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# Removal of zinc ion from water by sorption onto iron-based nanoadsorbent

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# Abstract

Batch and column experiments were conducted to investigate zinc removal from dilute aqueous solution (i.e. effluent) by sorption onto synthetic nanocrystalline akaganéite. Due to favorite characteristics, this material was shown to be a promising inorganic adsorbent prepared in the laboratory, following a new method of synthesis—previously published. The effects of adsorbent amount, zinc concentration, solution pH value, ionic strength and temperature variation on the treatment process were mainly investigated during this study. Typical adsorption models were determined searching the mechanism of sorption while the bed depth-service time model was applied to column (with granular material) experiments. © 2006 Elsevier B.V. All rights reserved.

Keywords: Akaganéite; Sorption; Industrial wastewater; Heavy metals

# 1. Introduction

The rapid industrialization and the increase in world population have all contributed to heavy metal pollution in ecosystems due to their high toxicities. Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because they do not degrade into less-harmful substances and can accumulate in soil and water reservoirs, which leads to harmful effects on living species if they enter into the food chain. Zinc, for example, is highly toxic and could be damaging to human health. Industries discharging waste streams that contain significant levels of zinc include steel works with galvanizing lines, zinc and brass metal works, zinc and brass platting, viscose rayon yarn and fiber production, ground wood pulp production and newsprint paper production. Zinc salts are also used in the inorganic pigments industry (e.g. zinc chromate) and high zinc levels have been reported in acid mine drainage. Waste concentrations of zinc range from less than 1 to more than  $48,000 \text{ mg L}^{-1}$  in various waste streams described in the literature. It is also known that high releasing of zinc into environment is also from non-point sources of pollution due to agricultural activities, sediment remobilization or entrainment, groundwater intrusion or from a combination of these sources [1].

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Having in mind the adverse effects of heavy metals environmental agencies set permissible limits for their levels in drinking water and other types of waters. The maximum allowable limit for zinc in discharged water was set by the Environmental Protection Agency to be 5 mg L<sup>-1</sup>. Considering the harmful effects of heavy metals, it is necessary to remove them from liquid wastes at least to a limit accepted by national and international regulatory agencies before their discharge to the environment. Treatment processes employed for zinc removal from wastewater may involve precipitation with disposal of the resultant sludge or recovery, membrane processes, ion exchange resins, although these are often expensive and ineffective at low metal concentrations. Therefore, there is a need for a cost effective treatment method that is capable of removing low concentrations of zinc from solution.

The adsorption on sorbents is reported to be one of the best methods for the removal of metal ions in low concentrations [2]. Several adsorbents can be applied for removal of heavy metals from wastewater; the choice of them depends on their adsorption capacity, availability and cost. Ding et al. [3] have studied the adsorption of arsenate, chromate, phosphate, lead and zinc ion on amorphous black ferric oxyhydroxide. Badruzzaman et al. [4] have used granular ferric hydroxide to identify and quantify mass transport processes of arsenate adsorption in packed beds. The adsorption of arsenate and salicylic acid onto granulated ferric hydroxide in fixed-bed adsorbents were also experimentally investigated and modelled by Sperlich et al. [5]. Liu et al. [6] reported the removal of copper, zinc and mercury from

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wastewater by an ion exchange chelating fiber. Shawabkeh et al. [7] studied the use of treated oil shale ash agricultural for the removal of copper and zinc ion from aqueous solutions. Natural zeolite and bentonite were studied by Sheta et al. [8] for the removal of zinc and iron. Pardo-Botello et al. [9] and Dabek [10] reported the use of activated carbon for the zinc removal. Raw and surfactant-modified montmorillonite was also used by Lin and Juang [11] to study the adsoption of zinc and copper. Norton et al. [12] found that the biological sludge can bind zinc anions effectively, while Trivedi et al. [13] studied nickel and zinc sorption to amorphous versus crystalline iron oxides.

Iron-based bonding materials have been widely used as adsorbents. Some of the reasons for selecting the iron-based bonding materials were that they are cheap, easily synthesized and they present low risks for adding a further pollutant to the system. The application of goethite and in situ-produced ferric hydroxide was demonstrated to be effective in the removal of heavy metals [14]; akaganéite, an iron oxyhydroxide, was previously effectively tested for arsenates [15,16] and chromates [17]. The aim of the present study is the examination of the ability of akaganéite to remove zinc ion from solutions, showing the possible advantage of this adsorbent if able to remove both anions and cations.

# 2. Experimental

#### 2.1. Materials

Akaganéite in the current study was prepared from ammonium carbonate reacted with hydrous ferric chloride, FeCl<sub>3</sub>·6H<sub>2</sub>O, according to an earlier published synthetic method [18]. For the fixed-bed experiments, akaganéite was prepared in the form of granules. This form of akaganéite was prepared under the same procedure as the nanostructured akaganéite but after the removal of chloride ion conventional freezing was followed [19].

The initial metal stock solution was prepared from the nitrate salt,  $Zn(NO_3)_2 \cdot 6H_2O$ . All chemicals were reagent grade and they were used without further purification. All solutions were prepared with deionised water and the glassware was cleaned by soaking in 10% HCl and rinsed with water. The background electrolyte was potassium nitrate (unless otherwise mentioned).

#### 2.2. Batch process for adsorptive material

The laboratory batch experiments for zinc ion removal from dilute aqueous solutions by the addition of the prepared sorbent were carried out using suitable conical flasks (100 mL sample volume) agitated with a reciprocal shaker (160 rpm) for 24 h. Constant temperature was maintained (25, 35 or 55 °C) in order to describe the adsorption results by known isotherm models (Freundlich and Langmuir equations). The pH of the suspension was modified, when needed, by addition of nitric acid (0.1 M) or sodium hydroxide solution (0.1 M). It is also noted that in all experiments the written pH values represent the final pH.

Zinc desorption experiments were carried out batchwise at constant temperature  $(25 \,^{\circ}C)$ . Samples of the sorbent loaded

with the maximum amount of zinc were placed for 24 h in aqueous solutions of different pH values and the amount of zinc released was determined.

The quantity of metal sorbed onto synthetic akaganéite (denoted as Ak) was expressed as percentage removal of zinc, R%, except for the sorption isotherms. The residual zinc after the application was chemically analysed by atomic absorption spectrophotometry (AAS), in the normal manner. The calibration curve enables the determination of zinc in the concentration range from 0.2 to 1.5 mg L<sup>-1</sup> and its sensitivity is 0.018 mg L<sup>-1</sup>. The electrokinetic measurements were carried out using a microelectrophoretic apparatus, and expressed as zeta-potential values.

# 2.3. Column process for adsorptive material

The set-up for the column tests consisted typically from a peristaltic pump and a vertical plastic column having inner diameter 1.6 cm and height 21 cm; a volumetric flow rate of 143 mL h<sup>-1</sup> was used. A fixed-bed of sorbent was formed in the column containing a predetermined mass of akaganéite, of 2.5, 5 or 15 g that corresponded to a column height of 1.2, 2.4 and 7.2 cm, respectively. All experiments were performed at room temperature in an upflow-operating mode; under these conditions the sorptive bed was not fluidised. Liquid samples were taken at different times from the column outlet in order to determine the residual concentrations of Zn(II) ion. In this case, the bed depth-service time (BDST) equation has been applied to the sorption results in order to model the column operation.

# 2.4. XPS measurements

The X-ray photoelectron spectroscopy (XPS) study was conducted by a SPECS LHS-10 UHV system at the Institute of Chemical Engineering and High Temperature Chemical Processes in Patras (Greece).

# 3. Results and discussion

#### 3.1. Batch adsorption experiments

An innovative, simple and low cost method was applied for the preparation of akaganéite (Ak), a nanocrystalline iron oxyhydroxide. The examined product, akaganéite, had high BET surface area ( $330 \text{ m}^2 \text{ g}^{-1}$ ) and definite pore size distribution; the produced material was examined in detail, i.e. by powder X-ray diffraction, TEM and nitrogen sorption measurement and they are presented in Table 1. The granulated form of akaganéite, denoted hereafter Akgranular, was also examined in detail and the results are also presented in Table 1.

A first look into the sorption of zinc ion by akaganéite, presented in Fig. 1a, revealed the necessary time for its removal. While in the beginning the process was fast showing a steep ascent, a less rapid decay succeeded; for complete metal removal ( $\sim$ 100%) almost 20 h were required. Quite similar observation was elsewhere recorded [20]. In order to investigate the mechanism of sorption and potential rate controlling step, such as

1.0-9.0

Surface properties of akaganéite and akaganéite granular					
Sample	Specific surface area, $S (m^2 g^{-1})$	Pore volume, $e$ (cm <sup>3</sup> g <sup>-1</sup> )	Range of pore diameters (nm)	Predominant pore diameter, D (nm)	
Ak <sub>nano</sub>	330	0.350	1.5-6.0	3.6	

0.237

Table 1 Su

234

mass transport and chemical reaction processes, kinetic models have been used to test experimental data. In case of strict surface adsorption, a variation in rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial solute concentration and the rate of adsorption will not be linear. Besides for adsorption on the outer surface of adsorbent, there is a possibility of transport of adsorbent ions from the solution to the pores of the adsorbent [21]. This possibility was tested in terms of a graphical relationship between amount of Zn adsorbed and square root of time (Fig. 1b). As it results from Fig. 1b the experimental data do not give straight line, thus the diffusion possibly does not play a key role to the mechanism of sorption.

Fig. 1c illustrates the comparison of experimental uptake data with theoretical predictions (curves) based on the Elovich, Lagergren, Ritchie and modified second-order kinetic equations. The best fit for the experimental series of this study was achieved by the application of Elovich kinetic equation:

$$q_{\rm t} = \frac{1}{\beta} \ln(1 + \alpha \beta t) \tag{1}$$

The parameter  $\alpha$  of the equation is the initial sorption rate, while the parameter  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption [22]. The agreement between the experimental data and the theoretical predictions based on the Elovich kinetic equation supports the heterogeneous sorption mechanism likely to be responsible for metal ion uptake [23].

Fig. 2 presents the influence of solution pH on the sorption of zinc ion using different background electrolytes. All the experiments were conducted at solution pH less than 7.5 because up to this pH region chemical precipitation of zincite could not take place, so zinc removal was due only to sorption. This pH range was defined by the thermodynamic aqueous speciation diagram of Zn, presented in Fig. 3, produced by a known computer program, Mineql+. Zinc removal was shown to be strongly affected by pH. It was observed that for a change from pH 5 to 7.5 the removal rates were changed from almost 0 to 95%.

Fig. 4 presents the fractions of  $SOH_2^+$  and SOH groups of akaganéite at various pH produced by pehametric titration. From the speciation of akaganéite it is concluded that zinc ion cannot be sorbed onto akaganéite at pH < 4 due to repulsive forces between the positively charged surface of akaganéite at this pH region and Zn<sup>2+</sup> ion. At the pH range of the experiments, an increase of the concentration of the neutral surface species (SOH) is observed, so the adsorption of Zn onto these SOH

species is performed increasingly according to the equations [24]:

3.5

 $p_{\text{IEP}}(-)$ 

7.3

7.3

$$\equiv \operatorname{Fe}^{\mathrm{s}}\operatorname{OH}^{\mathrm{o}} + \operatorname{Zn}^{2+} = \equiv \operatorname{Fe}^{\mathrm{s}}\operatorname{OZn}^{+} + \operatorname{H}^{+}, k_{1}$$
(2)

 $\equiv Fe^{w}OH^{o} + Zn^{2+} = \equiv Fe^{w}OZn^{+} + H^{+}, k_{2}$ (3)

Fig. 5 shows further the effect of ionic strength at constant pH and varying initial zinc concentrations. It was observed that the sorption of zinc was reduced with the existence in the solution of ionic strength (due possibly to ions competition to occupy surface sites) and this tension is well maintained over the full range of concentrations studied. This slight negative influence, however, it is believed that it cannot be a clear indication of physical sorption; according to Hayes et al. [25], the macroscopic observations of the ionic strength influence on ions adsorption by oxides, hydroxides and hydroxy-oxides comprised a method of differentiation between physical and chemical sorption. Quite similar observation was also recorded to the removal of arsenic and cadmium by akaganéite fixed-beds. Smaller aggregates of particles will have a shorter diffusion path, thus allowing the adsorbate to penetrate deeper into the adsorbent elementary particle more quickly, resulting in a higher rate of adsorption. In addition the total external surface area per unit volume for all smaller particles inside the column will be larger, providing more external surface for initial mass transfer to take place [16].

As it is generally accepted, the specific adsorption (i.e. chemisorption) of cations charges positively the colloids surfaces. Considering that the sorbed species are positively charged, the process is carried out easier to negatively charged or neutral sites, which meanwhile following sorption are decreased shifting the pH to higher pH values [26]. In this way, if zinc was chemisorbed, a higher  $p_{\text{IEP}}$  should be observed according to the next equation:

$$> \text{FeO}- + \text{Zn}^{2+} \rightarrow \text{FeO}-\text{Zn}^+$$
 (4)

The electrokinetic measurements of this system, presented as Fig. 6, showed that the  $p_{\text{IEP}}$  of akaganéite shifted from pH  $\sim$ 7.3–7.9, when zinc ion was sorbed. Therefore, chemisorption rather than physical sorption of zinc ion onto the adsorbent material may be concluded.

The influence of temperature for varying feed concentrations was also investigated (see Fig. 7a) and it was shown that zinc sorption was decreased as the temperature was increasing. Typical isotherm curves have been examined applying the Freundlich and Langmuir model, as it is often conducted in the literature. The Freundlich equation for dilute solution is given by Eq. (5):

$$Q_{\rm eq} = K_{\rm F} C_{\rm eq}^{1/n} \tag{5}$$

Akgranula



Fig. 1. (a) Effect of time on the adsorption of zinc at adsorbent (nanostructured akaganéite) dose  $1 \text{ g L}^{-1}$ , adsorbate concentration  $10 \text{ mg L}^{-1}$ , pH 6.5 and temperature 25 °C. (b) Evolution of adsorbent capacity with the square root of time at adsorbent (nanostructured akaganéite) dose  $1 \text{ g L}^{-1}$ , adsorbate concentration  $10 \text{ mg L}^{-1}$ , pH 6.5 and temperature 25 °C. (c) Comparison of experimental uptake data with theoretical predictions (curves) based on the Elovich, Lagergren, Ritchie and modified second-order kinetic equations at adsorbent (nanostructured akaganéite) dose  $1 \text{ g L}^{-1}$ , adsorbate concentration  $10 \text{ mg L}^{-1}$ , pH 6.5 and temperature 25 °C.



Fig. 2. Influence of pH and electrolyte type on zinc removal (conditions: [sorbent] = 1 g L<sup>-1</sup> nanostructured akaganéite,  $[Zn^{2+}]_{initial} = 10 \text{ mg L}^{-1}$ , I = 0.1 M, contact time = 24 h, temperature = 25 °C).



Fig. 3. Speciation diagram of zinc ( $[Zn^{2+}]_{initial} = 10 \text{ mg L}^{-1}$ , I = 0 M, temperature = 25 °C).



Fig. 4. Speciation diagram of akaganéite (I = 0 M, temperature = 25 °C).



Fig. 5. Influence of ionic strength on zinc removal for different initial zinc concentrations (conditions: [sorbent]=1 g  $L^{-1}$  akaganéite, pH 6.5, contact time = 24 h, temperature = 25 °C).

where  $Q_{eq}$  is the quantity of solute (Zn(II)) sorbed per unit weight of solid adsorbent (Ak),  $C_{eq}$  the concentration of solute in the solution at equilibrium, and  $K_F$  and 1/n are the constants indicating the adsorption capacity and the adsorption intensity, respectively. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (5):

$$\log Q_{\rm eq} = \log K_{\rm f} + \frac{1}{n} \log C_{\rm eq} \tag{6}$$

A familiar form of Langmuir equation for dilute solutions is given below:

$$\frac{C_{\rm eq}}{Q_{\rm eq}} = \frac{1}{K_{\rm L}Q_{\rm max}} + C_{\rm eq}\frac{1}{Q_{\rm max}}$$
(7)

where  $Q_{eq}$  and  $C_{eq}$  are previously denoted,  $K_L$  an energy term which varies as a function of surface coverage strictly due to variations in the heat of adsorption and  $Q_{max}$  is the maximum loading capacity. Taking into account the correlation coefficient



Fig. 6. Electrokinetic measurements, expressed as zeta-potential, of the nanostructured akaganéite as a function of solution pH, in presence and absence of the metal ion.



Fig. 7. (a) Adsorption isotherms of zinc for three different temperatures (conditions: [sorbent] =  $1 \text{ g L}^{-1}$  nanostructured akaganéite, pH 6.5, contact time = 24 h). (b) Adsorption isotherms of zinc for three different temperatures expressed by the logarithmic Freundlich equation.

 $(R^2)$  presented in Table 2 the experimental results present quite good agreement with both models.

Experiments at different temperatures followed with the granular sorbent, which was used in the fixed-bed attempts; the effect of temperature was similar with the nanostructured akaganéite

Table 2		
Freundlich and	Langmuir constants of akaganéite and akaganéite gra	mular

$I(\mathbf{C})$	Freundlich model			Langmuir model		
	$\overline{R^2}$	K <sub>F</sub>	1/n	$\overline{R^2}$	KL	$Q_{\max}$
Ak <sub>nano</sub>						
25	0,909	2.682	0.54	0.984	0,072	27.61
35	0.976	0.801	0.55	0.986	0.042	9.79
55	0.982	0.199	0.56	0.949	0.016	4.182
Akgranular						
25	0.956	0.755	0.60	0.983	0.026	13.95
35	0.949	0.536	0.60	0.994	0.044	7.74
55	0.935	0.426	0.59	0.946	0.034	6.91



Fig. 8. (a) Adsorption isotherms of zinc for three different temperatures (conditions: [sorbent] = 1 g  $L^{-1}$  granulated akaganéite, pH 6.5, contact time = 24 h). (b) Adsorption isotherms of zinc for three different temperatures expressed by the logarithmic Freundlich equation.

(Fig. 8). At zinc initial concentration higher than 50–60 mg L<sup>-1</sup>, the saturation of surface sites both for granular and nanostructured akaganéite occurs and the difference between two sorbents disappears. In this case, further, the Freundlich isotherm was better followed. This model, used often in industry, although it accepts the monolayer surface coverage of the sorbent. At 25 °C, a coefficient  $R^2$  of 0.956 was found;  $K_F$  was 0.755 and 1/*n* 0.6. The parameter  $K_F$  is known to be related with the strength of the sorption bond and as well as with the capacity of the sorbent. The other parameter, 1/*n*, is related with the heterogeneity of surface and the distribution of bonds.

Fig. 7b presents the results of the effect of temperature on zinc removal by akaganéite and Fig. 8b by granular akaganéite, using the logarithmic form of the Freundlich equation. From these figures the change of the respective enthalpy  $\Delta H$  of sorption was calculated by the means of the integrated form of the Clausius–Clapeyron equation given by the relation:

$$\Delta H = 2.303 R \frac{T_1 T_2}{T_2 - T_1} (\log C_{\text{eq}1} - \log C_{\text{eq}2})$$
(8)



Fig. 9. Zinc desorption (from an initial solution 50 mg L<sup>-1</sup> Zn<sup>2+</sup> at pH 6.5 with 5 g L<sup>-1</sup> nanostructured akaganéite contacted for 24 h);  $R_{Ak}$ % represents the percentage of Zn<sup>2+</sup> remaining on the surface of akaganéite and  $R_s$ % the percentage of zinc eluted in the solution.



Fig. 10. (a) Breakthrough curves for different quantities of akaganéite from an initial solution of  $10 \text{ mg L}^{-1} \text{Zn}^{2+}$  at pH 6.5. (b) Iso-removal lines for 20, 35 and 50% breakthrough; BDST model output, where *M* the quantity (in g) of sorbent inside the column.

![](_page_6_Figure_2.jpeg)

Fig. 11. XPS measurements for akaganéite after Zn adsorption.

For a constant  $Q_{\text{max}}$  value at three different temperatures  $(T_1 = 25 \text{ °C}, T_2 = 35 \text{ °C} \text{ and } T_3 = 55 \text{ °C})$  the concentrations of solute in the solution at equilibrium  $(C_{\text{eq1}}, C_{\text{eq2}} \text{ and } C_{\text{eq3}})$  were estimated.

 $\Delta H$  was the mean value of three calculations for three pairs of different temperatures (i.e. 298–308, 308–328 and 328–298 K)

and found to be:  $\Delta H = -30.77 \text{ kcal mol}^{-1}$  for powder akaganéite approximately, and  $\Delta H = -6.14 \text{ kcal mol}^{-1}$  for the granular, hence both exothermic; which also can be taken rather as figures belonging to the range of chemisorption (usually the limit is  $\Delta H_{\text{sorption}} = 2-10 \text{ kcal mol}^{-1}$  for physical sorption).

The results for zinc desorption for the pH range 4–12 are given in Fig. 9, where  $R_{Ak}$ % represents the percentage of Zn<sup>2+</sup> remaining on the surface of akaganéite and  $R_S$ % the percentage of zinc eluted in the solution. It was observed that even at low (acidic) pH values about 65% of zinc can be eluted, so the sorbent could be regenerated and reused.

#### 3.2. Column experiments

Based on the earlier batch experiments and the respective findings, the column tests were planned (Fig. 10a); as the ionic strength had almost negligible effect, it was not examined. In practical cases, the operation of fixed-bed adsorbers is expressed graphically by the breakthrough curves concept [19]. The following equation (Eq. (9)) was proposed [22] to describe the BDST model:

$$t = \frac{q_0}{C_0 V} M - \frac{1}{kC_0} \ln\left(\frac{C_0}{C_t} - 1\right) = aM + b$$
(9)

![](_page_6_Figure_11.jpeg)

Fig. 12. (a) Fe 2p core level photoelectron spectra of anions and cations on akaganéite, (b) Fe 2p core level photoelectron spectra of anions and cations on akaganéite after Zn adsorption, (c) O 1s core level photoelectron spectra of anions and cations on akaganéite and (d) O 1s core level photoelectron spectra of anions and cations on akaganéite after Zn adsorption.

where *t* is the service time (min),  $q_0$  the adsorption capacity (mol g<sup>-1</sup>),  $C_0$  the initial concentration of adsorbate (mM), *V* the applied flow rate (L min<sup>-1</sup>), *M* the mass of sorbent inside the column (g), *k* the rate constant of adsorption (L min<sup>-1</sup> mol<sup>-1</sup>) and  $C_t$  the respective effluent concentration of adsorbate (mM) at time *t*. From the iso-removal lines, i.e. the plots of *t* versus *M* regarding column operation under constant experimental conditions (except a sorbent dosage), the main parameters of BDST equation can be calculated. From the slope (*a*) of the respective lines the adsorption capacity ( $q_0$ ) can be calculated, while from the intercept (*b*) the rate constant of adsorption (*k*) can be found.

In Fig. 10b the iso-removal lines, of bed service to the respective adsorbent quantity for sorption of 20, 35 and 50%, are presented following the BDST equation in order to model the column operation. From the breakthrough curves, it is concluded that the respective straight line at 50% breakthrough is passing through the origin, confirming the reliability of the BDST model. The advantage of the BDST model is that the necessary quantity of sorbent for a pre-selected service time period can be directly calculated until a desirable breakthrough concentration, using the obtained parameters from the respective linear equation (t = aM + b).

#### 3.3. XPS measurements

XPS measurements were obtained for the sample of akaganéite after the sorption of zinc. The spectra recorded were a wide scan and the lines Fe 2p, and O 1s. All of them had a +4 eV binding energy shift due to electrostatic charging. The energy correction was done by considering that the main C 1s peak should appear at binding energy 284.6 eV.

Fig. 11 presents the typical XPS wide scan spectra for akaganéite after Zn adsorption. It is clear that a new peak at the BE of about 1070 eV appeared after Zn adsorption, that can be attributed to divalent zinc. The presence of this peak provides evidence of Zn being chemisorbed on the surface of akaganéite.

The peak of iron (Fe 2p), for the sample of akaganéite after Zn adsorption, was located at a binding energy (BE) of 710.7 eV (Fig. 12b). According to the literature [3] at this energy the iron of FeOOH–Zn is detected. A chemical shift in the peaks of iron following zinc sorption and the corresponding recorded for pure akaganéite, i.e. 711 eV (Fig. 12a) showed that there was interaction of the metal with the substrate (sorbent).

The O 1s peak was detected at BE 529.9 eV corresponding to the oxygen of oxide, with a small shoulder at 531.5 eV corresponding to –OH groups (Fig. 12d). A chemical shift in the peaks of O 1s following zinc sorption and the corresponding recorded for pure akaganéite, i.e. 530 and 531.7 eV, respectively (Fig. 12c), showed again that there was an interaction of the metal with the substrate.

The current data indicated that during zinc sorption onto akaganéite electron transfer between the substrate and the adsorbate occurred leading to the conclusion that zinc was probably chemisorbed onto the surface of akaganéite.

Table 3 Comparison of certain zinc  $Q_{\text{max}}$  values for various sorbents

Q <sub>max</sub> (mg/g)	$Q_{\rm max}~({\rm mg/g}{\rm m}^2)$	Sorbent	Reference
35	0.106	Akaganéite	This paper
3	-	River bed sediment	[27]
21.09	0.153	Sea nodule residue	[28]
2.9	0.007	Clinoptilolite	[8]
1.6	0.002	Philipsite	[8]
7.8	0.007	Chabazite	[8]
3.9	0.012	Analcime	[8]
2.9	0.003	Bentonite	[8]
7.8	0.097	Modified	[11]
		montmorillonite	
1.2	0.47	Coal	[2]
29.4	-	Biosolids	[12]
30.7	-	Silico-antimonate ion exchanger	[29]

#### 4. Conclusions

The sorption of zinc ion, existing in the dilute aqueous solution as  $Zn^{2+}$ , was investigated onto akaganéite, in two formations of nanocrystal and granulated material.

The mechanism of removal seemed rather to be a weak chemisorption, based also on the kinetics, the XPS measurements and the small change of the heat of sorption. The increase of temperature has brought a small reduction in zinc removal and the phenomenon was exothermic. The ionic strength of the solution was not strongly affecting the process. Table 3 presents a brief list of the published maximum load of various zinc adsorbents, including the present studied. Akaganéite, as compared to the other sorbent materials, has high sorption capacity. The column results were not enough satisfying compared to the effectiveness previously observed for arsenate oxyanions. This may be due to the fact that more contact time than the available contact time in the column is needed for the chemisorption of zinc ion leading to the conclusion that sorption at 50% breakthrough is far from reaching the equilibrium stage.

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