Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1138021

57 (2016) 22774–22778
October

Taylor & Francis
Taylor & Francis Group

Description of sorption kinetics of azo dye onto birch chips by means of fractional derivatives

Wladyslaw Kaminski*, Elwira Tomczak, Pawel Tosik

Faculty of Process and Environmental Engineering, Lodz University of Technology, Wolczanska 213, 90-924 Lodz, Poland, Tel. +48 42 631 37 08; Fax: +48 42 636 56 63; email: wladyslaw.kaminski@p.lodz.pl *(W. Kaminski)*

Received 22 May 2015; Accepted 30 December 2015

ABSTRACT

The adsorption kinetics is investigated in order to measure time necessary to reach equilibrium between the molecules of separated substance attracted to the sorbent surface and those left in the solution. Models of adsorption kinetics such as Lagergren's, Ho and McKay's, and Elovich's are quoted in technical articles. The application of pseudo-first-order Lagergren's kinetic model is recommended when physical adsorption is the dominant mechanism. On the other hand, when the process is mainly influenced by chemisorption, the pseudo-second-order model of Ho and McKay's as well as Elovich's equation are suggested. At the same time, no general method combining both mechanisms of adsorption is proposed. In the case of chemically complex sorbents and the mixed mechanism of sorption, this kind of approach is insufficient; however, such systems may be modelled using fractional derivatives . Recently, a considerable number of papers and monographs have been published on applying fractional derivatives. Most of them treat of solving linear equations and special functions such as the Mittag–Leffler function. This paper presents the results and mathematical description of azo dye adsorption kinetics on a natural plant-based sorbent.

Keywords: Sorption kinetics; Fractional derivatives; Plant sorbent

1. Introduction

Various types of dyes as well as huge amounts of water are consumed by the industry to produce food, pharmaceuticals, paper, fabrics, leather and plastics. Dyes can be found in wastewater entering industrial and municipal treatment plants. Being toxic, carcinogenic and mutagenic, they are extremely dangerous to the environment. Several methods of dye removal from wastewater have been developed and included the use of activated sludge, chemical coagulation, adsorption onto activated carbon, advanced oxidation, electrochemicaltechniques and membrane processes. Nevertheless, even advanced methods do not ensure a complete removal of dyes from water discharged into the ecosystem. Recently, an intensive research focus has been directed towards cheap adsorbents that could be used in both complex wastewater treatment systems and simple home sewage treatment plants [1]. It has been found that native and modified biomass of bacteria,

---

*Corresponding author.

Presented at EuroMed 2015: Desalination for Clean Water and Energy Palermo, Italy, 10–14 May 2015. Organized by the European Desalination Society.

fungi, algae and plants is able to effectively remove multiple fabric dyes through biosorption [2–10].

The current studies concentrate on testing potential adsorptive materials and a selected dye. Results are usually presented via description of the equilibrium state and sorption kinetics [11–14]. Equilibrium analysis serves to determine the capacities of selected materials with respect to the tested dye. Kinetics provides information about the estimated rate and duration of the process. In this paper, mathematical description of adsorption kinetics is based on the laboratory adsorption of Direct Blue 26 azo dye onto birch chips, previously subjected to thermal and chemical processing. The sorption kinetics is described using generalized form and fractional derivatives.

2. Numerical solution of sorption kinetics using fractional derivatives

In the literature, the most popular kinetic models describing experimental data are the pseudo-first-order, the pseudo-second-order and the Elovich equation. However, a change of the sorption mechanism is observed depending on pollutant concentration in the solution. In some cases, the sorption mechanism has both physical and chemical nature. When it is difficult to determine the mechanism of adsorption, i.e. to pick an equation defining the kinetics, fractional differential equations are suggested. It gives the opportunity to develop the three-parameter generalized equation for sorption kinetics.

Many reports on using fractional derivatives are available in technical articles. Fractional derivatives were used for different application e.g. drag release, description of non-Newtonian fluids and many others. This concept was successfully used to describe the sorption of heavy metal ions in our previous studies [1]. Additional examples are presented in the papers [15,16].

Employing the general equation for sorption kinetics involving fractional derivatives:

$$\frac{\mathrm{d}^{\alpha}q}{\mathrm{d}t^{\alpha}} = k_{\alpha}(q^{*} - q)^{n} \tag{1}$$

yields the following relation, which was accepted in presented calculations.

$$\frac{\mathrm{d}^{\alpha}(q^{*} - q)}{\mathrm{d}t^{\alpha}} = -k_{\alpha}\,(q^{*} - q)^{n} \tag{2}$$

Eq. (2) comprises four parameters that have to be determined using experimental data: k_{α}—kinetics constant, q*—equilibrium component concentration in the sorbent, n—reaction order, and α—derivative order. The equilibrium concentration q* (for every initial component concentration) should be established during the experiments and as such may be used in further calculations.

The initial condition introduced into the kinetics equation defines the zero concentration at the beginning of the process:

$$q(0) = 0 \tag{3}$$

A solution of the kinetics equation, for any n, can be derived using the Riemann-Liouville integrating operator J^{α}, for $\alpha > 0$ [17,18], when combined with the kinetics equation, gives:

$$J^{\alpha}\left(\frac{\mathrm{d}^{\alpha}(q^{*} - q)}{\mathrm{d}t^{\alpha}}\right) = J^{\alpha}(-k_{\alpha}(q^{*} - q(t))^{n}) \tag{4}$$

$$J^{\alpha}(-k_{\alpha}(q^{*} - q)^{n}) = \frac{-k_{\alpha}}{\Gamma(\alpha)}\int_{0}^{t}(t - \tau)^{\alpha - 1}(q^{*} - q(\tau))^{n}d\tau \tag{5}$$

where $\Gamma(\alpha)$ is the gamma function specified as follows:

$$\Gamma(x) = \int_{0}^{\infty} e^{-\tau}\cdot\tau^{x-1}d\tau \quad x \in R \tag{6}$$

For zero-order kinetics $n = 0$, the solution of Eq. (2) with initial condition (3) may be written as:

$$q = k_{\alpha}\frac{t^{\alpha}}{\Gamma(\alpha + 1)} \tag{7}$$

while for first-order kinetics $n = 1$, the following form is derived:

$$q = q^{*}(1 - E_{\alpha}(-k_{\alpha}t^{\alpha})) \tag{8}$$

where $E_{\alpha}(x)$ is the Mittag–Leffler function defined as:

$$E_{\alpha}(x) = \sum_{j=0}^{\infty}\frac{x^{j}}{\Gamma(\alpha j + 1)} \tag{9}$$

Only for zero-order reactions, the solution has a simple analytical form. In other cases, it takes the pattern of infinite series. In general case to solve, Eq. (2) is necessary to use a numerical method. The procedure of integration involving the predictor–corrector concept is presented below. This is an adaptation of procedure published by Diethelm et al. [19]. The subroutine can be used not only for fractional derivative equations but also for traditional derivative equations. Moreover, the procedure is very fast. The adaptation of this procedure to Matlab environment is demonstrated below:

$$\mathrm{sum}_B(j) = \sum_{i=1}^{j} B(i-1,\ k,\ \alpha)\cdot k_\alpha \cdot \left(q^* - q(t_j)\right)^n;\quad j = 1-m;\quad k = 1-j \tag{10}$$

$$q(t_{j+1}) = \frac{h^\alpha \cdot \mathrm{sum}_B}{\Gamma(\alpha+1)};\quad j = 1-m \tag{11}$$

$$\mathrm{sum}_A(j) = \sum_{i=1}^{j} A(i-1,\ k,\ \alpha)\cdot k_\alpha \cdot \left(q^* - q(t_j)\right)^n;\quad j = 1-m;\quad k = 1-j \tag{12}$$

$$q(t_{j+1}) = \frac{h^\alpha \cdot \left(\mathrm{sum}_A(j) + k_\alpha \cdot \left(q^* - q(t_{j+1})\right)^n\right)}{\Gamma(\alpha+2)};\quad j = 1-m \tag{13}$$

where

$$h = t_{\max}/m \tag{14}$$

$$A(i,\ k,\ \alpha) = \begin{cases} \text{if } i = 0; & = k^{\alpha+1} - (k-\alpha)\cdot(k+1)^\alpha \\ \text{if } i > 0; & = (k-i+2)^{\alpha+1} + (k-i)^{\alpha+1} \\ & \quad -2(k-i+1)^{\alpha+1} \\ \text{if } i = k+1; & = 1 \end{cases} \tag{15}$$

$$B(i,\ k,\ \alpha) = (k+1-i)^\alpha - (k-i)^\alpha \tag{16}$$

3. Materials and methods

Birch chips were used as the sorbent. The birch wood was mechanically cut into 1.0 cm × 0.5 cm × 0.1 cm pieces, washed and boiled in a pressure cooker at 130˚C for 2 h. To increase their sorption capacity, the birch chips were etched with 10% H_2SO_4 for 5 h at 60˚C. Following chemical pretreatment, the birch chips were dried at 105˚C for 2 h. The sorbent density was 494 kg d.m./m^3. Birch wood contained 40–50 wt% cellulose, 30–35 wt% hemi-celluloses, 20–25 wt% lignin and <5 wt% extractives. The SEM photo of a birch chip piece is presented in Fig. 1.

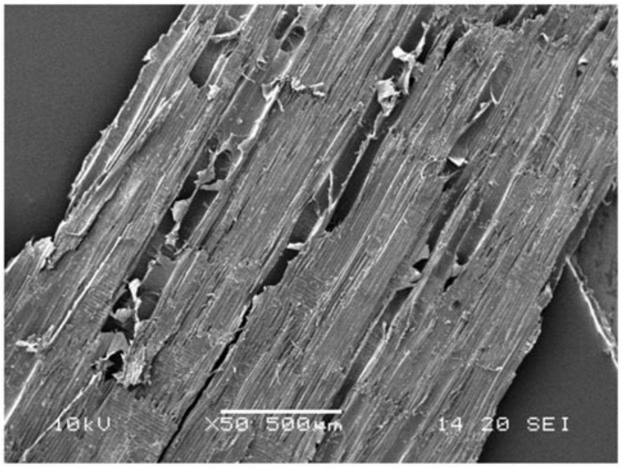

Fig. 1. SEM photo of the birch chip after thermal and chemical treatment.

Sorption kinetics studies were carried out at $T = 25$˚C and pH = $5 \div 6$. The experiments were conducted in glass flasks. In each flask, five grams of dry sorbent were placed and then 200 cm^3 of Direct Blue 26 solution (concentration of $100 \div 800$ mg/dm^3) were added. Afterwards, the flasks were shaken mechanically in a water bath until adsorption equilibrium was reached. During the process, dye concentration in the aqueous phase was measured using UV–vis Jasco V630 spectrophotometer.

Based on the experimental data, the kinetic constant k_α, equation order n and the differential coefficient α were calculated using the least squares method, numerical procedure given by Eqs. (10)–(16) and the evolutionary algorithm.

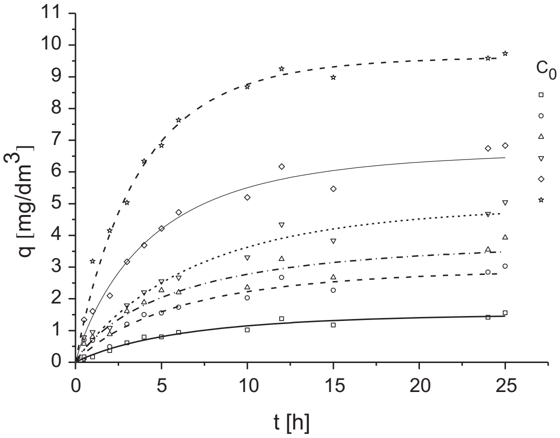

Fig. 2. Comparison of experimental and calculated data for birch chips and Direct Blue 26 dye.

Table 1
Coefficients of the sorption kinetics model (2) and statistical evaluation of results

c_0 (mg/dm^3)	q^* (mg/g)	k_α (1/h$^\alpha$)	α (–)	R^2	δ (mg/g)
100	1.56	0.168	0.92	0.969	0.086
200	3.03	0.179	0.89	0.938	0.228
300	3.93	0.201	0.82	0.946	0.266
400	5.05	0.155	0.93	0.971	0.262
500	6.83	0.243	0.87	0.975	0.328
800	9.73	0.280	0.95	0.987	0.378

4. Results and discussion

A preliminary assessment of the approximation results indicated that the reaction order n oscillated between 0.96 and 1.02. Hence, in further calculations, the reaction order equal to 1.0 was assumed. Simultaneously, this value helps to recognize that the investigated process is driven mostly by the mechanism of physical adsorption. Fig. 2 presents the experimental data and approximated adsorption kinetics. The kinetics constant, derivative order and statistical assessment of the experimental and calculated data (coefficients of determination and root-mean-square errors) are given in Table 1.

In the analysed cases, the derivative order varied from 0.82 to 0.95. This slight deviation from the traditionally accepted value of $\alpha = 1$ resulted in the improvement of statistical parameters. Therefore, the application of fractional derivatives to description of sorption kinetics allowed more accurate fit of the model to experimental data.

In order to compare the methods, calculations were conducted with α set to 1, i.e. assuming the first-order kinetics and changes of dye concentration in the sorbent with time expressed by an ordinary derivative. The results and statistical assessment are given in Table 2.

In order to compare the methods, calculations were conducted with α set to 1, i.e. assuming the first-order kinetics and changes of dye concentration in the sorbent with time expressed by an ordinary derivative. The results and statistical assessment are given in Table 2.

Table 2
Coefficients of pseudo-first-order sorption kinetics model (α = 1) and statistical evaluation of results

c_0 (mg/dm^3)	q^* (mg/g)	k_I (1/h)	R^2	δ (mg/g)
100	1.56	0.140	0.962	0.095
200	3.03	0.141	0.929	0.245
300	3.93	0.133	0.916	0.333
400	5.05	0.131	0.966	0.283
500	6.83	0.186	0.961	0.412
800	9.73	0.255	0.985	0.405

5. Summary and conclusions

The article presents sorption kinetics of Direct Blue 26 azo dye on birch chips – a natural plant-derived sorbent. Before the experiments, the birch chips were subjected to thermal and chemical treatment, which substantially increased their sorption capacity.

The general equation was proposed to model the sorption kinetics. The equation uses fractional derivatives and can be implemented for description of adsorption processes. The results of modelling the sorption kinetics were obtained using the predictor–corrector algorithm allowing quick numerical integration.

From the preliminary calculations, it can be concluded that physical adsorption is the dominant mechanism in the investigated process. The statistical assessment of experimental and approximated results confirmed the successful application of fractional derivatives in modelling the sorption kinetics.

In fact, using fractional derivatives gives more accurate results than the classic pseudo-first-order equation.

List of symbols

$A(i, k, \alpha)$ — constant (Eq. (15))
$B(i-1, k, \alpha)$ — constant (Eq. (16))
c_0 — initial concentration in the aqueous solution, (mg/dm^3)
$E_\alpha(x)$ — Mittag–Leffler function
h — step of calculations (h)
i, j, k — indexes
J^α — integration operator
k_α — kinetics constant (1/h$^\alpha$)
n — order of sorption kinetics
q — concentration of dyes in a sorbent (mg/g d.m.)
q^* — concentration of dyes in a sorbent at equilibrium (mg/g d.m.)
R — set of real numbers

R^2 — squared determination coefficient
t — time (h)
xs — real variable
α — derivative order
Γ — gamma function

References

[1] E. Tomczak, W. Kaminski D. Szczerkowska, Fractional derivatives for description of sorption kinetics in the plant sorbentmetal ions systems, Ecol. Chem. Eng. S 20(3) (2013) 499–507

[2] M. Anbia, S. Salehi, Removal of acid dyes from aqueous media by adsorption onto amino-functionalized nanoporous silica SBA-3, Dyes Pigm. 94 (2012) 1–9.

[3] P.S. Vankar, R. Sarswat, A.K. Dwivedi, R.S. Sahu, An assessment and characterization for biosorption efficiency of natural dye waste, J. Cleaner Prod. 60 (2013) 65–70.

[4] G. Bayramoglu, N. Adiguzel, G. Ersoy, M. Yilmaz, M.Y. Arica, Removal of textile dyes from aqueous solution using amine-modified plant biomass of *A. caricum*: Equilibrium and kinetic studies, Water Air Soil Pollut. 224(1640) (2013) 1–16.

[5] I.A. Aguayo-Villarreal, L.A. Ramírez-Montoya, V. Hernández-Montoya, A. Bonilla-Petriciolet, M.A. Montes-Morán, E.M. Ramírez-López, Sorption mechanism of anionic dyes on pecan nut shells (*Carya illinoinensis*) using batch and continuous systems, Ind. Crops Prod. 48 (2013) 89–97.

[6] O. Gulnaz, A. Sahmurova, S. Kama, Removal of Reactive Red 198 from aqueous solution by *Potamogeton crispus*, Chem. Eng. J. 174 (2011) 579–585.

[7] M.A. Ashraf, M. Hussain, K. Mahmood, A. Wajid, M. Yusof, Y. Alias, I. Yusoff, Removal of acid yellow-17 dye from aqueous solution using eco-friendly biosorbent, Desalin. Water Treat. 51(22–24) (2013) 4530–4545.

[8] W.C. Wanyonyi, J.M. Onyari, P.M. Shiundu, Adsorption of Methylene Blue dye from aqueous solutions using *Eichhornia crassipes*, Bull. Environ. Contam. Toxicol. 91 (2013) 362–366.

[9] P.S. Rani, R.L. Priya, M. Velan, Sorption behavior of freshwater aquatic fern *Azolla filiculoides* on red-wine dye, Desalin. Water Treat. 51(31–33) (2013) 6115–6129.

[10] E. Khosla, S. Kaur, P.N. Dave, Tea waste as adsorbent for ionic dyes, Desalin. Water Treat. 51(34–36) (2013) 6552–6561.

[11] A. Ayla, A. Çavuş, Y. Bulut, Z. Baysal, Çetin Aytekin, Removal of methylene blue from aqueous solutions onto *Bacillus subtilis*: Determination of kinetic and equilibrium parameters, Desalin. Water Treat. 51(40–42) (2013) 7596–7603.

[12] Y. Safa, H.N. Bhatti, Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk, Desalination 272 (2011) 313–322.

[13] A. Witek-Krowiak, Biosorption of malachite green from aqueous solutions by pine sawdust: Equilibrium, kinetics and the effect of process parameters, Desalin. Water Treat. 51(16–18) (2013) 3284–3294.

[14] H. Si, T. Wang, Z. Xu, Biosorption of methylene blue from aqueous solutions on β-cyclodextrin grafting wood flour copolymer: Kinetic and equilibrium studies, Wood Sci. Technol. 47 (2013) 1177–1196.

[15] R.P. Meilanov, D.A. Sveshnikova, O.M. Shabanov, The method of differential equations of fractional order for describing the kinetics of sorption, Russ. J. Phys. Chem. 77(2) (2003) 206–210.

[16] V.C. Friesen, D.P. Leitoles, G. Gonçalves, E.K. Lenzi, M.K. Lenzi, Modeling heavy metal sorption kinetics using fractional calculus, Math. Prob. Eng. 2015 (2015) ID549562, 1–8.

[17] D. Delbosco, L. Rodino, Existence and uniqueness for a nonlinear fractional differential equation, J. Math. Anal. Appl. 204 (1996) 609–625.

[18] N. Heymans, I. Podlubny, Physical interpretation of initial conditions for fractional differential equations with Riemann-Liouville fractional derivatives, Rheol. Acta 37 (2005) 1–7.

[19] K. Diethelm, N.J. Ford, A.D. Freed, A predictor-corrector approach for the numerical solution of fractional differential equations, Nonlinear Dyn. 29(1–4) (2002) 3–22.