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Adsorption of azo dyes onto a corncob in packed column at the constant velocity of front propagation

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ABSTRACT

Practical use of adsorption involves conducting the process in a packed bed column. The sorbent bed allows removing the contaminants from water or another solvent. Adsorption is most often applied to the treatment of aqueous solutions such as removal of hardness, heavy metal ions, colorants, pesticides, humus, and other organic and inorganic pollutants appearing in the water environment. Adsorption from low-concentration solutions is the main area of application of this process. Description of column adsorption presented in this paper uses a moving observer whose velocity is equal to the velocity of concentration front movement. This approach reduces the system of partial differential equations to ordinary differential equations. The method is able to predict the breakthrough time, saturation time as well as calculate the changes in concentrations with time and at different locations inside the column. Direct orange azo dye and properly prepared corncobs were used in the experiments. The column was operated at various initial dye concentrations, volumetric flow rates, and bed heights.

Keywords: Packed column; Adsorption dynamics; Azo dye

1. Introduction

The textile industry, despite evolving technology, modern machinery, and equipment, still produces considerable amounts of environmentally hazardous wastewater, which may be characterized by high salinity, alkaline pH, and above all, intense color. In the dyestuff industry, discoloration of wastewater is achieved mainly by applying highly efficient synthetic ion-exchange materials. Unfortunately, they are expensive and hard to dispose of. For these reasons, increasing attention has been focused around the possibility of using waste products, such as rye straw, vegetable peels, cereal seed husks, or corncobs, as natural sorbents. They are relatively cheap and biodegradable which makes them attractive replacements for synthetic substances [1,2].

Over the past few years, new low-cost sorbents have been looked for by the leading research centers. The investigated contaminants include heavy metal ions, dyes, phenols and their derivatives, and hydrocarbons. The key issue is to replace expensive traditional sorbents with cheaper waste-derived materials.

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However, to evaluate their effectiveness, proper experiments must be conducted including a specific group of compounds and the selected sorbent. Low-cost sorbents do not require regeneration—they may be incinerated, although the exhaust gases must be treated accordingly.

The main objective of this paper is to describe adsorption of an azo dye onto corncobs (low-cost adsorbent). The paper also presents a new approach to describe adsorption process in a packed column.

1.1. Characteristics of adsorbent and adsorbate

Cobs constitute the thick, hard, central core of maize. They are composed of 44–45% cellulose, 31–40% hemicellulose, and 8–15% lignin [3,4]. Corncob is an agricultural waste product and can be used in many application, e.g. as adsorbent. Apart from dye adsorption, corncobs are also reported to be widely used for removal of heavy metals from aqueous solutions [5–8]. They are also commonly used to obtain activated carbon, further utilized to adsorb water contaminants such as chlorophenol and dyes [9,10].

Corncobs used in this study were acquired from CHIPSI MAIS Germany and used in the form of hard granules, the size of approximately 0.005 m, humidity of ca. 10%, and density of 438.8 kg/m^3.

The direct orange 26 azo dye, of molecular formula $C_{33}H_{22}N_6Na_2O_9S_2$ and molecular weight 756.67 g/mol, CAS Number 3626-36-6. Dye (purity compatible with standard) used for the purpose of this study was supplied by Boruta-Zachem Kolor Sp. z o.o. (Poland). It is utilized for coloring home-cleaning products and cosmetics, and have several other applications (Order of the Minister of Health of 30th March 2005, Journal of Laws of 2005 No. 72 Item 642), and represents the azo compound group. Chemical structure of the azo dye is presented in Fig. 1.

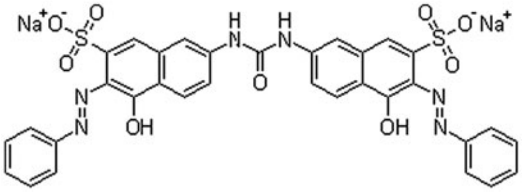

Fig. 1. Molecular structure of direct orange 26.

1.2. Mathematical description of adsorption dynamics

The starting point to characterize the adsorption mechanism in a packed column is the differential mass balance equation assuming that the concentration gradient in both the liquid and sorbent is a function of time and position [11,12]:

$$u_0\frac{\partial c(x,\ t)}{\partial x}+(1-\varepsilon)\rho_s\frac{\partial q(x,\ t)}{\partial t}+\varepsilon\frac{\partial c(x,\ t)}{\partial t}=\varepsilon D_{\text{eff}}\frac{\partial^2 c(x,\ t)}{\partial x^2(x,\ t)} \tag{1}$$

Therefore, the changes of concentration in the liquid $c(t,x)$ and sorbent $q(t,x)$ are functions of time and the distance from the inlet. The mass balance between the liquid stream and sorbent bed is calculated with the following initial and boundary conditions:

$c(0,x)=0,$
$q(0,x)=0,$
$c(t,0)=c_0$ for $t>0$

It entails the constant inlet concentration c_0.

Additionally, it has been assumed that the adsorption kinetics may be described by a pseudo-second-order equation:

$$\frac{\partial q}{\partial t}=k_2(q^*-q)^2 \tag{2}$$

and the concentration front moves at the constant velocity u_F. Such a concept was previously adopted in published works on adsorption kinetics in packed columns [13,14].

There is a possibility to transform partial differential Eqs. (1) and (2) into the system of ordinary equations by adopting a concept of the observer moving at the velocity of concentration front u_F. As the result, a new modified variable ξ defined by Eq. (3):

$$\xi=u_F t-x \tag{3}$$

may be employed. Calculating the derivatives of ξ with respect to time and distance and substituting derivatives in Eqs. (1) and (2) yields:

$$(\varepsilon u_F-u_0)\frac{dc(\xi)}{d\xi}+(1-\varepsilon)\rho_s u_F\frac{dq(\xi)}{d\xi}=\varepsilon D_{\text{eff}}\frac{d^2c(\xi)}{d\xi^2} \tag{4}$$

$$\frac{dq(\xi)}{d\xi}=\frac{k_2}{u_F}(q^*-q)^2 \tag{5}$$

Integrating Eq. (5) between the limits <0, ξ_0 > gives:

$$q(\xi_0)=q^*\frac{\alpha_2\xi_0}{1+\alpha_2\xi_0} \tag{6}$$

where

$$\alpha_2 = \frac{q^* k_2}{u_F} \tag{7}$$

$$\xi_0 = u_F t \tag{8}$$

Eq. (6) expresses the changes in concentration at the column inlet.

Integration of Eq. (5) between the limits $<\xi_0, \xi>$ yields:

$$q(\xi) = q^* \frac{\alpha_2 \xi}{1 + \alpha_2 \xi} \tag{9}$$

In subsequent calculations, an approximation of the derivative defined by Eq. (10) is accepted:

$$\frac{\mathrm{d}c(\xi)}{\mathrm{d}\xi} = \frac{(1-\varepsilon)\rho_s}{\left(1 - \varepsilon \frac{u_F}{u_0}\right)} \frac{\mathrm{d}q(\xi)}{\mathrm{d}\xi} \tag{10}$$

Integrating Eq. (4) between $<\xi_0, \xi>$ and applying approximation given by Eq. (10) finally results in:

$$c(\xi) = c_0 + \frac{(1-\varepsilon)\rho_s}{\left(1 - \varepsilon \frac{u_F}{u_0}\right)} (q(\xi) - q(\xi_0)) - \frac{\varepsilon D_{\mathrm{eff}}}{u_0 \left(1 - \varepsilon \frac{u_F}{u_0}\right)} \left(\frac{\mathrm{d}c(\xi)}{\mathrm{d}\xi} - \frac{\mathrm{d}c(\xi_0)}{\mathrm{d}\xi} \right) \tag{11}$$

2. Experiments

Adsorption dynamics studies were conducted using a laboratory column of 0.0345 m diameter and 0.70 m length packed with granulated corncobs giving bed porosity of $\varepsilon = 0.33$. The dye solution (flowing upwards) was fed with a dosing pump. Having passed through the bed, it was collected at predetermined intervals and analyzed quantitatively using UV–vis Jasco V630 spectrophotometer. pH and temperature of the solution were measured at the column inlet and outlet. Temperature was stabilized at approximately 25˚C, and pH was approximately equal to 5.6. To evaluate the adsorption model accuracy, it was necessary to perform experiments with different process parameters. Experiments were carried out for two different initial concentrations of dye solution $c_0 = 50$ and 75 mg/dm^3, three volumetric flow rates $Q = 50$, 100, and 200 cm^3/h, and two bed heights $H = 0.59$ and 0.29 m, which corresponded to masses of beds $m = 165$ and 85 g.

Granulated corncobs were washed and boiled for 3 h in a pressure cooker at 130˚C. To increase their adsorption capacity, corncobs were etched with 10% H_2SO_4 for 5 h at 60˚C. Following chemical pretreatment, the granulated corncobs were dried at 70˚C for 2 h. The procedure of pretreatment was developed based on the previous unpublished experience concerning corncobs. Application of sulfuric acid allowed cleaning raw corncob from resins and other contaminations, and due to pretreatment the structure of corncobs was more accessible to the azo dye. Hydroxyl groups from sorbent were able to create bounding with ionized sulfonic groups. Dye binding to the sorbent may be the result of weak van der Waals forces and strong ionic exchange interactions between ionized sulfonic groups of the dye and sorbent surface as per the following formula [15]:

$$\begin{aligned}&\text{Corncob–OH} + \text{H}^+ + {}^-\text{O}_3\text{S–Dye}\\&\quad = \text{Corncob–OH}_2^+ + \text{H}^+ + {}^-\text{O}_3\text{S–Dye}\end{aligned}$$

3. Results and discussion

The measurements of dye concentration at the column outlet were used to identify the unknown coefficients according to Eq. (11). The equilibrium dye concentrations in the sorbent q^* were determined experimentally and equaled 1.33 or 1.59 mg/g d.m., which corresponded to the initial dye concentrations at the column inlet of 50 and 75 mg/dm^3, respectively. Propagation velocity was assumed as constant and calculated using experimental and approximated values by dividing the bed height by breakthrough time (vide Table 1). Thus, values of two more variables, namely dispersion coefficient D_{eff} and kinetics constant k_2, had to be calculated, which was accomplished via an optimization procedure involving genetic algorithms.

Comparisons of experimental and approximated results, obtained for bed height of $h = 0.59$ m (165 g of sorbent) and initial dye concentrations of $c_0 = 50$ and 75 mg/dm^3, are presented in Figs. 2 and 3. Black dots represent approximated values (Eq. (11)). Figs. 4 and 5 demonstrate the changes in dye concentration q (mg/g) calculated using Eq. (9). Values of Eq. (9) coefficients are given in Table 1. Table 2 contains statistical assessment of the accepted model comprising coefficients of determination and root-mean-square errors.

Considering the values of dispersion coefficient D_{eff}, it may be said that dispersion is of little importance within the applied range of column flow rates.

Table 1
Coefficients of adsorption dynamics in the packed column

c_0	Coefficient	50 cm^3/h	100 cm^3/h	200 cm^3/h
50 mg/dm^3	k_2 (g/(mg min))	3.397e−04	2.061e−04	7.652e−04
	D_{eff} (m^2/min)	1.007e−05	3.285e−04	1.331e−09
	u_{F} (m/min)	9.365e−05	4.114e−04	8.183e−04
75 mg/dm^3	k_2 (g/(mg min))	3.334e−04	3.049e−04	6.750e−04
	D_{eff} (m^2/min)	3.498e−10	3.855e−09	1.902e−08
	u_{F} (m/min)	2.463e−04	6.985e−04	1.791e−03

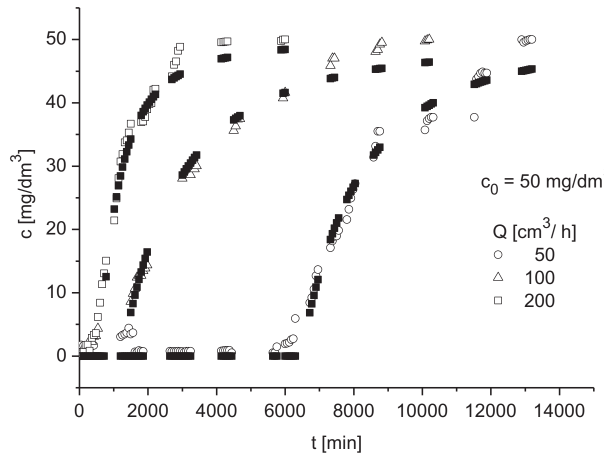

Fig. 2. Experimental and calculated changes in dye concentration at the column outlet for the initial concentration at the inlet equal to 50 mg/dm^3.

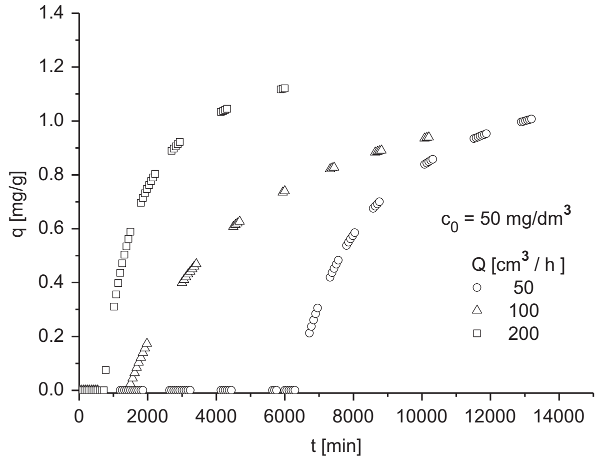

Fig. 4. Calculated changes in dye concentration in the sorbent at the column outlet for the initial concentration at the inlet equal to 50 mg/dm^3.

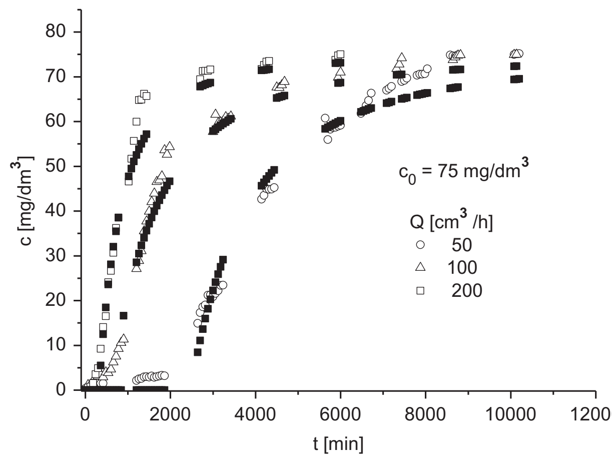

Fig. 3. Experimental and calculated changes in dye concentration in the solution at the column outlet for the initial concentration at the inlet equal to 75 mg/dm^3.

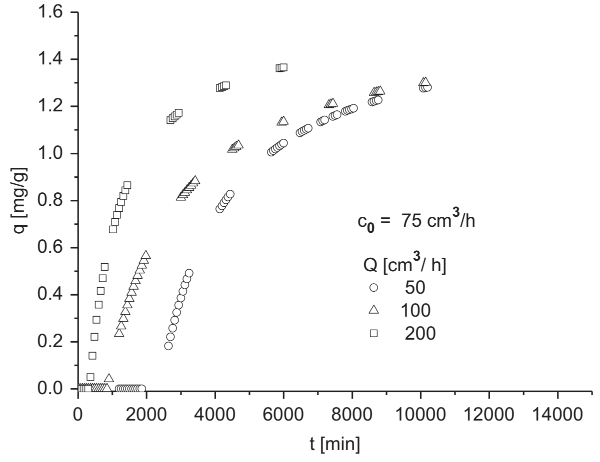

Fig. 5. Calculated changes in dye concentration in the sorbent at the column outlet for the initial concentration at the inlet equal to 75 mg/dm^3.

Table 2
Statistical assessment of experimental and calculated data

c_0	Coefficient	50 cm^3/h	100 cm^3/h	200 cm^3/h
50 mg/dm^3	R^2	0.959	0.982	0.959
	δ	3.381	2.356	3.653
75 mg/dm^3	R^2	0.982	0.979	0.977
	δ	3.833	3.965	4.172

In turn, low values of the kinetics constant suggest that adsorption on corncobs is slow and controlled by the internal diffusion.

The values shown in Table 2 confirm usefulness of the proposed model assuming constant velocity of the front propagation. Auxiliary coefficients for the model such as equilibrium concentration of dye in the sorbent q^* and the velocity of concentration front u_F were determined with accuracy less than ±5%.

4. Summary and conclusions

The article presents a mathematical model of adsorption in a packed column. The method of description refers to the Lagrange's view, i.e. an observer moving along the concentration front. Constant velocity of front propagation has been assumed. A mean value of propagation velocity was determined based on the breakthrough time of the column and applied in the calculations. The adsorption experiments were conducted using the direct orange 26 azo dye and thermally and chemically modified corncobs. The accepted model provides an accurate approximation, which was confirmed by statistical analysis of the obtained results.

List of symbols

c_0, c	—	initial or temporary concentration of dye in a solution (mg/dm^3)
D_{eff}	—	effective dispersion coefficient (m^2/min)
h	—	bed height (m)
k_2	—	kinetics constant (g/(mg min))
q	—	temporary concentration of dye in a sorbent (mg/g d.m.)
q^*	—	equilibrium concentration of dye in a sorbent (mg/g d.m.)
Q	—	volumetric flow rate (cm^3/h)
R^2	—	square determination coefficient (–)
t	—	time (min)
u_0	—	apparent linear velocity (m/min)
u_F	—	velocity of concentration front (m/min)
x	—	distance between the column inlet and specified place (m)
δ	—	root-mean-square error (g/mg)
ξ	—	coefficient defined by Eq. (3) (m)
ε	—	voidage of the bed (–)
ρ_s	—	density of sorbent (kg/m^3)

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