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Adsorption dynamics studies of azo dyes removal by biosorbent

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ABSTRACT

The aim of the study was to evaluate the process of azo dyes sorption onto plant sorbent as an alternative method of water treatment, allowing for the removal of harmful contaminants. The use of chemically modified rye straw to remove of Direct Orange 26 and Reactive Blue 81 from aqueous solutions was proposed in the paper. Experiments were carried out in a laboratory column for different volumetric flow rate, high of bed, and initial concentration of dye. The authors propose an approach completed with an experimental procedure which allows to describe the operation of adsorption columns during the startup, continuous work until breakthrough and to obtain concentration profiles prior to the column regeneration. Calculations were carried out in the Matlab computing environment. Assessment of statistical parameters confirmed that a good fit to experimental data for most of cases was obtained. It was found that that rye straw is an efficient sorbent for the removal of acid dye from water and that it may be used as an alternative biosorbent for the treatment of contaminated water.

Keywords: Rye straw; Azo dyes; Biosorption; Packed column; Dynamics modeling

1. Introduction

The water purification concerns of removal of many chemical compounds. Textile wastewater poses a potential threat to surface waters. It has a complex chemical composition and in most cases, dyes are the dominant compounds. With the development of science and technology, various methods for water purification have been developed and used. A number of methods, such as anaerobic decomposition, coagulation, filtration, or membrane separation, as well as biological methods, are used to remove dyes from industrial effluents. Adsorption is very effective for reducing dye concentration in effluents. Experiments aim at increasing efficiency of dye removal from aqueous solutions particularly by selecting suitable process parameters that should be provided. It is important that the process be cost effective so that innovative natural materials and industrial byproducts are investigated for this purpose. Biosorption is an alternative to physicochemical separation processes [1]. It is recommended to remove dyes by means of adsorption from diluted solutions. However, it is not easy to realize. In order to remove pollutants from the liquid solution by adsorption process, it is necessary to use solid adsorbents with a highly developed surface [2,3].

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Sorbent materials have various environmental applications, i.e. water filtration, separation, and purification. Rapid progress in nanotechnology and many others focused on biomass-based sorbent instead of traditional materials have produced a wide range of novel sorbents. The development and evaluation of novel sorbents requires a multidisciplinary approach encompassing environmental, nanotechnology, physical, analytical, and surface chemistry. The necessary evaluations cover not only the efficiency of these materials to remove contaminants from surface waters and groundwater, industrial wastewater, polluted soils and sediments, etc. but also the potential side effects of their environmental applications.

In the last decade, a growing interest is observed in inexpensive adsorbents to remove dyes, heavy metal ions, and others [4–6]. Biosorbents primarily fall into the following categories: bacteria, fungi, algae (living or dead sorbents), industrial wastes, agricultural wastes, natural residues, and other biomaterials (dead biomass). Modern studies are designed to investigate unconventional plant/natural lignocellulosic products and adsorbents such as: corncobs, banana fibers, sawdust, buckwheat and rice hull, peat, bran, etc. [7,8]. Dead biosorbents are more favorable as they cost less, can be regenerated and reused, and are easier to operate and maintain.

Azo dye–plant sorbent (rye straw) system was investigated in the paper. After initial studies with raw straw, further experiments involved chemically pretreated straw with a view to increasing its sorption capacity. The aim was to determine suitability of chemically modified rye straw for removing selected two azo dyes from aqueous solutions and provide a mathematical description of the process. Kinetic and equilibrium parameters were determined for the sorption process, necessary for calculations related with the dynamics of process carried out in adsorption column, which will comprise the main stage of the studies.

A mathematical model to calculate the concentration of solution at the column outlet and the concentration of adsorbed substance in the adsorbent, as well as breakthrough curves for different process conditions and column dimensions was proposed in the study.

2. Materials

Direct Orange 26—DO26 (molecular formula: $C_{33}H_{22}N_6Na_2O_9S_2$) and Reactive Blue 81—RB81 (molecular formula: $C_{25}H_{17}Cl_2N_7O_{10}S_3Na_3$) azo dyes were obtained from a local Boruta-Zachem Kolor Sp. z o.o. plant. They are used for coloring home cleaning products, cosmetics, and have several other applications and represent the azo compound group.

In experiments, a sorbent on the basis of the natural biosorbent rye straw (produced in central Poland in 2012) was prepared.

The procedure of chemical pretreatment was developed based on the previous experience with straw that had only been washed. To increase its sorption capacity, the straw was etched with 10% H_2SO_4 for 5 h at 60˚C. Following chemical pretreatment, the straw was washed and dried at 105˚C for 2 h. Because adsorption onto chemically preprocessed rye straw brought better results, this form of sorbent was used for the experiments.

Sorption equilibrium and kinetics studies (needed for the dynamics calculations) were carried out at constant temperature ($T = 25$˚C), at pH 6–7. Five grams of sorbent dm were placed into conical flasks and 200 cm^3 of the dye aqueous solutions was added. Initial dye concentrations were changed within the range 50–800 mg/dm^3.

3. The study of the packed column

The experimental setup for the sorption in a packed bed consisted of a glass column with a diameter of 3.45 cm and a length of 70 cm. The column was filled with pretreated dry rye straw of 100 g in mass which was corresponded to 0.58 m bed height. Additional experiments were performed for 0.28 m bed height. The voidage of the bed was 0.348. The density of the dried rye straw was 329 kg/m^3.

Before starting the sorption measurement, the bed was conditioned using redistilled water for 2 h. At time $t = 0$, aqueous solution of dye was pumped into the column from the bottom to the top of the bed and then to discharge. The column was fed with constant concentration of dye solution at the column inlet. Two initial concentrations were used i.e. 50 and 75 mg/dm^3. The experiments were carried out at a volumetric flow rate of 50, 100, 200, and 400 cm^3/h. Samples were taken at the column outlet and analyzed by means of UV–vis Jasco V630 spectrophotometer at the wavelength of 494 nm for Direct Orange 26 and 583 nm for Reactive Blue 81.

4. Mathematical description of sorption dynamics

The main goal of this study was to develop a simple method for modeling the adsorption process in a packed column. It is a new and original approach to solving the mass balance in the packed

column analytically. The authors propose an approach completed with an experimental procedure, which allows to describe the operation of adsorption columns during the startup, continuous work until breakthrough, and to obtain concentration profiles prior to the column regeneration. The system of partial differential equations describing adsorption in the column (mass balance—Eq. (1)) due to the assumption of a properly defined variable is transformed into the system of ordinary nonlinear equations, which enable identification of object parameters based on experiments.

The concentration is dependent both on time t and the axial position in the column x. To facilitate interpretation of results, introduction of the following variable was suggested:

$$\xi_0 = u_0 t \tag{1}$$

$$\xi = \begin{cases} u_0 t - x & \text{for } u_0 t > x \\ 0 & \text{for } u_0 t \leq x \end{cases} \tag{2}$$

This enabled the calculation of the concentration in the fluid $c(t,x)$ and the sorbent $q(t,x)$ as a function of time and distance from the inlet of the column. Assumptions of the model and detailed calculations were presented in [9].

$$u_0 \frac{\partial c(x,t)}{\partial x} + (1-\varepsilon)\rho_s \frac{\partial q(x,t)}{\partial t} + \varepsilon \frac{\partial c(x,t)}{\partial t} = \varepsilon D_{eff} \frac{\partial^2 c(x,t)}{\partial x^2(x,t)} \tag{3}$$

After the substitutions described in the paper [9,10], Eq. (3) takes the following form:

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

In the paper, it was assumed that concentration changes in the sorbent are in line with adsorption kinetics equation suitable for a given adsorbate–adsorbent system. In the case of the rye straw–azo dyes system, it was assumed that the dominant mechanism was chemical/mixed sorption and sorption kinetics was well described by the Elovich equation [11,12]:

$$\frac{dq}{dt} = k_E e^{-\beta q} \tag{5}$$

After taking into account the variable ξ, the following equation was obtained:

$$\frac{\partial q}{\partial t} = u_0 \frac{dq}{d\xi} = k_E \exp(-\beta q) \tag{6}$$

Using the Elovich equation, the concentration of azo dye in the sorbent $q(t,x)$ and the solution $c(t,x)$ in the column can be calculated from the following equations:

$$q(\xi) = \begin{cases} \frac{1}{\beta}\ln(\alpha_E \xi + 1) & x < u_0 t \\ 0 & x \geqslant u_0 t \end{cases} \tag{7}$$

$$\begin{cases} c = c_0 + \frac{\rho_s}{\beta}\ln\left(\frac{\alpha_E \xi + 1}{\alpha_E \xi_0 + 1}\right) - \frac{\varepsilon D_{eff}\alpha_E \rho_s}{\beta u_0 (1-\varepsilon)}\left(\frac{1}{\alpha_E \xi + 1} - \frac{1}{\alpha_E \xi_0 + 1}\right) & x < u_0 t \\ c = 0 & x \geqslant u_0 t \end{cases} \tag{8}$$

where

$$\alpha_E = \frac{k_E \beta}{u_0} \tag{9}$$

5. Results and discussion

The influence of initial concentration ($c_0 = 50$, 75 mg/dm^3) and solution flow rate ($Q = 50$, 100, 200, and 400 cm^3/h) on the breakthrough curve was determined using a mathematical model. Calculations were carried out in the Matlab computing environment to verify the model using evolutionary algorithms as a mathematical tool support.

Figs. 1–3 present the comparison of experimental results (points) and values calculated from the model

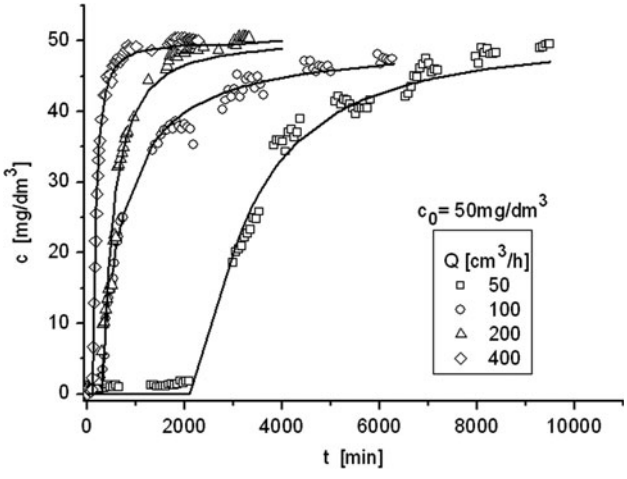

Fig. 1. Concentration changes of Direct Orange 26 in the solution at the column outlet.

(line) for Direct Orange 26. The breakthrough curves for volumetric flow rate $Q = 50\,cm^3/h$ and different initial concentrations of the solution are presented in Fig. 1. The longest breakthrough time, $t_B = 2{,}200$ min, for the smallest concentration was observed, while for the highest concentration, breakthrough time was $t_B =$ 125 min.

Fig. 2 compares the breakthrough curves depending on the initial concentration and on the bed heights, $h = 58$ and 28 cm. Based on the Eq. (7), the amount of adsorbed dye Direct Orange 26 on rye straw q (mg/g dm), depending on the process time, is depicted in Fig. 3.

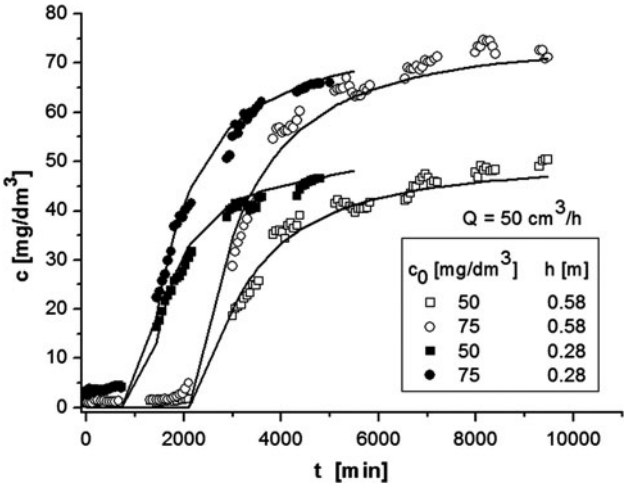

Fig. 2. Concentration changes of Direct Orange 26 in the solution at the column outlet for different heights of bed.

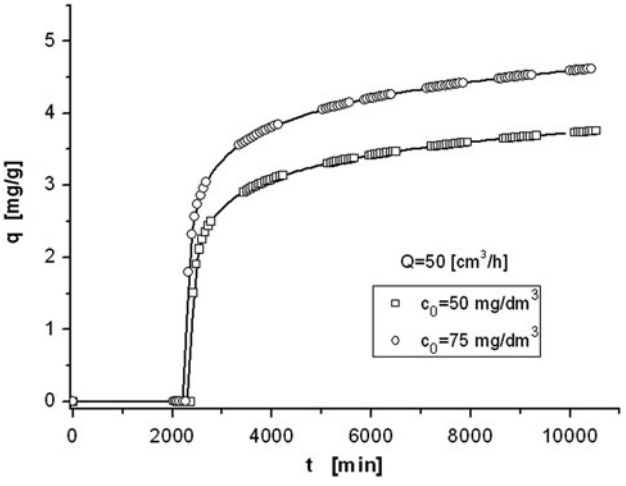

Fig. 3. Concentration changes of Direct Orange 26 in the sorbent at the column outlet.

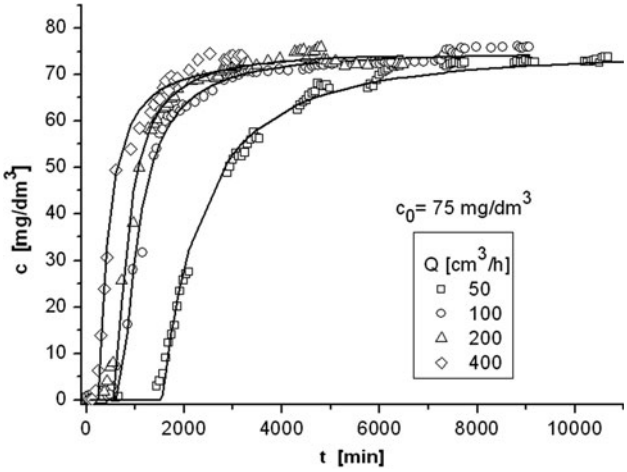

Fig. 4. Concentration changes of Reactive Blue 81 in the solution at the column outlet.

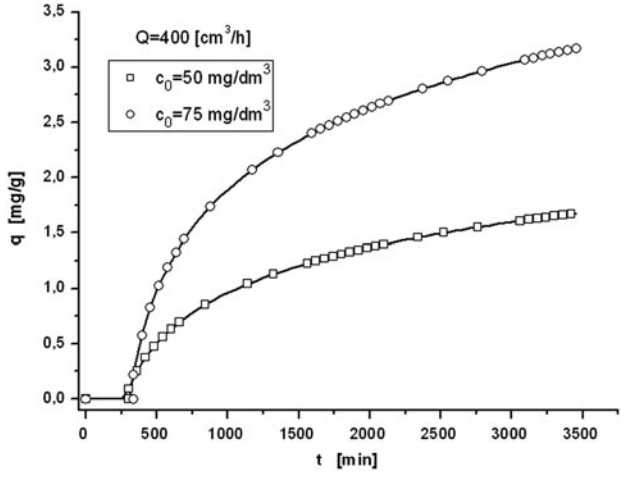

Fig. 5. Concentration changes of Reactive Blue 81 in the sorbent at the column outlet.

Figs. 4 and 5 present the comparison of experimental results and calculated values from the model for Reactive Blue 81. In Fig. 4, breakthrough curves for volumetric flow rate, $Q = 75\,cm^3/h$, and for four initial solution concentrations are presented. Similar to the Direct Orange 26, longest breakthrough time, $t_B =$ 1,480 min, was observed for the lowest concentrations and for the highest concentration, breakthrough time decreased to $t_B = 240$ min.

The calculation of adsorption profiles q (mg/g dm) during the process according to Eq. (7) is shown in Fig. 5.

Tables 1 and 2 summarize the calculated coefficients for mass balance in packed column and

Table 1
Model coefficients and statistical evaluation for Direct Orange 26

c_0 (mg/dm^3)	Q (cm^3/h)	k_E (mg/[g min])	β (g/mg)	D_{eff} (m^2/min)	α_E (1/m)	R^2	δ_m (mg/dm^3)
50	50	0.4288	2.408	0.0288	471.036	0.975	3.049
	100	0.0013	2.024	0.0079	0.612	0.990	1.799
	200	0.0006	7.743	0.5249	0.583	0.985	2.464
	400	0.0052	10.290	0.4085	3.060	0.997	0.874
75	50	0.4561	1.922	0.0336	400.385	0.976	4.602
	100	0.0022	1.012	0.0013	0.5101	0.992	2.347
	200	0.0014	3.395	0.2957	0.538	0.978	4.359
	400	0.0046	3.645	0.3970	0.9514	0.997	1.495

Table 2
Model coefficients and statistical evaluation for Reactive Blue 81

c_0 (mg/dm^3)	Q (cm^3/h)	k_E (mg/[g min])	β (g/mg)	D_{eff} (m^2/min)	α_E (1/m)	R^2	δ_m (mg/dm^3)
50	50	0.00025	24.853	0.3498	2.858	0.987	2.146
	100	0.00026	6.279	0.6210	0.378	0.965	3.147
	200	0.00123	1.272	0.5181	0.179	0.949	3.924
	400	0.00373	1.879	0.4234	0.399	0.984	2.153
75	50	0.00047	10.017	0.1899	2.177	0.996	1.784
	100	0.00134	12.162	0.3943	3.742	0.995	1.706
	200	0.02721	8.077	1.2633	25.101	0.990	2.263
	400	0.00921	1.102	0.3215	0.579	0.985	3.202

statistical evaluation expressed as the determination coefficient R^2 and the root-mean-square error δ_m.

6. Summary

In the paper, purification of water from colored substances was presented. Cheap, eco-friendly, and readily available biosorbent rye straw to remove of azo dyes was used. Excellent biosorbent was prepared from raw biomass using chemical pretreatment with sulfuric acid solution.

The paper presents a method involving experiments and calculations of sorption dynamics in packed column. A mathematical model to calculate the concentration of solution at the column outlet and the concentration of adsorbed substance in the adsorbent, as well as breakthrough curves for different process conditions and bed heights, were proposed in the study.

Appropriately, selected kinetics equation was used to calculate the dynamics i.e. to solve partial differential mass balance in the column. The model of process dynamics took into account the specificity of sorption described by the Elovich's equation (for chemical/mixed sorption). Identification of the column dynamics consisted in finding model coefficients k_E, β, and D_{eff}, and comparing the calculated with experimental data. Very good quality of experimental data approximation was confirmed by statistical evaluation.

It was determined that sorption on the modified rye straw was more favorable for Direct Orange 26 compared with Reactive Blue 81.

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List of symbols

c_0, c — initial or temporary concentration of dyes in a solution (mg/dm^3)
D_{eff} — effective dispersion (m^2/min)
h — bed height (m)
k_E — kinetics coefficient (mg/[g min])
q — concentration of dyes in a sorbent, sorption (mg/g dm)
Q — volumetric flow rate (cm^3/h)
t — time (min)
t_B — breakthrough time (min)

u_0 — apparent linear velocity (m/min)
x — distance between the two column heights considered (m)
β — kinetics coefficient (g/mg)
ξ — coefficient defined Eqs. (1 and 2) (m)
ε — voidage of the bed (–)
ρ_s — density of sorbent (kg/m^3)

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