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FRACTIONAL DERIVATIVES FOR DESCRIPTION OF SORPTION KINETICS IN THE PLANT SORBENT - METAL IONS SYSTEM

ZASTOSOWANIE POCHODNYCH UŁAMKOWYCH DO OPISU KINETYKI SORPCJI DLA UKŁADU SORBENT ROŚLINNY - JONY METALI

Abstract: It was examined if buckwheat hull has a potential to be used to adsorb heavy metal ions Zn(II), Cd(II), Co(II), Cu(II), Ni(II) from water. The research involved experiments aimed at the determination of sorption kinetics taking into consideration changes of concentration in a solution and sorbent over time. According to the literature data, kinetics is described with the use of pseudo first-order equations. Application of fractional derivatives for the description of sorption kinetics enables the development of the generalised sorption kinetics equation. Result analysis with this concept requires making a computational procedure using gamma functions and infinite series. Kinetics description using fractional derivatives will be equations with two parameters *i.e.* fraction of derivative α and the kinetics constant K dependent on the analysed sorbent-adsorbate system.

Keywords: fractional derivatives, biosorbents, heavy metal ions, buckwheat hull

Introduction

The use of adsorption for the purposes of environmental protection has been in focus of scientists both in Poland and worldwide for many years. Scientists paying attention at increasing the effectiveness of removal and recovery of heavy metal ions from aqueous solutions. The additional goal now is to reduce the process costs and more researchers are interested in innovative application of biomass named bioadsorbents.

Bioadsorbents may be represented by organic materials such as fungi [1], algae [2], sawdust [3, 4], rice hulls [5], peat [6], corn [7], wheat bran [8], sunflower seeds [9], chopped straw, sawdust, and nut or coffee shells and many others.

They are low cost adsorbents and they have several advantages such as:

- widely available and renewable,
- environment-friendly,
- good sorption capacity due to their unique chemical composition,
- cost effective,

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- easy to be physically or chemically modified,
- may be used as starting materials for the production of activated carbon.

Biosorption is an alternative to physico-chemical separation processes and may be combined with other separation processes. It has not been fully described as regards the mechanisms of the removal of chemical contaminants from water. According to the literature, the process is based on the plant sorbents' natural ability to bind heavy metals due to their chemical and surface structure. Chemical compounds binding occurs mainly in the main components of the biomass *ie* lignocellulose (cellulose, hemicellulose, lignin) and tannins, due to the presence of hydroxyl, carboxyl, carbonyl, thiol and amine groups in their chemical structure. Buckwheat hull as an innovative material is one of the new biosorbent. Botanically, buckwheat belongs to the knotweeds but is popularly considered cereal. The buckwheat central part (seed) is not attached to the coat (hull).

The hull is (pericarpium) composed of three primary layers, namely:

- epidermia - built of green and brown elongated or almost square prismatic cells with undulating walls;
- hypodermis - composed of thin fibrous cells in several rows,
- epidermie internal - external side of the hull composed of elongated, rectangular cells that form the pigment layer.

Buckwheat hull is thick, hard and brownish, silver and greenish to dark brown in shade. The color of the coat depends on the year of cultivation and vegetation conditions. Seed coat is 20-26% of the seed weight [11-13].

The aim of the present paper was to assess sorption capacity of pre-treated buckwheat hull for use as a potential adsorbent to remove heavy metal ions from aqueous solutions. Additionally, it was examined if analyte concentration had an effect on the sorption capacity of the material under study.

Experiments were carried out to determine sorption kinetics taking into account the changes in concentration of the solution and sorbent over time, which allowed for determining kinetic and equilibrium parameters of the sorption process necessary for the fractional derivative calculations.

Methodology and scope of research

Buckwheat hull (Pabianice Mill) was used as sorbent for the purposes of the experiment. The raw material was boiled at 90°C, washed with distilled water and dried at 105°C. Salts of heavy metals, namely $\text{CuSO}_4 \times 5\text{H}_2\text{O}$, $\text{NiSO}_4 \times 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$, $\text{CoSO}_4 \times 7\text{H}_2\text{O}$, $\text{Cd SO}_4 \times 8/3\text{H}_2\text{O}$ solved in deionized water were used as adsorbate. The salts for the preparation of aqueous solutions were purchased from Fluka, Germany.

Sorption equilibrium and kinetics studies were carried out at constant temperature ($T = 25^\circ\text{C}$), at pH = 5-6. Five grams of sorbent d.w. was placed into conical flasks and 200 cm³ of the heavy metals aqueous solution was added. Cations concentrations were changed with in the range 10-50 mg/dm³. Flasks containing the mixture of ions were shaken mechanically on a water bath until the adsorption equilibrium was achieved. During the adsorption process concentration of the metal ions was measured using Dionex ICS-1000 ion chromatography system (IonPac AS5A column). Based on that adsorbent's adsorption capacity was determined.

The amount of metal ions adsorbed onto buckwheat hull was determined using the following formula:

$$q_e = \frac{V}{m} \cdot (C_0 - C_e) \quad (1)$$

where:

- q_e - equilibrium amount of cations adsorbed per dry weight of sorbent [mg/g],
- V - solution volume in the flask [dm³],
- C_0 and C_e - initial and equilibrium cation concentrations in a solution [mg/dm³],
- m - mass of sorbent dry weight [g].

Mathematical description of sorption kinetics

Adsorbent should display not only high sorption capacity - calculated using the formula (1) but should also be selected to ensure that the process occurring on its surface is fast enough.

Kinetic equations using fractional derivatives will be two-parameter equations (fraction of derivative and kinetic constant), dependent on the analyzed sorbent-adsorbate system. Adsorption kinetics has been studied since it was first discovered that reaction rate had a decisive effect on the entire process, and in some cases could even limit it. Kinetics experiments aim at determining the time necessary to achieve equilibrium between the particles of the compound being separated in the solution and those adsorbed on the surface of the sorbent. The rate is dependent mainly on the type of sorbent and molecules being bound.

In the literature two models of adsorption kinetics are widely used, namely the Lagergren's pseudo first-order, Ho and McKay's pseudo second-order model.

The pseudo first-order equation has the following form [14]:

$$\frac{dq}{dt} = K_1 \cdot (q_e - q_t) \quad (2)$$

where K_1 is the pseudo first order sorption rate constant, q_e , q_t are the values of amount of metal ions adsorbed on the surface of the sorbent at equilibrium and at any time t , respectively.

The pseudo second-order sorption kinetics may be expressed as follows [15]:

$$\frac{dq}{dt} = K_2 \cdot (q_e - q_t)^2 \quad (3)$$

where K_2 is the pseudo second order sorption rate constant.

The present paper proposes a new approach to kinetics calculations. In a general case of mixed adsorption when it is difficult to unmistakably define its mechanism, *ie* to decide which of the equations (2) or (3) should be applied to describe the kinetics, it is suggested that fractional derivatives be used. This approach allows to create a generalized description of sorption kinetics. Result analysis according to this concept requires elaborating a computational procedure using gamma functions and infinite series. Kinetics equations using fractional derivative are equations with two parameter *ie* fraction of derivative and kinetics constant dependent on the analyzed sorbent-adsorbate system. The similar approach authors presented for the description of sorption kinetics of dyes in the paper [16].

Many papers and monographs have appeared recently concerning fractional derivatives. Most of them are devoted to the solvability of fractional differential equation.

Derivatives of integer order $\alpha \in N$, eg $\alpha = 1$ $d^\alpha f/dt^\alpha$ are classical and well defined. The fractional-order derivatives $\alpha \in <0,1>$ were defined by Riemann-Liouville [17] by the following equation:

$$\frac{d^\alpha f(t)}{dt^\alpha} = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t (t-\tau)^{-\alpha} f(\tau) d\tau \quad (4)$$

where $\Gamma(z)$ denotes the gamma function

$$\Gamma(z) = \int_0^\infty e^{-u} u^{z-1} du \quad z \in R \quad (5)$$

In the present paper, we suggest that adsorption kinetics be described by an equation of the general form:

$$\frac{d^\alpha (q^* - q)}{dt^\alpha} = -K(q^* - q)^n \quad (6)$$

with an initial condition:

$$q(0) = 0 \quad (7)$$

The solution of equation (6) comprises three main elements: α - fractional order of derivative, K - kinetic constant and n - kinetic order.

For zero order kinetics $n = 0$ the equation (6) should be transformed to:

$$\frac{d^\alpha q}{dt^\alpha} = K_0 \quad (8)$$

Solution of equation with condition (7) has the following form:

$$q = K_0 \frac{t^\alpha}{\Gamma(\alpha + 1)} \quad (9)$$

For the first order kinetics $n = 1$ solution of equation (6) has the following form:

$$q = q^* (1 - E_\alpha(-K_1 t^\alpha)) \quad (10)$$

where $E_\alpha(x)$ is the defined Mittag-Leffler function

$$E_\alpha(x) = \sum_{j=0}^{\infty} \frac{x^j}{\Gamma(\alpha j + 1)} \quad (11)$$

Interpretation of results

During the measurements the solution composition was analysed, every 15 minutes frequently in the initial period, and then less frequently near equilibrium (1 h). Kinetic measurements were carried out until the 25th h, but equilibrium was reached after 5 h. The changes of concentration in 5-component solution of initial concentration of $C_0 = 20 \text{ mg/dm}^3$ are presented in Figure 1.

Fig. 1. The sorption kinetics for buckwheat husk - Cu(II), Zn(II), Ni(II), Co(II), Cd(II) system ($C_0 = 20 \text{ mg/dm}^3$)

Next, using equation (1), the changes of metal ion concentrations q in the absorbent for $C_0 = 20 \text{ mg/dm}^3$ were calculated, as shown in Figure 2. Points corresponding to experimental data were described by curves obtained from equation (9) presenting the application of fractional derivative.

Fig. 2. Comparison of experimental and calculated data for buckwheat husk - Cu(II), Zn(II), Ni(II), Co(II), Cd(II) system

K_1 and α were determined based on genetic algorithms in the Matlab computing environment using own procedure.

Based on the analysis of kinetics for metal ion-buckwheat hull system it was found that copper ions are adsorbed the most strongly, other ions being adsorbed on a lower level, with Co(II) ions on the lowest level. Mathematical description of sorption kinetics with the proposed equation is satisfactory.

Table 1 presents α , K_1 values for 5 analysed heavy metal ions and additionally statistical evaluation of experimental data approximation using the fractional differential equation. Where R^2 is determination coefficient, and δ is mean squared error.

Table 1

Statistical evaluation and the coefficients in the equation (9)

Ion	α	K_1	R^2	δ
Cu(II)	0.8206	1.8976	0.9762	0.0440
Zn(II)	0.7030	2.4623	0.8863	0.0946
Ni(II)	0.7063	2.4456	0.9301	0.0765
Co(II)	0.9844	1.1776	0.7853	0.2478
Cd(II)	0.7751	2.1166	0.8296	0.1183

Fig. 3. Comparison of sorption kinetics approximation for Cu(II), $C_0 = 20 \text{ mg/dm}^3$

Figure 3 compares data approximation quality for Cu(II) ions using fractional derivative and pseudo-first order equation. In this case, values obtained for differential equation were $\alpha = 0.8206$, $K_1 = 1.8976 \text{ 1/h}$ and $k_1 = 1.379 \text{ 1/h}$ using the classical kinetic model respectively. Analysis of both cases shows that a better mathematical description is obtained with the use of fractional derivative, especially as regards high speed process. When it comes to slow speed sorption, the experiment is described well by both models.

Conclusion

The paper describes kinetics of sorption of heavy metal ion mixture onto a natural sorbent (buckwheat hull), this low-cost sorbent can be used in the process of adsorption of heavy metal ions. It was found that copper ions are adsorbed the best, other ions being adsorbed on a lower level, and while cobalt ions are worst adsorbed.

The application of a generalised equation for sorption kinetics description was proposed. The equation uses fractional derivatives and may be used for different mechanisms of adsorption process. It was assumed that physical adsorption is the dominant mechanism in presented case.

Experimental data approximation for all of the analysed ions was successful, as confirmed by statistical evaluation. The results of the comparison of mathematical description using the classical pseudo-first order equation and the equation with fractional derivative provided evidence in favour of the latter one.

References

- [1] Dhankhar R, Hooda A. Fungal biosorption - an alternative to meet the challenges of heavy metal pollution in aqueous solutions. *Environ Technol.* 2011;32:5-6. DOI:10.1080/09593330.2011.572922.
- [2] Hamdy AA. Biosorption of heavy metals by marine algae. *Current Microbiology.* 2000;41:232-238. DOI: 10.1007/s002840010126.
- [3] Argun ME, Dursun S, Ozdemir C, Karatas M. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *J Hazard Mater.* 2006;141(1):77-85. DOI: 10.1016/j.jhazmat.2006.06.095.
- [4] Baral SS, Dasa SN, Rath P. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. *Biochem Eng J.* 2006;31:216-222. DOI: 10.1016/j.bej.2006.08.003.
- [5] Mohan S, Gandhimathi R, Sreelakshmi G. Isotherm studies for heavy metal adsorption on rice husk. *Asian J Water, Environ Pollut.* 2008;5:71-78.
- [6] Gundogan R, Acemioglu B, Alma MH. Copper(II) adsorption from aqueous solution by herbaceous peat. *J Colloid & Inter Sci.* 2004;269:303-309. DOI:10.1016/S0021-9797(03)00762-8.
- [7] Igwe JC, Abia AA. Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk. *Electron J Biotechnol.* 2007;10(4). DOI: 10.2225/vol10-issue4-fulltext-15.
- [8] Nameni M, Alavi Moghadam MR, Arami M. Adsorption of hexavalent chromium from aqueous solutions by wheat bran. *Int J Environ Sci Technol.* 2008;5:161-168.
- [9] Sun G, Shi W. Sunflower stalks as adsorbents for the removal of metal ions from wastewater. *Industr Eng Chem Res.* 1998;37:1324-1328. DOI:10.1021/ie970468j.
- [10] Witek-Krowiak A, Szafran R, Modelski S. Atrakcyjne i tanie sorbenty do usuwania metali ciężkich z wód. *Przem Chem.* 2011;90(1):128-131.
- [11] Jurga R. Prawie wszystko o ziarnie gryki i jej przetworach. *Przegląd Zbożowo-Młynarski.* 2010:6-10.
- [12] Kowalewski W, Gałązka R, Gąsiorowska T. Technologia czyszczenia i przerobu gryki na kaszę. *Przegląd Zbożowo-Młynarski.* 2004:28-30.
- [13] Zawadzki K. Gryka jako alternatywa dla pszenicy. *Przegląd Zbożowo-Młynarski.* 2007:27.
- [14] Lagergren S. Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar.* 1898;24(4):1-39.
- [15] Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochem.* 1999;34:451-465.
- [16] Tomczak E, Kaminski W. Description of Azo dyes sorption kinetics using fractional derivatives. *International Conference on Environment, Malaysia.* 2012:530-536.
- [17] Delbosco D, Rodino L. Existence and uniqueness for a nonlinear fractional differential equation. *Math Anal Appl.* 1996;204(2):609-625.

ZASTOSOWANIE POCHODNYCH UŁAMKOWYCH DO OPISU KINETYKI SORPCJI DLA UKŁADU SORBENT ROŚLINNY - JONY METALI

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Abstrakt: W pracy wykorzystano łuskę gryki do procesu sorpcji jonów metali ciężkich Cu(II), Ni(II), Zn(II), Co(II) i Cd(II) z roztworów wodnych. Wyznaczone zostały maksymalne pojemności sorpcyjne oraz stałe kinetyczne i równowagowe. Obliczone wartości pozwoliły na zastosowanie równań różniczkowych ułamkowych do opisu kinetyki sorpcji oraz uzyskania uogólnionego równania kinetyki sorpcji. Opracowanie wyników według tej koncepcji wymaga napisania procedury obliczeniowej wykorzystującej funkcje gamma oraz szeregi nieskończone. Równania kinetyki z wykorzystaniem pochodnych ułamkowych są równaniami o dwóch parametrach. Są to ułamek pochodnej i stała kinetyczna zależne od analizowanego układu sorbent - adsorbat.

Słowa kluczowe: ułamkowe równania różniczkowe, biosorbenty, metale ciężkie, łuska gryki