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SORPTION KINETICS OF Cd(II) IONS ON FERMENTED GRAPE MARC

The sorption kinetics of Cd(II) ions on the biosorbent which is waste in wine production has been investigated. The sorption process took place relatively quickly, enabling one to achieve equilibrium within a period of 15–20 min only, depending on initial concentration of the sorbate. Kinetic models of pseudo-first and pseudo-second order, model of diffusion in a fluid film and Weber's and Morris' intraparticle diffusion model were used to describe the experimental results. The pseudo-second order kinetic model described the sorption process with a high correlation coefficient ($R^2 = 0.998$) better than the other kinetic models. The mass transfer coefficient decreases upon increasing the initial concentration of the solution, which can be explained by the fact that the mechanism of binding of Cd(II) ions to the surface of the sorbent is ion exchange followed by discharge of exchangeable cations from the surface. Characteristic constants in the Weber–Morris model increase upon increasing the initial concentration of the solution.

1. INTRODUCTION

Rapid development of various industries and technologies and relatively low level of environmental protection leads to increased pollution of ecosystems with heavy metals. Cadmium and other heavy metals are not biodegradable and have a tendency to accumulate in living organisms, causing various diseases [1]. Therefore, cadmium should be removed efficiently from waste waters and from ecosystems in general.

Disadvantages of the conventional methods of wastewater treatment (ion exchange, precipitation, ultrafiltration, electrochemical processes, etc.) have been reported [2], as well as the benefits of heavy metal sorption on different sorbents. The other advantage of biosorption is using easily available and waste biomass as a sorbent. In recent years,

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numerous studies have been carried out in order to find new, easily available and inexpensive biosorbents for the removal of cadmium such as: various algae [3, 4], rice husk [5], orange peels [6], tea waste [7] and various types of sawdust [8, 9].

Whether full or partial sorption will be performed depends on its rate. Analysis of kinetic parameters gives information about the dominant mechanisms of mass transfer. In this way, kinetic studies may help in assessing the possibility of using any material as a potential sorbent for the removal of impurities from solutions [10]. Large number of kinetic models is proposed to determine sorption rates. The most commonly used are models of pseudo-first and pseudo-second order as well as the Weber and Morris intra-particle diffusion model.

Experimental results [11] showed that grape marc is a cellulosic material of multi-layered structure whose layers are interconnected by a system of channels and pores, which form a relatively large specific surface area. The presence of pores is suitable for diffusion of metal ions and their adsorption on numerous internal active centers. The advantages of using this biosorbent are its efficiency in removing Cd(II) ions at various pH and for various grain sizes of the sorbent. In that sense, the costs of its preparation are reduced and its application in industrial conditions is greatly facilitated.

The goal of this research was to investigate kinetics of sorption of Cd(II) on fermented grape marc as well as the mechanisms of mass transfer.

2. EXPERIMENTAL

Sorbent. Grape marc from the wine production after draining off under a pressure of $2 \cdot 10^5$ Pa was washed with distilled water, then rinsed with dilute hydrochloric acid, and again washed with distilled water to remove Cl^- ions. The sorbent was dried at ambient temperature and at 60°C to constant weight, and granulated on a steel laboratory blender (ITNMS, Laboratory for preparation of raw materials, Belgrade). Then it was sifted through a standard steel sieve to obtain fractions of appropriate particle size: <0.5 mm, 0.5–1 mm, 1–2 mm, >2 mm. Before using in experiments, the biomass was again treated with dilute HCl, rinsed with distilled water to remove Cl^- ions and dried at 60°C to constant weight.

Materials and analyses. Cd(II) solutions ($20\text{--}400$ $\text{mg}\cdot\text{dm}^{-3}$) were made by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (p.a.) in distilled water. Their concentrations were determined by the atomic absorption spectrophotometry (AAS) using the AA-6800 instrument (Shimadzu, Japan) at 228.8 nm. pH was measured using a WTW inoLab pH 720 pH-meter.

Sorption experiments. Preliminary kinetic experiments were conducted to assess the time, taken for attaining the equilibrium. One set of experiments was done using aqueous solution of Cd(II) ions with initial concentration from 20 $\text{mg}\cdot\text{dm}^{-3}$ to 400 $\text{mg}\cdot\text{dm}^{-3}$.

The amount of the grape marc was maintained constant, equal to 0.1 g in 100 cm³ solution in each of the batch experiments. During the sorption process, the solutions were mixed on a reciprocal shaker (Heidolph), after which they were filtrated, and filtrates were stabilized with 1 cm³ of concentrated HNO₃ and saved for examination of the contents of metals.

The amount of metal ions adsorbed per unit mass of the biosorbent q_t was calculated by the following equation:

$$q_t = \frac{c_0 - c_e}{S} V \quad (1)$$

where c_0 is the initial metal ion concentration (mg·dm⁻³), c_e is the equilibrium metal ion concentration (mg·dm⁻³), V is the volume of metal ion solution (dm³) and S is the weight of the biosorbent (g).

Four of the main models proposed in the literature have been selected for the adjustment of the experimental results obtained and to determine the kinetic parameters of the biosorption of Cd(II) onto grape marc.

Pseudo-first order kinetic model. The pseudo-first order model describes the sorption rate that is proportional to the number of available binding sites on the sorbent surface. This model is described by the Lagergren equation [12]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are the adsorption capacities at equilibrium and after time t , respectively; k_1 (min⁻¹) is the constant rate of pseudo-first order adsorption.

The constant k_1 can be obtained from the slope of the time dependence of $\ln (q_e - q_t)$, and q_e can be calculated from its intercept on the ordinate.

Pseudo-second order kinetic model. Unlike the kinetic model of the pseudo-first order which can be applied only in the initial phases of the sorption process, the pseudo-second order model is useful during the whole process and it is described by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 (g·mg⁻¹·min⁻¹) is the constant rate of the pseudo-second order adsorption. The values of q_e and k_2 can be obtained from the slope and the intercept of time dependence t/q_t , respectively.

Diffusion in a fluid film. Results of examination of the kinetics of sorption processes were used to determine the mass transfer coefficients. The sorption process is complex and is carried out in four consecutive steps: transport of Cd(II) ions in the bulk fluid [13], diffusion through the film of fluid (boundary layer) around the sorbent particles (external diffusion), diffusion through the film in the pores of the sorbent (internal diffusion) and sorption on the particle surface. Each of these stages may influence the rate of the overall process.

The Mathews–Weber model [14] is used to describe the external mass transfer:

$$\ln \frac{c_t}{c_0} = -k_f a t \quad (4)$$

where c_0 and c_t ($\text{mg} \cdot \text{dm}^{-3}$) are concentrations of metal ions in solution at the beginning of the process and after time t , respectively, $k_f a$ is the volumetric mass transfer coefficient which can be calculated from the slope of the time dependence of $\ln(c_t/c_0)$.

Intraparticle diffusion model. One of the most commonly used models for the diffusion within the sorbent particles is the Weber–Morris model [15] given by the equation:

$$q_t = k_{id} t^{1/2} + C \quad (5)$$

where k_{id} ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$) is a constant of the diffusion rate, and C is a constant related to the thickness of the adsorption boundary layer.

It is possible to define present resistance for the mass transfer by using this model, as well as limiting stage of the overall sorption process. Equation (5) is a straight line in the coordinate system q_t vs. $t^{1/2}$. If the line passes through the origin, the thickness of the boundary layer and thus the resistance for mass transfer through the film is negligible. Therefore, the only limiting stage of the sorption process is diffusion within the particles.

3. RESULTS AND DISCUSSION

All the results, generated from AAS, were used to calculate the Cd(II) uptake by biosorbent. The amount of metal adsorbed (q_t) vs. contact time is shown in Fig. 1. It can be seen that the shape of the curve does not depend on the initial concentration of the solution. Sorption is a heterogeneous process, and each curve is composed of two parts corresponding to the fast stage, and the slow stage of the process. The largest amount of metal is adsorbed in the first 5 min of the process, similarly as in the case of sorption of Cd(II) on coconut copra meal [16] and on a pomelo peel [17]. The fast stage at the beginning

of the process is caused by the large driving force for the mass transfer due to large differences in the concentrations of metals in solution and on the surface of the sorbent, as well as a large number of available active sites on the surface of the sorbent [9, 18]. The sorption capacity of the sorbent increases until the equilibrium is established, which is attained after 15–20 min depending on the initial concentration of the solution. Short period of time needed for establishing the equilibrium or high process rate indicate that the cadmium ions bind to active sites on the surface of the sorbent without a significant share of diffusion within the particles.

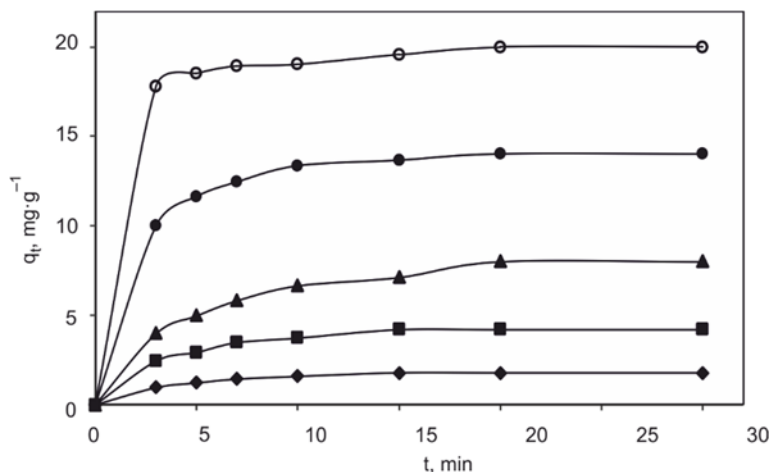


Fig. 1. Time dependences of metal uptake by grape marc; c_0 of the solution ($\text{mg}\cdot\text{dm}^{-3}$): \blacklozenge – 20, \blacksquare – 50, \blacktriangle – 100, \bullet – 200, \circ – 400

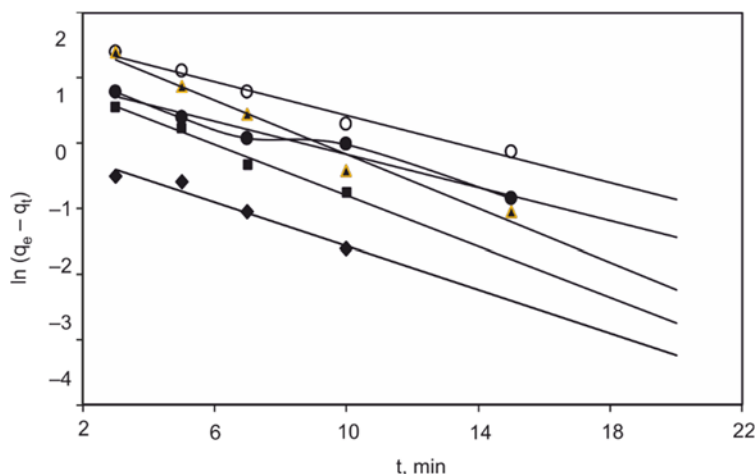


Fig. 2. Kinetic model of the pseudo-first order process for the sorption of Cd(II) on grape marc; c_0 of the solution ($\text{mg}\cdot\text{dm}^{-3}$): \blacklozenge – 20, \blacksquare – 50, \blacktriangle – 100, \bullet – 200, \circ – 400

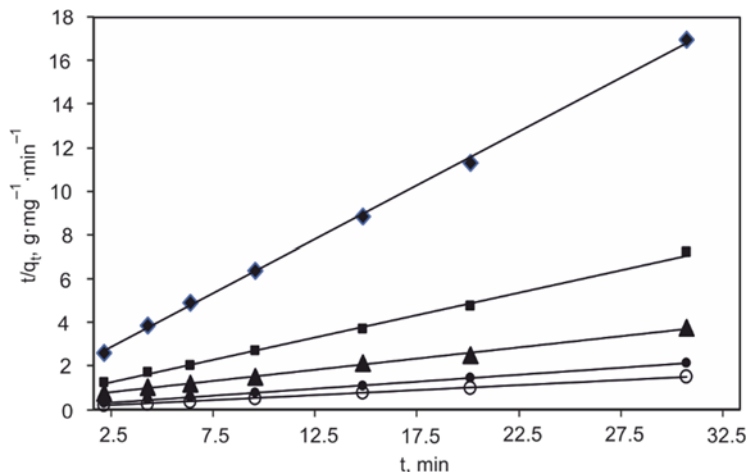


Fig. 3. Kinetic model of the pseudo-second order process for the sorption of Cd(II) on grape marc; c_0 of the solution ($\text{mg}\cdot\text{dm}^{-3}$): \blacklozenge – 20, \blacksquare – 50, \blacktriangle – 100, \bullet – 200, \circ – 400

The results, obtained in the study, were used to investigate the kinetics of the Cd(II) ions adsorption on the surface of grape marc. Based on kinetic models of pseudo-first order and pseudo-second order (Figs. 2, 3), kinetic parameters of sorption process were calculated (Table 1).

Table 1

Kinetic parameters of the sorption of Cd(II) ions
on the grape marc for the pseudo-first and pseudo-second order models

c_0 [$\text{mg}\cdot\text{dm}^{-3}$]	$q_{e, \text{exp}}$ [$\text{mg}\cdot\text{g}^{-1}$]	Pseudo-first order model			Pseudo-second order model		
		q_e [$\text{mg}\cdot\text{g}^{-1}$]	k_1 [min^{-1}]	R^2	q_e [$\text{mg}\cdot\text{g}^{-1}$]	k_2 [$\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$]	R^2
20	1.77	1.109	0.166	0.959	1.921	0.242	0.998
50	4.19	3.129	0.194	0.981	4.587	0.091	0.997
100	8.00	5.596	0.129	0.979	9.174	0.028	0.997
200	14.00	6.672	0.206	0.974	14.706	0.056	0.999
400	20.00	0.083	0.126	0.964	20.408	0.096	0.999

The values of calculated parameters indicate that the pseudo-second order model demonstrates the best compliance with the experimental results. The values of R^2 are higher those corresponding to the pseudo-first order model and theoretical value of q_e obtained by application of the pseudo-second order are closer to experimentally obtained values. These facts indicate that the sorption of Cd(II) on the grape marc undergoes via the mechanism of the second order, i.e., it is a chemisorption mechanism.

The pseudo-second order model is often used to describe the kinetics of sorption of heavy metals onto various biosorbents [9, 17–22].

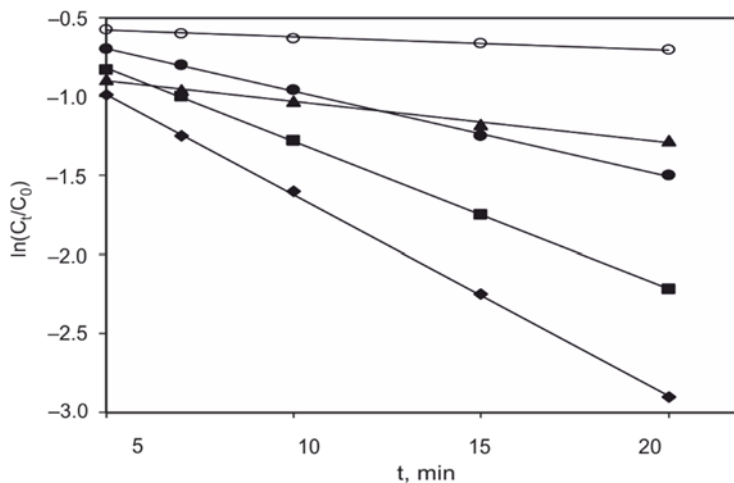


Fig. 4. Mathews and Weber's model of external mass transfer in the sorption process of Cd(II) ions on the grape marc; c_0 of the solution ($\text{mg} \cdot \text{dm}^{-3}$): ◆ – 20, ■ – 50, ▲ – 100, ● – 200, ○ – 400

The dependences given in Fig. 4 were obtained using the Mathews and Weber model. The values of volumetric mass transfer coefficients which define diffusion of metal ions through the boundary layer of fluid are given in Table 2.

Table 2

Volumetric mass transfer coefficients through the film of fluid during the sorption of Cd(II) ions from solutions

c_0 [$\text{mg} \cdot \text{dm}^{-3}$]	20	50	100	200	400
$k_f a$ [$\text{dm}^3 \cdot \text{min}^{-1}$]	0.126	0.096	0.061	0.021	0.004

The value of the mass transfer coefficient decreases upon increasing the initial concentration of the solution, which can be explained by the fact that the mechanism of binding of Cd(II) ions to the surface of the sorbent is ion exchange, followed by discharge of exchangeable cations from the surface. Transfer of Cd(II) ions through the film of fluid is hindered by diffusion of cations in the opposite direction, as well as by the electrostatic repulsion of positively charged ions. The quantity of released cations and the resistance to diffusion of Cd(II) through the boundary layer increases upon increasing concentration of Cd(II) ions in solution, which causes a decrease of the volumetric coefficient of mass transfer.

In Figure 5, q_t vs. $t_{1/2}$ dependences have been plotted. They are multilinear, which suggests various mechanisms of the sorption process. For shorter times, the dependences relate

to the diffusion within film fluid, and later to the diffusion within the pores [9, 15]. Namely, at the beginning of the sorption, Cd(II) ions diffuse through the boundary layer to the surface of grape marc [23]. Then metal ions gradually diffuse within the particles of the sorbent which determines the overall rate of the process. A part of the curve parallel to the abscissa represents the equilibrium state.

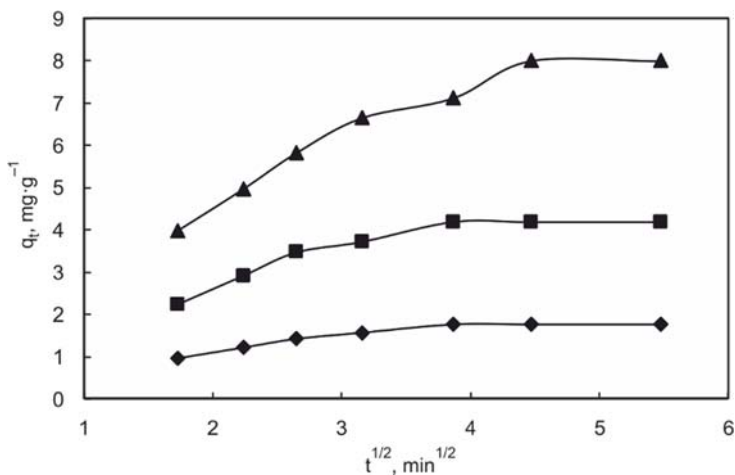


Fig. 5. The Weber–Morris model of the sorption process of Cd(II) ions on the grape marc; c_0 of the solution ($\text{mg}\cdot\text{dm}^{-3}$): ◆ – 20, ■ – 50, ▲ – 100, ● – 200, ○ – 400

The values of the k_{id} coefficients for the two stages of the sorption at various initial concentrations of Cd(II) ions are shown in Table 3. The lines relating to the initial period of the sorption process do not pass through the beginning of coordinate system and the correlation coefficients are also relatively low (Table 3) which indicates that diffusion in the pores is not the only factor that determines the rate of the process. This could be a consequence of differences in the rate of mass transfer in the initial and final phase of the sorption process, due to the decrease in the metal ion concentration.

Table 3

Parameters of the Weber–Morris model for the sorption of Cd(II) ions on the grape marc at various initial sorbate concentrations^a

c_0 [$\text{mg}\cdot\text{dm}^{-3}$]	$k_{id,1}$ [$\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$]	R^2	$k_{id,2}$ [$\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$]	R^2
20	0.511	0.899	0.157	0.791
50	1.337	0.888	0.368	0.791
100	1.998	0.929	1.094	0.952

^a $k_{id,1}$ – constant of diffusion rate within film fluid, $k_{id,2}$ – constant of diffusion rate within the pores.

It is evident that diffusion through the barrier layer is a limiting factor in the process, although the rates of stirring are high and therefore diffusion within the particles is not the only limiting factor. Since the sorption process at the beginning is fast, values of $k_{id,1}$ are always higher than the values of $k_{id,2}$. This can be explained by the fact that by decreasing the pore size, the length of free path of the molecules within the pore decreases, which causes reduction of sorption speed and process parameters [24]. It is evident that coefficients of slopes increase with the increasing of initial concentration of solution which can be due to the fact that the Weber–Morris model based on Fick's law, according to which an increase in the concentration gradient causes the faster diffusion and adsorption [25].

The values of R^2 of the pseudo second order kinetic model are higher than the value of R^2 of diffusion within particles model, which confirms that the basic mechanism of binding of Cd(II) ions is chemisorption. But, the examined sorption process is complex, and represents a combination of surface chemisorption and diffusion within particles.

4. CONCLUSION

Results of examination of the time dependences indicate that the sorption of Cd(II) on the fermented grape marc is very fast. Experimental results were analyzed in terms of the pseudo-first and pseudo-second order kinetic models as well as the external diffusion model of mass transfer and model of diffusion within sorbent particles. Upon increasing initial concentration of solution, the volumetric mass transfer coefficients decrease while the values of characteristic constants in the Weber–Morris model increase. The kinetics of the sorption process is controlled by chemisorption as well as by diffusion. The used biosorbent is industrial waste material, inexpensive, readily available and very efficient to remove heavy metals from both natural and waste waters. By using it, the problems of waste reusing and water waste treatment are both solved.

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