# Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones

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Received March 8, 2010; revised August 3, 2010

In this work single and four-component adsorption kinetics was studied for removal of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  from aqueous solutions with activated carbon from apricot stones. The adsorption equilibrium was calculated by the Langmuir model for single- and multi-component systems. Comparison of three kinetic models for internal diffusion control was performed. The steep initial part of the kinetic curve was accounted for by an intercept term in the linear representation of the models of Weber and Morris, Boyd and the moment method. The Weber and Morris model was found to correlate best with the experimental data. The intraparticle diffusion coefficients for the individual ions are in the range  $1-3x10^{-8}$  cm<sup>2</sup>/s. Similar results were obtained by the moment method applied to homogeneous solid phase diffusion control. Lower values of the kinetic parameters were obtained in four-component solutions. The calculated summary diffusion coefficient in the multi-component system is close to that obtained for single-component solutions with the same total initial ion concentration.

Keywords: adsorption kinetics; diffusion coefficient, active carbon, heavy metals

# INTRODUCTION

The kinetic study has the important practical task to determine the degree of utilization of the adsorption capacity as a function of the time of contact between the liquid and the solid. Therefore, different models are used to fit the obtained kinetic curves in order to define the rate parameters and explain the mechanism of mass transfer. Most studies dealing with heavy metals adsorption on low-cost adsorbents use the statistical approach of the best-fit model that compares the correlation coefficients of models with different physical background and applies as a criterion the acceptable description of the whole kinetic curve or as large part of it as possible. Kinetic investigations with activated carbons usually apply first-order [1,3-10,12] and second-order reaction models [1,5-7,9,10]. For porous sorbents as activated carbons, however, diffusional effects may be quite important and the physical meaning of the evaluated rate constants has to be consequently determined in order to get insight into the transfer mechanism. Usually comparison with other mass transfer models [6,11,12,24] is performed, like the Boyd model [1,5,7,13] and the intraparticle diffusion model of Morris and Weber [1-5,9-12]. The

moment method is less used, because of its original limitation to systems with linear equilibrium. Its application to batch adsorption uptake curves with nonlinear isotherms [15] enhances the scope of its utilization, including the adsorption of heavy metals [16, 17]. The obtained rate constant is related to the traditional mathematical models used for describing solid phase mass transfer, like the linear driving force model, the homogeneous solid phase or the pore diffusion model, as well as to more complicated structures like biporous sorbents [16].

The *Weber and Morris model* or intraparticle diffusion model is of major interest because the internal diffusion determines the adsorption rate in most of the liquid systems. Eq. (1) is a general representation of the kinetics, where the intercept is related to the mass transfer across the boundary layer and the expected value of the exponent is 0.5 (for Fickian diffusion and plate geometry).

$$q = k_{in}t^n + c \tag{1}$$

Both processes are generally observed for adsorption kinetics on activated carbons – the external mass transfer from the solution to the liquid-solid interface and the diffusion of the adsorbed species inside the porous particle. The Weber and Morris model (eq. 2) describes the time evolution of the concentration in adsorbed state, where the rate constant ( $k_{in}$ ) is obtained from the plot of q versus  $t^{0.5}$  and is related to the respective

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intraparticle diffusion coefficient (D) according to eq.(3).

$$q = k_{in} t^{0.5} \tag{2}$$

$$k_{in} = 6 \frac{q_0}{R} \sqrt{\frac{D}{\pi}}$$
(3)

The different mechanisms of mass transfer are manifested as different slopes in the linear plot of q versus  $t^{0.5}$ , obtained by piecewise linear regression. They correspond to different consecutive stages of mass transfer and intraparticle diffusion in the macro-, meso- and microporous structure of the adsorbent [5].

The *Boyd's model* is often used to obtain insight into the mechanism of the adsorption kinetics. Originally proposed for intraparticle diffusion in a spherical particle, it is better known as the Boyd's film-diffusion model. When applied to external mass transfer, it supposes a linear dependence through the origin between  $F = \frac{q}{q_e}$  (the fractional

approach to equilibrium) and t (time):  $\ln(1-F) = kt$ . Here k denotes the external mass transfer coefficient.

The general solution of the model, applied to solid phase control, is:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 Bt\right),$$
 (4)

where the rate coefficient *B* is related to the effective diffusion coefficient ( $D_{\text{eff}}$ ) and the particle radius as  $B = \pi^2 D_{\text{eff}}/R^2$ .

By applying Fourier transform, the relation between the fractional approach to equilibrium F and the rate coefficient B is written as:

$$Bt = \left(\sqrt{\pi} - \sqrt{\pi - (\pi^2 F/3)}\right)^2 \text{ for } F < 0.85 \quad (5a)$$

and  $Bt = -0.498 - \ln(1 - F)$  for F>0.85 (5b)

The linear plot between the time and the right side of the above expressions, f(F), is used to evaluate the rate parameter B. The observance of an intercept is an indication for the effect of a second mass transfer mechanism (external mass transfer).

#### The method of moments

The main idea of the method is to connect the Laplace transform solution of the mass balance equations with the statistical characteristics of the corresponding concentration curves. The time evolution of the liquid phase concentration is given by the mass balance equation:

$$\frac{dc}{dt} = -\beta \frac{dq}{dt},\tag{6}$$

where  $\beta$  denotes the solid-liquid ratio  $\beta = V_e/V_1$ .

The dimensionless representation of eq. (6) is:  $\frac{d\bar{c}}{dt} = -\beta K \frac{d\bar{q}}{dt}$ Equilibrium is suggested between the final solid and liquid phase concentrations, denoted by the slope of the isotherm  $K = \frac{q_e}{c_e}$ . The change in the solid phase concentration is described according to the model of mass transfer:

For the linear driving force model  $\frac{dq}{dt} = k_s(q_e - q)$ , where the rate constant  $k_s$  is defined as the solid phase mass transfer coefficient [s<sup>-1</sup>]. The solution for the solid phase concentration in this case is:

$$\frac{q}{q_e} = \left[1 - \exp\left(-\frac{t}{\mu_1}\right)\right] \tag{7a}$$

or in dimensionless form:

$$\ln(1 - \frac{q}{q_e}) = -\frac{t}{\mu_1} \tag{7b}$$

Here the first absolute moment of the uptake curve is inversely proportional to the rate constant  $k_s = \frac{1}{\mu_1}$ . This solution is formally identical to that for

a first-order reaction model  $\ln(q_e - q) = \ln q_e - k_1 t$ .

b) For the homogeneous solid phase diffusion model the change in the volume averaged solid phase concentration is due to diffusion flux across the boundary (r = R):

$$\frac{dq}{dt} = \frac{3}{R} D_a \frac{q}{\partial r} \bigg|_{r=R}$$
(8)

Here *a* denotes the local adsorbed concentration. Fick diffusion is supposed inside the spherical particle:

$$\frac{dq}{dt} = \frac{D_a}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right) \tag{9}$$

The relation between the moment of the uptake curve  $(\mu'_1)$  and the diffusion coefficient  $(D_a)$  is given as:

$$\mu_{1}^{'} = \frac{R^{2}}{(1 + \beta K)! 5D_{a}}$$
(10)

Relations for other diffusion models are given in [16] and [17]. The equilibrium parameter K was originally defined for a linear isotherm. It was later shown that it may be treated as the local slope of the isotherm at the equilibrium concentration  $c_e$  [17].

Despite the large number of articles concerning the adsorption of heavy metals on low cost adsorbents, very few of them are dealing with the multi-component kinetic behaviour of such systems. In the case of adsorption on activated carbon from apricot stones (ACAS) only single component kinetics for batch removal of chromium [14] and gold ions [23] is reported. The authors [14] compare different kinetic models with the results being in favour of the pseudo first-order reaction model.

The aim of the present paper was to investigate the adsorption kinetics of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ on ACAS in single- and four-component solutions. Three kinetic models for solid phase diffusion control were discussed and compared in order to obtain the rate parameters of the adsorption process, based on the microporous nature of the activated carbon and the suggested ion exchange mechanism [18].

#### **EXPERIMENTAL**

Single and four-component solutions containing Pb(NO<sub>3</sub>)<sub>2</sub>, CdCl<sub>2</sub>, ZnSO<sub>4</sub>  $\times$  7H<sub>2</sub>O and CuSO<sub>4</sub>  $\times$ 5H<sub>2</sub>O with total concentration of about 1.5 mmol/l were used in the kinetic experiments. ACAS, supplied by the Institute of Organic Chemistry, Bulgarian Academy of Sciences, was used, whose properties and adsorption equilibrium were reported earlier [18]. The kinetic curves were obtained by several parallel runs with different contact times. The other experimental conditions were: particle size 1.8 mm; mass of dry solid 0.5 g  $(M_s)$ ; volume of metal ion solution 50 ml  $(V_l)$ . The liquid phase concentration c(t) was measured by atomic absorption spectrometry (Perkin-Elmer 5000). The solid phase concentration q(t) was calculated from the mass balance:  $V_l(c_0 - c) = M_s q$ , where  $c_o$  is the initial concentration in the solution, mmol/l.

### RESULTS AND DISCUSSON Single component adsorption kinetics

Figs.1a) to d) present the kinetic curves for the individual ions in dimensionless coordinates:  $q/q_e$  vs. time. The equilibrium value  $q_e$  was calculated

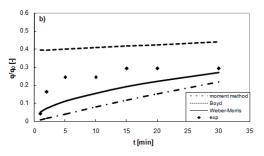


Fig.1a. Dimensionless experimental and calculated kinetics for  $Pb^{2+}$ .

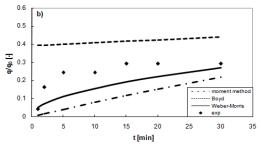
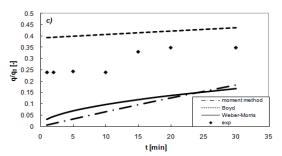


Fig.1b. Dimensionless experimental and calculated kinetics for  $Cd^{2+}$ .



**Fig.1c**. Dimensionless experimental and calculated kinetics for  $Cu^{2+}$ .

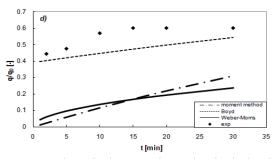


Fig.1d. Dimensionless experimental and calculated kinetics for  $Zn^{2+}$ .

by the Langmuir isotherm [18], whose equilibrium parameters  $(q_m \text{ and } b)$  are shown in Table 1. The slope of the isotherm (K) is determined at the equilibrium concentration  $c_e$ , which was calculated by the mass balance in the liquid phase:

$$V_{l}(c_{0} - c_{e}) = M_{s}(q_{e} - q_{0}) = M_{s}q_{e} = M_{s}\frac{q_{m}bc_{e}}{1 + bc_{e}}$$
(11)

Ion	$q_m$	b	$c_0$	$q_e$	K	S
	[mmol/g]	[l/mmol]	[mmol/l]	[mmol/g]	[-]	[-]
Pb	0.0762	11.534	1.544	0.0692	81.09	0.092
Cu	0.1222	5.774	1.26	0.0858	210.26	0.298
Cd	0.01196	1.203	1.245	0.0549	78.55	0.543
Zn	0.0935	1.064	1.485	0.0482	48.15	0.484

Table 1. Equilibrium parameters and conditions for the individual ions in single-component solutions

Table 2. Rate parameters for the individual ions in single-component solutions

	Method of moments				Boyd's model		Weber and Morris model		
	k.	$D_a \times 10^8$	$R^2$	В	$D_{eff} \cdot \times 10^8$	$R^2$	k <sub>in</sub>	$D \times 10^8$	$R^2$
Ion	$[\min^{-1}]$	[cm <sup>2</sup> /s]		$[\min^{-1}]$	$[cm^2/s]$		[mmol/gmin <sup>-1/2</sup> ]	[cm <sup>2</sup> /s]	
$Pb^{2+}$	0.0126	6.262	0.680	0.0072	9.86	0.69	0.0035	3.01	0.74
$\mathrm{Cd}^{2+}$	0.0082	4.135	0.59	0.0027	3.69	0.70	0.0027	2.84	0.73
$Cu^{2+}$	0.0067	1.944	0.81	0.0031	4.245	0.82	0.0026	1.08	0.79
$Zn^{2+}$	0.0124	8.424	0.70	0.0096	13.15	0.71	0.0021	2.23	0.83

Only experimental values for the initial concentrations  $(c_o)$  were necessary in this case. The final equilibrium values were predicted by the isotherm. This approach is also useful for situations when the plateau of the kinetic curve is not reached

or is poorly defined. The parameter  $S = \frac{1}{1 + bC_0}$ 

in Table 1 characterizes the nonlinearity of the isotherm (S=1 applies for a linear isotherm, S=0 – for a rectangular one). It is close to the highly favourable (rectangular) isotherm for Pb<sup>2+</sup>, as can be seen in Table 1. For the other three ions the values of *S* correspond to different nonlinearity (0.3-0.5), far from the linear case.

# 1. Morris and Weber model

The experimental kinetics of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and  $Zn^{2+}$  adsorption on ACAS is characterized by a sharp increase in the adsorbed concentration during the first 1-2 min, followed by a lower uptake rate, which can be described by the Weber and Morris model in the form of eq. (1):  $q = k_{in}t^{0.5} + c$ . The kinetic curve, in fact, exhibits a different initial slope (dotted line in Fig. 2) and the intercept c is an extrapolation of its second linear 'diffusion' part to the ordinate (solid line in Fig. 2). The initial part is connected to faster mass transfer through the boundary layer and/or adsorption on the solid surface, followed by slow diffusion inside the particles. The obtained rate constants  $k_{in}$  are shown in Table 2, as well as the intraparticle diffusion coefficients D calculated by eq. (3). The values obtained for  $k_{in}$  are in the order reported in the literature for adsorption on low-cost activated carbons from plant materials. Depending on the initial concentration of lead ions, values of  $k_{in}$  =

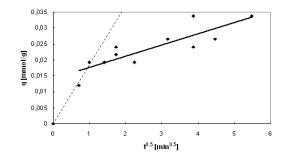


Fig.2. Morris and Weber linear plot for lead ions in single-component solution

0.2 ÷ 1.85 mg/g·min  $^{1/2}$  were found in [1]. They correspond to the  $k_{in,Pb}$  presented in Table 2, if recalculated in the dimensions of [1], i.e. 0.724 mg/g min<sup>-1/2</sup>. The Morris and Weber model gives values of  $k_{in}$  in the range 0.83-5.94 mg/g min<sup>-1/2</sup> for lead adsorption on palm shell-based activated carbon [5]. Kinetic data for  $Cr^{2+}$  adsorption on ACAS are reported in [14] for comparable experimental conditions (pH=3, d=1.6 mm,  $c_o$ =1-2 mmol/l). In the authors' representation - percentage of ion adsorption vs time [h], the results for  $k_{in}$  in Table 2 should be: Cd<sup>2+</sup>-37.5, Pb<sup>2+</sup>-39.68, Zn<sup>2+</sup>-33.86 and Cu<sup>2+</sup>=23.17 h<sup>-1/2</sup>, i.e. of the same order as those, reported in [14] (33.5 - 37.3  $h^{-1/2}$ ). The obtained intraparticle diffusion coefficients (Table 2) are in the range  $1-3\cdot10^{-8}$  cm<sup>2</sup>/s, which is physically reasonable for internal diffusion. The comparison with the coefficients of molecular diffusion also supports the conclusion for a rate limiting internal diffusion mechanism. The reported values for molecular diffusion of free ions in aqueous solutions are in the order of  $10^{-6}$  cm<sup>2</sup>/s (Pb<sup>2+</sup> - 9.5·10<sup>-6</sup> cm<sup>2</sup>/s, Cd<sup>2+</sup> - 6.52-7.2 ·10<sup>-6</sup> cm<sup>2</sup>/s, Cu<sup>2+</sup> - 6.47-7.3·10<sup>-6</sup> cm<sup>2</sup>/s, Zn<sup>2+</sup> - 6.37-7.2·10<sup>-6</sup>  $cm^{2}/s$  [19-22]).

#### 2. Boyd's model

linear representation in coordinates А  $\left(\sqrt{\pi} - \sqrt{\pi - (\pi^2 F/3)}\right)^2$  vs t was used to obtain the kinetic parameter B and the respective effective diffusion coefficient. As can be seen from Table 2, the  $D_{eff}$  values are higher  $(3.7 \cdot 10^{-8} - 1.3 \cdot 10^{-7} \text{ cm}^2/\text{s})$ than those, obtained with the Morris and Weber model. Similar results are reported in [1], where  $D_{eff,Ph}$  is about three times higher (3.1.10<sup>-7</sup> cm<sup>2</sup>/s). Our values for B are about one order of magnitude lower than those, reported in [5] for the film diffusion model and lower or comparable to those, obtained in [13] (0.013–0.014 min<sup>-1</sup>), where pore diffusion inside the particles was found to play an important role. The correlation coefficients are generally lower, except for Cu<sup>2+</sup>. The presence of an intercept shows that diffusion is not the only observed mechanism of transfer.

# 3. The moment method-application

The  $n^{th}$  absolute moment of a concentration curve c(t) is defined as:

$$\mu'_{n} = \frac{1}{\mu_{0}} \int_{0}^{\infty} t^{n} \frac{d^{j}c}{dt^{j}} dt \qquad (12)$$

where: j=1 for an uptake curve obtained from batch experiment;  $\mu'_0 = \int_0^\infty \frac{d^j c}{dt^j} dt = c_0$  and  $c_o$  is the

initial concentration.

 $\mu_1$  can be calculated directly from the experimental kinetic curve for analysis of the adsorption rate. When the plateau of this curve was not reached or was poorly defined, the solution of the LDF model was used. Eq. (7a) applies for batch type experiment. Its linearized form (eq. 7b) in coordinates  $\ln(1-\frac{q}{q_e})$  vs t gives the value of  $\mu'_1$  and the corresponding solid phase mass transfer coefficient  $(k_s = \frac{1}{\mu_1})$ . Linear regression with intercept was used again to separate the initial part of the kinetic curve from the subsequent linear one. Results for  $k_s$  are shown in Table 2. These values can also be compared to the reported rate constants for a first order reaction model, as the rate expressions are identical. The obtained values are in line with the reported ones in the literature for lead adsorption on low-cost activated carbons:  $0.0151-0.0161 \text{ min}^{-1}$  [13],  $0.0117-0.127 \text{ min}^{-1}$  [5].

The kinetic curves for the different ions gave  $k_s$  values in a close variation range of 0.007 to 0.013, which was also observed for Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> adsorption on activated carbons [24, 25]. Despite the lower correlation coefficients, the calculated diffusion coefficients were in the same order (10<sup>-8</sup> cm<sup>2</sup>/s) as those, obtained by the other two models.

Figs. 1a) to d) present the comparison of the results from the calculation of the slopes of the kinetic curves by utilizing the different models. The calculations were done according to eq. 2, 4 and 7a. In order to better visualize the results, the intercepts of the calculated linear regression equations were not included in Fig.1, which explains the displacement of the calculated curves from the experimental data. These intercepts were explained by the initial fast mass transfer through the liquid film around the particle and they were easily accounted for by a diffusion model with an appropriate boundary condition:

$$-D_{a}\frac{\partial q}{\partial r}\Big|_{r=R} = k_{f}(c\Big|_{r=R} - c)$$
(13)

Here  $k_f$  denotes the external mass transfer coefficient [m/s]. Simplified models like Morris and Weber, Boyd and the moment method usually suggest a first order boundary condition  $(c|_{r=R} = c)$ , i.e. no mass transfer resistance across the liquid film. As can be seen in Fig.1, the moment method gives similar results as the Morris and Weber model, which is to be expected, as they have similar theoretical background. The analysis of the results in Table 2 and Fig. 1 leads to the conclusion that the best description of the kinetic data is provided by the Morris and Weber model. The correlation coefficients with this model are higher and the scatter of the diffusion coefficients is less pronounced, which is in agreement with the similar time evolution of the experimental data obtained for the different ions.

#### Multi-component adsorption kinetics

The experimental kinetic curves for the individual ions in a four-component solution are shown in Fig. 3. Dimensionless solid phase concentrations  $q/q_e$  are used. The equilibrium value  $q_e$  was calculated by the extended Langmuir model for multi-component adsorption:

$$q_{e,i} = \frac{q_{mi}b_i c_{e,i}}{1 + \sum_{i=1}^N b_j c_{e,j}}$$
(14)

Here  $c_{ej}$  is the concentration of the *i*<sup>th</sup> ion in the solution;  $q_{mi}$  and  $b_j$  are single-component isotherm parameters, as they are shown in Table 1. Table 3 shows the equilibrium characteristics for the multi-component kinetic runs. Initial liquid phase concentrations are presented together with the calculated  $q_{ej}$  and the slope of the isotherm ( $K_i$ ) for the respective ions at equilibrium concentration  $c_{e,i}$ . The latter was calculated by the mass balance in the liquid phase:

$$V_{l}(c_{0,i} - c_{e,i}) = M_{s}q_{e,i} = M_{s}\frac{q_{m,i}b_{i}c_{e,i}}{1 + \sum_{j=1}^{4}b_{j}c_{e,j}}$$
(15)

where  $\sum_{1}^{4} b_j c_{e,j} = const$  for each kinetic experiment. The rearrangement of eq. (15) gives:

$$c_{e,i} = \frac{c_{0,i}}{\left(\frac{\beta q_{m,i} b_i}{1 + const} + 1\right)}$$
(15a)

where  $\beta = \frac{M_s}{V_l}$ . Further summation on i=1 to 4

gives 
$$\sum_{i=1}^{4} b_i c_{e,i} = const = \sum_{i=1}^{4} \frac{b_i c_{0,i}}{\left(\frac{\beta q_{m,i} b_i}{1 + const} + 1\right)},$$

where the unknown parameter is the constant (  $\sum_{i=1}^{4} b_i c_{e,i}$ );  $c_{o,i}$  is the measured initial concentration

in the solution. The equilibrium liquid phase concentrations  $c_{e,i}$  were calculated by eq. (15a). For the initial concentrations shown in Table 3, the value of

$$\frac{1}{1+\sum_{j=1}^{4}b_{j}c_{e,j}}$$

was evaluated to 0.385. Table 3 also presents the summary adsorption in the four-component system, which can be compared to the  $q_e$  values in Table 1 with approximately the same initial loading.

 Table 3. Equilibrium parameters and conditions for the individual ions in 4-component solution

Ion	$C_0$	$q_e$	K
	[mmol/l]	[mmol/g]	[-]
$Pb^{2+}$	0.081	0.006	338.4
$Cu^{2+}$	0.403	0.0294	271.4
$\mathrm{Cd}^{2^+}$	0.436	0.0155	55.3
$Zn^{2+}$	0.566	0.0157	38.3
Sum	1.485	0.0666	45.0

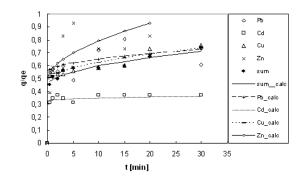


Fig. 3. Dimensionless experimental and calculated kinetic curves in four-component solution.

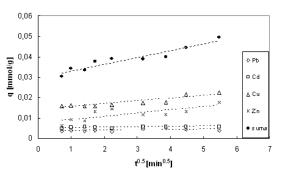


Fig. 4. Morris and Weber linear plots for the individual ions in four-component solution.

The individual ions exhibit similar kinetic behaviour, as can be seen from the dimensionless representation in Fig. 3. The  $Cu^{2+}$  data practically coincide with the summary adsorption curve in a multi-component solution. Stronger deviation is obtained for the  $Cd^{2+}$  ions, where much slower kinetics was observed. Fig. 4 illustrates the Morris and Weber plots of the multi-component kinetic data. The calculated rate parameters are shown in Table 4.

Morris-Weber Boyd Ion  $D \cdot \times 10^8$  $D \cdot \times 10^7$  $R^2$ В  $R^2$ k<sub>in</sub> [mmol/gmin<sup>1/2</sup> [min<sup>-1·</sup>  $[cm^2/s]$  $[cm^2/s]$ Pb 0.0002 1.215 0.27 0.0101 1.383 0.15 Cd 0.049 0.0001 0.42 0.0012 0.16 0.37 Cu 0.0014 2.668 0.83 0.0206 2.82 0.899 0.59 Zn 0.0016 1.228 0,0284 3.89 0.11 0.90 0.922 0.0033 2.872 0.0180 2.47 Sum

Table 4. Rate parameters for the individual ions in 4-component solution

The results with Boyd's model are analogous to those, observed in single-component solutions. Lower correlation coefficients and up to one order of magnitude higher diffusion coefficients were calculated  $(10^{-7} \text{cm}^2/\text{s})$ , compared to the Morris and Weber model. The  $k_{in}$  values in the 4-component solution were lower, as can be seen from the comparison of the results in Tables 4 and 2. The difference between the individual diffusion coefficients D is more pronounced. This can be explained by the competition of the diffusing ions in the multi-component system, but also by errors coming from the calculated equilibrium, which was predicted and not directly measured from the plateau of the experimental curve. Best correlation was obtained for the summary adsorption kinetics, as well as for Cu<sup>2+</sup>, which was best adsorbed in the multi-component system [18]. The summary diffusion coefficient was practically the same as that, obtained for single-component adsorption with the same initial loading. Comparison of the experimental kinetic curves with the calculations of the Morris and Weber model (Eq. 2), including the intercept term, is shown in Fig. 4. Despite the scatter of the experimental points and the low correlation coefficients, the observed agreement is satisfactory.

# CONCLUSIONS

The adsorption kinetics of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup> and  $Zn^{2+}$  in single- and four-component aqueous solutions with activated carbon from apricot stones was successfully described by the model of Weber and Morris. The intraparticle diffusion coefficients for the individual ions are in the range of 1 to  $3x10^{-1}$ <sup>8</sup> cm<sup>2</sup>/s, which is reasonable for the case of internal diffusion control. These values give a satisfactory description of the observed kinetics after the first 1–2 min. The initial part of the kinetic curves was described by the formal inclusion of an intercept term. A more detailed diffusion model including the appropriate boundary condition is needed to account for the combined effect of the external mass transfer and internal diffusion. Lower rate parameters were observed in the multi-component solutions. Despite the lower correlation coefficients in this case, the agreement between the experimental data and the kinetics calculated by the model of Morris and Weber was satisfactory. The moment method gave similar values for the rate of internal mass transfer and the respective diffusion coefficient. This result was expected, because of the similar physical background of the two models. The obtained effective diffusion coefficients with the Boyd model were usually greater, but still in the range expected for internal diffusion control. Best correlation coefficients were obtained with the Morris and Weber model. The calculated summary diffusion coefficient in the 4-component solution was close to that obtained in single-component solutions for the same total initial concentration. No kinetic studies were found in the literature for adsorption of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on ACAS. The comparison with the reported rate parameters for other low-cost activated carbons in similar systems is encouraging for further investigation of the adsorption behaviour of ACAS in a fluidized bed column.

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# СРАВНЕНИЕ НА РАЗЛИЧНИ КИНЕТИЧНИ МОДЕЛИ ПРИ АДСОРБЦИЯ НА МЕТАЛНИ ЙОНИ С АКТИВЕН ВЪГЛЕН ОТ КАЙСИЕВИ ЧЕРУПКИ

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## Постъпила на 8 март, 2010 г.; коригирана на 3 август, 2010 г.

# (Резюме)

В тази работа е изследвана кинетиката на едно- и четири-компонентна адсобция на  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$  и  $Zn^{2+}$  йони от водни разтвори с активен въглен от кайсиеви черупки. За описание на едно и многокомпонентно равновесие е използван моделът на Лангмюир. Направено е сравнение на три кинетички модела за вътрешно дифузионен контрол. Първоначалната стръмна част на кинетичната крива бе определена от отреза на линейното представяне на моделите на Вебер и Морис, Бойд и моментния метод. Най-добро съвпадение с експерименталните данни са получени с модела на Вебер и Морис. Коефициентите на вътрешна дифузия за отделните йони са в диапазона  $1-3 \cdot 10^{-8} cm^2/s$ . Подобни резултати са получени и при използване на моментния метод. Получени са по-ниски стойности на кинетичните параметри за четирикомпонентен разтвор. Стойността на сумарният дифузионен коефициент за многокомпонентна система е близък до този получен за еднокомпонентен разтвор със същата концентрация.