

Adsorption of Cd, Cu and Zn from aqueous solutions onto ferronickel slag under different potentially toxic metal combination

Jong-Hwan Park, Seong-Heon Kim, Se-Won Kang, Byung-Hwa Kang, Ju-Sik Cho, Jong-Soo Heo, Ronald D. Delaune, Yong Sik Ok and Dong-Cheol Seo

ABSTRACT

Adsorption characteristics of potentially toxic metals in single- and multi-metal forms onto ferronickel slag were evaluated. Competitive sorption of metals by ferronickel slag has never been reported previously. The maximum adsorption capacities of toxic metals on ferronickel were in the order of Cd (10.2 mg g^{-1}) > Cu (8.4 mg g^{-1}) > Zn (4.4 mg g^{-1}) in the single-metal adsorption isotherm and Cu (6.1 mg g^{-1}) >> Cd (2.3 mg g^{-1}) > Zn (0.3 mg g^{-1}) in the multi-metal adsorption isotherm. In comparison with single-metal adsorption isotherm, the reduction rates of maximum toxic metal adsorption capacity in the multi-metal adsorption isotherm were in the following order of Zn (93%) > Cd (78%) >> Cu (27%). The Freundlich isotherm provides a slightly better fit than the Langmuir isotherm equation using ferronickel slag for potentially toxic metal adsorption. Multi-metal adsorption behaviors differed from single-metal adsorption due to competition, based on data obtained from Freundlich and Langmuir adsorption models and three-dimensional simulation. Especially, Cd and Zn were easily exchanged and substituted by Cu during multi-metal adsorption. Further competitive adsorption studies are necessary in order to accurately estimate adsorption capacity of ferronickel slag for potentially toxic metals in natural environments.

Key words | competitive adsorption, ferronickel slag, Freundlich isotherm, Langmuir isotherm, potentially toxic metals, three-dimensional simulation

Jong-Hwan Park
Seong-Heon Kim
Jong-Soo Heo
Dong-Cheol Seo (corresponding author)
 Division of Applied Life Science (BK21 Plus) &
 Institute of Agriculture and Life Science,
 Gyeongsang National University,
 Jinju 660-701,
 Republic of Korea
 E-mail: drseodc@gmail.com

Byung-Hwa Kang
 Department of R&D, Hyoseok, Co., Ltd,
 857 Kumho-dong, Gwangyang,
 Republic of Korea

Ronald D. Delaune
 Department of Oceanography and Coastal Sciences,
 School of the Coast and Environment,
 Louisiana State University,
 Baton Rouge, LA 70803,
 USA

Yong Sik Ok
 Korea Biochar Research Center & Department of
 Biological Environment,
 Kangwon National University,
 Chuncheon 200-701,
 Republic of Korea

Se-Won Kang
Ju-Sik Cho
 Department of Bio-Environmental Sciences,
 Suncheon National University,
 Suncheon, 540-950,
 Republic of Korea

INTRODUCTION

Demand for water among the agricultural and private sectors has significantly increased due to increasing economic development and population growth. Water pollution by toxic metals being discharged from industrial effluents has become a worldwide problem during recent years. Therefore, wastewater containing potentially toxic metals needs to be treated and recycled to secure alternative sources of water (Ali 2010).

Adsorption is a widespread method for metal treatment, with great efficiency and low expense among various treatment technologies. Various sorbents, such as natural

materials and synthetic products, have been developed (Gupta *et al.* 2009).

The ferronickel slag of the electric arc furnace represents about 80–90% of the feeding material. Maragkos *et al.* (2009) reported that a vast quantity of slag is generated in the ferronickel production, creating a serious problem for every ferronickel plant worldwide. In South Korea, approximately 1 million tons of ferronickel slag are annually produced, and about 20–30% of ferronickel slag is utilized in the cement industry or in the production of construction material (Ministry of Agriculture Food & Rural Affairs 2011).

Most applications of ferronickel slag are: for road construction, to replace the limestone aggregates and the production of cement, concrete, and construction materials (Kirillidi & Frogoudakis 2005; Fidancevska *et al.* 2007; Vassilev *et al.* 2007). However, a large quantity of ferronickel slag has to be disposed. Ferronickel slag can be used as sorbents due to chemical stability and high recycling probabilities.

Toxic metal adsorption depends not only on ferronickel slag characteristics but also on the nature of the toxic metals involved and on their competitive behavior for ferronickel slag adsorption sites. Using synthetic minerals and soils, competitive adsorption of toxic metals has been indirectly assessed either by single or binary system experiments (Brummer *et al.* 1988; Harter 1992). Several approaches are used for competitive sorption and selectivity sequences of toxic metals by using various sorbents, such as goethite, hydroxyapatite, activated carbon, and soils (Gupta *et al.* 2003; Karami 2013; Zhao *et al.* 2014). None of these studies considered the ferronickel slag for potentially toxic metals adsorption; especially, the competitive sorption of potentially toxic metals by ferronickel slag has never been reported.

The goal of this study was to investigate the adsorption characteristics of potentially toxic metals in single- and multi-metal forms by ferronickel slag in order to estimate the toxic metal adsorption capacity of ferronickel slag in natural environments. The specific objectives were: (1) to investigate single- and multi-metal adsorption characteristics of ferronickel slag in a batch experiment; (2) to compare the adsorption capacities of toxic metals on ferronickel slag in single- and multi-metal adsorption isotherms in the batch experiment using both Freundlich and Langmuir adsorption models; and (3) to compare three-dimensional simulation graphics using the data obtained from the adsorption experiment under single- and multi-metal adsorption conditions.

MATERIALS AND METHODS

Materials

Ferronickel slag, which is a by-product of the manufacture of ferronickel and used in stainless steel, is from the Gwangyang Iron and Steel Works, POSCO, South Korea. Major physico-chemical characteristics of ferronickel slag were analyzed, and the results are shown in Supplementary Table S1 (see the Supplementary Material, available with the online version of this paper). The Fourier transform infrared (FTIR) spectra and X-ray diffraction (XRD) for ferronickel slag are shown in Supplementary Figures S1 and S2, respectively (available

with the online version of this paper). The bulk density, porosity, surface area, and pH of ferronickel slag were 1.74 g cm^{-3} , 34%, $0.09 \text{ m}^2 \text{ g}^{-1}$, and 7.5, respectively.

Characterization of potentially toxic metal solutions

Potentially toxic metals (Cd, Cu and Zn) were used in the study. Stock solutions ($1,000 \text{ mg L}^{-1}$) of Cd ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), Cu ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$), and Zn ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were prepared by dissolving exact quantities of the respective salts (GR grade, Fisher Scientific, USA) in distilled water. The toxic metals stock solution was further diluted to the required experimental concentration.

Batch experiment 1

Both single- and multi-metal adsorption experiments were conducted to evaluate the adsorption characteristics of ferronickel slag for the potentially toxic metals. Adsorption behaviors of the potentially toxic metals on ferronickel slag were evaluated using both the Freundlich and Langmuir adsorption isotherm models.

Single-metal adsorption isotherms of potentially toxic metals were obtained by weighing 1.0 g of ferronickel slag, from each test, in glass Erlenmeyer flasks. Thereafter, 50 mL of solution containing specific concentrations of the toxic metals was added to the flask. Multi-metal adsorption isotherms were investigated by following the same procedure as the single-metal experiment and using the same concentration ratio for the selected toxic metals. For each toxic metal, concentration levels of 0, 2.5, 5, 10, 20, 40, 80, 160, and 320 mg L^{-1} were individually evaluated (three replicates for each treatment). The initial pH of the solutions were adjusted to 7 by adding either 0.1 M HCl or 0.1 M NaOH solutions. The leaching test of ferronickel slag using different solutions (water, H_2SO_4 , HCl, HNO_3) was performed by Kim *et al.* (2011, 2013). According to previous studies, the toxic metals were leached in the acid solution, but were not leached into the water (neutral pH). For this reason, the leaching test of ferronickel slag was not considered.

All samples were equilibrated for 24 hours, after providing sufficient time for the system to reach equilibrium, on a shaking rotator (KASI KSI-200L, Korea) at constant room temperature (25°C). After settling, a 30 mL aliquot of the supernatant was filtered through a Whatman GF/C filter ($0.45 \mu\text{m}$) and, then, analyzed for toxic metal concentrations. The toxic metal concentrations in the single- and multi-metal adsorption experiments were determined by using inductively coupled plasma with optical emission

spectroscopy (ICP-OES, Perkin Elmer Optima 4300 DV). The amount of toxic metal adsorption by ferronickel slag was calculated from the concentration reduction in solution. Statistical analysis of data was conducted by using SAS software (SAS 9.3, SAS Institute Inc., Cary, NC, USA).

Batch experiment 2

Adsorption characteristics of metals in the ferronickel slag were studied at three temperatures (10, 20, and 30 °C) at pH 7 using the procedures described previously. The maximum adsorption capacities of metals by the ferronickel slag at different temperatures were evaluated using the Langmuir adsorption isotherm equations.

Adsorption models

Adsorption isotherms were determined using the Freundlich and Langmuir models. The details of Freundlich and Langmuir models are supplied in the Supplementary Material. Kinetic experiments were completed to establish the time required for the sorption system to reach equilibrium.

Speciation of metals

Aqueous speciation of metals as a function of pH was studied using the computer program Visual MINTEQ, Version 2.30 (Gustafsson 2004). The solution speciation of the metals was modeled because the hydrolysis behavior of metal ions has been found to influence sorption processes (James & Healy 1972).

Analysis methods

Chemical composition and physical properties of the slags were analyzed (see the Supplementary Material).

RESULTS AND DISCUSSION

Speciation of metals

The speciation of each of the metals in the single- and multi-metal adsorption systems are shown in Supplementary Figure S3 (available with the online version of this paper). Curves from single- and multi-metal adsorption systems are similar. Cadmium appears predominantly as Cd^{2+} species over pH 2–9. The concentration of Cd species such as CdNO_3^+ and $[\text{Cd}_2(\text{OH})]^{3+}$ is lower in solution and does

not change results over the pH range. Copper appears predominantly as Cu^{2+} species at pH <5.0. The concentration of various Cu hydroxyl species (CuOH^+ , $[\text{Cu}_2(\text{OH})_2]^{2+}$, $[\text{Cu}(\text{OH})_4]^{2-}$, $\text{Cu}(\text{OH})_2(\text{aq})$ and $[\text{Cu}(\text{OH})_3]^-$) increases at pH >5.0 in both adsorption systems. The concentration of CuNO_3^+ , $[\text{Cu}(\text{OH})_4]^-$ and $[\text{Cu}_2(\text{OH})]^{3+}$ is lower in solution and does not significantly change with the pH. Zinc appears predominantly as Zn^{2+} species, the concentration of which sharply decreases at pH >8. The concentration of ZnNO_3^+ and $[\text{Zn}_2(\text{OH})]^{3+}$ is negligible.

Potentially toxic metal adsorption characteristics of ferronickel slag in single- and multi-metal conditions

The single- and multi-metal adsorption isotherms for the three toxic metals on ferronickel slag in the batch experiment are shown in Figure 1(a). Single-metal adsorption isotherms for the three toxic metals on ferronickel slag exhibited different shapes and retention quantities. The single-metal adsorption

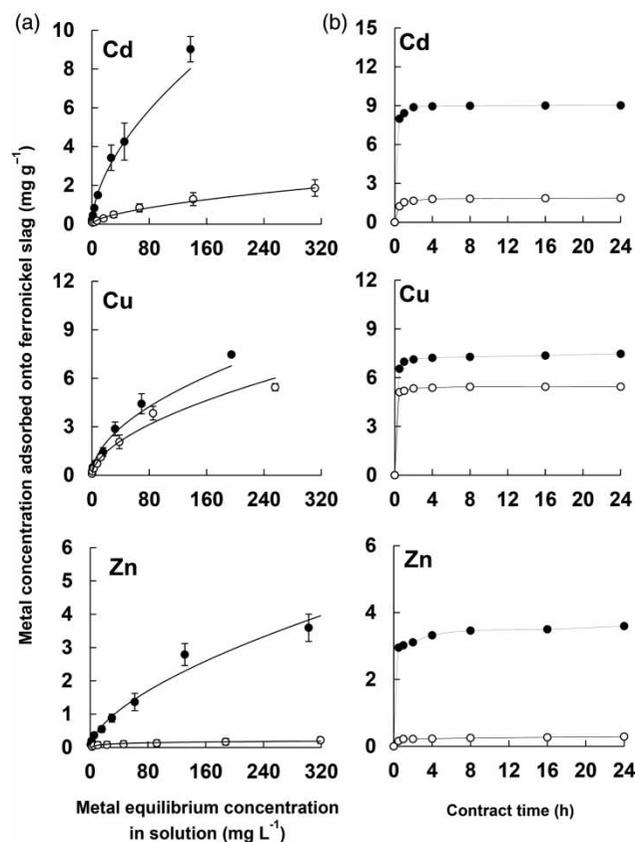


Figure 1 | Single- and multi-metal adsorption isotherms (a) for the three potentially toxic metals (Cd, Cu, and Zn) on ferronickel slag in the batch experiment. Adsorption kinetics (b) of the three toxic metals as a function of contact time in the single- and multi-metals system. (●) Single-metal adsorption isotherm, (○) Multi-metal adsorption isotherm.

isotherms of Cu were L-1 curve type, based on the classification system of Giles *et al.* (1960). This isotherm type indicates a relatively high affinity of the ferronickel slag particles for the studied metals at the added toxic metal concentrations (Sposito 1989). According to Limousin *et al.* (2007), the ratio between the toxic metal concentration of the compound remaining in solution and that adsorbed onto the solid decreased when the solute concentration increased.

Competition between ions affected adsorption of all toxic metals. As compared to single-metal adsorption, the initial linear part of the multi-metal adsorption isotherms was shorter and the knee was sharper. Cadmium and Zn isotherms were L-2 type for competitive retention, reflecting no surface precipitation. The L-2 curve reached a strict asymptotic plateau (ferronickel slag has a limited sorption capacity), suggesting a theoretical monolayer was achieved. The Cu isotherms for ferronickel slag were L-1 type, which does not reach any plateau (ferronickel slag as a solid does not show clearly a limited sorption capacity). L type isotherms are often difficult to identify as belonging to either the first or second sub-group (Limousin *et al.* 2007). Stumm (1992) reported that, when attachment of Cu to the sorbent is strong, ions tend to spread out over the surface. For low-surface coverage (lowest equilibrium concentration of competitive isotherms), all competing ions were retained whereas isotherms tend to show greater affinity for Cu than for either Cd, Ni, or Zn at higher equilibrium concentrations (Echeverría *et al.* 1998).

Adsorption kinetics

The results of adsorption kinetic measurements are shown in Figure 1(b). These indicate that sorption onto ferronickel

slag at pH 7.0 reached equilibrium within 30 min, with no evidence of additional adsorption up to 24 h. For example, at 30 min, around 80% of the metals are adsorbed in the single-element system except Zn. Available metal adsorption results show that the uptake of adsorbate species is fast at the initial stages of the adsorption period, and thereafter it becomes slower near the equilibrium. The results agree with previous observations by Xue *et al.* (2009) regarding the adsorption kinetics of metals (Cu, Cd, Pb, and Zn) on basic oxygen furnace slag. This initial fast reaction is characteristic of metal sorption on ferronickel slag and has been attributed to adsorption on high affinity surface sites or on sites with higher bonding strength to the metal (Flogeac *et al.* 2007). All curves of metal adsorption have a nearly similar trend. However, some differences are observed between the adsorption systems. The amount of single metal adsorbed decreases in the multi-metal system in comparison with the single-metal system. This is attributed to the effect of competitive adsorption of metals.

Comparison between single- and multi-metal adsorption capacities of ferronickel slag using Freundlich and Langmuir isotherm models

The adsorption capacities (K) for the toxic metals by ferronickel slag were determined by using the Freundlich isotherms and were in the following order of Cd (0.4779) > Cu (0.4226) >> Zn (0.1166) under single-metal conditions and Cu (0.2669) >> Cd (0.0655) > Zn (0.0217) under multi-metal conditions (Table 1). The adsorption capacity of each metal on ferronickel slag in single-metal conditions was generally higher than that in multi-metal conditions. Especially, the Cd adsorption in

Table 1 | Determination of the parameters for the Freundlich and Langmuir adsorption isotherm by test fit approach in batch experiment of single- and multi-metal adsorption to ferronickel slag

| Metals | Treatments | Freundlich adsorption isotherm | | | Langmuir adsorption isotherm | | |
|--------|--------------|-------------------------------------------|--------|---------|-------------------------------------------|-------|--------|
| | | Equation | K^a | $1/n^b$ | Equation | a^c | b^d |
| Cd | Single-metal | $y = 0.5728x - 0.3207 (r = 0.9964^{***})$ | 0.4779 | 0.5728 | $y = 0.0976x + 3.2565 (r = 0.9152^*)$ | 10.2 | 0.0300 |
| | Multi-metal | $y = 0.5836x - 1.1835 (r = 0.9886^{***})$ | 0.0655 | 0.5836 | $y = 0.4421x + 37.525 (r = 0.9613^{***})$ | 2.3 | 0.0118 |
| Cu | Single-metal | $y = 0.5263x - 0.3741 (r = 0.9929^{***})$ | 0.4226 | 0.5263 | $y = 0.1194x + 4.6369 (r = 0.9249^*)$ | 8.4 | 0.0258 |
| | Multi-metal | $y = 0.5620x - 0.5737 (r = 0.9963^{***})$ | 0.2669 | 0.5620 | $y = 0.1633x + 6.7027 (r = 0.9709^{***})$ | 6.1 | 0.0243 |
| Zn | Single-metal | $y = 0.6112x - 0.9332 (r = 0.9958^{***})$ | 0.1166 | 0.6112 | $y = 0.2273x + 18.495 (r = 0.9405^*)$ | 4.4 | 0.0123 |
| | Multi-metal | $y = 0.4141x - 1.6644 (r = 0.9653^{***})$ | 0.0217 | 0.4141 | $y = 3.3295x + 221.29 (r = 0.9388^*)$ | 0.3 | 0.0150 |

^a K : adsorption capacity of toxic metal.

^b $1/n$: an empirical parameter related to the intensity of sorption.

^c a : maximum adsorption capacity of toxic metal (mg g^{-1}).

^d b : binding strength constant of toxic metal.

*** denotes significance at 5.0 and 1.0% levels.

the multi-metal adsorption isotherm was 7.3 times lower than the single-metal adsorption isotherm, indicating that the rate of reduction in Cd adsorption capacity was highest among all the tested metals. On the other side, the reduction rate in Cu adsorption capacity under multi-metal conditions was 1.6 times lower compared to single-metal conditions. The $1/n$ values for ferronickel slag in the single- and multi-metal adsorption isotherms in this study were less than unity, representing a favorable adsorption process.

Using ferronickel slag, the maximum adsorption capacities (a ; mg g⁻¹) of the toxic metals that were determined from the Langmuir isotherms followed the order of Cd (10.2) > Cu (8.4) >> Zn (4.4) under single-metal conditions and Cu (6.1) >> Cd (2.3) > Zn (0.3) under multi-metal conditions (Table 1). The maximum metal adsorption capacities of ferronickel slag in multi-metal conditions were lower than those in single-metal conditions.

Based on the above results, the reduction rates of maximum toxic metal adsorption capacity in the multi-metal adsorption isotherm were in the order of Zn (93%) > Cd (78%) >> Cu (27%) in comparison with single-metal adsorption isotherm (Supplementary Figure S5, available with the online version of this paper). The reduction rate of maximum Cu adsorption capacity was lowest among the tested toxic metals whereas that for Zn was highest. Our results showed that adsorption of both Cd and Zn was more affected by the competing toxic metals than was Cu. Namely, Cd and Zn could be easily exchanged and substituted by Cu whereas Cu had more effective competition ions against Cd and Zn for adsorption sites in the ferronickel slag.

The a_{metal} (single-metal adsorption)/ a_{metal}^* (multi-metal adsorption) ratios were generally greater than unity, suggesting that the simultaneous presence of multi-metals reduced the adsorption capacity for each metal due to competition for sorption sites in ferronickel slag. The $a_{\text{metal}}/a_{\text{metal}}^*$ ratio followed the order of $a_{\text{Zn}}/a_{\text{Zn}}^*$ (14.6) >> $a_{\text{Cd}}/a_{\text{Cd}}^*$ (4.52) > $a_{\text{Cu}}/a_{\text{Cu}}^*$ (1.36), indicating that adsorption of Cd and Zn was more affected by competing metals than was Cu. In other words, Cu exhibited effective competition for sorption sites in the ferronickel slag in the presence of Cd and Zn. Toxic metals mainly adsorbed to specific adsorption sites at low metal concentrations (Saha et al. 2002). On the other hand, the sorbent lost some of its ability to bind toxic metals as the adsorption sites overlapped at higher metal inputs, thereby becoming less specific for a particular toxic metal. This result in turn induced reduction of toxic metal sorption (Saha et al. 2002). In the presence of Cd and Zn, the Cu can successfully compete for sorption sites on different colloidal surfaces (Fontes & Gomes 2003). The maximum

adsorption capacity (a) for Cd was higher than that for Cu in single-metal adsorption experiment whereas a values for Cd were lower than Cu in multi-metal adsorption experiment. The ratios of $a_{\text{Cd}}/a_{\text{Cu}}$ (single-metal adsorption) and $a_{\text{Cd}}^*/a_{\text{Cu}}^*$ (multi-metal adsorption) were 1.22 and 0.37, respectively, indicating that the ratio of $a_{\text{Cd}}/a_{\text{Cu}}$ was higher than that of $a_{\text{Cd}}^*/a_{\text{Cu}}^*$ in the ferronickel slag.

To select the optimum adsorption isotherm for ferronickel slag, comparison of calculated values including R^2 values and average relative error (data not shown) was carried out using the Freundlich and Langmuir isotherms for single-metal and multi-metal adsorption of the three potentially toxic metals. Based on the results, the Freundlich model for ferronickel slag provides a slightly better fit than the Langmuir model for potentially toxic metal adsorption in all stages.

Effect of temperature on toxic metal adsorption in the ferronickel slag

The effect of temperature on adsorption of toxic metals by the ferronickel slag at 10, 20 and 30 °C are shown in Supplementary Figure S4 (available with the online version of this paper). In the single- and multi-metal adsorption systems, the adsorption capacity (a) of the metal on the ferronickel slag determined by Langmuir isotherms at different temperatures were in the order of 30 °C ≥ 20 °C > 10 °C for Cd. Similar results were obtained for Cu and Zn (30 °C ≥ 20 °C > 10 °C) with the highest level of adsorption measured at 30 °C. The adsorption capacities of the toxic metals on the ferronickel slag increased slightly with temperature increase. According to McKay et al. (1982) and Giles et al. (1974), the enhancement of metal adsorption capacity on increasing the temperature may be due to increase in the mobility and diffusion of adsorbate species. Dimitrova (1996) reported that the endothermic nature of the process can basically be related to increased hydrolysis and slag surface solubility.

Comparison between single- and multi-metal adsorption behaviors on ferronickel slag using three-dimensional simulation

The three-dimensional (3D) simulation graphs, shown in Supplementary Figure S6 (available with the online version of this paper), can be used to effectively predict the relationships between toxic metals under the single and competitive adsorption systems. The 3D simulation graphs can be successfully used to estimate the adsorption behaviors of toxic metals under single and competitive adsorption conditions.

The 3D simulation graphs of toxic metals in both single- and multi-metal adsorption systems are shown in Supplementary Figure S6.

In the 3D adsorption plot under single-metal adsorption conditions (Supplementary Figure S6a), the simulation diagram showed that Cu adsorption increased as Zn and Cd adsorption increased, and Cu adsorption increased with increasing Cd adsorption and decreasing Zn adsorption under multi-metal adsorption condition (Supplementary Figure S6b). These two 3D adsorption plots illustrated the differences between single-metal and multi-metal adsorption conditions. These results were mainly attributed to the differences in Cu adsorption capacities between single (lower Cu adsorption capacity than Cd) and competitive (highest Cu adsorption capacity among metals) adsorption conditions. As a consequence, toxic metal adsorption patterns under single-metal adsorption conditions were different from those under multi-metal adsorption conditions. Single and competitive adsorption systems were necessary to estimate toxic metal adsorption efficiencies of ferronickel slag.

Toxic metals rarely occur alone, and their associations and interactions with one another and with other components in natural environments are known to influence their transport between the aqueous solution and the solid surface. Although the adsorption of toxic metal ions is influenced by environmental factors in soils or sorbents, the toxic metal ion ratios substituted by other competitive metal ions in a multi-metal adsorption system were consistent over a wide range of metal concentration (Chen et al. 2011).

CONCLUSION

Single-metal and multi-metal adsorption of potentially toxic metals using ferronickel slag was performed in order to estimate the adsorption behavior of toxic metals. The toxic metal adsorption capacities of ferronickel slag were determined by using Freundlich and Langmuir adsorption models and were in the order of $Cd > Cu > Zn$ in the single-metal adsorption isotherm and $Cu > Cd > Zn$ in the multi-metal adsorption isotherm. The reduction rates of maximum toxic metal adsorption capacity in the multi-metal adsorption isotherm were in the order of $Zn (93\%) > Cd (78\%) \gg Cu (27\%)$ compared to the single-metal adsorption isotherm. The Freundlich model fits the data better than the Langmuir model using correlation coefficients for toxic metal adsorption on ferronickel slag. Copper was the most often retained cation under multi-metal conditions whereas Zn and Cd most significantly

lost their adsorption capacity. Toxic metal adsorption patterns obtained from the three-dimensional simulation graphs in the single-metal adsorption system were different from those in the multi-metal adsorption system. Results demonstrated that further competitive adsorption studies for ferronickel slag are necessary for accurate estimation of adsorption in natural environments.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea grant funded by the Korea Government (Ministry of Education, Science and Technology), NRF-2014R1A1A2007515.

REFERENCES

- Ali, I. 2010 The quest for active carbon adsorbent substitutes: inexpensive adsorbents for toxic metal ions removal from wastewater. *Separation & Purification Reviews* **39**, 95–171.
- Brummer, G. W., Gerth, J. & Tiller, K. G. 1988 Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite I. Adsorption and diffusion of metals. *European Journal of Soil Science* **39**, 37–52.
- Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B. & Hay, A. G. 2011 Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource Technology* **102**, 8877–8884.
- Dimitrova, S. V. 1996 Metal sorption on blast-furnace slag. *Water Research* **30** (1), 228–232.
- Echeverría, J. C., Morera, M. T., Mazkiarán, C. & Garrido, J. J. 1998 Competitive sorption of heavy metal by soils. Isotherm and fractional factorial experiments. *Environmental Pollution* **101**, 275–284.
- Fidancevska, E., Vassilev, V., Milosevski, M., Parvanov, S., Milosevski, D. & Aljihmani, L. 2007 Composites based on industrial wastes III. Production of composites from Fe–Ni slag and waste glass. *Journal of the University of Chemical Technology and Metallurgy* **42** (3), 285–290.
- Flogeac, K., Guillon, E. & Aplincourt, M. 2007 Competitive sorption of metal ions onto a north-eastern France soil: isotherms and XAFS studies. *Geoderma* **139**, 180–189.
- Fontes, M. P. F. & Gomes, P. C. 2003 Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils. *Applied Geochemistry* **18**, 795–804.
- Giles, C. H., McEwan, T. H., Nakhawa, S. N. & Smith, D. 1960 Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society* **3**, 3973–3993.

- Giles, C. H., Smith, D. & Huitson, A. 1974 [A general treatment and classification of the solute adsorption isotherm. I. Theoretical.](#) *Journal of Colloid Interface Science* **47**, 755–765.
- Gupta, V. K., Jain, C. K., Ali, I., Sharma, M. & Saini, V. K. 2003 [Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste.](#) *Water Research* **37**, 4038–4044.
- Gupta, V. K., Al Hayat, M., Singh, A. K. & Pal, M. K. 2009 [Nano level detection of Cd\(II\) using poly\(vinyl chloride\) based membranes of Schiff bases.](#) *Analytica Chimica Acta* **634**, 36–45.
- Gustafsson, J. P. 2004 *Visual MINTEQ Version 2.30: A Computer Program for Speciation.* Department of Land and Water Resources Engineering, KTH, Sweden.
- Harter, R. D. 1992 [Competitive sorption of cobalt, copper and nickel ions by a calcium-saturated soil.](#) *Soil Science Society America Journal* **56**, 444–449.
- James, R. O. & Healy, T. W. J. 1972 [Adsorption of hydrolyzable metal ions at the oxide–water interface. I. Co\(II\) adsorption on SiO₂ and TiO₂ as model systems.](#) *Journal of Colloid Interface Science* **40**, 42–52.
- Karami, H. 2013 [Heavy metal removal from water by magnetite nanorods.](#) *Chemical Engineering Journal* **219**, 209–216.
- Kim, E. Y., Choi, S. W., Kim, V., Li, Y. & Park, J. H. 2011 [The extraction ability of Mg and Fe components from ferronickel slag depending on their particle size and hydrochloric acid concentration.](#) *Korea Society of Waste Management* **28**, 672–679.
- Kim, E. Y., Choi, S. W., Kim, V., Li, Y. & Park, J. H. 2013 [The dissolution of magnesium and iron from ferronickel slag depending on aging condition.](#) *Applied Chemistry for Engineering* **24**, 350–356.
- Kirillidi, Y. & Frogoudakis, E. 2005 [Electric arc furnace slag utilization.](#) In: *Proceedings of the 9th International Conference on Environmental Science and Technology, Rhodes, Greece*, pp. 768–772.
- Limousin, G., Gaudet, J. P., Charlet, L., Szenknect, S., Bathès, V. & Krimissa, M. 2007 [Sorption isotherms: a review on physical bases, modeling and measurement.](#) *Applied Geochemistry* **22** (2), 249–275.
- Maragos, I., Giannopoulou, I. P. & Panias, D. 2009 [Synthesis of ferronickel slag-based geopolymers.](#) *Minerals Engineering* **22** (2), 196–203.
- McKay, G., Blair, H. S. & Gardner, J. R. 1982 [Adsorption of dyes on chitin. I. Equilibrium studies.](#) *Journal of Applied Polymer Science* **27**, 3043–3057.
- Ministry of Agriculture Food & Rural Affairs 2011 *Technical Development and Products for Agricultural Utilization from Ferro-Nickel Slag.* Report for the Ministry of Agriculture Food and Rural Affairs, Korea.
- Saha, U. K., Taniguchi, S. & Sakurai, K. 2002 [Simultaneous adsorption of cadmium, zinc, and lead on hydroxyaluminum- and hydroxyaluminosilicatemontmorillonite complexes.](#) *Soil Science Society America Journal* **66**, 117–128.
- Sposito, G. 1989 *The Chemistry of Soils.* Oxford University Press, New York.
- Stumm, W. 1992 *Chemistry of the Solid-Water Interface.* Wiley, New York.
- Vassilev, V., Fidancevska, E., Milosevski, M., Parvanov, S., Milosevski, D. & Hristova-Vasileva, T. 2007 [Composites based on industrial wastes IV. Production of porous composites from Fe–Ni slag and waste glass.](#) *Journal of the University of Chemical Technology and Metallurgy* **42** (4), 369–376.
- Xue, Y., Hou, H. & Zhu, S. 2009 [Competitive adsorption of copper \(II\), cadmium \(II\), lead \(II\) and zinc \(II\) onto basic oxygen furnace slag.](#) *Journal of Hazardous Materials* **162**, 391–401.
- Zhao, X. Y., Zhu, Y. J., Zhao, J., Lu, B. Q., Chen, F., Qi, C. & Wu, J. 2014 [Hydroxyapatite nanosheet-assembled microspheres: hemoglobin-templated synthesis and adsorption for heavy metal ions.](#) *Journal of Colloid and Interface Science* **416**, 11–18.

First received 4 August 2015; accepted in revised form 27 October 2015. Available online 6 November 2015