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# Adsorption of zinc on natural sediment of Tafna River (Algeria)

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## Abstract

The environmental impact of metal additions to sediment depends on its sorption ability. The paper presents a study of zinc adsorption using the experiment data on natural sediment of Tafna River in northwest of Algeria. The effect of various operating variables, namely initial concentration, mass of sediment, and contact time, have been studied. The optimum contact time needed to reach equilibrium is of the order of 30 min and is independent of initial concentration and mass of zinc ions. The extent of adsorption increases with increase of concentration, and with decrease of adsorbent mass. The content of carbonate in sediment increases the adsorption indicating the active support material towards zinc ions.

A batch sorption model, which assumes the pseudo-second-order mechanism, is developed to predict the rate constant of the sorption, the equilibrium sorption capacity and the initial sorption rate with the effect of initial zinc ion concentration and sediment dose. Various thermodynamic parameters, such as  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ , have been calculated. The thermodynamics of zinc ion/sediment system indicates spontaneous, endothermic and randomness nature of the process.

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# 1. Introduction

Due to heavy metals, pollution remains a serious environmental and public problem. Chemical precipitation has been traditionally employed to remove heavy metals. However, metal removal via coagulation-precipitation is, in many cases, insufficient to meet strict regulatory requirements. Adsorption has been shown to be a feasible alternative method for removing metals. The concentration and mobility of these metals in sediments has been widely studied in the last decades [1–5].

Adsorption on sediment is an important process that controls dissolved metal concentration, bioavailability, and toxicity in natural environments [6,7].

Zinc is an essential element for both man and animals and is necessary for functioning various enzyme systems where its deficiency leads to growth retardation. Low intake of zinc results in retardation of growth; immaturity and anemia, condition known as 'zinc deficiency syndrome'. Symptoms of zinc toxicity in human being include vomiting, dehydratation, electrolyte imbalance, abdominal pain, nausea lethargy ness, dizziness and lack of muscular coordination. Zinc imparts undesirable, bitter astringent taste to water at levels above 5.0 mg/L [8]. Toxic concentrations of zinc above recommended value cause adverse effect in the morphology of fish by inducing cellular breakdown of gills. Zinc deficiency in human body may also result in infantilism, impaired wound healing and several other diseases.

A several studies are reported in this area of research. Jenne [9] discussed the role of clay sized minerals in trace element sorption by soils and sediments. Fu and Allen [10] studied the adsorption of cadmium by oxic sediments using a multisided binding model. Bajracharya et al. [11] studied the effect of zinc and ammonium ions on the adsorption of cadmium on sand and soil. They reported that the ions suppress the adsorption capacity significantly.

The purpose of this work is to understand the adsorption mechanism of zinc by natural sediments samples collected from downstream Tafna River (northwest of Algeria) with a view per-

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haps to demonstrate the role of sediments in controlling metal pollution. A batch metal removal experiments were carried out. A kinetic study of the metal uptake of the sediment allowed the calculation of parameters according to pseudo-second-order sorption kinetic models. Adsorption isotherm was determined, and allowed to obtain thermodynamic parameters.

# 2. Materials and methods

# 2.1. Sampling and sample characterization

The River Tafna is one of the important rivers in north west Algeria, having a length of 170 km, and a basin area of about 7245 km<sup>2</sup>. It is continuously exposed to industrial, urban and agricultural wastes including a large number of metal ions. This investigation has been discussed in a previous work [12]. Samples used in the experiment, were collected at Tafna River few years ago (at the reference site "Pierre du Chat", in 16 January 2002). The water quality is controlled by the Water Agency Protection (ANRH). The river is approximately 20 km away from the sea and drains a heavily populated and agriculture area.

The collected samples were stored in hermetically sealed plastic bags until treatment in the laboratory. They were dried out overnight at room temperature in a horizontal laminar-flow hood (class 100 clean air) and crushed using an agate mortar to obtain a fine powder, followed by separation through a sieve to obtain the lower fraction ( $<63 \,\mu$ m). This fraction represents more than 95% of the sediments (granulometric analyses by CILAS 850 granulometer). For total metal determination, the sediment was mineralized with an acid mixture of HF+HCl+HNO<sub>3</sub> (volume ratio of 2:12:6) in Teflon flasks at 120 °C. The partitioning into the different fractions by the BCR sequential extraction procedure was also applied to the fine fraction ( $<63 \mu m$ ) [13]. Specific surface area (SSA) was determined, respectively, by BET method using a Quantasorb.Jr apparatus with an adsorption of nitrogen at 77 K. The sample was outgassed at 180 °C during 5 h at vacuum of  $10^{-4}$  Torr. The total organic Carbon was obtained by using an elementary analyzer using CHNS LECO 932. The mineralogy was evaluated by X-ray diffraction (Table 1).

Sample preparation for X-ray analysis included crushing and acidic treatment. The powdery samples are then analysed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer

Table 1 Characteristics of the water and sediment samples

	Pierre du Chat (water)		
Temperature (°C)	15.5		
pH	8.31		
Conductivity (µs/cm)	2.05		
Oxygen (mg $L^{-1}$ )	0.13		
Redox potentiel (mv)	-68		
	Pierre du Chat (sediment)		
$\overline{\text{SSA}(\text{m}^2\text{g}^{-1})}$	17.19		
TOC (%)	1.11		
Mineralogy	Quartz, calcite, dolomite		

equipped with a copper anode. Such an apparatus allows working with a sample under a given atmosphere at different temperatures. The values of  $2\theta$  were used to estimate the observed reflections of maximum intensity.

The aqueous zinc solutions  $(ZnCl_2, Prolabo)$  were prepared by dissolving the exact quantities of  $ZnCl_2$  in demineralised water (*milli-Q*). Other reagents used in this study were of analytical grade.

# 2.2. Batch sorption experiments

Kinetic experiments were carried out to evaluate the potential adsorption of the natural sediment from the Tafna River. Different parameters related to the sediment, metal and medium can influence the zinc adsorption. In this context, the influence of various experimental parameters such as contact time, initial concentration in zinc, mass of sediment, on the kinetics were studied with a goal of optimization. Details explaining the chosen abbreviations are given in Table 2.

Adsorption isotherms were achieved in a 1 L by mixing 1 g of metal solution, (i.e. buffer solution at pH  $\sim$ 7) at 20 ± 1 °C, under ambient light. The sediment was equilibrated by mechanical shaking. The mixture was stirred for 24 h, allowing the adsorption to reach equilibrium. A mechanical agitator at 400 rpm was used to provide a reproducible and homogenous mixing; the mixture was filtered off afterwards. Several solutions with different initial concentration were prepared.

Adsorption kinetics were performed according to the same procedure for predefined times, at appropriate time intervals. In effect, 10 mL aliquots were sampled and filtered through a 0.45  $\mu$ m pore size, 25 mm diameter Millipore syringe-driven filter unit and swinex. The pH values were controlled at all the experiments. The amount of metal adsorbed ( $q_t$ ) per gram of sediment (mg/g) at time t, was calculated as follows:

$$q_t = (C_0 - C_t) \frac{V}{m_{\text{ads}}} \tag{1}$$

 $C_0$  and  $C_t$  are the metal concentration in liquid phase at the initial and time *t* (in mg/L), respectively,  $m_{ads}$  is the weight of the sediment (g), *V* is the volume of this solution (L).

All solutions were then filtered through  $0.45 \,\mu m$  Millipore membrane filters and acidified with HNO<sub>3</sub>. The resulting solutions were stored at 4 °C until ICP-AES analysis.

Table 2						
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$\overline{C_0}$	Metal concentration in liquid phase at the initial time (mg/L)
$C_t$	Metal concentration in liquid phase at time $t$ (mg/L)
mads	Adsorbent amount in the solution (g/L)
k	Rate constant of the pseudo-second-order model (g/mg/min)
$q_{\rm e}$	Maximum amount of sorbed metal at time $t (mg/g)$
$q_t$	Amount of sorbed metal at equilibrium (mg/g)
Ce	Metal concentration in liquid phase at equilibrium (mg/L)
$K_D$	The equilibrium constant (L/mg)
R	The gas constant = $8.314 \times 10^{-3}$ kJ/mol/K
$\Delta G^{\circ}$	The change in free energy (kJ/mol)
$\Delta H^{\circ}$	The change in enthalpy (kJ/mol)
$\Delta S^{\circ}$	The change in entropy (kJ/mol/K)

Each solution was individually analyzed by ICP-AES and standard solutions were prepared in their specific batch solutions to avoid any analytical deviation.

All reagent used in this study were of analytical grade (Merck, Germany) and *milli-Q* deionized water (Millipore system) was used throughout all experiments.

An inductively coupled plasma atomic emission spectrometer [ICP-AES, Varian model Liberty (II) axial view] was used for determination of zinc. The ICP-AES was equipped with a pneumatic V-Groove nebuliser, inert PTFE spray chamber Sturmun-Master. The optimal instrumental condition were: plasma power 1.0 kW; photomultiplicator tension 650 V; integration 2 s; background correction in dynamic mode; nebulizer pressure 300 kPa; argon auxiliary flow 1.5 L/min and pomp peristaltic rate 15 rpm. The wavelength chosen for Zn is 213.856 nm (with 0.9 µg/L detection limit). In order to determine the precision of the analytical processes, samples were analyzed twice. The average values of the variation coefficients obtained were  $\leq$ 10%). All pH measurements were done with a pH meter (model WTW Multiplane P3).

## 3. Results and discussion

The water and sediment characteristics of River Tafna are given in Table 1. The total organic carbon content of the sediment is 1.11%. Fig. 1 shows a characteristic X-ray diffraction spectrum of the sediment. The presence of large quantities of quartz (SiO<sub>2</sub>), calcites and dolomites can be clearly distinguished. The amount of quartz will be reduced during sample treatment, because the size of SiO<sub>2</sub> particles often exceeds the sizes considered in this work. In particular, CaCO<sub>3</sub> and CaMgCO<sub>3</sub> are found in large quantities. Therefore, it can be assumed that at least Ca and Mg may be considered as major elements in this analysis. X-ray results obtained for different sites of the river (not shown) yielded the same general behaviour, which means that the geological situation does not change significantly as a function of the sites chosen for sample collection.



Fig. 1. X-ray spectrum of sediments collected from Tafna River at "Pierre du Chat".



Fig. 2. Effect of contact time on the adsorption of zinc by sediment for various initial zinc concentrations.

#### 3.1. Contact time

The adsorption data of the zinc uptake versus contact time at different initial concentrations is presented in Fig. 2. The results show that equilibrium time required for the adsorption of Zn by the sediment is almost  $\sim$ 30 min of shaking. However, for subsequent experiments, the samples were left for 24 h to ensure equilibrium; these results are confirmed for all the experiments (as function of the initial Zn concentration and the mass sediment taken). Besides, these results indicate that the sorption process can be considered very fast because of the largest amount of zinc attached to the sorbent within the first 30 min of adsorption; these observations are in agreement with previous works of Hatje et al. and Jain et al. [4,5].

During the course of zinc removal by sediment in *milli-Q* water, we noticed an evolution of the initial pH of the solution from 6 to 9 at the equilibrium (Fig. 3). This can been interpreted by a competition between  $Zn^{2+}$  ions and  $H_3O^+$  for binding sites. Similar observations have been made by other researchers with other metal ion-material systems [14,15]. In order to limit the pH variation, we have used in some experiments a buffer solution (pH ~7) and natural water from the same site of sediment sampling. In these cases the pH variations are not significant (Fig. 3).

The results obtained in Fig. 2, indicate that the curves have the same shape. The time required to reach equilibrium is not vari-



Fig. 3. pH profile of zinc sorption by sediment.

able (30 min). We also notice that the capacity of zinc removal by sediment at the equilibrium, increases with an increase of initial zinc concentration. As it can be seen, the remaining concentration of zinc becomes asymptotic to the time axis after 30 min of shaking. The experimental results of zinc sorption on sediment at various concentrations are shown in Fig. 2. It is apparent, that the amount of zinc ions sorbed at equilibrium, increases with an increase in initial sorbate concentration. The removal of zinc increases from 0.12 to 25.45 mg/g (Table 3) by increasing the initial zinc concentration from 0.17 to 26.10 mg/L at 20 °C.

In order to investigate the mechanism of sorption, the kinetics constants of sorption are determined by using pseudo-second-order equation [16–20]. The pseudo-second-order kinetic expression has been applied to the solid–liquid sorption systems

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k(q_\mathrm{e} - q_t)^2 \tag{2}$$

where *k* is the pseudo-second-order rate constant of adsorption (g/mg/min). After integrating Eq. (2) for boundary conditions t=0 to t=t and  $q_t=0$  to  $q_t=q_t$ , the following form can be obtained:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t\tag{3}$$

 $q_e$  and  $q_t$  are the amounts of metal ion sorbed (mg/g) at equilibrium and at time *t*, respectively

$$ht = kq_{\rm e}^2 \tag{4}$$

where *h* is the initial sorption rate (mg/g/min) as  $q_t/t$  approches 0.

By plotting  $t/q_t$  versus t, a straight line can be obtained (Fig. 4) and therefore  $q_e$  can be calculated. The values of sorption capacity, ( $q_e$ ), and rate kinetic constant, (k), are determinated from the slope and intercepts, respectively.

The pseudo-second-order coefficients of determination  $(R^2)$ , the rate parameters (k), the equilibrium sorption capacity  $(q_e)$ and initial sorption rate (h), for various initial zinc concentrations are presented in Table 3. The data show a good agreement with the pseudo-second-order model (Fig. 4) and the regression coefficients for the linear plots were higher than 0.989 for all the systems studies. The sorption curves are typical for effect of initial metal ion concentration on the sorption kinetics. Similar results have been reported for the sorption of dye onto peat

Table 3

Pseudo-second-order rate constants for the effect of initial Zn (II) concentration

$\overline{C_0 \text{ (mg/L)}}$	$q_{\rm e} ~({\rm mg/g})$	h (mg/g/min)	k (g/mg/min)	$R^2$	
0.17	0.12	0.13	8.900	1.000	
0.54	0.19	0.12	3.137	0.999	
0.90	0.65	0.14	0.330	0.987	
1.20	0.81	0.41	0.627	0.996	
2.36	1.94	2.24	0.595	0.999	
3.33	2.92	3.11	0.364	0.999	
12.02	11.72	6.19	0.045	0.999	
15.40	14.88	12.09	0.055	1.000	
22.34	22.68	13.16	0.026	0.999	
26.10	25.45	36.36	0.056	1.000	



Fig. 4. Linearization of zinc sorption kinetics by sediment: pseudo-second-order rate at different initial concentrations.

and pith [17,23]. Table 3 shows that the equilibrium sorption capacity increases from 0.12 to 25.45 mg/g. The values of the rate constant are found to decrease from 8.9 to 0.056 g/mg/min whilst the initial sorption rate increases from 0.13 to 36.36 mg/g.

The kinetics results of Fig. 2 can be used to determine whether particle diffusion is the rate-limiting step for zinc adsorption on sediment. According to Weber and Morris [21], for most adsorption processes, the uptake varies almost proportionately with  $t^{1/2}$  rather than with the contact time, *t*. Therefore, plot of zinc adsorbed,  $C_t$  versus  $t^{1/2}$ , is presented in Fig. 5. The plots have linear portion and a plateau. The linear portion is attributed to the intraparticle diffusion and the plateau to the equilibrium. The experiments were conducted at pH equal to 7 to avoid any precipitation.

The deviation of the curve from the origin indicates that intraparticle transport is not the only rate-limiting mechanism [22] and that some other mechanisms are involved.

## 3.2. Effect of sediment mass

In the goal to determine the required sediment quantity for a maximal removal of zinc, the effect of sediment mass on the kinetic of zinc removal was studied; the experiments were achieved in one liter of solution (initial concentration of zinc 2.5 mg/L). Fig. 6 shows that the capacity of zinc sorption increases with decrease of the quantity of sediment introduced.



Fig. 5. Plots of zinc adsorption vs. square root of time for various initial zinc concentrations.



Fig. 6. Zinc adsorption capacity  $(q_t)$  as a function of the sediment mass (initial concentration 2.5 mg/L).

This result is in agreement with those reported by Venkataraman et al. [24] and Sampedro et al. [25] using other metal ions-material systems. The authors have explained this decrease by the formation of aggregates at higher mass concentration, which decreases the effective sorption area or a shortage of metal concentration in solution. From the curves of Fig. 7, it can also be seen that the sediment mass has not an influence on the contact time necessary to reach equilibrium. This may be expected because, for a fixed initial solute concentration, the increase of the total sediment doses provide a greater surface area (or sorption sites), although the specific sorption capacity decreases from 7.11 to 0.24 mg/g of sediment with the increasing doses (from 0.2 to 8 g/L), as shown in Fig. 6. This result is due to the fact that the smaller amount of sediment, the higher amount of the metal contact per unit weight of the sediment. The adsorption capacities are much improved by minimum effective substrate.

Fig. 8 illustrates a series of plot of  $t/q_t$  versus time for sorption of zinc (II) with sediment varying from 0.5 to 8 g/L, on the basis of the pseudo-second-order model [20]. The coefficient of determination,  $(R^2)$ , the rate constant, (k), the equilibrium sorption capacity,  $(q_e)$  and the initial sorption rate, (h), of sorption at various masses at initial concentration 2.5 mg/L are shown in Table 4. The rate of the zinc (II) sorption process appears to be controlled by a chemical process, in accordance with the pseudo-second-order reaction mechanism.



Fig. 7. Effect of sediment mass on the sorption kinetics of zinc by sediment (initial concentration 2.5 mg/L).



Fig. 8. Linearization of zinc sorption kinetics by sediment: pseudo-second-order rate at different masses.

Table 4 Pseudo-second-order rate constants for the effect of different masses

Mass of sediment (g)	$q_{\rm e}~({\rm mg/g})$	h (mg/g/min)	k (g/mg/min)	<i>R</i> <sup>2</sup>	
0.5	4.42	6.13	0.314	1.000	
0.8	2.67	1.64	0.230	0.999	
1	1.31	0.95	0.553	1.000	
2	0.81	1.37	2.104	1.000	
4	0.51	1.33	5.204	1.000	
6	0.24	0.81	13.904	1.000	

## 4. Role of carbonate phase

Role of carbonate phase [13] on the adsorption of zinc ions is shown in Fig. 9 for fixed initial concentration of zinc (26.10 mg/L). These plots reveal that for crude sediment, the adsorption of zinc is higher (25 mg/g). Furthermore, it is observed that the adsorption capacity decreases for sediment after carbonate phase extraction by acid treatment at pH  $\sim$ 5 (6.54 mg/g).

The results shown in Fig. 10 are consistent with the pseudosecond-order model [20] and the regression coefficients for the linear plots were higher than 0.994 for both sediments (Table 5). The equilibrium sorption capacity decrease from 25.58 mg/g (crude sediment) to 7.41 mg/g (after carbonate phase extraction). The values of the rate constant are found between 0.041



Fig. 9. Role of carbonate phase on the adsorption of zinc ions by sediment at  $20\,^\circ\text{C}$ .



Fig. 10. Linearization of zinc sorption kinetics by both of sediments (crude sediment and after carbonate phase extraction): pseudo-second-order rate.

and 0.055 mg/g/min and the initial sorption rate increases from 26.79 mg/g (crude sediment) to 3.02 mg/g (after carbonate phase extraction).

# 5. Effect of temperature

The temperature range used in the study was from 20 to 40 °C. Adsorption increases with increasing temperature, due to the increase in number of active sites. Thermodynamic parameters such as free energy change ( $\Delta G^{\circ}$ ), enthalpy change ( $\Delta H^{\circ}$ ) and entropy change ( $\Delta S^{\circ}$ ) are determined using the following equation [26,27]:

$$\Delta G^{\circ} = -RT \ln K_{\rm d} \tag{5}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{6}$$

where  $\Delta G^{\circ}$  is the change in free energy (kJ/mol);  $\Delta H^{\circ}$  the change in enthalpy (kJ/mol/K); *T* the absolute temperature, *R* the gas constant = 8.314 × 10<sup>-3</sup> kJ/mol *K*; and *K*<sub>d</sub> the equilibrium constant. This latter may be defined as

$$K_{\rm d} = \frac{C_{\rm Ae}}{C_{\rm e}} \tag{7}$$

where  $C_{Ae}$  and  $C_{e}$  are the equilibrium concentration (mg/L) of the metal ion on the adsorbent and in solution, respectively.

By using Eqs. (5) and (6), Eq. (7) can be rewritten as

$$\ln K_{\rm d} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H}{RT} \tag{8}$$

when  $\ln K_d$  is plotted versus 1/T, a straight line with slope  $\Delta H^{\circ}/R$  and intercept  $\Delta S^{\circ}/T$  are obtained Fig. 11. The thermodynamic parameters for the adsorption process are given in Table 6.

Positive values of  $\Delta H^{\circ}$  suggest the endothermic nature of the adsorption of zinc on natural sediment. While negative values

Table 5 Pseudo-second-order rate constants for the both of sediment (crude sediment and after carbonate phase extraction)

Nature of sediment	$q_{\rm e}$	h	k	$R^2$
Crude sediment	25.58	26.738	0.041	1.000
After carbonate phase extraction	7.41	3.019	0.055	0.994



Fig. 11. Van't Hoff plot for adsorption of zinc by natural sediment of Tafna River.

Table 6 Thermodynamic parameters for the adsorption of zinc ions on natural sediment of Tafna River

Ce (mg/L)	$\Delta H^{\circ}$ (kJ/mol)	$\Delta S^{\circ}$ (kJ/K/mol)	$\Delta G^{\circ}$ (kJ/mol)		mol)	
			298 K	303 K	313 K	
22.34	24.574	0.083	-0.042	-0.882	-1.722	

of  $\Delta G^{\circ}$  indicate the feasibility of the process and the spontaneous nature of the sediment [5]. However, the negative value of  $\Delta G^{\circ}$  decreases with increasing temperature, showing that the spontaneous nature of adsorption of zinc is inversely proportional to the temperature. The positive value of  $\Delta S^{\circ}$  reflects the affinity of sediment for zinc ions and suggests some structural changes in zinc and sediments. In addition, positive value of  $\Delta S^{\circ}$  exhibits the increasing randomness at the solid/liquid interface during the sorption of zinc ions on sediment. Similar findings were also observed by Namasivayam and Ranganathan [28]. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. Enhancement of adsorption capacity of adsorbent at higher temperatures may be attributed to the activation of the adsorbent surface [5].

#### 6. Equilibrium of adsorption

To study equilibrium of zinc removal by sediment, the approach more frequently used consists in measuring the isotherm of adsorption. It represents the quantity of metal removed (q) against the equilibrium concentration of metal ion in the solution. It corresponds to the equilibrium distribution of metal ions between the aqueous and solid phases when the concentration increases. This equilibrium time has been chosen on the basis of results of the kinetics of zinc removal by sediment. For information, this contact time needed to reach equilibrium dependents on experimental conditions. As shown in Fig. 12, the isotherm for zinc adsorption is type III, according to the classification of Brunauer [29]. Type III isotherms are characterized principally by heats of adsorption, which are less



Fig. 12. Sorption isotherm of zinc by sediment at 20 °C.

than the adsorbate heat of liquefaction. Thus, as adsorption proceeds, additional adsorption is facilitated since adsorbate interaction with an adsorbed layer is greater than that with the adsorbent surface. This type of isotherm is applicable for the adsorption of gases according to the BET classification.

There is another type of classification proposed by Giles et al. [30]. In our case the isotherm obtained should be of type S, for weak concentration. However when adsorption involves solids of heterogeneous structure, the use of theorical models are often inappropriate.

#### 7. Conclusion

The results obtained in this study confirm that sediment can remove zinc ion from aqueous solution and the adsorption performances are strongly affected by their initial concentration. The kinetics of zinc sorption on natural sediment is based on the assumption of the pseudo-second-order mechanism. The carbonate phase plays an important role in the adsorption process.

The kinetic data suggest that the adsorption of zinc on sediments is an endothermic process, which is spontaneous at the low temperature. The uptake of zinc is controlled by intraparticle diffusion mechanism. The application to experimental results of the isotherm type III shows that the model applies satisfactorily with the concentration and the mass sediment used in the experiments.

Experimental results obtained are encouraging and may be extended to other aquatic ecosystems.

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