

Kinetic model for the sorption of copper ions onto sugar beet shreds

Mirjana M. Brdar, Marina B. Šćiban, Dragana V. Kukić, Tatjana M. Došenović

University of Novi Sad, Faculty of Technology, Serbia

Abstract

Adsorption kinetics is of great significance to evaluate the performance of adsorption process. The kinetics of copper ions adsorption onto different sized sugar beet shreds has been considered. Sugar beet shreds are very promising adsorbents due to their convenient chemical composition and availability in relatively large quantities in many countries. Experimental data were fitted with pseudo-first and pseudo-second-order kinetic models. Also, we used the intraparticle diffusion model for further analysis of kinetics. The coefficient of determination indicates that the pseudo-second-order equation, obtained by using non-linear least square method, was the most appropriate model for the description of copper ions adsorption onto sugar beet shreds. The adsorption capacities at equilibrium, for a particle size of 224–400 μm , 400–750 μm and 750–1000 μm , are 10, 9 and 8.6 mg/g, respectively. By using intraparticle diffusion model proposed by Weber and Morris, it was obtained that there exist two different stages in adsorption: fast initial adsorption which is further limited by intraparticle diffusion.

Keywords: adsorption, sugar beet shreds, kinetic models, pseudo-first order, pseudo-second order, intraparticle diffusion model.

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Wastewaters of many industries, such as metal plating facilities, mining operations, fertilizer industries, tanneries, paper industries, production of batteries, pesticides, etc., contain heavy metals which are of major concern due to their toxicity, bioaccumulation tendency and non-biodegradability. Consequently, it is necessary to remove metal ions from effluents [1]. Conventional precipitation method of heavy metals removal from wastewaters has serious limitations regarding efficiency, operating conditions and sludge production. The use of different biomass, such as wood and agro-industry waste, as adsorbent is an alternative technology for removing metal ions from wastewaters that is called biosorption [2]. Advantages of biosorption over conventional methods are low cost, high efficiency for dilute solutions, minimal amount of sludge, no additional nutrient requirement and possibility of biosorbent regeneration and metal recovery [3]. Agro-industry waste and by-products of cellulosic origin are convenient low-cost adsorbents because they are inexhaustible and non-hazardous materials. In this study, the dried sugar beet shreds, a by-product of sugar industry, are investigated as adsorbents. Sugar beet shreds which are usually used as animal feed, a source of pectin or as a substrate for bioethanol production, also have certain adsorption properties. If production of bioethanol from sugar beet, as a fuel, increases in the future, the sugar beet shreds will be obtained in large

quantities as by-products. On the other hand, more than 40% of shreds dry matter is pectic substance. Pectin is known to strongly bind metal cations in aqueous solutions due to a number of carboxyl functional groups. Therefore, sugar beet shreds are very promising adsorbents [4]. The aim of this paper is to research influence of adsorbent particle size on adsorption kinetics.

In order to use agro-industrial waste material as adsorbent, in actual treatment plants for removing of heavy metals from wastewaters, it is necessary to conduct adsorption kinetic experiments [5,6]. Kinetic studies provide information about possible mechanism of adsorption and reactions that occur on the adsorbent surface. They can also help in understanding the rate controlling step of the mass transfer process which affects the overall rate of adsorption. In recent years, several mathematical models have been proposed to describe adequately the kinetic process of adsorption [7–9]. According to [7] the most crucial factor for effective system design is predicting the rate of adsorbate removal. Adsorption kinetics of copper ions onto other different adsorbent has been investigated in many papers [10–13].

In this study, the kinetic studies have been carried out by batch reactions with various particle sizes of sugar beet shreds as adsorbents. The pseudo-first and pseudo-second-order equation were analyzed, as well as the intraparticle diffusion model. The method of least square was used to predict which model better match the experimental data. Mathematica 6, Wolfram Research software tool was used for calculation.

Correspondence: M.M. Brdar, University of Novi Sad, Faculty of Technology, Bul. cara Lazara 1, 21000 Novi Sad, Serbia.

E-mail: mbrdar@tf.uns.ac.rs

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EXPERIMENTS

Materials

Water solution of CuSO_4 concentration of about 50 mg/L was prepared by diluting 0.25 mol/L stock salt solution with demineralised water, just before experiments. pH adjustment was made using HNO_3 solution. All chemicals used were of analytical reagent grade.

Dry sugar beet shreds were obtained from nearby sugar refinery. They were milled on a laboratory mill (MiagBraunschweig DOXY 71b/4) and sieved through a set of sieves (Bühler MLU-300) in order to obtain different particle size. Three different ranges of particle size were used in experiments: 224–400 μm , 400–750 μm and 750–1000 μm .

Batch adsorption studies

The batch experiments were carried out by shaking 5 g of sugar beet shreds of different particle size in 1 L of aqueous solution of Cu(II) at pH 4. Experimental pH value is chosen to be under the pH value that induces copper hydroxide precipitation [14]. Suspensions were shaken at different time intervals (2 to 180 min). After reaction time, suspensions were filtered through a filter paper (Macherey-Nagel 651/120). Concentrations of copper ions in aqueous solutions were determined before (c_0) and after (c) adsorption process by complexometric titration [15]. Experiments were duplicated and results were averaged.

The amount of heavy metal ions adsorbed per specified amount of adsorbent (q) was calculated as follows:

$$q = \frac{c_0 - c}{m} \quad (1)$$

where m is a mass of adsorbent per liter of solution.

Kinetic models

Adsorption kinetics depends on the sorbate–sorbent interactions and experimental conditions. Various models can be used to analyze the kinetics of sorption process. Two of them, pseudo-first-order and pseudo-second-order model, have been widely used to describe sorption without any assumption of process conditions [16].

Pseudo-first-order model was introduced by Lagergren in 1898 [17]. It was the first model which describes kinetic of adsorption and it can be presented as follows:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2)$$

where q_e and q are the adsorption capacities at equilibrium and time t , respectively, and k_1 is the pseudo-first-order constant for the kinetics model.

In many manuscripts the Lagergren equation was applicable only to first 20 or 30 min of adsorption [18]. This kinetic model has been mostly used to describe the adsorption of pollutants from wastewater in different fields.

Literature survey has shown that the number of publications referring to other kinetic models such as the pseudo-first-order model, intraparticle diffusion model and Elovich equation are about one-third of that to the pseudo-second-order model [19]. Pseudo-second-order model is expressed with the following equation:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (3)$$

where q_e and q are the adsorption capacities at equilibrium and time t , respectively, and k_2 is the pseudo-second-order constant for that model. It was suggested by Ho and McKay [20]. All of the constants, both in pseudo-first and pseudo-second order model, have been calculated from the experimental results.

Nonlinear regression methods for determining the parameters of these two kinetic models for the experimental data were used [21]. Which model better describes the fit of the experimental data is determined by some error function. Since non-linear regression implicitly minimizes the sum of squares of the errors to determine the equation parameters, the coefficient of determination R^2 was chosen as the error function for the kinetic model analysis. Mathematica 6, Wolfram Research software tool was used for calculation.

Since the above two equations could not definitely reveal the adsorption mechanism, another kinetic model named intraparticle diffusion model was used in the present study. This model was discovered by Weber and Morris [22]. They found that in many adsorption cases solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t , so this model has the following interpretation

$$q = k_{\text{int}} t^{1/2} + a \quad (4)$$

where k_{int} is the intraparticle diffusion rate constant and a is a constant for any experiment. Equation (4) can be written as:

$$q_{\text{ref}} = k_{\text{int}} t_{\text{ref}}^{1/2} + a \quad (5)$$

After some simple calculation we obtain:

$$\frac{q}{q_{\text{ref}}} = 1 - R_i \left[1 - \left(\frac{t}{t_{\text{ref}}} \right)^{1/2} \right] \quad (6)$$

where $R_i = k_{\text{int}} t_{\text{ref}}^{1/2} / q_{\text{ref}}$, which is defined as the initial adsorption factor of the intraparticle diffusion model. Also, R_i can be expressed as:

$$R_i = 1 - \frac{a}{q_{\text{ref}}} \quad (7)$$

When $a = 0$, *i.e.*, $R_i = 1$, there is no initial adsorption behavior in an absorption system. When $R_i = 0.1$, the initial point is at $q/q_{\text{ref}} = 0.9$, which means that the initial adsorption has already reached 90%; later on, the adsorption proceeds following intraparticle diffusion mechanism. The R_i value is divided into four zones: $0.9 < R_i < 1$ is called weakly initial adsorption (zone 1); $0.5 < R_i < 0.9$ intermediately initial adsorption (zone 2); $0.1 < R_i < 0.5$ strongly initial adsorption (zone 3) and $R_i < 0.1$ approaching completely initial adsorption (zone 4).

If the adsorption process follows the intraparticle diffusion model, a plot of q against $t^{1/2}$ should be a straight line. The intraparticle diffusion rate constant, k_{intr} , can be calculated from the slope of the straight line. Nevertheless, it is common to observe multilinearity on the above mentioned plot, which reveals the different stages in adsorption involving external mass transfer and intraparticle diffusion [23].

RESULTS AND DISCUSSION

The kinetic studies have been carried out by batch reactions with various particle sizes of sugar beet shreds as adsorbents (Figure 1). The removal of copper ions by shreds with different particle sizes showed that the adsorption capacity and removal rate were increased with a decrease in particle diameter. The explanation is in the following, the higher adsorption with smaller adsorbent particle is attributed to the fact that smaller particles yield larger specific surface area. Also, the surface area of small particles is more accessible which facilitates adsorbate diffusion to the active sites.

Therefore, using adsorbents with smaller particles can be achieved faster as well as more efficient adsorption.

In this paper, the pseudo-first and pseudo-second order kinetic models were used to determine the rate of adsorption. In Table 1 the kinetic parameters for experimental data were presented obtained by using pseudo-first and pseudo-second-order model. Both equations give high coefficient of determination for all experimental data. The higher coefficient of determination for pseudo-second-order equation suggested that it was better model to explain kinetics of adsorption for experimental data. Figures 2–4 show the pseudo-first and pseudo-second-order equations obtained by using the non-linear methods for different particle sizes, 224–400 μm , 400–750 μm and 750–1000 μm , respectively.

Table 1. Kinetic parameters obtained from experimental data for different particle size

Particle size	Parameter	Pseudo-first	Pseudo-second
224–400 μm	q_e	9.2868	10.0000
	k	0.3807	0.0558
	R^2	0.9585	0.9883
400–750 μm	q_e	8.3400	9.0000
	k	0.3343	0.0521
	R^2	0.9336	0.9824
750–1000 μm	q_e	7.8902	8.6000
	k	0.2727	0.0436
	R^2	0.9437	0.9863

The coefficient of determination in Table 1 showed that the best model to describe the kinetics of adsorption is pseudo-second-order equation. The experimental adsorption capacities at equilibrium (q_e , Figure 1) best matches with values obtained by pseudo-second-order equation.

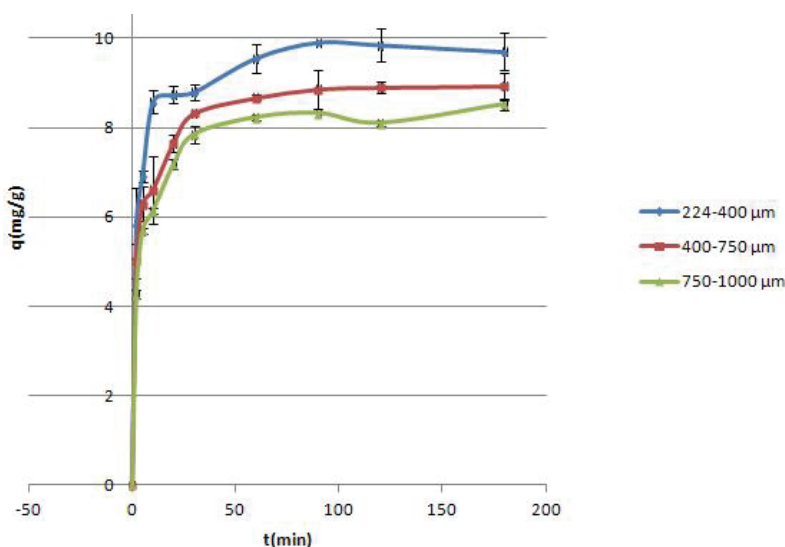


Figure 1. Effect of contact time and particle size of sugar beet shreds on the adsorption of copper ions.

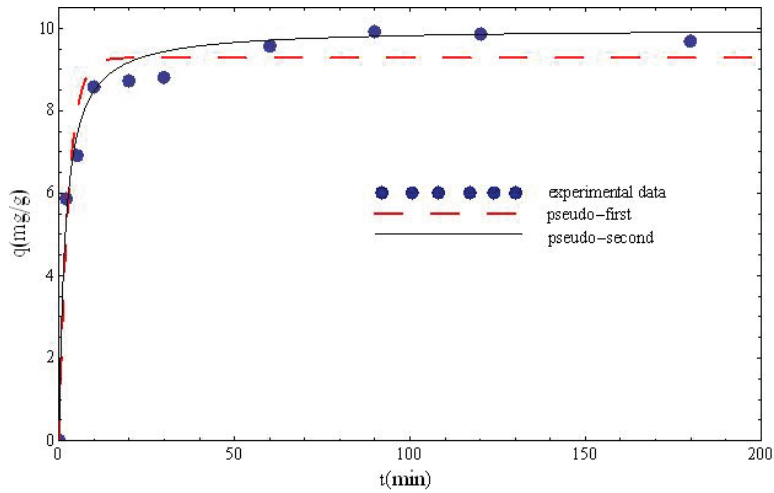


Figure 2. Pseudo-first and pseudo-second-order kinetic equations obtained by using the non-linear methods at particle sizes 224–400 μm .

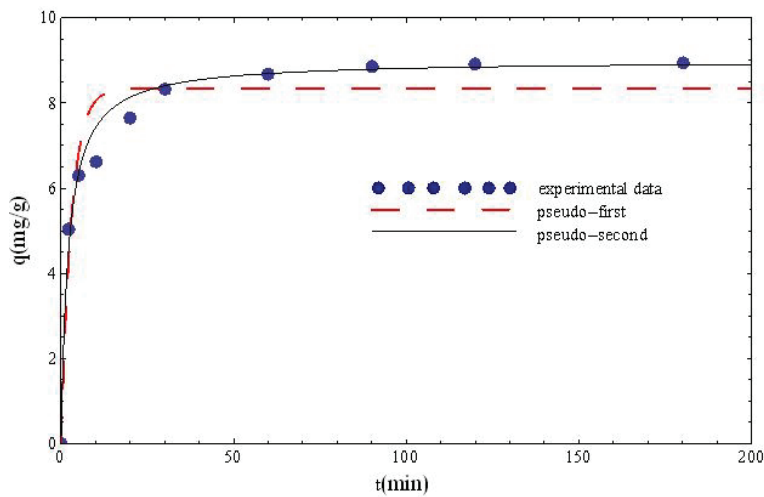


Figure 3. Pseudo-first and pseudo-second-order kinetic equations obtained by using the non-linear methods at particle sizes 400–750 μm .

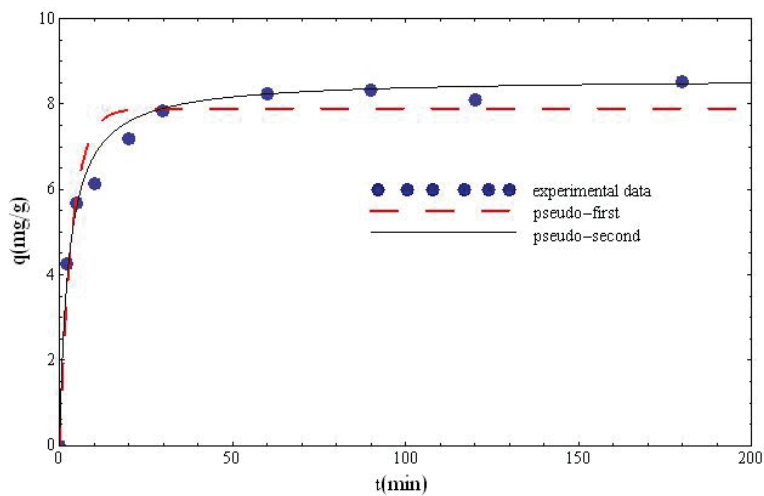


Figure 4. Pseudo-first and pseudo-second-order kinetic equations obtained by using the non-linear methods at particle sizes 750–1000 μm .

ond-order kinetics model (Table 1). This is another confirmation of the success of this model.

In Figure 5 it is observed that there are two linear portions which elucidate the two adsorption stages. The first adsorption stage is external mass transfer at initial period and the second is intraparticle diffusion. The slope of the linear portion suggests that the rate of intraparticle diffusion k_{int} , listed in Tables 2 and 3, increases with decreasing of particle size. The first adsorption state is represented by rapid adsorption (zone 1) while the second state is represented by deceleration (zone 3). Further, the first straight portion is attributed to a macropore diffusion process and the second linear portion can be ascribed to a micropore diffusion process. It is clear from Figure 5 that the first stage is faster than the second one. The slope decreases with increasing of particle size, which can be explained by poor accessibility of larger particles pores surface for the adsorbates.

CONCLUSIONS

The kinetics of adsorption of copper ions from water solution by sugar beet shreds was explained using the pseudo-first and pseudo-second-order kinetic and intraparticle diffusion models. The adsorption equilibrium for copper ions adsorption onto different sized sugar beet shreds was reached in 30 min. The adsorption capacity and removal rate were increased with a decrease in sugar beet shreds particle diameter. The coefficient of determination showed that the best model to describe the kinetics of adsorption is pseudo-second-order equation. The adsorption capacities at equilibrium, for a particle size of 224–400 μm , 400–750 μm and 750–1000 μm , are 10, 9 and 8.6 mg/g, respectively. By using intraparticle diffusion model proposed by Weber and Morris, it was obtained that there exist two different stages in adsorption: fast initial adsorption which is further limited by intraparticle diffusion.

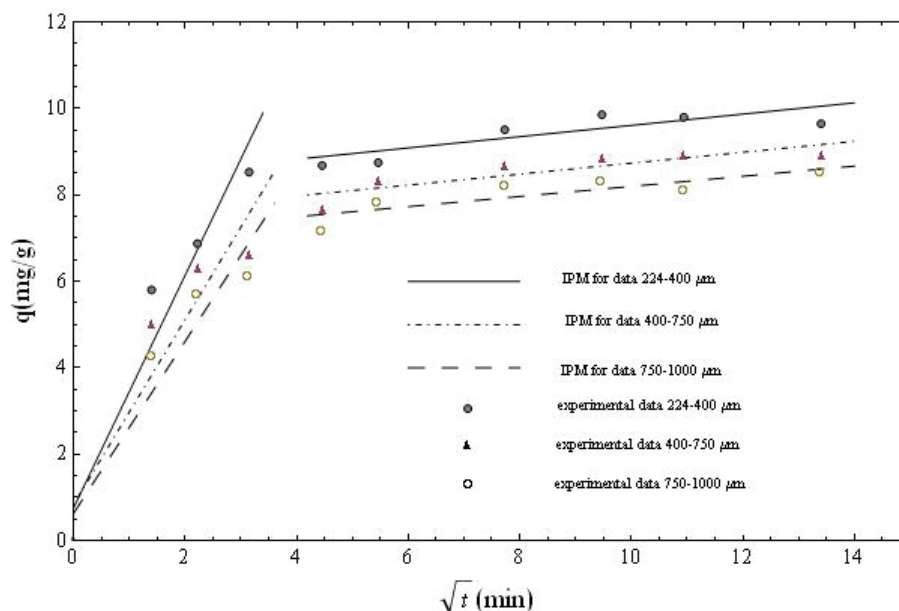


Figure 5. Intraparticle diffusion plot for the sorption of copper ions onto sugar beet shreds.

Table 2. First adsorption stage – intraparticle diffusion model for zone 1

Particle size	k_{int}	a	R_i	R^2
224–400 μm	2.6899	0.7586	0.9241	0.9667
400–750 μm	2.1396	0.8364	0.9071	0.9363
750–1000 μm	1.9905	0.6324	0.9265	0.9546

Table 3. Second adsorption stage – intraparticle diffusion model for zone 3

Particle size	k_{int}	a	R_i	R^2
224–400 μm	0.1304	8.3052	0.1695	0.9576
400–750 μm	0.1265	7.4694	0.1701	0.9688
750–1000 μm	0.1171	7.0269	0.1829	0.9325

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REFERENCES

- [1] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manage.* **92** (2011) 407–418.
- [2] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy

- metal ions from aqueous solutions – A review, *Biore-source Technol.* **99** (2008) 6017–6027.
- [3] S.O. Lesmana, N. Febriana, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Studies on potential applications of biomass for the separation of heavy metals from water and wastewater, *Biochem. Eng. J.* **44** (2009) 19–41.
- [4] V.M. Dronnet, C.M.G.C. Renard, M.A.V. Axelos, J.-F. Thibault, Binding of divalent metal cations by sugar-beet pulp, *Carbohydr. Polym.* **34** (1997) 73–82.
- [5] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents, *Rev. Separ. Purif. methods* **29** (2000) 189–232.
- [6] R.B. Garcia-Reyes, J.R. Rangel-Mendez, Adsorption kinetics of chromium(III) ions on agro-waste materials, *Bioresource Technol.* **101** (2010) 8099–8108.
- [7] W. Plazinski, W. Rudzinski, A. Plazinska, Theoretical models of sorption kinetics including a surface reaction mechanism: A review, *Adv. Colloid Interf. Sci.* **152** (2009) 2–13.
- [8] H. Qiu, L. Lv, B. Pan, Q. Zhang, W. Zhang, Q. Zhang, Critical review in adsorption kinetic models, *J. Zhejiang Univ. Sci., A* **10** (2009) 716–724.
- [9] S.S. Gupta, K.G. Bhattacharyya, Kinetics of adsorption of metal ions on inorganic materials: A review, *Adv. Colloid Interf. Sci.* **162** (2011) 39–58.
- [10] A.E. Ofomaja, E.B. Naidoo, Biosorption of copper from aqueous solution by chemically activated pine cone: A kinetic study, *Chem. Eng. J.* **175** (2011) 260–270.
- [11] K.S. Tong, M. Jain Kassim, A. Azraa, Adsorption of copper ion from its aqueous solution by a novel biosorbent *Uncaria gambir*: Equilibrium, kinetics, and thermodynamic studies, *Chem. Eng. J.* **170** (2011) 145–153.
- [12] B. Al-Rashdi, C. Tizaoui, N. Hilal, Copper removal from aqueous solutions using nano-scale diboron trioxide/titanium dioxide (B_2O_3/TiO_2) adsorbent, *Chem. Eng. J.* **183** (2012) 294–302.
- [13] E. Demirbas, N. Dizge, M.T. Sulak, M. Kobya, Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, *Chem. Eng. J.* **148** (2009) 480–487.
- [14] M. Šćiban, M. Klačnja, Wood sawdust and wood originate materials as adsorbents for heavy metal ions, *Holz Roh Werkstoff* **62** (2004) 69–73.
- [15] I. Sajo, *Complexometry*, 1st ed., Muszakikonykiado, Budapest, 1973 (in Hungarian)
- [16] W. Rudzinski, W. Plazinski, Kinetics of solute adsorption at solid/solution interfaces: a theoretical development of the empirical pseudo-first and pseudo-second order kinetic rate equations, based on applying the statistical rate theory of interfacial transport, *J. Phys. Chem., B* **110** (2006) 16514–16525.
- [17] S. Lagergren, Zurtheorie der sogenannten adsorption gelöesterstoffe, *Kungliga Svenska Vetenskapsakademien. Handlingar* **24** (1898) 1–39.
- [18] Y.S. Ho, G. McKay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbent, *Trans. IChemE* **76**, B (1998) 332–340.
- [19] F.-C. Wu, R.-L. Tseng, S.-C. Huang, R.-S. Juang, Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: A mini-review, *Chem. Eng. J.* **151** (2009) 1–9.
- [20] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* **34** (1999) 451–465.
- [21] Y.S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods, *Water Res.* **40** (2006) 119–125.
- [22] W.J. Weber, Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* **89** (SA2) 31–39.
- [23] X.Y. Yang, B. Al-Duri, Kinetic modeling of liquid phase adsorption of reactive dyes on activated carbon, *J. Coll. Interf. Sci.* **287** (2005) 25–34.

IZVOD

Kinetika adsorpcije jona bakra na izluženim repinim rezancima šećerne repe

Mirjana M. Brdar, Marina B.Šćiban, Dragana V. Kukić, Tatjana M. Došenović

Univerzitet u Novom Sadu, Tehnološki fakultet, Srbija

(Naučni rad)

Otpadne vode mnogih industrija, kao što su industrija prerade metala, eksploatacija ruda, proizvodnja đubriva, papira, baterija, prerada kože, itd, sadrže teške metale koji predstavljaju problem sa stanovišta zaštite životne sredine jer su toksični, imaju tendenciju biakumulacije i nisu biorazgradljivi, pa ih je neophodno ukloniti iz efluenta. Među mnogobrojnim dostupnim tehnikama najbolje rezultate je pokazala adsorpcija aktivnim ugljem, međutim, njenu primenu uveliko ograničava visoka cena. Potraga za novim, jeftinijim adsorbentima poput biomase dovela je do razvoja nove tehnologije poznate pod nazivom biosorpcija. Prednosti ove metode su, osim niže cene, visoka efikasnost i mogućnost regeneracije adsorbenta. Poljoprivredni otpad, koji u svojoj strukturi sadrži celulozu, je vrlo pogodan za ove svrhe jer je jeftin i dostupan u velikim količinama. Izluženi rezanci šećerne repe se obično koriste kao stočna hrana, izvor pektina ili supstrat za proizvodnju bioetanola, ali imaju i sposobnost adsorpcije jona teških metala. Oko 40% suve materije repinih rezanaca čini pektin koji veže katjone metala iz vodenih rastvora zbog brojnih funkcionalnih grupa koje sadrži. Za ocenu efikasnosti procesa adsorpcije značajno je određivanje kapaciteta adsorbenta, kinetike adsorpcije i ostalih uslova rada koji će dati najbolje rezultate pri primeni nekog adsorbenta. U ovom radu ispitana je kinetika adsorpcije jona bakra na izluženim repinim rezancima šećerne repe. Eksperimenti su izvedeni šaržno primenom rezanaca šećerne repe različitih veličina čestica: 224–400 μm , 400–750 μm i 750–1000 μm . Ravnoteža u procesu adsorpcije je postignuta nakon 30 min, a kapacitet i brzina adsorpcije su rasli sa smanjenjem veličina čestica adsorbenta. Za opisivanje kinetike adsorpcije su primenjene nelinearne jednačine pseudo-prvog i pseudo-drugog reda, kao i model difuzije unutar čestica. Za proračun je korišćen softver Mathematica 6. Rezultati su pokazali da je jednačina pseudo-drugog reda dobijena nelinearnom metodom najmanjih kvadrata najbolji model za opisivanje adsorpcije jona bakra na izluženim rezancima šećerne repe. Modelom difuzije unutar čestica je pokazano da postoje dva stanja prilikom adsorpcije. Prvo stanje karakteriše brza adsorpcija (zona 1), dok u drugom dolazi do zasićenja, te brzina adsorpcije opada (zona 3).

Ključne reči: Adsorpcija • Rezanci šećerne repe • Kinetički modeli • Pseudo-prvi red • Pseudo-drugi red • Model difuzije unutar čestice