

TOMASZ SUPONIK (ORCID: 0000-0002-4251-4275)<sup>1</sup>

CARMEN MIHAELA NECULITA (ORCID: 0000-0002-8388-7916)<sup>2</sup>

## REACTIVITY OF nZVI IN THE REMOVAL OF Cu(II) AND Zn(II) FROM SYNTHETIC MINE DRAINAGE

Adsorption properties, including isotherms and kinetics, of nano zero-valent iron (nZVI) for Cu(II) and Zn(II) removal from synthetic mine drainage were evaluated in batch tests. The influence of contact time, nZVI doses, pH, ionic strength, temperature, and concentration on nZVI adsorption properties was assessed. The removal of Cu(II) and Zn(II) increased with pH from 3 to 7 and then stabilized up to pH 10. Moreover, the increased Cu(II) adsorption capacity upon increasing temperature and a positive enthalpy change ( $\Delta H$ ) indicate that the adsorption process is endothermic. The results also showed that the adsorption equilibrium for Cu(II) and Zn(II) was achieved after 50 and 30 min, respectively. Kinetics were best described by a pseudo- $n$ th order model, with the order of sorption of 2.231 and 1.363, and the rate constants of 0.0008 and 0.0679  $\text{mg}^{1-n} \cdot \text{g}^{n-1} / \text{min}$ , for Cu(II) and Zn(II), respectively. The correlation between the amount of metals adsorbed on nZVI surface and the residual amount of metals in water during isothermal tests was best described by the nonlinear Sips model. Using this model, high  $q_{\text{max}S}$  were found: 286.6 mg/g and 142.6 mg/g, for Cu(II) and Zn(II), respectively, as indication of their high sorption capacity.

### 1. INTRODUCTION

Mining industry produces and handles high volume of waste materials, often disposed in dumps and tailings impoundment facilities. Exposure of these waste to weathering leads to contaminants leaching, including Zn(II) and Cu(II), into natural waters. The intensity of metal leaching varies due to climate change, which is often associated with long periods of drought, followed by short, intense precipitation. Depending on

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<sup>1</sup>Silesian University of Technology (SUT), Gliwice, Poland, corresponding author, e-mail address: Tomasz.Suponik@polsl.pl

<sup>2</sup>Canada Research Chair in Contaminated Mine Water Treatment, Research Institute on Mines and Environment (RIME), University of Quebec in Abitibi-Temiscamingue (UQAT), QC, Canada.

these changes, different methods of discharging surface runoff and leachate into the environment (i.e., different, variable drainage systems) and different methods of treating leachate and groundwater should be used.

To limit and control metal leaching, nano zero-valent iron (nZVI) can be used. The high efficiency of nZVI in contaminant removal from groundwater as well as from industrial wastewater is well established [1]. The advantages of using nZVI in the treatment of contaminated water over other reactive materials have been studied previously [2]. In addition, several nZVI production techniques and nZVI characteristics have been published elsewhere [3]. In Poland, where there are companies producing zinc and copper, leachate from dumps and tailing contain mainly Zn(II) and Cu(II), and nZVI can be used to remove these and other metals under various physicochemical and weather conditions.

The type of metal removed, the presence of other accompanying contaminants, and the physicochemical parameters of water influence the treatment efficiency. When referring to surface and groundwater contaminated by waste disposal sites, copper and zinc in the cationic form should be the priority, based on their toxicity and persistent properties. Copper is an essential trace element for living organisms, but its intake at high levels can cause detrimental health effects [4]. Cu(II) and Zn(II) ions have a toxic effect on humans and ecosystems [4].

Based on the Eh–pH diagrams, zinc exists in divalent ionic form in water at pH up to 8.5 [5]. Then, from pH 8.5 to about 11, Zn(OH)<sub>2</sub> and the cationic species such as Zn(OH)<sup>+</sup> are more common. Similarly, copper exists mainly in the form of Cu<sup>2+</sup> in water at pH up to 7 [6]. At pH from 7 to 9.5, cationic species such as Cu(OH)<sup>+</sup>, Cu<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>, and Cu<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup> dominate. At higher pH, Cu(OH)<sub>2</sub> and the anionic species such as Cu(OH)<sub>3</sub><sup>-</sup> and Cu(OH)<sub>4</sub><sup>2-</sup> are more common. Therefore, zinc and copper ions in the specified pH intervals are in the divalent form.

The application of ZVI to remove zinc and copper in their cationic forms from water has been investigated before [1, 4, 7, 8]. Some authors claim that the removal of heavy metals from water using ZVI takes place as a result of the adsorption of this reactive material onto the surface or iron corrosion products [8, 9]. On the contrary, other authors reported that the dominant mechanism for removing metal ions – with a standard potential very close to or more negative than that of iron – is sorption/surface complex formation [10]. The types of compounds precipitated on the ZVI surface as a result of the removal of metal ions from water were discussed earlier for Zn(II) [11] and Cu(II) [12].

In the present study, the adsorption properties of nZVI were investigated to provide the scientific and technical grounds for its using for the removal of Cu and Zn from leachate under various physicochemical and weather conditions. The influence of contact time, nZVI doses, pH, ionic strength, temperature, and concentration on nZVI adsorption properties was analyzed using batch tests.

## 2. MATERIALS AND METHODS

*Synthesis of nZVI.* nZVI particles were prepared by the reduction of ferrous iron Fe(II) to Fe(0). The preparation method was detailed elsewhere [13]. Sodium borohydride was used as a reducing agent [3]. Precisely, through titration at a rate of 1.0 cm<sup>3</sup>/s, the solution of 0.4 mol/dm<sup>3</sup> NaBH<sub>4</sub> was added to the 0.1 mol/dm<sup>3</sup> FeCl<sub>2</sub>×4H<sub>2</sub>O solution, at a volume ratio of 1:1. The resultant solution was mixed in a flask reactor with a stirrer at 120 rpm for an additional 30 min after the titration. The iron particles were then separated from the solution using vacuum filtration and stabilized with a large volume of deionized water (>100 cm<sup>3</sup>/g) to wash, and, in the end, with 100 cm<sup>3</sup> of diluted ethanol (~30%) once.

*Characterization of nZVI.* After drying, the nZVI was characterized for mineralogy, by X-ray diffraction (XRD), and for other characteristics, including grain size distribution and specific surface. The mineralogy was carried out using the PANalytical EMPYREAN multifunction X-ray diffractometer. The PDF4+ database was used to identify chemical compounds. For the grain size distribution, a laser granulometer (Malvern Nano S-90) was used. To determine the specific surface, the BET multi-point method was applied using Micromeritics Gemini 2360 surface area analyzer. The measurement principle was based on the nitrogen adsorption on the sample surface at a constant temperature of liquid nitrogen (77–78 K).

*Reactivity of nZVI – batch tests.* Several sets of laboratory experiments were performed in a parametric study on the efficiency of nZVI for Cu(II) and Zn(II) removal from water, including nZVI dosage ( $1.72 \times 10^{-5}$ – $6.90 \times 10^{-3}$  g/cm<sup>3</sup>), contact time (5–120 min), initial pH (3–10), temperature (from 11–29 °C), ionic strength (0.001–1 mol/dm<sup>3</sup> for NaCl) and initial concentrations of copper (4.5–161.3 mg/dm<sup>3</sup>) and zinc (4.0–192.5 mg/dm<sup>3</sup>). For all these tests, the synthetic mine drainage was prepared in advance. Copper and zinc ion solutions were prepared by dissolving the ACS purity metal salts (CuSO<sub>4</sub>×5H<sub>2</sub>O or ZnSO<sub>4</sub>×7H<sub>2</sub>O) in distilled water. The concentrations of metal in water varied depending on the experiment and were always higher than the Polish regulatory criteria according to Journal of Laws 2019 item 1311.

The tests were conducted using a programmable MULTI BIO RS-24 BIOSAN rotator equipped with plastic tubes filled with metal solution. Then, 0.01 g of nZVI was added into each solution. In the case of tests carried out for the different doses of nZVI, the mass of added varied as following: 0.001, 0.006, 0.01, 0.06, 0.1, and 0.4 g. To eliminate the headspace (a gaseous phase above the solution) the total volume of the sample in the tube amounted to 58 cm<sup>3</sup>. The doses of nZVI were:  $1.72 \times 10^{-5}$ ,  $1.03 \times 10^{-4}$ ,  $1.72 \times 10^{-4}$ ,  $1.03 \times 10^{-3}$ ,  $1.72 \times 10^{-3}$ ,  $6.90 \times 10^{-3}$  g/cm<sup>3</sup>, respectively. Except when the temperature effect was studied, all the experiments were carried out at a laboratory temperature of 23±2 °C. For each sample in the rotator (40 rpm), a 2 min orbital rotation was

applied followed by a 6 s reciprocal motion (with the turning angle of  $90^\circ$ ) with vibration. This sequence of shaking was repeatedly reiterated. The sequence continued for 120 min, except for kinetic measurements. In the kinetic tests, the sequences were continued for 5, 15, 30, 45, 60, and 120 min. The equilibrium shaking time was determined based on the adsorption kinetics studies. For the tests in which the initial pH was different, the pHs of the solutions were adjusted by slow titration with hydrochloric acid ( $0.01 \text{ mol/dm}^3$ ) or with sodium hydroxide ( $0.01 \text{ mol/dm}^3$ ), while investigating the effect of the increased ionic strength (IS) on adsorption, various NaCl doses were added to the water samples. The ionic strength ranged from 0.001 to  $1 \text{ mol/dm}^3$ . Except for these tests, all experiments were carried out at the initial pH 5.3 for Cu(II) solution and 5.8 for Zn(II) solution, and without the addition of sodium chloride.

After shaking the samples, the solutions were passed through a filter paper with the pore size of  $0.45 \mu\text{m}$  and then the residual solid phase was separated from liquid by centrifugation at 8000 rpm for 5 min. All experimental data were the average of duplicate determinations. The relative uncertainty of the data was 4%. Variations in the metal ion concentrations resulting from the use of nZVI were calculated from:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where:  $q_t$  is the amount of metal ions adsorbed by mass of nZVI ( $\text{mg/g}$ ),  $C_0$  is the initial concentration of metal ions in water ( $\text{mg/dm}^3$ ),  $C_t$  is the residual concentration of metal ions in water ( $\text{mg/dm}^3$ ),  $V$  is the volume of solution ( $\text{dm}^3$ ),  $m$  is the mass of nZVI used in the test (g).

To estimate the removal efficiency  $\eta$  of Cu(II) and Zn(II), the following equation was used:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

The equilibrium distribution coefficient ( $\text{dm}^3/\text{mg}$ ) was calculated from:

$$K_d = \frac{q_t}{C_t} \quad (3)$$

Three non-linear mathematical models were used in the study, i.e., Freundlich (eq. (4)), Langmuir (eq. (5)), and Sips models (eq. (6)).

$$q_{eq} = K_F C_{eq}^{1/n_F} \quad (4)$$

where:  $q_{eq}$  is the amount of metal ions adsorbed by the mass of nZVI at equilibrium ( $\text{mg/g}$ ),  $C_{eq}$  is the equilibrium concentration of metal ions in water after batch test

(mg/dm<sup>3</sup>),  $K_F$  is the Freundlich sorption equilibrium constant (mg/g)(dm<sup>3</sup>/mg)<sup>1/n</sup>,  $n_F$  is the Freundlich exponent.

$$q_{eq} = \frac{q_{\max L} K_L C_{eq}}{1 + K_L C_{eq}} \quad (5)$$

where:  $K_L$  is Langmuir equilibrium constant (dm<sup>3</sup>/mg),  $q_{\max L}$  is the maximum sorption capacity in the Langmuir model (mg/g).

Sips isotherm is a combination of the Langmuir and Freundlich isotherms and is calculated based on the following equation

$$q_{eq} = \frac{q_{\max S} K_S C_{eq}^{1/n_S}}{1 + K_S C_{eq}^{1/n_S}} \quad (6)$$

where:  $K_S$  is the Sips equilibrium constant (dm<sup>3</sup>/mg)<sup>1/n</sup>,  $q_{\max S}$  is the Sips maximum adsorption capacity (mg/g),  $n_S$  is the Sips model exponent.

To determine the time dependence of Cu(II) and Zn(II) removal, the pseudo-first (eq. (7)), pseudo-second (eq. (8)) and pseudo- $n$ th order (eq. (9)) nonlinear kinetic models were used

$$q_t = q_e (1 - \exp(-k_1 t)) \quad (7)$$

where:  $q_t$  and  $q_e$  are the amounts of metal (mg) adsorbed on nZVI (g) at time  $t$  (min) and at equilibrium, respectively (mg/g),  $k_1$  is the rate constant of the first order reaction (1/min);

$$q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \quad (8)$$

where:  $k_2$  is the rate constant of the second order reaction, g/mg·min.

$$q_t = q_e \frac{q_e}{(1 + (n-1) q_e^{n-1} k_n t)^{1/(n-1)}} \quad (9)$$

where:  $n$  is the reaction kinetic order,  $k_n$  is the rate constant of the  $n$ th order reaction (mg<sup>1-n</sup>·g<sup>n-1</sup>/min).

To assess the effect of temperature on the efficiency of metal removal from water, thermodynamic parameters such as enthalpy change ( $\Delta H^\circ$ , kJ/mol), entropy change  $\Delta S^\circ$ , J/(mol·K) and free energy change ( $\Delta G^\circ$ , kJ/mol) were calculated [14, 15] at four temperatures: 284, 291, 297 and 302 K. The following equations were used (for  $K_d$  see eq. (3)).

$$\Delta G^\circ = -RT \ln K_d \quad (10)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} = \frac{\Delta H^\circ}{RT} \quad (11)$$

where:  $R$  is the universal gas constant (8.314 J/(K·mol)),  $T$  is the temperature (K).

*Measurement methods.* During the tests, ca. 20 cm<sup>3</sup> of aliquot samples were collected and used for determining the following physicochemical parameters: pH, oxidation-reduction potential (ORP), temperature, and electrical conductivity ( $EC$ ). All these parameters were measured on unfiltered samples, by electrometric methods with the Knick PORTAMESS meters. Copper, zinc, and sulfate concentrations in water were determined using a UV-VIS DR5000 Hach Lange spectrophotometer.

### 3. RESULTS AND DISCUSSION

#### 3.1. CHARACTERISTICS OF nZVI

The diffraction pattern of nZVI is shown in Fig. 1a, while the grain size distribution is presented in Fig. 1b. Only iron in the metallic form was found on the surface of nZVI, and the size of the iron particles was between 30 nm and 400 nm, as an indication that they can form a colloidal suspension under appropriate conditions. These findings are consistent with those reported in a previous study, which found particles ranging from few nm up to 900 nm, with the average particle size around 60 nm [3].

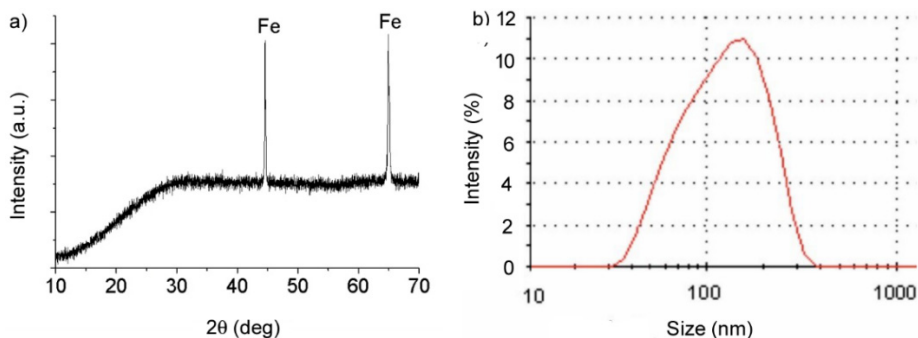


Fig. 1. Diffraction pattern of synthesized nZVI (a), and its grain size distribution (b)

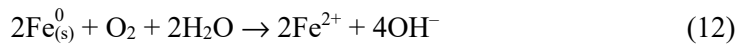
Based on the XRD pattern, a freshly prepared nZVI synthesized on the montmorillonite consisted mainly of Fe(0) (at a  $2\theta$  value of 44.9°) [16]. The nZVI showed very weak oxide signals in the XRD pattern, indicating that the material was mildly oxidized during preparation. In turn, the apparent peaks at the  $2\theta$  of 44.9° and 35.8° could indicate

the presence of both, ZVI ( $\alpha$ Fe) and iron oxide (FeO) crystalline phases [3]. The degree of oxidation of nZVI depends on the freshness of the sample.

The specific surface area of the nZVI synthesized was 15.5 m<sup>2</sup>/g. These findings are consistent with previously reported: 14.5 m<sup>2</sup>/g [3] and 20.0 m<sup>2</sup>/g [1]. In another study, the BET surface area for nZVI supported with kaolinite varied from 6.9 to 9.6 m<sup>2</sup>/g [17].

### 3.2. ADSORPTION PROPERTIES OF nZVI

The concentration of both metal ions in water decreased dynamically with the increase of the nZVI dose (Fig. 2a). This observation was especially obvious for low nZVI doses. The decrease in zinc concentration was slower as compared to copper. During the process, pH increased while ORP and *EC* decreased (Figs. 2b, c). These observations are similar to those in a previous study using grain-size iron [18]. In the present study, the oxidation of ZVI to ferrous (Fe<sup>2+</sup>) and ferric (Fe<sup>3+</sup>) iron caused an increase in pH, a decrease in ORP, the consumption of dissolved oxygen (DO) and generation of hydrogen:



The rate of hydrogen formation (eq. (13)) is much slower compared to the oxidation of Fe(0) with oxygen (eq. (12)) [19]. All changes were particularly noticeable for low doses of nZVI. In principle, the formation of hydroxide precipitates, such as Fe(OH)<sub>2</sub>, prevents the accumulation of OH<sup>-</sup> in solution by their consumption in the neutralization reaction of secondary or residual acidity generated by iron hydrolysis. This effect contributes to a self-regulating mechanism that maintains the pH at a stable level. In addition, the *EC* of the solutions decreased with increasing dose of nZVI, due to the increase in the pH value and the presence of DO in the solutions, probably leading to the formation of a precipitate.

The SO<sub>4</sub><sup>2-</sup> concentrations for both solutions also decreased gradually with increasing nZVI doses. To be noted that sulfate removal was not obvious in the case of granulated iron [11]. However, nano-Fe has a larger specific surface area than granulated iron. This can explain much better properties of nZVI for sulfate removal from water.

Determination of the kinetics of metal ions and sulfate uptake by nZVI is essential and necessary for modeling and designing the process on a larger scale. Adsorption of Cu(II), Zn(II), and SO<sub>4</sub><sup>2-</sup> on nZVI was tested at 10 different time intervals (Fig. 3). The results show that the adsorption equilibrium for Cu(II) and Zn(II) was achieved after about 50 and 30 min, respectively. Beyond this time, there was no further increase in adsorption. Adsorption of Cu(II) and Zn(II) was the fastest in the first 15 min of the process.

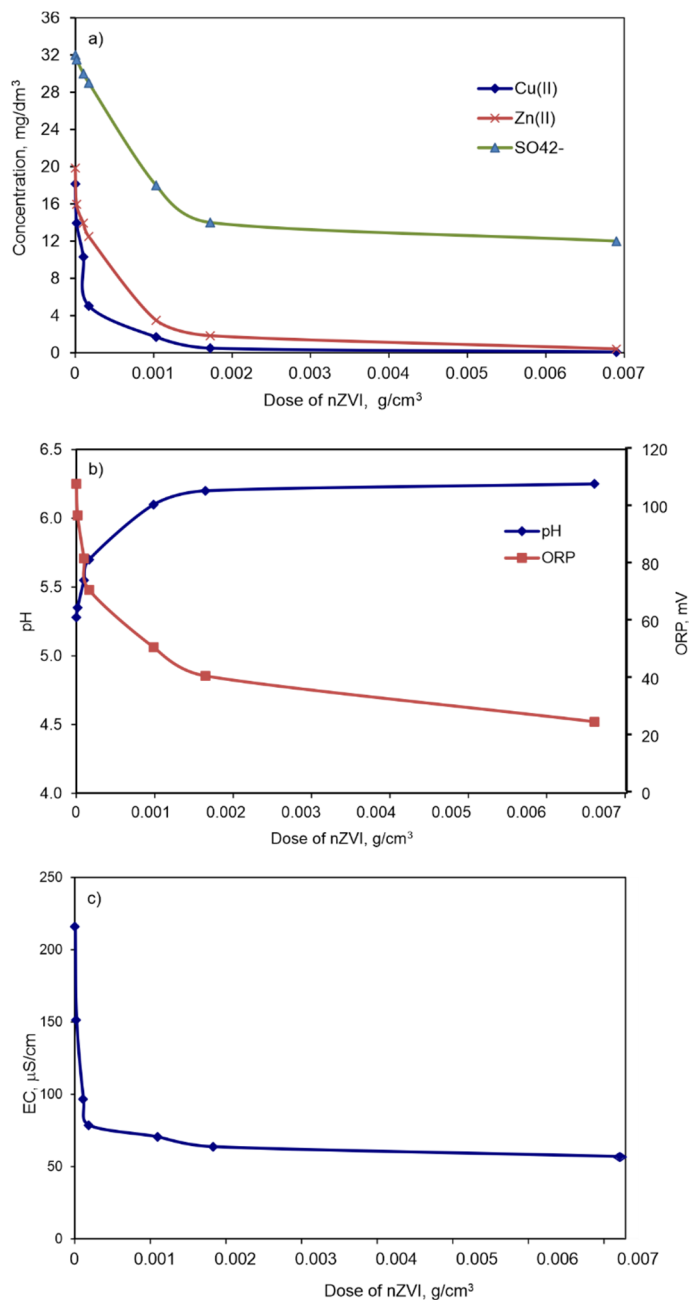


Fig. 2. Dependences of: a) concentration of Cu(II), Zn(II) and SO<sub>4</sub><sup>2-</sup>, b) pH, and c) EC on nZVI doses; process parameters: initial concentration of Cu(II), Zn(II) and SO<sub>4</sub><sup>2-</sup> 18.15, 19.85 and 32.0 mg/dm<sup>3</sup>, contact time 120 min, initial pH 5.3 for Cu(II) solution and 5.8 for Zn(II) solution, temperature 24 °C for Cu(II) solution and 22 °C for Zn(II) solution



Then, it slowly reached equilibrium. Within the first 15 min, all active sites on the surface of nZVI were probably free and the concentration of metals in the solution was high. Afterwards, few active sites remained available, and a slow increase in copper and zinc ions uptake was observed. Previously, sorption of Cu(II) on rapeseed meal modified with magnetite nanoparticles reached equilibrium after a longer time, of about 80 min [20]. In the case of sulfates (Fig. 3), it seems that the maximum adsorption capacity (and adsorption equilibrium) was not achieved and their uptake was slow.

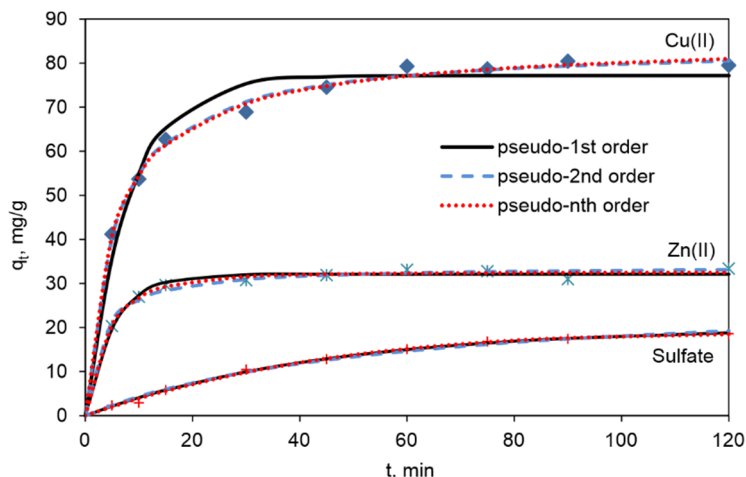


Fig. 3. Kinetics of Cu(II), Zn(II) and  $\text{SO}_4^{2-}$  sorption on nZVI;  $T$  20 °C, pH for Cu 5.3,  $C_{0(\text{Cu})} = 18.90 \text{ mg/dm}^3$ , pH for Zn 5.8,  $C_{0(\text{Zn})} = 19.45 \text{ mg/dm}^3$ , pH for sulfate 5.8,  $C_{0(\text{sulfate})} = 36 \text{ mg/dm}^3$

The rate constants ( $k_1$ ,  $k_2$ ,  $k_n$ ) and other parameters of the kinetic models, as well as the coefficients for pseudo-first, pseudo-second, and pseudo- $n$ th order models, are given in Table 1. The pseudo- $n$ th order model had the highest  $R^2$  value for all analyzed substances. The kinetic order of sorption determined based on this model for copper, zinc, and sulfate ions was 2.231, 1.363, and 0.746, respectively. As such, for sulfates, the reaction coefficient hardly changes over time, while that for copper is directly proportional to the square of concentration.

The amount of copper and zinc ions adsorbed on nZVI after reaching equilibrium for non-linear modeling using the  $n$ th-order model was 86.46 and 32.50 mg/g, respectively. The rate constants for Cu(II), Zn(II), and sulfate was 0.0008, 0.0679, and 0.0469  $\text{mg}^{1-n} \cdot \text{g}^{n-1} / \text{min}$ , respectively. The kinetic order of Cu(II) sorption, determined based on non-linear modeling using the  $n$ th order model, was previously reported 1.30 [20]. The rate constant for this model was 0.0121  $\text{mg}^{1-n} \cdot \text{g}^{n-1} / \text{min}$ . In another study, the kinetics of Cu(II) and Zn(II) removal by nZVI supported with bentonite were evaluated [21]. Using a pseudo-first order linear model at 35 °C, a lower rate of Zn(II) removal, as compared to Cu(II) was obtained. In the present study,  $k_1$  decreased from 0.1620 to 0.0568  $\text{min}^{-1}$  as the

initial Cu(II) concentration increased from 20 to 100 mg/dm<sup>3</sup>, and the equilibrium time increased from 15 to 20 min. In the case of Zn(II) removal,  $k_1$  decreased from 0.1427 to 0.0111 min<sup>-1</sup>, and the equilibrium time increased from 20 to 40 min.

Table 1

Parameters for kinetic models

Ions	Pseudo-first order			Pseudo-second order			Pseudo- $n$ th order			
	$k_1$ [1/min]	$q_{el}$ [mg/g]	$R^2$	$k_2$ [g/(mg·min)]	$q_{ell}$ [mg/g]	$R^2$	$k_n$ [mg <sup>1-n</sup> ·g <sup>n-1</sup> /min]	$q_{en}$ [mg/g]	$n$	$R^2$
Cu(II)	0.1245	77.14	0.9769	0.0022	84.14	0.9969	0.0008	86.46	2.231	0.9971
Zn(II)	0.1905	32.07	0.9982	0.0101	33.90	0.9980	0.0679	32.50	1.363	0.9988
SO <sub>4</sub> <sup>2-</sup>	0.0228	20.10	0.9998	0.0006	28.08	0.9997	0.0469	18.67	0.746	0.9999

The sorption capacity of nZVI increased dynamically for the initial concentration of metal ions in mine drainage from 4 to 80 mg/dm<sup>3</sup> (Fig. 4). Then, the capacity increased slower. In the case of sulfates, sorption capacity increased throughout the entire range of initial concentrations, i.e., from 10 to 200 mg/dm<sup>3</sup>.

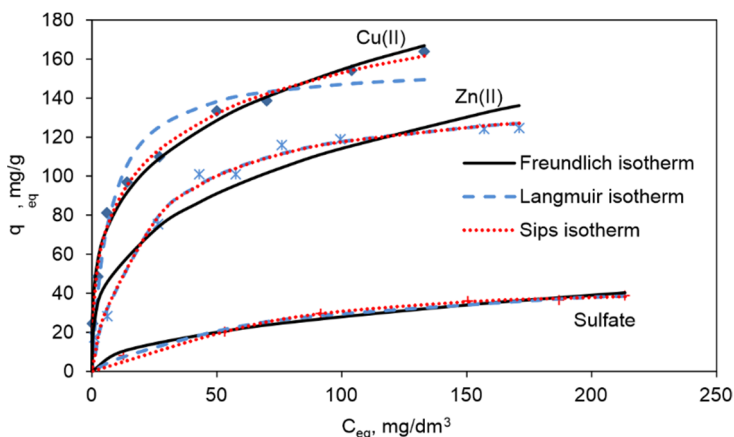


Fig. 4. Sorption equilibrium of Cu (II), Zn(II), and sulfate on nZVI;  
 $T$  23 °C, pH for Cu 5.3, pH for Zn 5.8, pH for sulfate 5.8

The high  $R^2$  values indicate that the results obtained correlate well with the selected equilibrium adsorption equations (Table 2). The Sips model has the highest  $R^2$  value for all substances tested (Table 2). It ranged from 0.9847 for Zn(II) to 0.9946 for sulfates.

High values of  $q_{maxS}$  in Sips's theory,  $q_{maxL}$  in Langmuir's theory, and  $K_F$  in Freundlich's theory indicate the high adsorption capacity of this material for the analyzed metal ions. These values were 286.6 mg/g, 157.2 mg/g, 45.32 (mg/g)·(dm<sup>3</sup>/mg)<sup>1/n</sup> for Cu(II), and 142.6 mg/g, 142.7 mg/g and 25.26 (mg/g)·(dm<sup>3</sup>/mg)<sup>1/n</sup> for Zn(II), respectively. Based on these data, it can be concluded that nZVI has better properties concerning Cu(II)

removal from water than Zn(II). For sulfate removal, these parameters were 42.16 mg/g, 52.3 mg/g, 3.08 (mg/g)·(dm<sup>3</sup>/mg)<sup>1/n</sup>, as an indication of low sorption capacity of iron concerning this substance.

Table 2

Adsorption isotherm parameters for nZVI used in the batch tests

Ions	Freundlich isotherm			Langmuir isotherm			Sips isotherm			
	$K_F$ [(mg/g)(dm <sup>3</sup> /mg) <sup>1/n</sup> ]	$n_F$	$R^2$	$K_L$ [dm <sup>3</sup> /mg]	$q_{maxL}$ [mg/g]	$R^2$	$K_S$ [dm <sup>3</sup> /mg] <sup>1/n</sup>	$q_{maxS}$ [mg/g]	$n_S$	$R^2$
Cu(II)	45.32	3.753	0.9857	0.1460	157.2	0.9399	0.1622	286.6	0.4246	0.9934
Zn(II)	25.26	3.052	0.9254	0.0471	142.7	0.9846	0.0473	142.6	1.0035	0.9847
SO <sub>4</sub> <sup>2-</sup>	3.08	2.086	0.9721	0.0131	52.3	0.9945	0.0011	42.1	1.7014	0.9946

For Cu(II) removal by rapeseed meal modified with magnetite nanoparticles, the same parameters were  $q_{maxS}$  63.1 mg/g,  $K_F$  17.98 (mg/g)·(dm<sup>3</sup>/mg)<sup>1/n</sup>, at 25 °C [20]. This indicates that nZVI has twice the Cu(II) removal capacity of the rapeseed meal. In another study, the sorption of Cu(II) on walnut shell supported by nZVI was evaluated [22]. The  $q_{maxL}$  and  $K_F$  at 20 °C were 398.4 mg/g and 199.8 (mg/g)·(dm<sup>3</sup>/mg)<sup>1/n</sup>, respectively, indicating that this material had higher Cu(II) capture capacity.

The feasibility of using carboxymethyl cellulose (CMC)-stabilized nZVI for the removal of Cu(II) from water was also assessed [23]. The Freundlich isotherm parameters for this material were  $K_F = 9.1559$  (mg/g)(dm<sup>3</sup>/mg)<sup>1/n</sup> and  $n = 3.042$  (equivalent to  $1/n = 0.329$ ). To be noted that  $1/n$  is a function of the force with which the metal ions are sorbed by the adsorbent. The lower the value  $1/n$  (towards zero), the greater the sorption intensity is. Since in the study,  $1/n$  for Cu(II) and Zn(II) was 0.266 and 0.328 (Table 2), respectively, the affinity of copper for nZVI is greater. It should be noted here that the ionic strength of solutions was small compared to natural water.

### 3.3. INFLUENCE OF pH, IONIC STRENGTH, AND TEMPERATURE ON THE ADSORPTION OF Cu(II) AND Zn(II) IONS

For most adsorbents, pH affects the removal of metal ions from water (Fig. 5). Moreover, pH had a greater influence on Cu(II) removal than on Zn(II). Removal of Cu(II) and Zn(II) increased with pH from 3 to 7 (in the case of Zn(II) up to 9) and then maintained at the same level with pH up to 10. The maximum removal of Cu(II) and Zn(II) by nZVI was observed under alkaline conditions. Under these conditions, nZVI has twice as much adsorption capacity for Cu(II) than for Zn(II).

The distribution of components between the dissolved and precipitated phases analyzed using Visual MINTEQ 3.1 showed that all analyzed components: Cu(II), Zn(II) and SO<sub>4</sub><sup>2-</sup> under applied conditions, were 100% dissolved and 0% precipitated. For example, for copper they were in the form of: Cu<sup>2+</sup>, CuSO<sub>4(aq)</sub>, SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> for pH 3.01 and CuOH<sup>+</sup>,

$\text{Cu}(\text{OH})_3^-$ ,  $\text{Cu}(\text{OH})_2$  (aq),  $\text{Cu}_2(\text{OH})_2^{2+}$ ,  $\text{Cu}_3(\text{OH})_4^{2+}$  and  $\text{SO}_4^{2-}$  for pH 10.07, while for zinc:  $\text{Zn}^{2+}$ ,  $\text{ZnSO}_4$  (aq),  $\text{Zn}(\text{SO}_4)_2^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$  for pH 3.07 and  $\text{Zn}(\text{OH})_2$  (aq),  $\text{Zn}(\text{OH})_3^-$ ,  $\text{ZnOH}^+$  and  $\text{SO}_4^{2-}$  for pH 10.39. This proves that the removal of metals (Cu(II) and Zn(II)) from water under the analyzed conditions was caused by sorption on nZVI.

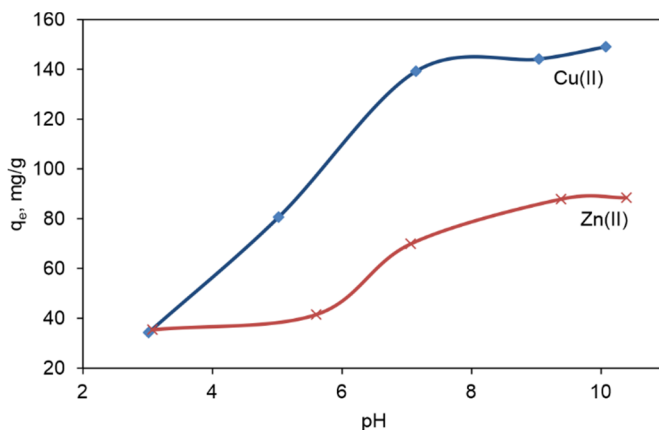
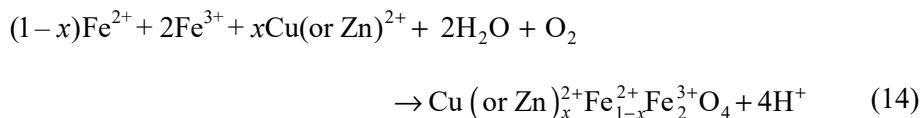


Fig. 5. pH dependences of Cu(II) and Zn(II) adsorption on Nzvi; nZVI dosage  $1.72 \times 10^{-4}$  g/cm<sup>3</sup>,  $C_{0(\text{Cu})}$  19 mg/dm<sup>3</sup>,  $C_{0(\text{Zn})}$  20 mg/dm<sup>3</sup>, contact time 120 min, temperature 21 °C

The formation of copper in its metallic form and of CuO are the basic processes of Cu(II) removal from water at low pH (pH 3), while under circum-neutral solution magnetite was probably formed: copper replaced iron creating  $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$  (where  $x \leq 1$ , eq. (14)) and, to a lesser degree,  $\text{Cu}_2\text{O}$ ,  $\text{Cu}^0$  and/or  $\text{CuO}$  and/or  $\text{Cu}_2\text{S}$  [12]. In the case of deoxygenated acidic conditions in water and for nZVI in the presence of kaolinite clay,  $\text{Cu}^0$  and  $\text{Cu}_2\text{O}$  have been formed on the surface of iron [4, 17]. Moreover, these results were confirmed for pure nZVI, with which Cu(II) ions were removed mainly via a redox mechanism that resulted in the formation of  $\text{Cu}_2\text{O}$  and  $\text{Cu}^0$  [6]



For the removal of Zn(II) from water,  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  (where  $x \leq 1$ , eq. (14)) was the main compound generated on nZVI over a wide range of pH (4.5–9.5) [11]. The formation of magnetite (in its pure form) was previously investigated [6, 24]. The latter has noted a slow development of iron oxides, primarily in the forms of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ . Kishimoto et al. [7] reported that the iron hydroxide formed in earlier stages was finally oxidized and transformed into iron oxides.

Ionic strength affects Cu(II) adsorption on nZVI, while having a slight effect on the effectiveness of Zn(II) removal (Fig. 6). The adsorption decreases with NaCl concentration increases from 0.001 to 1.0 mol/dm<sup>3</sup>, suggesting that Na<sup>+</sup> greatly affects Cu(II) adsorption. The amount of copper adsorbed on nZVI ( $q_{eq}$ ) decreased from 80 mg/g for 0.001 mol/dm<sup>3</sup> of NaCl additive to 20 mg/g when the concentration of NaCl was 1.0 mol/dm<sup>3</sup>. For the same NaCl concentration,  $q_{eq}$  for Zn(II) removal decreased from 30 to 15 mg/g.

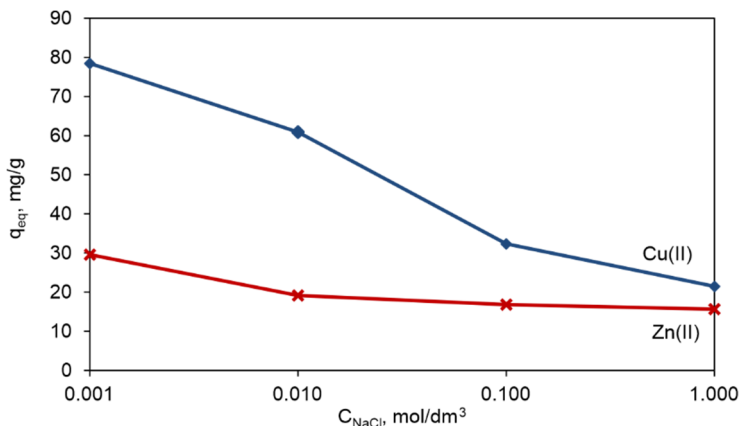


Fig. 6. Dependences of Cu(II) and Zn(II) adsorption on nZVI on ionic strength; nZVI dosage  $1.72 \times 10^{-4}$  g/cm<sup>3</sup>,  $C_{0(Cu)}$  18 mg/dm<sup>3</sup>,  $C_{0(Zn)}$  20 mg/dm<sup>3</sup>, contact time = 120 min, temperature 20 °C, initial pH = 5.3 for Cu(II) solution and 5.8 for Zn(II) solution

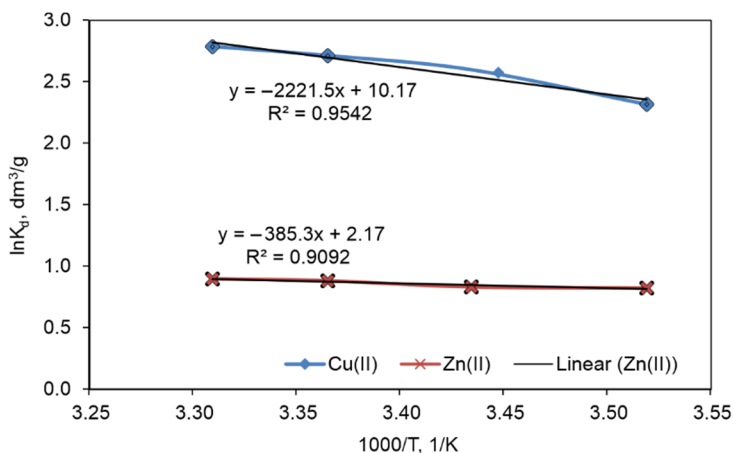


Fig. 7. Temperature dependences of Cu(II) and Zn(II) adsorption on nZVI;  $C_0$  20 mg/dm<sup>3</sup>, nZVI dosage  $1.72 \times 10^{-4}$  g/cm<sup>3</sup>,  $C_{0(Cu)}$  19 mg/dm<sup>3</sup>,  $C_{0(Zn)}$  20 mg/dm<sup>3</sup>, contact time 120 min, initial pH 5.3 for Cu(II) solution and 5.8 for Zn(II) solution

The Cu(II) adsorption capacity increased with the increasing temperature in the solution (Fig. 7). This suggests that the adsorption process is endothermic. At the same

time, Zn(II) uptake is almost independent of temperature. The thermodynamic parameters (enthalpy change ( $\Delta H^\circ$ ), entropy change ( $\Delta S^\circ$ ) and free energy change ( $\Delta G^\circ$ )), which were calculated by using the equations (3), (10) and (11) and the linear functions (Fig. 7) are presented in Table 3. Positive  $\Delta H^\circ$  values for both metals show that Cu(II) and Zn(II) adsorption processes on nZVI are endothermic, while negative  $\Delta G^\circ$  indicates that they are spontaneous in the analyzed temperatures.

The adsorption of Zn(II) and Pb(II) on montmorillonite supported nZVI was found favored for Zn(II) over Pb(II), under the same conditions [16]. The authors interpreted the negative  $\Delta G^\circ$  and  $\Delta H^\circ$  as an indication of a spontaneous and exothermic adsorption process.

Table 3

Thermodynamic parameters of Cu(II) and Zn(II) adsorption on nZVI

Ions	$\Delta H^\circ$ [kJ/mol]	$\Delta S^\circ$ [J/(mol·K)]	$\Delta G^\circ$ [kJ/mol]			
			284 K	291 K	297 K	302 K
Cu(II)	18.47	84.55	-5.47	-6.28	-6.69	-6.99
Zn(II)	3.20	18.03	-1.94	-2.01	-2.17	-2.25

#### 4. CONCLUSION

In the presented study, the parameters of Cu(II) and Zn(II) removal from synthetic mine drainage using nano zero-valent iron were determined to characterize the treatment process. These parameters are to be used as input data for the hydrodynamic and hydrochemical model of the aquifer under the coal waste dump to assess the effectiveness of removing ionic metals from leachate and polluted groundwater under climate change conditions, mainly with higher and lower precipitation.

The nZVI showed high adsorption capacity in removal of tested metal ions from contaminated water. The maximum adsorption capacity ( $q_{max}$ ) for Cu(II) and Zn(II) was 286.6 mg/g and 142.6 mg/g, respectively. The adsorption process was spontaneous, endothermic, and relatively fast at the tested temperatures and concentrations. The equilibrium time was 30 min and 50 min for Zn (II) and Cu (II), respectively. pH and ionic strength affect the removal of metal ions from water, and have a greater effect on Cu(II) uptake than on Zn(II). Based on these results, nZVI has better removal efficiency for Cu(II) than for Zn(II). Finally, this material seems promising enough for metal removal from leachate and polluted groundwater of mining waste dumps.

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