

# Reactivity of nano zero-valent iron in permeable reactive barriers

Katarzyna Pawluk\*, Joanna Fronczyk, Kazimierz Garbulewski

Warsaw University of Life Sciences – SGGW, Faculty of Civil and Environment Engineering, Nowoursynowska 159, 02-773 Warsaw, Poland

\*Corresponding author: e-mail: katarzyna\_pawluk@sggw.pl

In this paper, the ability of nZVI to remove heavy metals (Cd, Cu, Ni, Pb, Zn) from multicomponent aqueous solutions was investigated through batch experiments. The experimental data were fitted to a second-order kinetic model based on solid capacity. The data for copper and lead fitted well into the second-order kinetic model, thus suggesting that the adsorption had a physical character. The values of the removal ratio and the second-order rate constant indicated that the order of adsorption priority of nZVI was as follows:  $Pb > Cu > Zn > Cd > Ni$ . The adsorption isotherm data were described by the most conventional models (Henry, Freundlich, and Langmuir). Equilibrium tests showed that copper and zinc were removed from the solution by adsorption processes, i.e., complexation and competitive adsorption. The test results suggested that the removal processes using nZVI are more kinetic than equilibrium. The study demonstrated that nZVI is favorable reactive material; however, comprehensive investigation should be performed for further *in situ* applications in PRB technology.

**Keywords:** contaminated groundwater, permeable reactive barrier, nano zero-valent iron, reactivity.

## INTRODUCTION

To design a permeable reactive barrier (PRB), the characterization of contaminants and groundwater conditions is required. Contaminants and groundwater parametrization are important for the appropriate choice of reactive materials that fill the treatment zone of the PRB. In PRB technology, the capacity of reactive materials in natural attenuation processes (sorption, redox, precipitation, and biodegradation) is a crucial parameter in the selection of suitable materials<sup>1, 2</sup>. Moreover, the intensity of these processes closely correlates with the velocity of groundwater flow through the PRB. A well-designed PRB should be a chemical barrier for pollutants. This means that the PRB should effectively reduce the concentration of pollutants but not change groundwater flow conditions.

Heavy metals, which are the common contaminants in groundwater, are emitted from industrial plants, municipal waste disposal sites, vehicle transport, etc.<sup>3</sup>. In practice, several methods for removing heavy metals are applied: chemical precipitation<sup>4, 5</sup>, ion exchange<sup>6</sup>, electrolytic processes<sup>7</sup>, adsorption<sup>8, 9, 10</sup>, reverse osmosis, and membrane processes<sup>11, 12</sup>. PRB technology is one of the low-cost methods introduced in the last decade for groundwater remediation<sup>13</sup>. Nowadays, numerous reactive materials have been used in the treatment zone of PRBs, e.g., zero-valent iron, activated carbon, zeolite, and organic matter<sup>14, 15</sup>. Nanoscale zero-valent iron (nZVI), which comprises submicrometer particles of iron metal, has also been used in PRB. nZVI has a number of advantages compared to granular ZVI: greater surface area and the possibility of more rapid contaminants degradation. nZVI has been demonstrated to be effective for the treatment of both organic compounds (TCE, PCE, DCE, and VC) and inorganic contaminants (heavy metals)<sup>16, 17</sup>.

The aim of this study is to evaluate the ability of nZVI in removing heavy metals from multicomponent solutions. Recently, more and more experiments involving batch tests have been carried out with multicomponent solutions that (in contrast to the one-component solution)

better reflect conditions seen in the environment<sup>18–21</sup>. The objective is to investigate the adsorption kinetics and isotherm models of removing Cd, Cu, Ni, Pb, and Zn in acid environment conditions. Batch tests may be used to develop an understanding of reaction pathways and the mechanism of sorption reactions. The preliminary test results including kinetic and equilibrium data demonstrate that nano zero-valent iron may be recommended for environmental protection using PRB technology.

## EXPERIMENTAL

### Material

In this study, nano zero-valent iron powder (nZVI) was used as the reactive medium. nZVI with the specific surface ( $S_{BET}$ ) equal to 2.1 m<sup>2</sup>/g and specific gravity equal to 7.8 was purchased from Hepurtechnologies (USA).

### Multicomponent aquatic solution

All experiments were performed using dilute simulated waste water, which was prepared using analytical reagents of cadmium, copper, nickel, lead, and zinc (CHEMPUR, Poland). Chloride ions (150 mg/L) were added to the analytical solution. The initial pH ( $pH = 4.0 \pm 0.2$ ) of the aquatic solutions was adjusted with 1M HCL/1M NaOH using a pH meter (SCHOTT, Germany). The initial electrical conductivity of the solution was 31 mS/cm; the oxygen reduction potential (ORP) was 313 mV.

### Kinetic and equilibrium tests

Batch kinetic tests were conducted as follows: in the first stage, 2.0 g of nZVI was added to 100 mL of solution (PE flask) with a constant concentration of heavy metals (30 mg/L); in the second stage, the flasks were sealed and placed in a rotary shaker at 15 rpm (GFL, Germany) at room temperature of  $21 \pm 2^\circ\text{C}$ . To determine the equilibrium time, the contents of flasks were agitated until the concentrations of metal ions were measured following 1, 3, 6, 10, 24 and 48 hours.

For the batch equilibrium tests, a given amount of nZVI, i.e., 2.0 g, was used. The initial concentrations of

heavy metals ranged from 0 to 110 mg/L. All samples were agitated for 48 hours. In order to minimize inaccuracy, this research used aqueous solutions without adsorbents as control samples as well as conducted double-blind (distilled water with adsorbent) tests.

pH, temperature, electrical conductivity and ORP were measured using a digital meter (SCHOTT Instruments GmbH, Germany) at the beginning and the end of experiments. The final concentration of the aquatic solutions was analyzed using an Atomic Adsorption Spectrometer ICP – AAS (Thermo Scientific, USA).

The removal ratio  $R$  (%) of metal by nZVI was calculated using the equation:

$$R (\%) = (C_0 - C)100 / C_0 \quad (1)$$

where:  $C_0$  and  $C$  are the initial and final metal concentrations (mg/L).

The data for the kinetic tests were analyzed using the first (equation 2) and the second order (equation 3) models as follows:

$$C_s = C_0 \exp(-k_1 t) \quad (2)$$

$$C_s = 1 / (k_2 t + 1 / C_0) \quad (3)$$

where:  $C_s$  is the adsorbates concentration after time  $t$  (mg/L),  $C_0$  is the initial concentration of the solute adsorbate (mg/L),  $k_1$  is the first-order rate constant (1/h), and  $k_2$  is the second-order rate constant (1/(mg · L<sup>-1</sup> · h)).

Moreover, the partition coefficients for each metal were obtained by fitting Henry (equation 4), Freundlich (equation 5), and Langmuir (equation 6) models to the data using Solver, MS Excel's data analysis tool (Microsoft). The adsorption models can be expressed mathematically by the following equations, respectively:

$$q_e = K C_e \quad (4)$$

$$q_e = K_F C_e^{N_F} \quad (5)$$

$$q_e = C_{a,max} K_L C_e / (1 + K_L C_e) \quad (6)$$

where:  $q_e$  is the adsorption capacity of nZVI at equilibrium (mg/g),  $C_e$  is the concentration of metal ions in the equilibrium solution (mg/L),  $K$ ,  $K_F$ , and  $K_L$  are, respectively, the constants for Henry (L/g), Freundlich (L/g), and Langmuir (L/g),  $N_F$  is the heterogeneity factor (-), and  $C_{a,max}$  is the maximum amount of adsorbate (mg/g).

## RESULTS AND DISCUSSION

The kinetic test results are presented in Figures 1 and 2. For the purposes of kinetic studies, the second-order rate constant for heavy metals was determined. The Figures show the final concentration of each metal in the multicomponent solution as a function of time. All the metals used in this study were removed at various times and in diverse intensities. Time after which equilibrium was attained was less than 24 hours for all tested metals. The adsorption processes of zinc occurred

less intensely than for lead and copper, however, it was still satisfactory. The correspondence between the data and the equation indicates that copper and lead follow a second-order reaction. For Cu, Pb and Zn, the fitted lines illustrate the two-step adsorption process. This consists of a rapid adsorption process and a relatively slow stage of adsorption, during which equilibrium is reached. The final removal ratios  $R$  for each metal from the solution were as follows: Cd – 24%, Cu – 96%, Ni – 8%, Pb – 97%, and Zn – 73%. From the values of the removal ratio and the second-order rate constants (Table 1), the order of adsorption priority on nZVI was as follows: Pb > Cu > Zn > Cd > Ni.

Analysis of equilibrium conditions may lead to the conclusion that copper and zinc are removed from the solution by adsorption processes, i.e., complexation and competitive adsorption. Due to the limited adsorption sites on the surface of nZVI, the removal pathways

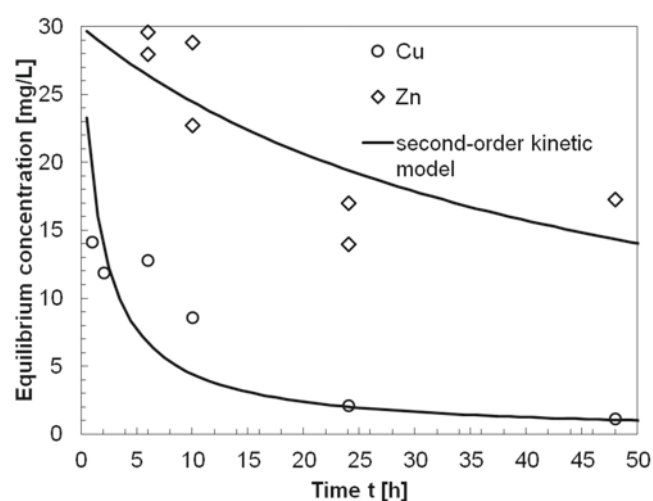


Figure 1. Adsorption kinetic of Cu and Zn on nZVI

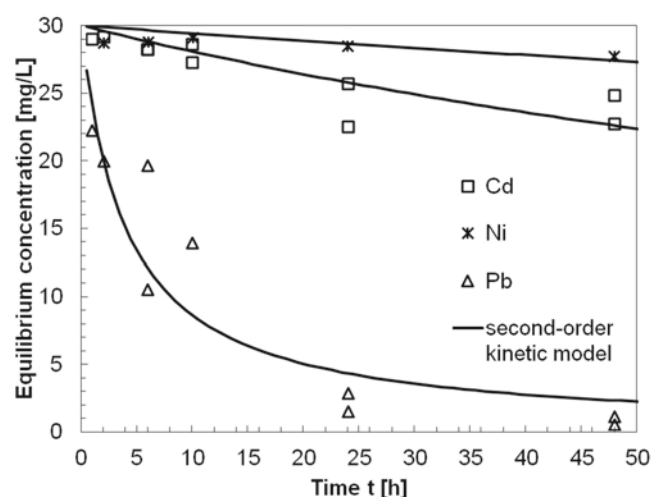


Figure 2. Adsorption kinetic of Cd, Ni and Pb on nZVI

Table 1. Experimental conditions and kinetic parameters

Second order kinetic equation	Metals				
	Cd	Cu	Ni	Pb	Zn
Second order constant $k_2$ [1/(mg/L)h]	0.0002	0.0193	0.00007	0.0082	0.0008
Determination coefficient $R^2$	0.69	0.65	0.45	0.78	0.89
Removal ratio $R$ [%]	24	96	8	97	73
pH	4.03–5.44				
Electrical conductivity [mS/cm]	7.97–9.37				
ORP [mV]	149–237				

of cadmium, nickel, and lead involve cementation and metal hydroxide precipitation. The equilibrium studies are illustrated in Figures 3 and 4. The copper removal data were well described by the Freundlich and Henry models, which probably indicate multilayer adsorption<sup>22</sup>. nZVI is a good adsorbent for Cu, as the constant  $N_F$  ranged from 0.2 to 0.8<sup>23</sup>. The data fitted well into the Freundlich and Henry models, where the determination coefficients were, respectively, 0.97 and 0.91. The equilibrium capacities of zinc could be related to chemisorption or monolayer adsorption, as the Langmuir model fits well into the experimental data with a determination coefficient of 0.99. The calculated constants are shown in Table 2. The removal processes by nZVI are rather kinetic than equilibrium. Therefore, the adsorption of Pb, Ni, and Cd was not described by the Henry, Freundlich and Langmuir equilibrium models.

Inorganic contaminants are removed from aqueous solutions by nZVI in the following processes: cementation, adsorption, and precipitation<sup>1, 24</sup>. The intensity of the processes mentioned above is difficult to determine, as single and multiple reaction pathways are possible. This appears to be due both to the physical and chemical

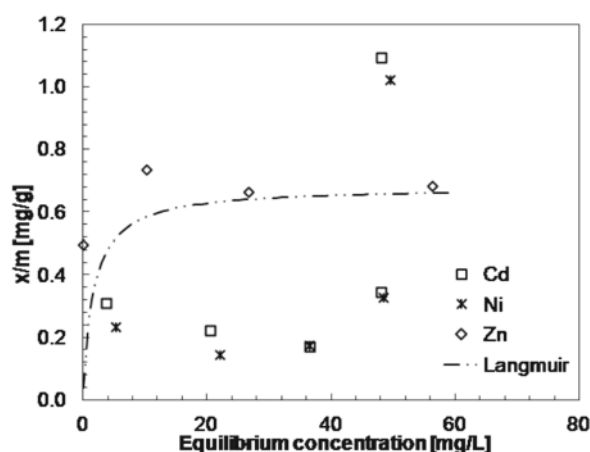


Figure 3. Adsorption of Cd, Ni, and Zn

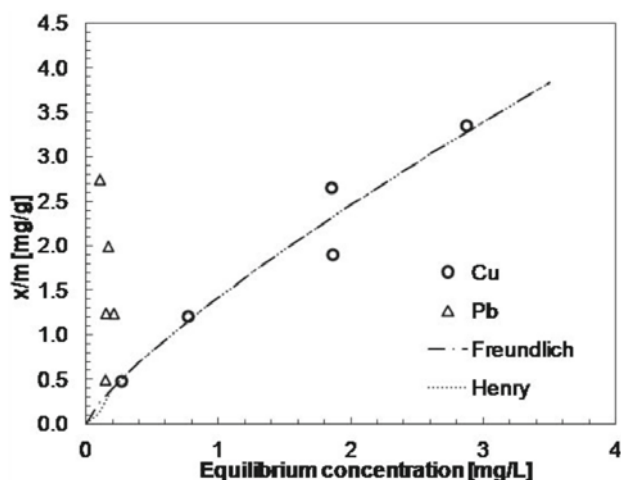


Figure 4. Adsorption of Cu and Pb

Table 2. The constants of the adsorption models

Metals	Henry model		Freundlich model			Langmuir model		
	$K_D$ [L · g <sup>-1</sup> ]	$R^2$	$K_F$ [L · g <sup>-1</sup> ]	$N_F$	$R^2$	$C_{amax}$ [mg · g <sup>-1</sup> ]	$K_L$ [L · g <sup>-1</sup> ]	$R^2$
Cu	1.21	0.91	1.47	0.79	0.97	—	—	—
Zn	—	—	—	—	—	0.68	0.6	0.99

characteristics of nZVI and to the solutions used in the experiments. nZVI has a strong ability to govern the redox chemistry of a solution. In the acid environment of the laboratory tests, the cementation processes were highly effective. The removal of cadmium, nickel, and lead in the experiments may be explained by the re-oxidation of heavy metals with accumulated  $Fe^{3+}$ .

The difference between removal ratios obtained at lower pH values are shown in Figure 5. In these conditions, the positively charged surface of the reactive material becomes dominant, which induces the repulsive forces between the sorbent and the metal. This may decrease the adsorption processes<sup>3</sup>.

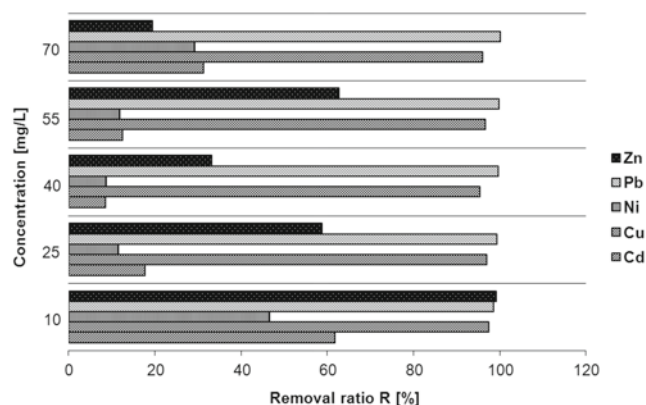


Figure 5. The metal removal ratio R (%) from aqueous solutions for different initial concentrations

## CONCLUSIONS

This study allows the following conclusions to be drawn:

Based on the corrosion theory of iron, the removal processes of metals by nZVI are better described by a kinetic rather than equilibrium model. During corrosion, more ferrous iron precipitates and new adsorption sites for metal binding at the surface are formed.

The mechanisms of metal removal by nZVI depend on the metal species and experimental conditions.

The values of the second-order rate constants for copper and lead indicate relatively high removal rates from the multicomponent solution.

Due to the limited adsorption sites on the surface of nZVI, the removal pathway of copper and zinc was through adsorption processes. On the other hand, cadmium, nickel, and lead were removed by cementation processes, which are connected to ferrous oxide precipitation.

nZVI permeable reactive barriers are an efficient method for remediation of groundwater contaminated by a mixture of heavy metals (Cd, Cu, Ni, Pb, and Zn).

Additional comprehensive research studies should be performed for further *in situ* application.

## ACKNOWLEDGMENT

This research was supported by grant No. NN523 561638 obtained from the National Science Centre of the Republic of Poland.

This publication has been co-financed with the European Union funds by the European Social Fund.

## LITERATURE CITED

- Gavaskar, A. (1999). Design and construction techniques for permeable reactive barriers. *J. Hazard. Mater.* 68, 41–71.
- Yong, R.M. & Mulligan, C.N. (2004). *Natural attenuation of contaminants in soils*. Boca Raton, FL, USA: Lewis Publishers.
- Nassar, N.N. (2012). Kinetics, Equilibrium and thermodynamic studies on the adsorptive removal of nickel, cadmium and cobalt from wastewater by superparamagnetic iron oxide nanoadsorbents. *Can. J. Chem. Engin.* 90, 1231–1238. DOI: 10.1002/cjce.20613.
- Ku, Y. & Jung, I.L. (2001). Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. *Water Res.* 35, 135–144. DOI: 10.1016/S0043-1354(00)00098-1.
- Zhu, S., He, W., Li, G., Zhou, X., Zhang, X. & Huang, J. (2012). Recovery of Co and Li from spent lithium-ion batteries by combination method of acid leaching and chemical precipitation. *T. Nonferr. Metal. Soc.* 22, 2274–2281. DOI: 10.1016/S1003-6326(11)61460-X.
- Smara, A.R., Delimi, R., Chainet, E. & Sandeaux, J. (2007). Removal of heavy metals from diluted mixtures by a hybrid ion-exchange/ electrodialysis processes. *Sep. Sci. Technol.* 57, 103–110. DOI: 10.1016/j.seppur.2007.03.012.
- Dermentzis, K.I., Davidis, A.E., Dermentzi A.S. & Chatzichristou, C.D. (2010). An electrostatic shielding-based coupled electrodialysis/electrodeionization process for removal of cobalt ions from aqueous solutions. *Water Sci. Technol.* 62 (8), 1947–1953. DOI: 10.2166/wst.2010.547.
- Hernández-Montoya, V., Pérez-Cruz, M.A., Mendoza-Castillo, D.I. & Moreno-Virgen, M.R. (2013). Competitive adsorption of dyes and heavy metals on zeolitic structures, *J. Environ. Manage.* 116, 213–221. DOI: 10.1016/j.jenvman.2012.12.010.
- Lee, T. (2011). Microwave preparation of raw vermiculite for use in removal of copper ions from aqueous solutions. *Environ. Technol.* 32, 1195–1203. DOI:10.1080/09593330.2010.531055.
- Treviño-Corderoa, H., Juárez-Aguilara, L.G., Mendoza-Castilloa, D.I., Hernández-Montoyaa, V., Bonilla-Petricioleta, A. & Montes-Moránb, M.A. (2013). Synthesis and adsorption properties of activated carbons from biomass of *Prunus domestica* and *Jacaranda mimosifolia* for the removal of heavy metals and dyes from water, *Ind. Crop. Prod.* 42, 315–323. DOI:10.1016/j.indcrop.2012.05.029.
- Landaburu-Aguirre, J., García, V., Pongrácz, E. & Keiski, R.L. (2009). The removal of zinc from synthetic wastewaters by micellar-enhanced ultrafiltration: statistical design of experiments. *Desalination* 240, 262–269. DOI:10.1016/j.desal.2007.11.077.
- Sampera, E., Rodríguez, M., De la Rubia, M.A. & Prats, D. (2009). Removal of metal ions at low concentration by micellar-enhanced ultrafiltration (MEUF) using sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS). *Sep. Purif. Technol.* 65, 337–342. DOI:10.1016/j.seppur.2008.11.013.
- Gavaskar, A., Gupta, N., Sass, B., Janosy, R. & Hicks, J. (2000). *Design guidance for application of permeable reactive barriers for groundwater remediation*. Columbus, Ohio. Retrived January 16, 2013 from CLU-IN: [http://www.cluin.org/conf/itrc/prbll\\_061506/prb-2.pdf](http://www.cluin.org/conf/itrc/prbll_061506/prb-2.pdf)
- Fu, F. & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* 92(3), 407–418. DOI: 10.1016/j.jenvman.2010.11.011.
- Naftz, D.L., Morrison, S.J., Fuller, C.C. & Davis, J.A. (2002). *Handbook of groundwater remediation using permeable reactive barriers: application to radionuclides, trace metal, and nutrients*. Amsterdam, Denmark: Elsevier Science.
- Kenneke, J.F. & McCutcheon, S.C. (2003). Use of pretreatment zone and zero-valent iron for the remediation of chloroalkenes in an oxic aquifer. *Environ. Sci. Technol.* 37(12), 2829–2835. DOI:10.1021/es0207302.
- Wilkin, R.T., Su, C.M., Ford, R.G. & Paul, C.J. (2005). Chromium-removal processes during groundwater remediation by a zero-valent iron permeable reactive barrier. *Environ. Sci. Technol.* 39, 4599–4605. DOI: 10.1021/es050157x.
- Velazquez-Jimenez, L.H., Pavlick, A. & Rangel-Mendez, J.R. (2013). Chemical characterization of raw and treated agave bagasse and its potential as adsorbent of metal cations from water. *Ind. Crop. Prod.* 43, 200–206. DOI: 10.1016/j.indcrop.2012.06.049.
- Doskočil, L. & Pekař, M. (2012). Removal of metal ions from multi-component mixture using natural lignite. *Fuel Process. Technol.* 101, 29–34. DOI: 10.1016/j.fuproc.2012.02.010.
- Zhang, M. (2011). Adsorption study of Pb(II), Cu(II) and Zn(II) from simulated acid mine drainage using dairy manure compost. *Chem. Eng. J.* 172, 361–368. DOI: 10.1016/j.cej.2011.06.017.
- Xue, Y., Hou, H. & Zhu, S. (2009). Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag. *J. Hazard. Mater.* 162, 391–401. DOI: 10.1016/j.jhazmat.2008.05.072.
- Ho, Y.S., Porter, J.F. & McKay, G. (2002) Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, *Water Air Soil Poll.* 141, 1–33.
- Esmaili, A., Kalantari, M. & Saremnia, B. (2012). Biosorption of Pb (II) from aqueous solutions by modified of two kinds of marine algae, *Sargassum glaucescens* and *Gracilaria Corticata*. *Pol. J. Chem. Tech.* 14(2), 22–28. DOI: 10.2478/v10026-012-0066-5.
- Wilkin, R.T. & McNeil, M.S. (2003). Laboratory evaluation of zero-valent iron to treat water impact by acid mine drainage. *Chemosphere* 53, 715–725. DOI:10.1016/S0045-6535(03)00512-5.