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Kinetics of azo dyes sorption onto low-cost sorbents

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ABSTRACT

Removal of dyes from wastewater is of paramount importance for water quality. Biological methods alone are not capable of dealing with such pollution. Even small amounts of dye in water are highly visible and difficult to remove using conventional methods. Dyes are chemically complex, and advanced techniques such as chemical and photo-oxidation, adsorption or membrane separation must be used for their removal. Adsorption is commonly used at a final stage of dye removal process when high-purity water is required. Sorption kinetics is a key parameter for assessing sorbent efficiency in removing dyes. Results of tests on sorption kinetics of selected azo dyes (Reactive Blue 81, Reactive Red 120, Direct Orange 26 and Direct Black 22) are presented in the paper. Sorption tests were carried out using rye straw with and without thermal and chemical pre-treatment processes. Experimental data were analysed using the relevant kinetic equations. In most cases, the equation used was the Elovich model.

Keywords: Natural sorbent; Sorption kinetics; Azo dyes

1. Introduction

Dyes and huge amounts of water are used by many industries for the production of food, pharmaceuticals, paper, fabrics, leather and plastics. Dyes are one of the components of wastewater entering industrial and municipal wastewater treatment plants. Being toxic, carcinogenic and mutagenic, they are extremely dangerous for the environment. Several methods of dye removal from wastewater have been developed and include the use of activated sludge, chemical coagulation, adsorption onto activated carbon, advanced oxidation, electrochemical techniques and membrane processes [1]. However, even advanced methods do not ensure complete removal of dyes from water discharged into the environment. Intensive research has recently been focused on cheap adsorbents that could be used both in complex wastewater treatment solutions and in simple home sewage treatment plants. It was found that native and modified biomass of bacteria, fungi, algae and plants effectively removed multiple fabric dyes through biosorption [2–10].

Currently, studies are underway to find cheap natural sorbents that would replace activated carbon and zeolites widely used for their separation properties. Low-cost sorbents produced from biomass are an

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important group of materials with sufficiently high dye removal capacity and selectivity.

The paper is focused on testing the potential materials and selected dyes. Results are described by the analysis of equilibrium and sorption kinetics. Equilibrium analysis is to determine the capacity of a selected material with respect to the tested dyes. Kinetics provides information about the estimated rate and duration of the process [4–13].

2. Modelling of sorption kinetics

Mathematical description of adsorption kinetics uses the results of experiments concerning equilibrium for the system under study. Equilibrium is described by the Langmuir, Freundlich and Dubinin–Radushkevich equations. Sorption kinetics is described by models listed in Table 1. Eqs. (1) and (2) are de facto one-parameter equations where the calculated value is constant k (k_{I} or k_{II}). The equations are presented in the literature in a slightly different form with q_{e}, and sorption rate constant k *is* shown as values calculated simultaneously based on the experiments. The two values q_{e} and k (k_{I} or k_{II}) should be determined independently, and then experimental data, described by kinetic equations in modified coordinates, should fit a straight line starting from the origin of the coordinates system. Simultaneous determination of q_{e} and constant k may result in errors in estimated q_{e}. Eqs. (3) and (4) are two-parameter equations. In Eq. (3), k_{E} and coefficient of equation β must be determined based on experimental data. Assuming that $k_{\mathrm{E}}\beta t >> 1$ and with an approximation in modified coordinates, k_{E} and β can be determined simultaneously. Eq. (4) is also a two-parameter equation. k_{N} and order of sorption kinetics n are the estimated coefficients. If the order of sorption kinetics is assumed, then Eq. (4) with modified coordinates yields a straight line starting from the origin of the coordinates system. If assuming that the n value is impossible, then linearisation of Eq. (4) is also not possible. Simultaneous determination of all coefficients in Eqs. (1)–(5) can be achieved based on the non-linear approximation using e.g. the Lavenberg–Marquardt algorithm.

A generalised sorption kinetics equation was proposed by Tomczak et al. [14] applying fractional derivatives. Eq. (5) has four parameters, namely sorption capacity q_{e}, adsorption rate constant k_α, order of reaction n and order of derivative α, which come in the range <0, 1>. Assuming that q_{e} is known and order of reaction is equal to 1, the kinetic equation can be integrated analytically. In a general case, the kinetic equation can be integrated numerically, and thus, sorption rate constant, order of sorption kinetics n and order of derivative α can be determined.

3. Material and methods

Dyes used for the purposes of this study were supplied by Boruta-Zachem Kolor Sp. z o.o. in Zgierz. They are used for colouring home-cleaning products and cosmetics, and have several other applications (Order of the Minister of Health of 30 March 2005, Journal of Laws of 2005 No. 72 Item 642), and represent the azo compound group. Chemical structure and properties of azo dyes are presented in Table 2.

Rye straw was used as a sorbent. The straw was mechanically cut into 1 cm pieces, washed and boiled in a pressure cooker at 130˚C for 2 h. To increase its sorption capacity, the straw was etched with 10%

Table 1
Description methods for sorption kinetics

No	Name of Eq.	Form of Eq.	Solution	Linear form after transformation
(1)	Pseudo-first-order	$\frac{\mathrm{d}q}{\mathrm{d}t} = k_{\mathrm{I}}(q_{\mathrm{e}} - q)$ $q(0) = 0$	$q = q_{\mathrm{e}}(1 - \exp(-k_{\mathrm{I}}t))$	$\ln\left(1 - \frac{q}{q_{\mathrm{e}}}\right) = -k_{\mathrm{I}}t$
(2)	Pseudo-second-order	$\frac{\mathrm{d}q}{\mathrm{d}t} = K_{\mathrm{II}}(q_{\mathrm{e}} - q)^2$ $q(0) = 0$	$q = q_{\mathrm{e}}\frac{k_{\mathrm{II}}q_{\mathrm{e}}t}{1+k_{\mathrm{II}}q_{\mathrm{e}}}$	$\frac{q_e}{q} - 1 = \frac{1}{k_{II}q_{\mathrm{e}}}\frac{1}{t}$
(3)	Elovich model	$\frac{\mathrm{d}q}{\mathrm{d}t} = k_{\mathrm{E}}\exp(-\beta q)$ $q(0) = 0$	$q = \frac{\ln(1+\beta k_{\mathrm{E}}t)}{\beta}$	For $k_{\mathrm{E}}\beta t >> 1$ $q = \frac{\ln(k_{\mathrm{E}}\beta)}{\beta} - \frac{1}{\beta}\ln(t)$
(4)	Generalised model	$\frac{\mathrm{d}q}{\mathrm{d}t} = k_{\mathrm{N}}(q_{\mathrm{e}} - q)^n$ $q(0) = 0$	$q = q_{\mathrm{e}}\left(1 - \left(1 - \frac{k_{\mathrm{N}}t(1-n)}{q_{\mathrm{e}}^{1-n}}\right)^{\frac{1}{1-n}}\right)$	If n is assumed $1 - (1 - \frac{q}{q_{\mathrm{e}}})^{1-n} = \frac{k_N t(1-n)}{q_{\mathrm{e}}^{1-n}}$
(5)	Fractional derivative	$\frac{\mathrm{d}^\alpha q}{\mathrm{d}t^\alpha} = k_\alpha(q_{\mathrm{e}} - q)^n$ $q(0) = 0$	For $n = 1$ $q = q_{\mathrm{e}}(1 - E_\alpha(-k_\alpha t^\alpha))$ $E_\alpha(x) = \sum_{j=0}^{\infty}\frac{x^j}{\Gamma(\alpha j+1)}$	Not applicable

Table 2
Characteristics of the tested dyes

Name of the dyestuff	Molecular formula	Molecular weight	CAS number
Reactive Blue 81	$C_{25}H_{17}Cl_2N_7O_{10}S_3Na_3$	811.51	75030-18-1
Reactive Red 120	$C_{44}H_{30}Cl_2N_{14}O_{20}S_6$	1,338.09	61951-82-4
Direct Black 22	$C_{44}H_{32}N_{13}Na_3O_{11}S_3$	1,083.97	6473-13-8
Direct Orange 26	$C_{33}H_{22}N_6Na_2O_9S_2$	756.67	3626-36-6

H_2SO_4 for 5 h at 60˚C. Following chemical pre-treatment, the straw was dried at 105˚C for 2 h. The procedure of chemical pre-treatment was developed based on the previous experience with straw that had only been washed. Sorption kinetics studies were carried out at T = 25˚C and pH 5–6. Five grams of dry weight sorbent were placed in glass flasks and 200 cm^3 solution of dye concentration of 100–800 mg dm^{-3} was added. Flasks with the mixture were shaken mechanically in a water bath until adsorption equilibrium was reached. During the process, dye concentration in the water phase was measured using UV–vis Jasco V630 spectrophotometer.

4. Discussion

Based on the initial results, it was determined that considerable sorption effects are observed for Reactive Blue 81 and Direct Orange 26. Results of equilibrium studies were one order higher than for Reactive Red 120 and Direct Black 22. For example, for the initial concentration of 100 mg dm^{-3} equlibrium concentrations in the sorbent were 0.11 and 0.36 mg g^{-1} d m for Direct Black 22 and Reactive Red 120, while for Reactive Blue 81 and Direct Orange 26, they were 3.4 and 4.0 m g^{-1} d m, respectively. That is why two latter dyes were used for complete kinetics analyses.

Table 3
Kinetics coefficients and statistical evaluation of results for Reactive Blue 81

c_0 (mg dm^{-3})	Coefficients β (g mg^{-1}) and k_E (mg g^{-1} h^{-1})	Statistical evaluation R^2 and χ^2
100	1.778 ± 0.096	0.975
	7.147 ± 1.461	0.021
200	0.849 ± 0.067	0.957
	3.069 ± 0.607	0.104
300	0.548 ± 0.026	0.987
	2.903 ± 0.298	0.065
400	0.512 ± 0.017	0.991
	11.016 ± 1.104	0.069
500	0.402 ± 0.011	0.994
	6.737 ± 0.475	0.059
800	0.296 ± 0.007	0.996
	7.854 ± 0.455	0.073

Table 4
Kinetics coefficients and statistical evaluation of results for Direct Orange 26

c_0 (mg dm^{-3})	Coefficients β (g mg^{-1}) and k_E (mg g^{-1} h^{-1})	Statistical evaluation R^2 and χ^2
100	1.657 ± 0.105	0.942
	26.099 ± 7.562	0.0283
200	0.756 ± 0.049	0.969
	12.343 ± 2.555	0.110
300	0.494 ± 0.0364	0.954
	6.261 ± 1.076	0.219
400	0.419 ± 0.027	0.969
	12.900 ± 2.324	0.306
500	0.306 ± 0.0132	0.987
	9.747 ± 0.969	0.192
800	0.147 ± 0.014	0.958
	6.351 ± 0.984	2.021

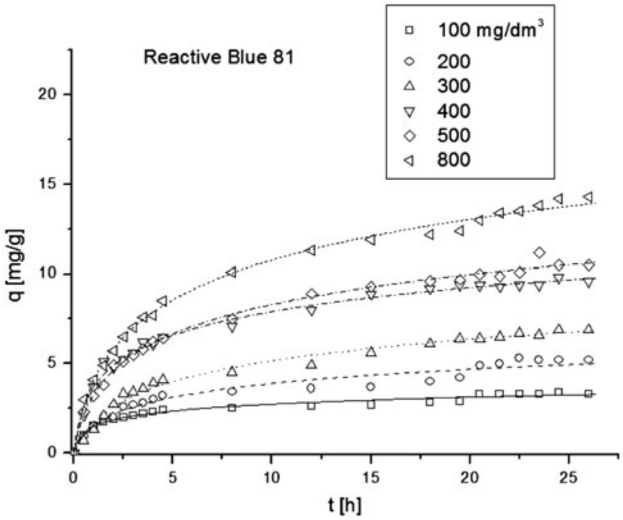

Fig. 1. Comparison of experimental and calculated data for Reactive Blue 81.

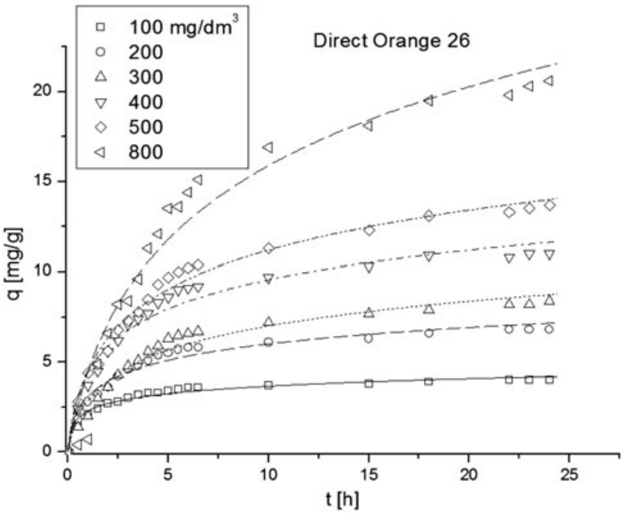

Fig. 2. Comparison of experimental and calculated data for Direct Orange 26.

Kinetics was described using equations listed in Table 1. Based on the statistical evaluation, taking into account determination coefficient and χ^2, best fit of equations describing sorption kinetics was obtained for the Elovich model. The coefficients obtained in Elovich model, that is, constant k_E and coefficient β, as well as statistical evaluation are presented in Tables 3 and 4.

Experimental and calculated data using Elovich model equations were compared in Figs. 1 and 2.

Statistical coefficients and the presented plots show that Elovich model fits very well with the experimental data. Direct Orange 26 has higher sorption capacity on modified straw than Reactive Blue 81. The use of Elovich model demonstrates that sorption on modified straw is of mixed nature and combines physical and chemical adsorption.

5. Conclusions

(1) Modified straw allows for effective adsorption of Direct Orange 26 and Reactive Blue 81 dyes from water solutions. No effective removal of Reactive Red 120 or Direct Black 22 was observed.

(2) Adsorption kinetics of Direct Orange 26 and Reactive Blue 81 may be described by Elovich model that ensures the best statistical evaluation.

(3) In Elovich model, constants k_E and β are dependent on the initial concentration of the solution.

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Symbols

c_0 — initial concentration (mg dm^{-3})
$E_\alpha(x)$ — Mittag–Leffler function (−)
k_I — first-order adsorption rate constant (h^{-1})
k_{II} — second-order adsorption rate constant (mg g^{-1} h^{-1})
k_E — Elovich adsorption rate constant (mg g^{-1} h^{-1})
k_α — α order adsorption rate constant (h$^{-\alpha}$)
n — order of adsorption rate (−)
q — concentration in the sorbent (mg g^{-1} d m)
q_e — concentration in the sorbent at equilibrium (mg g^{-1} d m)
R — determination coefficient (−)
t — time (h)
α — order of derivative (−)
β — Elovich adsorption coefficient (g mg^{-1})

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