The sorption of metal ions on nanoscale zero-valent iron

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Abstract. The injection of the colloidal suspensions of nano-iron (nZVI) into an aquifer is a novel method of removing metal ions from acidic water. In the batch tests, the equilibrium study of the sorption of metal ions, Cu(II) and Zn(II), on Green Tea nanoscale Zero-Valent Ion (GT-nZVI) was carried out. The sorption of metal ions on this reactive material was described using the Langmuir, Freundlich and Sips models. This last model described in a better way the sorption equilibrium in the tested range of concentrations and temperature. The value of determination coefficient (R^2) for the Sips model, for copper and zinc, was 0.9735 to 0.9995, respectively. GT-nZVI has very good properties in removing Cu(II) and Zn(II) from acidic water. The high values of $qmax_S$, the maximum adsorption capacity in the Sips model, amounting to 348.0 and 267.3 mg/g for Cu(II) and Zn(II), indicate the high adsorption capacity of GT-nZVI. The analyzed metals have good or very good affinity with GT-nZVI.

1 Introduction

Waste materials resulting from the mining of non-ferrous metal ores and hard coal, as well as from the manufacturing process of non-ferrous metals, accumulated at industrial waste disposal sites contain metal minerals and, as a result, may affect the quality of ground and surface water in the southern areas of Poland. The leachate from these places may contain various toxic metals which may cause a risk to the environment.

In order to protect ground and surface water from leachates containing metal contaminants the suspension of nano-ZVI may be injected into contaminated aquifer [1]. In the study, the nanoscale zero-valent iron was obtained by reducing Fe(II) with a solution of green tea (GT). The polyphenols were responsible for the reduction properties of this tea [2]. GT is an effective, cheap and environmentally friendly alternative to other ways of obtaining nZVI. In accordance with Hoag et al. [3] the polyphenolic matrix can act as a capping agent that protects the iron nanoparticles from premature oxidation. In this way, the effect of removing metal ions by zero-valent iron can be intensified by biosorption on the coating of polyphenolic compounds. Biosorption on them is the process of selectively binding compounds (e.g. metal ions) on the surface of biological material by the presence of specific functional groups. The quality and quantity of these groups is not the same for each biosorbent. Therefore, the binding mechanism of the selected compounds is different. It may be based on physical adsorption, chelation [4], complexation, micro precipitation or ion exchange [5].

The processes of the removal of metal ions from water (directly) on Fe(0) are: reductive precipitation that lead to the metallic form, co-precipitation with iron in the form of oxides and/or hydroxides, precipitation as a result of an increase in pH and adsorption on the surface of iron corrosion products [6]. The type of processes depends on the type of metal removed, the other accompanying substances and the physicochemical conditions in the ZVI bed, mainly the pH of the water.

The aim of the study was to assess the equilibrium sorption of metal ions, Cu(II) and Zn(II), on GT-nZVI. The equilibrium of these processes were described using the Langmuir, Freundlich and Sips models.

2 Materials and methods

2.1 Synthesis of GT-nZVI

Nanoscale zero-valent iron particles was prepared in aqueous solutions by way of the reduction of ferrous iron Fe(II) using a solution of green tea (GT). The method was inspired by article written by Mystrioti et al. [7]. A method of preparing the suspension of green tea nanoscale zero-valent iron GT-nZVI was presented in the papers [1, 7, 8]. The 1:2 volume ratio of the GT solution to the Fe(II) solution were vigorously mixed in a flask reactor (see Fig. 1) at room temperature for an additional 15 minutes after the titration of GT. The solutions in the flask were mixed with a mechanical stirrer at 120 rpm. Through titration at a rate of 1.0 cm^3/s, the solution of GT was introduced to reduce ferrous ions to zero-valent iron Fe(0).

The Loyd brand of green tea was the source of polyphenolic compounds. An immersion of dry green tea in deionized water at a temperature of 80-90ºC for 30 minutes, was the way of preparing the solution. It was filtered with the vacuum filtration, using a filter paper of 0.45 μm pore size. The ratio of green tea leaves to deionized water, amounted to 1g/50ml, while the ratio of

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$FeCl_2 \cdot 4H_2O$ to deionized water was 1.35g/50ml. $FeCl_2x4H_2O$ was dissolved in deionised water and stirred under strong ultrasonic agitation a short time before introducing the GT solution [1].

The pH, conductivity and oxidation-reduction potential (ORP) in the GT-nZVI suspensions were 1.73, 10.7 mS/cm and 499 mV, respectively.
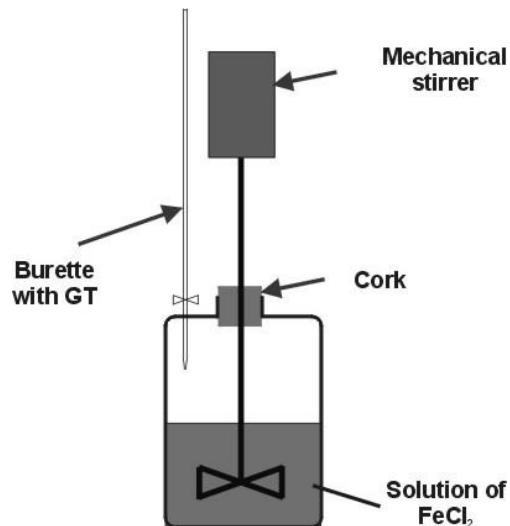

Fig. 1. Laboratory set-up for GT-nZVI synthesis [1].

2.2 Characteristics of the batch test

The several of experiments were done to study the capability of GT-nZVI in the removal of Cu(II) and Zn(II) from water in different initial concentrations of metals. For all these tests, the wastewater was prepared before. Metal ion solutions (copper, zinc) were prepared by dissolving the appropriate metal salts ($CuSO_4x5H_2O$, $ZnSO_4x7H_2O$) in distilled water. Always only one metal salts was dissolved in water. The concentrations of metal in the solutions were always higher than the allowable concentration of individual metals, within the meaning of legal regulations provided in the Journal of Laws, 2014, item 1800. The concentrations were in the ranges of 10 - 500 mg/dm³, while the pHs for the solution of copper, zinc were 4.7, 5.3, respectively.

The tests were conducted in a programmable MULTI BIO RS-24 BIOSAN rotator equipped with plastic tubes filled with metal solution. Then the 0.5 ml of GT-nZVI was added into each of the solution. The 0.5 ml of suspension corresponds to 0.0067 g of dry matter obtained after the evaporation of water. This mass was used, as a mass of GT-nZVI, for calculations of the parameters of isotherms. However, this material is not consistent with the amount of GT-nZVI. The mass of iron is much lower. Using a lower weight, the sorption capacity of GT-nZVI would be much higher. In accordance with Mystrioti et al. [8], it was found that only ca. 27% of the total Fe was reduced to its elemental state. Namely, the produced GT-nZVI suspensions contained approximately 1.3 g/dm³ of Fe in the form of nZVI solid particles and 3.7 g/dm³ in the form of Fe(II) aqueous ions.

In order to eliminate the headspace (a gaseous phase above the solution) the total volume of the sample in the tube amounted to 58 cm³. All these experiments were carried out in a laboratory temperature of 22ºC±2 ºC.

A two-minute orbital rotation was applied for each sample in the rotator (40 rpm), after which a six-second reciprocal motion (with a turning angle equal to 90°) with vibration followed. This sequence of shaking was repeatedly reiterated. The sequence continued for 120 minutes.

2.3 Measurement methods

After shaking the samples, the solutions were passed through filter paper of 0.45 μm pore size and assessed. The temperature, pH, the redox potential and the electrolytic conductivity were determined using electrometric methods (with the following meters: PORTAMESS 913 pH with a SenTix 41 combination electrode; PORTAMESS 913 pH with a POLYPLAST ORP electrode; PORTAMESS 913 Cound). Also, the following determinations were made with regards to water:
- concentrations of Cu_{tot}: Spectrophotometer DR5000 HachLange by the bicinchoninate method (method 8506 of Hach Co.), at wavelength 560 nm,
- concentrations of Zn_{tot}: Spectrophotometer DR5000 HachLange by the Zincon method (method 8009 of Hach Co.), at wavelength 620 nm,
- concentrations of SO_4^{2-}: Spectrophotometer DR5000 HachLange by the SulfaVer 4 method (method 8051 of Hach Co.) at wavelength 450 nm.

The measurements were carried out four times. The results were calculated as an arithmetic mean.

2.4 Mathematical description

The changes in the concentration of metal ions as a result of the use of GT-nZVI were calculated in accordance with the equation:

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

where :
q_t – the amount of metal ions adsorbed by the mass of nZVI, mg/g,
C_0 – the concentration of metal ions in water before the batch test, mg/dm³,
C_t the concentration of metal ions in the water after 120 minutes, mg/dm³,
V – the volume of solution, dm³,
m – the mass of nZVI used in the test, g.

In order to determine the correlation between the amount of metals adsorbed on the surface of GT-nZVI and the amount of metals remaining in the solution, the three nonlinear mathematical models were used being the Freundlich (eq. 2) [9] and Langmuir (eq.3) [10] and Sips models.

$$q_{eq} = K_f \cdot C_{eq}^{\frac{1}{n_f}} \qquad (2)$$

where :

q_{eq} – amount of metal ions adsorbed by the mass of nZVI at equilibrium, mg/g,

C_{eq} – the equilibrium concentration of metal ions in water after batch test, mg/dm^3,

K_f – Freundlich sorption equilibrium constant, (mg/g)(dm^3/mg)$^{1/n}$,

n_f – Freundlich exponent.

$$q_{eq} = \frac{q_{maxL} \cdot K_L \cdot C_{eq}}{1 + K_L \cdot C_{eq}} \qquad (3)$$

where :

K_L – Langmuir equilibrium constant, dm^3/mg,

q_{maxL} – maximum sorption capacity in the Langmuir model, mg/g.

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms and is given in the form [11].

$$q_{eq} = \frac{q_{maxS} \cdot K_S \cdot C_{eq}^{\frac{1}{n_S}}}{1 + K_S \cdot C_{eq}^{\frac{1}{n_S}}} \qquad (4)$$

where :

K_S – the Sips equilibrium constant, (dm^3/mg)$^{1/n}$,

q_{maxS} – the Sips maximum adsorption capacity, mg/g,

n_S – the Sips model exponent.

3 Results and discussion

For the GT-nZVI, the sorption isotherms of metal ions were determined as a function of their concentration. Figures 2, 3 show isotherms for Cu(II), Zn(II), respectively. As was presented in these Figures, the sorption capacity of GT-nZVI increased for the initial concentration of metal ions in the solution in the range of 10 to 100 mg/dm^3. Then the capacity grew much slower.

The obtained results correlate well with the selected equations of adsorption equilibrium (see Table 1). This is evidenced by the high or very high values of R^2. The higher values of R2 in the Sips model, for the both of metals, indicate the best suitability fitting to the results of the experiments. These were 0.9735 and 0.9995, for copper and zinc, respectively.
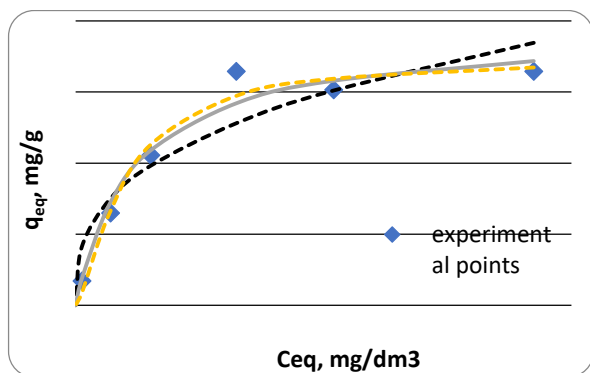

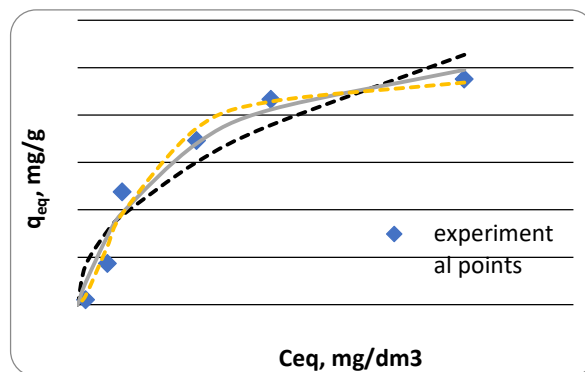**Fig. 2.** Equilibrium of the sorption of Cu (II) on GT-nZVI.

Fig. 3. Equilibrium of the sorption of Zn(II) on GT-nZVI.

Based on the data presented in the table 1, it can also be said that GT-nZVI has very good properties in removing copper and zinc from water.

The high values of qmax$_L$, in Langmuir's theory, qmax$_S$, in Sip's theory, and Kf, in Freundlich's theory, indicate the high adsorption capacity of this material for all analyzed metal ions.

These values were 387.4 mg/g, 348.0 mg/g, 43.33 (mg/g)(dm^3/mg)$^{1/n}$, for Cu(II), and 305.2 mg/g, 267.3 mg/g and 45.64 (mg/g)(dm^3/mg)$^{1/n}$, for Zn(II). It should be noted here that ionic strength of solutions was small compared to natural waters.

1/n is a function of the force with which the metal ions are sorbed by the adsorbent. The lower the 1/n (towards zero), the greater the affinity of the substance.

For both tested metals, the value of 1/n below 1 indicates a normal Sips isotherm and Freundlich isotherm, and the adsorption becomes more heterogeneous as the value of 1/n gets closer to zero.

Yang et al. [12] studied also the sorption of copper on adsorbent. This was the walnut shell supported nanoscale zero-valent iron. It was prepared from sodium borohydride, iron(II) chloride tetrahydrate, and walnut shell by liquid phase chemical reduction.

The values of q$_{maxL}$ and K$_L$, in the Langmuir model, and K$_f$ and 1/n$_f$, in the Freundlich model, were, in the study of Yang et al. [12], 398.4 mg/g, 0.029dm^3/mg and 199.8 (mg/g)(dm^3/mg)$^{1/n}$, 0.084, at ca. 20°C. These values are of similar magnitude as was obtained with the use of GT-nZVI.

Another study on the sorption of copper on iron was presented by Ayob et al. [13]. They investigated the feasibility of using carboxylmethyl cellulose (CMC)-stabilized nano zero valent iron (nZVI) particles for immobilization of Cu2+ in water. The parameters of Freundlich's isotherm for this material were K$_f$ = 9.1559 (mg/g)(dm^3/mg)$^{1/n}$ and n = 3.042.

In conclusion, it can be said that nano-iron has very good properties in the removal of metal ions from water. The process of water purification by Fe (0) was probably intensified by biosorption on the coating of polyphenolic compounds. This may be evidenced by the fact that the concentration of sulphates (see Table 2) also decreased, unlike the observations presented in the paper [14]. The parameters such as pH and ORP (see Table 2) were varied in the same way as in the case of Fe(0) in the form of fine grain steel [14] or in the form of rector with steel sheets

positioned in parallel inside. This is proof that Fe(0) itself is reactive.

However, the changes in the values of pH, ORP and sulphate concentrations were very small, because a small amount of GT-nZVI was added to the solutions.

Table 1. The equilibrium parameters of sorption obtained from the Freundlich, Langmuir and Sips isotherms.

The type of metal removed from the solution	Freundlich			Langmuir			Sips			
	K_f (mg/g) $(dm^3/mg)^{1/n}$	n_r	R^2	K_L dm^3/mg	q_{maxL} mg/g	R^2	K_S $(dm^3/mg)^{1/n}$	q_{maxS} mg/g	n_S	R^2
Cu(II)	43.33	2.864	0.8645	0.0170	387.4	0.9637	0.0037	348.0	1.434	0.9735
Zn(II)	45.64	3.218	0.7965	0.0264	305.2	0.9567	0.0010	267.3	2.006	0.9995

Table 2. The change in the value of pH, ORP and sulphate concentrations according to initial metal ions concentration. The positive value means an increase after batch tests, while negative a decrease. The table presents the average values for the analyzed parameters/substances.

Parameter /substance	The change in the value of the parameter/substance for the initial concentration of metal ions:					
	10 mg/dm³	50 mg/dm³	100 mg/dm³	200 mg/dm³	300 mg/dm³	500 mg/dm³
pH	+0.11	+0.10	+0.06	+0.03	+0.01	0.01
ORP, mV	-24	-21	-18	-12	-11	-4
SO_4^{2-}, mg/dm³	-36	-48	-61	-88	-92	-110

4 Conclusion

This study has shown that GT-nZVI is a good material for removing metal ions from acid mine water. This is determined by:

- the very good sorption capacity of GT-nZVI - In Sips model, the q_{maxS}, were 348.0 and 267.3 mg/g, for copper and zinc, respectively,

- the good affinity of copper and zinc with GT-nZVI - The low value of 1/n, in the Sips theory, amounting to 0.697 and 0.499 for copper and zinc, respectively,

- the dual action of F(0) and biosorbent - The process of water purification by Fe(0) was probably intensified by biosorption on the coating of polyphenolic compounds,

- the size of GT-nZVI and other properties – This material has a large surface area, is inexpensive to use, compared with other reactive materials, and environmentally friendly and, if kept stable, can spread without clogging the pores of the aquifer.

The obtained results of experiments correlate the best with the Sips theory. The determination coefficient (R^2) was 0.9735 and 0.9995 for copper and zinc, respectively.

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