and Clark models are suboptimal.

The table 1 indicates that the mass transfer coefficients for the Thomas and Clark models (k_T, k_{CL}) show a linear increase with flow rate, but a significant decrease in these parameters occurs at the highest flow rate (20 mL min^{-1}) [15]. This can be attributed to the reduced contact time between the adsorbate and adsorbent in the column due to the high fluid flow velocity. The parameter a of the Yan model decreases with increasing flow rate for both adsorbents, while the adsorption capacity at breakthrough time (q_{Yan}) increases.

In this context, it can be inferred that the superior fit of the Yan model to the data suggests that the adsorption mechanism of AM on the surfaces of NaZC and HZC is governed by intraparticle diffusion, characterized by the rapid approach of C/C_0 to 1, a factor not accounted for by the other models.

4. Conclusions

This study clearly demonstrates the feasibility of AM adsorption in a fluidized bed column using the alternative adsorbents NaZC and HZC. The model that best predicts the experimental data is the Yan model, indicating that mass transfer is governed by intraparticle diffusion. This finding facilitates and enables the scale-up to real processes, which generally contribute to the maintenance, cleaning, and sustainable management of water bodies.

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