

Kinetic Study of Zinc Retention Onto a River Sediment

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Heavy metals discharges in water bodies pose a significant threat to the aquatic ecosystems and human health. Small doses of zinc have an important metabolic role, but overdoses may pose toxic effects onto the aquatic wildlife. Sediments in water bodies act as metals accumulators and food source for the benthic biota. The role of sediments in the bio-geochemical cycles of zinc in water bodies is partially known. In this paper a kinetic study of zinc retention onto a sediment core sampled from Arges river (nearby Crivina, Giurgiu County) is presented. The study was done in order to develop a chemodynamic model of zinc dispersion into a river stream. Based on the experimental results, as variation of concentration in time, and in order to assess the zinc retention rates, the pseudo-1st order, pseudo-2nd order and Elovich models were used. The calculations show that Elovich model has the best applicability. Based on these data, it was drawn up a mathematic correlation between retention rate and zinc concentration in the aqueous phase and sediment, based on a first order Langmuir kinetic model. The calculation results shown that the model can be successfully used to describe the kinetics of zinc retention on the chosen sediment.

Keywords: kinetics, Langmuir, sediment, sorption, zinc

Major sources of zinc pollution are represented by non-ferrous mining industry, electroplating, thermal plating, corrosion protection. Zn poses an important role in metabolic processes, acting as microelement but exceeding doses may pose toxic effects [1, 2]. How long the toxicity of organic micropollutants is directly related to their bioaccumulation rates, the toxicity of heavy metals depend on their nature, speciation, and the target organism [3-5].

As follows from literature, the most selective method used for removal of Zn²⁺ ions from the industrial wastewaters solutions is extraction. However, apparatus and installation to carry out extraction on a commercial scale are too expensive for some factories. Therefore, cheaper alternative methods are demanded. Ion exchange seems to be a proper solution. Production of synthetic fibres using the viscose method requires acidic baths whose main components are zinc sulphate, sulphuric acid and sodium sulphate. Industrial wastewaters containing Zn²⁺ ions are the most toxic of all that are developed in this process. Their disposal into rivers causes serious damages in particular of its high Zn²⁺ content [4-6].

In the last decade researchers have followed different sequential extraction techniques for the fractionation of metals in sediments of different river systems. Rauret et al. studied the speciation of copper and lead in the sediments of River Tenes (Spain) while Pardo et al. studies the speciation of zinc, cadmium, lead, copper nickel and cobalt in the sediments of Pisuerga River, Spain, in order to establish the extent to which these are polluted and their capacity to remobilization. Jardo and Nickless investigated the chemical association of zinc, cadmium, lead and copper in soils and sediments of England and Wales. In most samples, these four metals were associated with all the chemical fractions. Tessier et al. studied speciation of cadmium, cobalt, copper, nickel, lead, zinc, iron and manganese in water and sediments of St. Francois river, Quebec, Canada [7].

Rivers as one of the basic resources of surface water have ecologic and notable economic value. The hydrochemical composition and quality of water and the sediments of river beds have always been influenced by natural (geologic) and unnatural (pollution) factors. The polluting elements entry, based on natural and human activities is one of the most important issues which mankind faces today. Together with the fast industrial and economic growth and producing many kinds of chemical substances as well as the consumption increase, human enters many kinds of contaminants to the nature which endangers both man and environment [5]. The importance of water resources especially surface water for supplying water needs, declares the important need of maintaining them from pollution, with entering effluents to the main system, consisting urban, industrial and agricultural sewage, they contain microbial and contaminants such as heavy metals. Although the noted metals in low concentration act as micro-nutrients in a food chain, their accumulation in high concentrations cause toxicities and adverse environmental effect and as a result endangers water ecosystem and of course the consumers. Measuring the heavy metals concentration alone, would not show their pollution intensity. Therefore in recent years to get rid of such problem, the Muller geochemical index is used to measure the intensity of pollution. In addition the accumulation of metal in sediments provides researchers with suitable information about environmental conditions. [6]. The sediments are ultimate accumulation of heavy metals in aquatic environments, in some cases they can act as sources of contaminations in water themselves [8]. The contaminants remains in the sediment for quite a long time, but due to biological activities and physical and chemical changes they can enter the surface waters, therefore measuring the heavy metal concentration can show a real picture of aquatic environment pollution [6].

To determine the pollution effect, the sources and concentrations of pollutants in aquatic environment need

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assessment and monitoring [9]. The amount of pollution in aquatic environment can be determined by analysis of water, sediments and marine organisms [10-21].

In this paper the influence of temperature on the kinetics of zinc retention on a sediment core was studied.

Experimental part

The kinetic experiments were done in batch systems, by contacting synthetic aqueous solutions of $ZnSO_4$ with sediment, at a mass ratio $L/S = 50/1$, by considering the total mass of sediment. Location of the sampling point was preferred due to its accessibility and its relevance, being placed upstream of the most important freshwater supply of Bucharest municipality.

Sediment core was sampled from Arges River bed, nearby the locality Crivina, Giurgiu County, about 600 m upstream the supply of water treatment plant Rosu. The sampling point DMS coordinates are $44^{\circ}25'47.29''$ N and $25^{\circ}46'4.93''$ E, as shown in figure 1.



Fig. 1. Sampling point location (<http://maps.google.ro>)

During the sampling process, the following on site measurements were done:

- air temperature: 6 °C;
- water temperature: 9 °C;
- water pH: 7.42;
- oxygen demand (DO): 6.42 mg/L;
- electric conductivity: 242 μ S/cm;
- sampling depth: 30 cm.

Techniques used for sediment characterization are presented in table 1.

The grain size distribution of sediment, determined according to the procedure mentioned in table 1, is:

- coarse fraction (> 63 μ m): 49.9%;
- silt (2 ÷ 63 μ m): 40.0%;
- clays (< 2 μ m): 10.1%.

In table 2 is presented the content of heavy metals in sediment, reported to the reactive fraction of the sediment (< 63 μ m).

Data presented in table 2 show high concentrations of Zn and Cr in sediment, significantly exceeding the levels of concern (LOC), how long the Cu concentration reaches the LOC value.

The kinetic study of zinc retention on the sediment was done by contacting synthetic aqueous solutions of $ZnSO_4$ with sediment samples, in the following working conditions:

- aqueous phase volume: 100 mL;
- sediment mass: $2 \pm 2 \cdot 10^{-4}$ g (as total mass of dry sediment);
- working temperatures: 5, 10, 17, and $25 \pm 1^{\circ}$ C;
- contact times: 0.5, 1, 2, 4, 6, 8, 10, 15, and 20 min.;
- initial zinc concentration in aqueous phase: 0.1, 0.2, 0.3, 0.5, 1.0, 1.5, and 2 mg/L.

At the established contact time, the phase separation was done by vacuum filtration, and concentration of Zn in aqueous phase was measured by atomic absorption spectrometry (AAS model CONTRA 300). To ensure the temperature control, was used an incubator model FOC 225E - Velp Scientifica.

Hydrodynamic conditions were ensured by using a shaker model HEIDOLPH UNIMAX.

Table 1
TECHNIQUES USED FOR SEDIMENT CHARACTERIZATION

Indicator	Principle	Working conditions	Reference	Value
Humidity	Weight loss at drying	105 °C	ISO 11465-1998	1.08%
Organic matter	Weight loss at ignition	400 – 450 °C	[4]	6.05%
Heavy metals, mg/kg	Digestion in <i>aqua regia</i>	24 h at room temperature, 2 h boiling under reflux	ISO 11466-1999	table 2
Cation exchange capacity, meq/100 g	Saturation with NH_4Ac , reextraction of NH_4^+ with NaCl	Mixing for 8 h, Kjeldahl analysis	ISO 11260-2001	21.8
Grain size distribution	Sedimentation in aqueous suspension		Romanian standard: STAS 7184/10-79	

Table 2
CONTENT OF HEAVY METALS IN SEDIMENT

Metal	Cu	Cr, total	Zn	Pb
Concentration, mg/kg	40.42	181.63	195.61	26.45
Levels of concern (LOC), mg/kg	40	100	150	85

Results and discussions

The experimental results were obtained as variation in time of Zn^{2+} concentration in aqueous phase. This way were built the kinetic integral curves concentration – time $C(t)$. To determine the variation of Zn^{2+} concentration in sediment was used the mass balance equation (1):

$$q_t = q_0 + \frac{V \cdot (C_0 - C_t)}{m_s \cdot \omega_r} \quad (1)$$

where:

- V – volume of aqueous phase (mL);
- C_0 – zinc concentration in aqueous phase before phase contact ($mg \cdot L^{-1}$);
- C_t – zinc concentration in aqueous phase at the moment t ($mg \cdot L^{-1}$);
- m_s – mass of sediment (g);
- q_t – concentration of zinc in sediment at the moment t ($mg \cdot kg^{-1}$);
- q_0 – concentration of zinc in sediment before phase contact ($mg \cdot kg^{-1}$);
- ω_r – the reactive fraction of sediment.

Using equation (1) was calculated the variation of zinc concentration in the reactive fraction of sediment, q_r and were built the integral kinetic curves $q(t)$.

In order to calculate the zinc retention rate in sediment, expressed as differential kinetic curves $q(t)$, were used three kinetic models: the pseudo-1st order, the pseudo-2nd order and Roginsky – Zeldovich (Elovich) model.

Differential form of the pseudo-1st order model is expressed according to equation (2):

$$\frac{dq_t}{dt} = k_1(q^* - q_t) \quad (2)$$

where:

- q_t – zinc concentration in the reactive fraction of sediment at moment t ;
- q^* – zinc concentration in the reactive fraction of sediment at equilibrium;
- k_1 – constant of the pseudo-1st order kinetic model (min^{-1}).

Considering the boundary conditions $t = 0 \rightarrow q = q_0$, and at the moment $t \rightarrow q = q_r$ results the integral form of the pseudo-1st kinetic order:

$$\ln \left(\frac{q^* - q_t}{q^* - q_0} \right) = -k_1 t \quad (3)$$

which can be expressed in the linear form

$$\ln(q^* - q_t) = \ln(q^* - q_0) - k_1 t \quad (3')$$

The pseudo 1st model parameters were calculated by linear regression, considering the variable changes in equation (3') $x = t, y = \ln(q^* - q_t)$.

Differential form of the pseudo-2nd order model is expressed according to equation (4):

$$\frac{dq_t}{dt} = k_2(q^* - q_t)^2 \quad (4)$$

where:

- q_t – zinc concentration in the reactive fraction of sediment at moment t ;
- q^* – zinc concentration in the reactive fraction of sediment at equilibrium;
- k_2 – constant of the pseudo-2nd order kinetic model ($kg \cdot mg^{-1} \cdot min^{-1}$).

Considering the boundary conditions $t = 0 \rightarrow q = q_0$, and at the moment $t \rightarrow q = q_r$ results the integral form of the pseudo-2nd kinetic order:

$$\frac{1}{q^* - q_t} = \frac{1}{q^* - q_0} + k_2 t \quad (5)$$

which can be expressed in the linear form

$$\frac{t}{q_t - q_0} = \frac{1}{k_2(q^* - q_0)^2} + \frac{1}{q^* - q_0} t \quad (5')$$

Model parameters were calculated considering in equation (5') the variable changes $x = t, y = \frac{t}{q_t - q_0}$.

Model Elovich is an empirical model, applicable for chemisorption processes, and its differential form is characterized by the equation (6):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (6)$$

Considering the boundary conditions $t = 0 \rightarrow q = q_0$, and at the moment $t \rightarrow q = q_r$ the integral form of the Elovich model can be expressed according to equation (7):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln \left[t + \frac{1}{\alpha\beta} \exp(\beta q_0) \right] \quad (7)$$

If the term $\alpha\beta \gg 1$, the term $\frac{1}{\alpha\beta} \exp(\beta q_0)$ can be neglected, and equation (7) has the form:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (7')$$

otherwise, the term is a time-dimension parameter, t_0 , and equation (7) becomes

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t + t_0) \quad (7'')$$

Model parameters, α and β , were calculated by linear regression, by using the variable changes $x = \ln(t), y = q_r$ and considering the term $t_0 = 0$. After the calculation of the

model parameters, the term $\frac{1}{\alpha\beta} \exp(\beta q_0)$ was calculated too, and if its value was significant, it was re-introduced in equation (7''), and the regression calculation was done again, until the difference between two iterations was smaller than 10^{-4} min.

To validate each individual kinetic curve, and in order to select the most appropriate kinetic model, was used the relative standard deviation, defined according to equation (8):

$$\Delta q(\%) = 100 \cdot \sqrt{\frac{\sum_{i=1}^n [(q_{exp,i} - q_{calc,i}) / q_{exp,i}]^2}{(n-1)}} \quad (8)$$

For each individual kinetic curve $q(t)$, the model was considered as appropriate if $\Delta q(\%) \leq 2\%$.

The kinetic curves for zinc retention on the sediment are presented in figures 2 – 13.

The shapes of the integral kinetic curves $C(t)$ show that retention process is a very fast one, in the first minutes of contact zinc concentration in aqueous phase decreases with an order of magnitude.

The regressions calculations results are presented in tables 3 – 6.

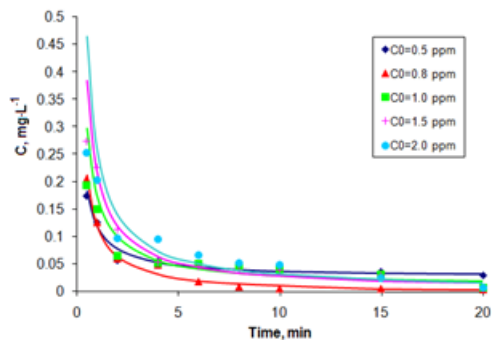


Fig. 2 Integral kinetic curves for zinc retention on sediment at the temperature 5 °C, $C(t)$

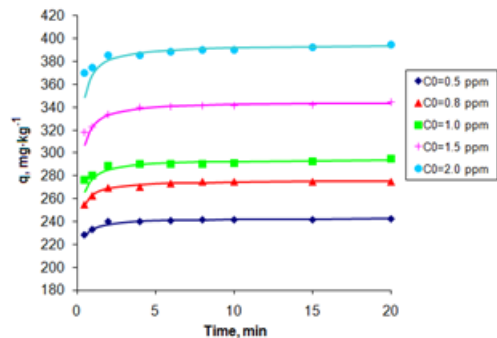


Fig. 3 Integral kinetic curves for zinc retention on sediment at the temperature 5 °C, $q(t)$

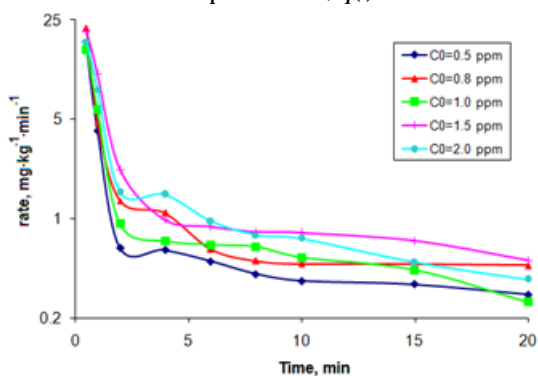


Fig. 4. Differential kinetic curves for zinc retention on sediment at the temperature 5 °C, $q(t)$

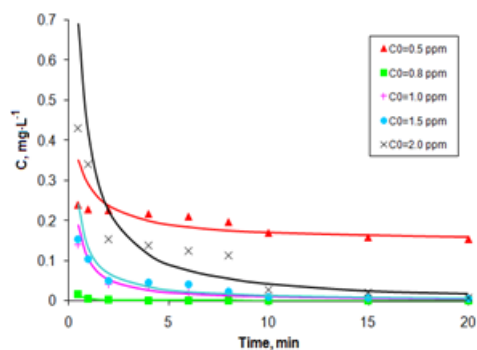


Fig. 5. Integral kinetic curves for zinc retention on sediment at the temperature 10 °C, $C(t)$,

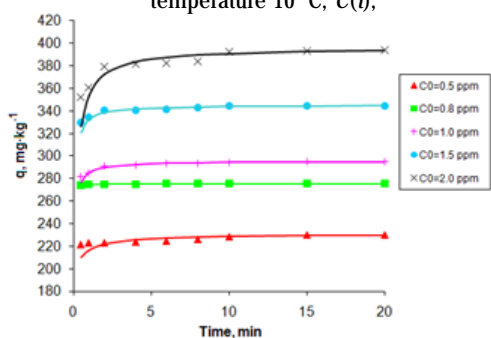


Fig. 6. Integral kinetic curves for zinc retention on sediment at the temperature 10 °C, $q(t)$

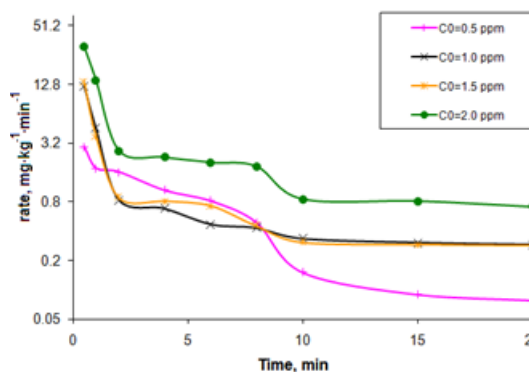


Fig. 7. Differential kinetic curves for zinc retention on sediment at the temperature 10 °C, $q(t)$

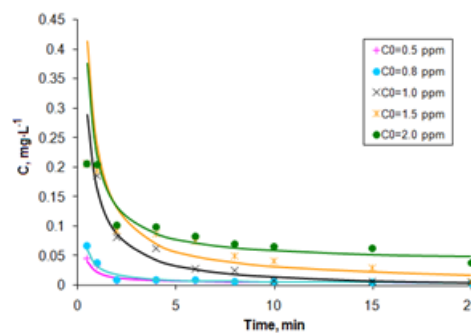


Fig. 8. Integral kinetic curves for zinc retention on sediment at the temperature 17 °C, $C(t)$

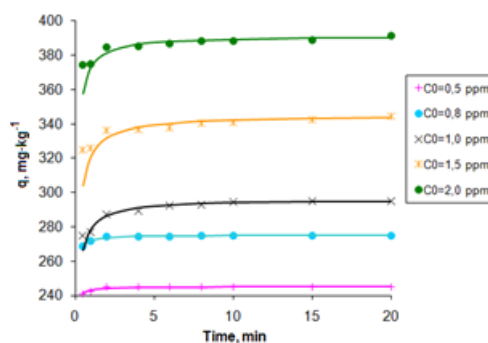


Fig. 9. Integral kinetic curves for zinc retention on sediment at the temperature 17 °C, $q(t)$

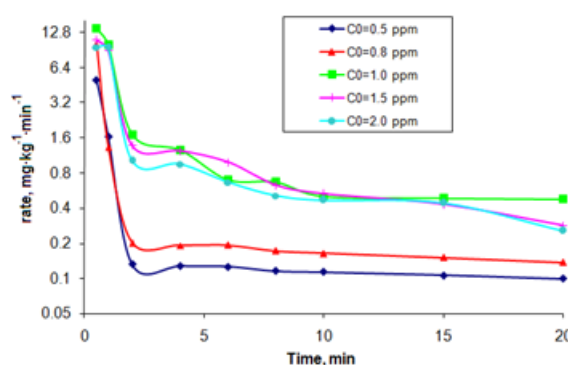


Fig. 10. Differential kinetic curves for zinc retention on sediment at the temperature 17 °C, $q(t)$

Data in tables 3 – 6 show that the applicability of the selected models varies from each kinetic curve to another. Generally, the pseudo-1st order model has a limited applicability in order to calculate the zinc retention rate. The pseudo-2nd order model has a better applicability, but with limitations, how long Elovich model turned the better fits in most of the cases. Thus, model Elovich was selected to calculate the retention rate values of zinc retention on the sediment.

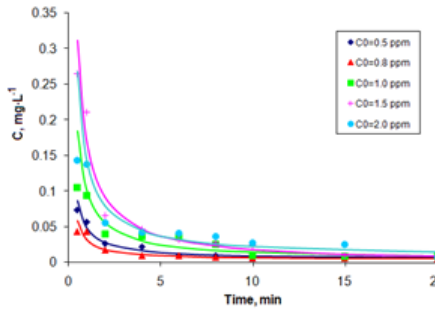


Fig. 11. Integral kinetic curves for zinc retention on sediment at the temperature 25 °C, $C(t)$

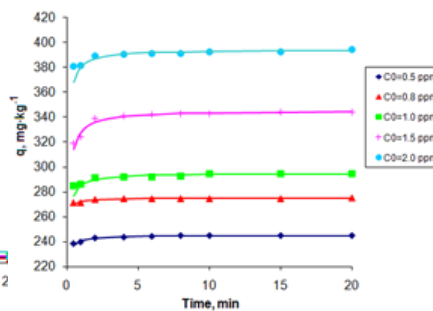


Fig. 12. Integral kinetic curves for zinc retention on sediment at the temperature 25 °C, $q(t)$

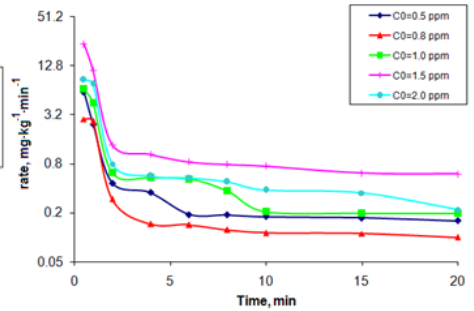


Fig. 13. Differential kinetic curves for zinc retention on sediment at the temperature 17 °C, $q(t)$

Table 3
REGRESSIONS CALCULATIONS RESULTS FOR THE KINETIC STUDY AT 5 °C

Model	$C_0, \text{mg}\cdot\text{L}^{-1}$	0.1	0.2	0.3	0.5	0.8	1.0	1.5	2.0
Pseudo-1	<i>slope</i>	-0.2707	-0.3281	-0.2917	-0.3987	-0.4599	-0.2335	-0.2957	-0.2225
	<i>intercept</i>	0.3007	2.0800	2.3654	2.8972	3.0519	2.9046	3.3735	3.2046
	R^2	0.9784	0.8167	0.9737	0.7879	0.9572	0.7854	0.8055	0.9090
	k_1, min^{-1}	0.2707	0.3281	0.2917	0.3987	0.4599	0.2335	0.2957	0.2225
	$\Delta q(\%)$	1.164%	5.213%	3.884%	5.104%	2.535%	2.768%	1.936%	1.424%
Pseudo-2	<i>slope</i>	0.0999	0.0496	0.0337	0.0211	0.0125	0.0101	0.0067	0.0050
	<i>intercept</i>	0.0148	0.0193	0.0145	0.0053	0.0023	0.0021	0.0011	0.0008
	R^2	0.9999	0.9997	0.9997	0.9999	1.0000	0.9997	0.9999	0.9999
	$k_2, \text{kg}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	0.6722	0.1273	0.0788	0.0844	0.0674	0.0493	0.0392	0.0332
	$q^*, \text{mg}\cdot\text{kg}^{-1}$	205.62	215.79	225.24	242.93	275.84	294.54	345.00	395.01
$\Delta q(\%)$	4.107%	5.586%	6.970%	2.115%	1.047%	4.942%	3.189%	4.561%	
Elovich	<i>slope</i>	0.3481	2.1744	2.6865	3.6134	5.2186	4.5381	7.2281	6.3981
	<i>intercept</i>	204.6248	209.99	217.56	233.43	262.36	281.62	325.44	376.33
	R^2	0.9557	0.8751	0.9255	0.8411	0.8822	0.8859	0.9086	0.9412
	α	$6.6\cdot 10^{254}$	$1.9\cdot 10^{42}$	$3.98\cdot 10^{35}$	$4.12\cdot 10^{28}$	$3.56\cdot 10^{22}$	$4.06\cdot 10^{27}$	$2.59\cdot 10^{20}$	$2.24\cdot 10^{26}$
	β	2.8726	0.4599	0.3722	0.2767	0.1916	0.2204	0.1383	0.1563
	t_0, min	0	0.0013	0.0003	0	0	0	0	0
	$\Delta q(\%)$	0.998%	6.265%	3.764%	4.885%	3.431%	2.243%	2.061%	1.065%

Table 4
REGRESSIONS CALCULATIONS RESULTS FOR THE KINETIC STUDY AT 10 °C

Model	$C_0, \text{mg}\cdot\text{L}^{-1}$	0.2	0.3	0.5	0.8	1.0	1.5	2.0
Pseudo-1	<i>slope</i>	-0.3584	-0.0771	-0.1188	-0.1247	-0.2734	-0.3141	-0.2331
	<i>intercept</i>	1.2619	0.3960	2.3777	-0.6173	2.3747	2.6464	3.6633
	R^2	0.8524	0.4126	0.9539	0.7017	0.9787	0.9672	0.9434
	k_1, min^{-1}	0.3584	0.0771	0.1188	0.1247	0.2734	0.3141	0.2331
	$\Delta q(\%)$	6.518%	5.751%	2.974%	0.570%	2.078%	1.118%	2.810%
Pseudo-2	<i>slope</i>	0.0502	0.0334	0.0285	0.0125	0.0100	0.0067	0.0050
	<i>intercept</i>	0.0070	0.0016	0.0195	0.0001	0.0012	0.0006	0.0013
	R^2	1.0000	1.0000	0.9961	1.0000	1.0000	1.0000	0.9996
	$k_2, \text{kg}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	0.3629	0.7092	0.0415	1.4305	0.0853	0.0695	0.0186
	$q^*, \text{mg}\cdot\text{kg}^{-1}$	215.510	225.587	230.733	275.410	295.486	345.315	396.135
$\Delta q(\%)$	3.292%	3.466%	17.954%	0.199%	2.124%	2.521%	6.440%	
Elovich	<i>slope</i>	1.1455	1.0101	2.3302	0.3437	3.6146	3.8011	11.1714
	<i>intercept</i>	212.676	223.260	222.078	274.572	285.830	334.768	363.612
	R^2	0.6932	0.6136	0.8473	0.6489	0.9018	0.9140	0.9271
	α	$4.88\cdot 10^{80}$	$9.84\cdot 10^{95}$	$5.71\cdot 10^{41}$	$2.48\cdot 10^{350}$	$7.95\cdot 10^{34}$	$6.75\cdot 10^{38}$	$1.53\cdot 10^{15}$
	β	0.8730	0.9900	0.4291	2.9097	0.2767	0.2631	0.0895
	t_0, min	0	0	0	0	0	0	0
	$\Delta q(\%)$	5.863%	3.710%	4.169%	0.401%	1.586%	1.022%	2.156%

Table 5
REGRESSIONS CALCULATIONS RESULTS FOR THE KINETIC STUDY AT 17 °C

Model	C ₀ , mg·L ⁻¹	0.1	0.2	0.3	0.5	0.8	1.0	1.5	2.0
Pseudo-1	slope	-0.4288	-0.3999	-0.4856	-0.3365	-0.2605	-0.3527	-0.1399	-0.1409
	intercept	0.7621	0.3613	2.3617	0.7938	1.0540	3.0551	2.8861	2.6412
	R ²	0.9879	0.9361	0.9845	0.8410	0.8573	0.9772	0.9424	0.8824
	k ₁ , min ⁻¹	0.4288	0.3999	0.4856	0.3365	0.2605	0.3527	0.1399	0.1409
	Δq(%)	1.367%	0.928%	4.943%	2.075%	2.004%	2.074%	1.901%	1.525%
Pseudo-2	slope	0.0995	0.0512	0.0334	0.0202	0.0126	0.0100	0.0067	0.0051
	intercept	0.0165	0.0028	0.0109	0.0008	0.0005	0.0021	0.0013	0.0005
	R ²	0.9999	1.0000	0.9997	1.0000	1.0000	0.9999	0.9998	0.9999
	k ₂ , kg·mg ⁻¹ ·min ⁻¹	0.6021	0.9260	0.1025	0.5030	0.3226	0.0480	0.0355	0.0493
	q*, mg·kg ⁻¹	205.656	215.122	225.591	245.117	275.148	295.998	344.904	391.295
	Δq(%)	3.706%	0.648%	4.870%	0.996%	0.560%	3.909%	6.002%	3.455%
Elovich	slope	0.4948	0.3276	2.9601	1.0353	1.4748	5.9385	5.3973	4.5924
	intercept	204.318	214.250	217.782	242.605	271.532	279.898	328.667	378.055
	R ²	0.9163	0.7053	0.9010	0.7531	0.7456	0.9223	0.9422	0.8984
	α	1.1·10 ¹⁷⁹	3.8·10 ²⁸³	2.7·10 ³²	6.2·10 ¹⁰¹	1.35·10 ⁸⁰	1.75·10 ²¹	1.51·10 ²⁷	2.59·10 ³⁶
	β	2.0210	3.0529	0.3378	0.9659	0.6781	0.1684	0.1853	0.2177
	t ₀ , min	0	0	0.0006	0	0	0	0	0
	Δq(%)	2.009%	1.142%	4.798%	1.534%	1.402%	2.374%	1.219%	1.038%

Table 6
REGRESSIONS CALCULATIONS RESULTS FOR THE KINETIC STUDY AT 25 °C

Model	C ₀ , mg·L ⁻¹	0.1	0.2	0.3	0.5	0.8	1.0	1.5	2.0
Pseudo-1	slope	-0.4321	-0.3431	-0.3656	-0.3662	-0.3493	-0.3516	-0.3230	-0.1513
	intercept	2.1562	2.2542	1.7842	1.8408	1.3492	2.4313	3.0375	2.3691
	R ²	0.9563	0.9791	0.8169	0.9014	0.8768	0.9339	0.9647	0.8741
	k ₁ , min ⁻¹	0.4321	0.3431	0.3656	0.3662	0.3493	0.3516	0.3230	0.1513
	Δq(%)	17.346%	9.405%	4.273%	1.574%	0.710%	1.123%	3.033%	1.283%
Pseudo-2	slope	0.1010	0.0498	0.0336	0.0202	0.0126	0.0101	0.0067	0.0050
	intercept	0.1454	0.0319	0.0050	0.0020	0.0005	0.0011	0.0009	0.0004
	R ²	0.9920	0.9993	1.0000	1.0000	1.0000	0.9999	1.0000	1.0000
	k ₂ , kg·mg ⁻¹ ·min ⁻¹	0.0701	0.0778	0.2284	0.2013	0.3414	0.0903	0.0507	0.0670
	q*, mg·kg ⁻¹	205.512	215.690	225.339	245.076	275.079	295.054	345.400	394.394
	Δq(%)	12.838%	8.115%	1.568%	1.330%	0.860%	3.290%	1.818%	2.449%
Elovich	slope	1.8902	2.8213	1.7744	1.8414	1.1616	2.7380	6.9671	3.6734
	intercept	199.750	207.889	220.902	240.325	272.098	287.320	327.381	384.033
	R ²	0.9278	0.8980	0.8037	0.8891	0.8489	0.9132	0.8530	0.8810
	α	1.48·10 ⁴⁶	2.83·10 ³²	2.07·10 ³⁴	8.84·10 ³⁶	6.2·10 ¹⁰¹	1.03·10 ⁴⁶	1.78·10 ²¹	9.29·10 ⁴⁵
	β	0.5290	0.3544	0.5636	0.5431	0.8609	0.3652	0.1435	0.2722
	t ₀ , min	0.1118	0.0129	0	0	0	0	0	0
	Δq(%)	9.299%	8.622%	4.198%	1.729%	0.788%	1.110%	2.588%	0.446%

To describe the mathematical correlation between retention rate and zinc concentration in liquid, respectively in solid phase, a Langmuirian kinetic model was used. The general equation of such a model, at constant temperature, is expressed by equation (9) [22]:

$$\frac{d\theta_t}{dt} = k_s \cdot C_t \cdot (1 - \theta_t)^s - k_d \cdot \theta_t^2 \quad (9)$$

where:

$\frac{d\theta_t}{dt}$ - retention (sorption) rate (min⁻¹);

k_s, k_d - the kinetic constants of the sorption, respectively desorption processes;

C_t - zinc concentration in aqueous phase (mg·L⁻¹);

θ - surface coverage degree, representing the ratio of covered surface, according to Langmuir model hypotheses;

s - number of sites on solid surface which are involved in the sorption of a single solute unit.

Term θ_t in equation (9) can be mathematically defined as the ratio between zinc concentration in sediment, q_t and a theoretically maximum achievable concentration in solid phase, q_{max}. Thus, for a 1st order model, s = 1, equation (9) can be rewritten in the form presented in equation (10) [22]:

$$\frac{dq_t}{dt} = k_s \cdot C_t \cdot (q_{max} - q_t) - k_d \cdot q_t \quad (10)$$

where:

Table 7
RESULTS OF REGRESSION CALCULATIONS FOR THE DETERMINATION OF LANGMUIRIAN MODEL PARAMETERS

Temperature, °C	Linear model parameters			Langmuirian model parameters			
	a_0	a_1	a_2	$k_s, l \cdot mg^{-1} \cdot s^{-1}$	k_d, s^{-1}	$q_{max}, mg \cdot kg^{-1}$	R^2
5	$-9.977 \cdot 10^{-3}$	112.51	-0.1092	0.1092	$9.977 \cdot 10^{-3}$	1029.9	0.8509
10	$-3.273 \cdot 10^{-3}$	342.68	-0.8034	0.8034	$3.273 \cdot 10^{-3}$	426.56	0.8549
17	$-2.165 \cdot 10^{-3}$	121.06	-0.2170	0.2170	$2.165 \cdot 10^{-3}$	557.81	0.8405
25	$-3.827 \cdot 10^{-3}$	143.09	-0.2096	0.2096	$3.827 \cdot 10^{-3}$	682.77	0.8997

$\frac{dq_t}{dt}$ – the zinc retention rate on sediment;
 C_t – zinc concentration in aqueous phase in moment t .

In this case, equation (10) can be expressed in the linear form [22]

$$\frac{1}{q_t} \frac{dq_t}{dt} = k_s \cdot q_{max} \cdot \frac{C_t}{q_t} - k_s \cdot C_t - k_d \quad (11)$$

Model parameters, k_s , k_d and q_{max} were calculated by two variables linear regression, after doing the variable

changes $y = \frac{1}{q_t} \frac{dq_t}{dt}$, $x_1 = \frac{C_t}{q_t}$, $x_2 = C_t$. In this case, equation (11) can be expressed as:

$$y = a_1x_1 + a_2x_2 + a_0 \quad (12)$$

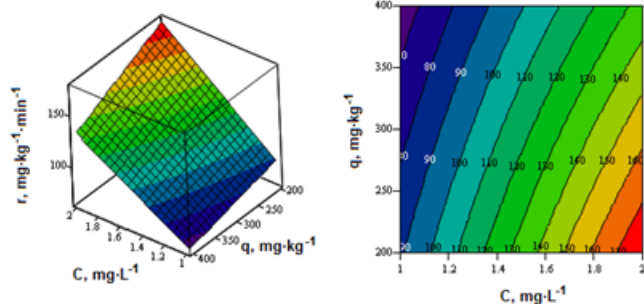


Fig. 14. Dependence of zinc retention rate on zinc concentration in aqueous phase, respectively in sediment, at 5 °C. a) Surface plot; b) Contour plot

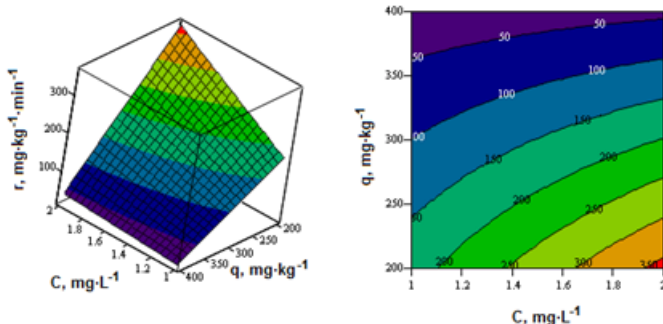


Fig. 15. Dependence of zinc retention rate on zinc concentration in aqueous phase, respectively in sediment, at 10 °C. a) Surface plot; b) Contour plot

The results of regression calculations are shown in table 7.

Data in table 7 show that the 1st order Langmuirian kinetic model can be successfully used to establish, in assessment purposes, a correlation between retention rate of zinc in sediment and zinc concentration in aqueous phase, respectively in solid phase, at neutral pH, regardless the temperature value. Such a correlation may represent a useful tool in order to assess the behavior of zinc ions in water bodies in case of an accidental discharge.

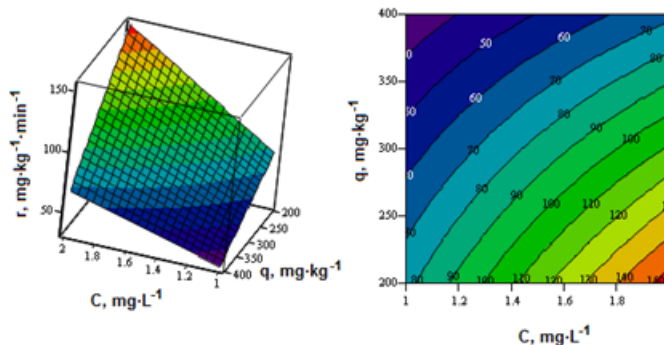


Fig. 16. Dependence of zinc retention rate on zinc concentration in aqueous phase, respectively in sediment, at 17 °C. a) Surface plot; b) Contour plot

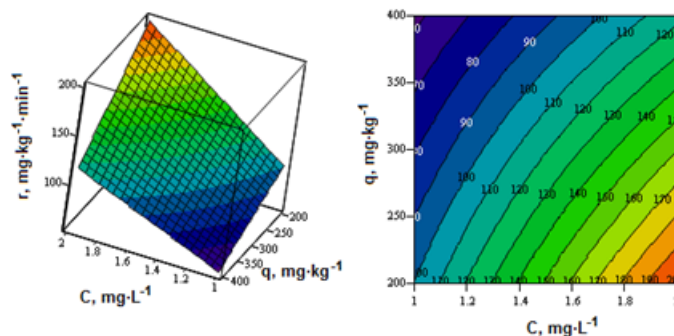


Fig. 17. Dependence of zinc retention rate on zinc concentration in aqueous phase, respectively in sediment, at 25 °C. a) Surface plot; b) Contour plot

In figures 14 – 17 are represented the dependences of zinc retention rates on sediments as dependence of zinc concentrations in aqueous, respectively solid phase.

Conclusions

Mathematical description of heavy metals behavior in water bodies can represent a useful tool to predict the long term consequences of a major accidental discharge. In this paper, the authors intended to establish a correlation between zinc concentration in aqueous phase and sediment, and zinc retention rate, in order to assess zinc behavior and its spatial and temporal distribution.

Results show that, regardless the high level of initial sediment contamination, zinc retention process is a very fast one, the largest amounts of zinc being retained in the first minutes after the phase contact.

The first step was to determine the most appropriate way to determine the zinc retention rate on sediment. To achieve this goal, the Pseudo-1st order, Pseudo-2nd order and Elovich models were used. The regression results show that the model Elovich offers the best correlation between input data and output data, thus it can be satisfactorily used to draw up the differential kinetic curves. Based on these data, the zinc retention rates on sediment were calculated by using Elovich model.

These results were used to establish a mathematic correlation between zinc retention rate on sediment and

zinc concentration in aqueous phase, respectively in solid phase. This way, the use of a Langmuirian first order kinetic model represents in a future research a good approach, as long as the Pearson correlation coefficients reach values in the range 0.84 – 0.90.

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