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Removal of As(V) from aqueous system using steel-making by-product

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ABSTRACT

For As(V) removal aqueous system, 3 types slag which is a waste product from steel making process was used. Arsenic was mainly removed by Ca-As precipitation such as form $Ca_3(AsO_4)_2$. The removal efficiency of arsenic on slag was affected by iron oxide contents because arsenic was removed by adsorption on iron oxide. The experimental results were well fitted by pseudo-second-order and Langmuir isotherm model compared to other models. Arsenic was completely removed by Slag Y and Slag J within 12 h, 0.5 g and 0.7 g of Slag Y and Slag J are sufficient to remove arsenic of 20 mg/l arsenic. The removal efficiency increases with the decrease of initial pH and the decrease of initial arsenic concentration. The calcium that is a major component comes from dissolution of the lime (CaO). The calcium concentration increased at low initial pH because the solubility of the lime (CaO) increases at acidic condition. The equilibrium pH sharply increase after reaction because of creation of hydroxide ion.

Keywords: Arsenic; Langmuir; Precipitation; Pseudo-second-order; Steel making slag

1. Introduction

Arsenic contamination in the aqueous streams has been a global problem including Bangladesh, Vietnam, India, Taiwan and western United States [1]. Arsenic contamination caused by industrial wastes and agricultural chemicals as well as natural source [2] has been more and more serious. Therefore, an innovative technology for arsenic removal is urgently needed. Arsenic, one of the pollutants, was greatest threat to human health and eco-systems. World Health Organization and United States Environmental Protection Agency have been strengthened arsenic regulation levels and more and more countries have adopted the value of the new standard [3]. Although the standard of arsenic was strengthened, the number of injured countries and peoples has been increased gradually.

Generally, arsenic exists anionic forms such as AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$ and $H_3AsO_3^{2-}$ in natural aqueous system [4]. The speciation of arsenic is highly depended on the solution pH. Arsenite (As(III)) and arsenate (As(V)) are stable at natural aqueous systems [5]. Common technologies for arsenic removal from aqueous system are adsorption [6,7], anion exchange [8], reverse osmosis, precipitation and coagulation [9]. Recently, iron oxide is a good adsorbent for arsenic because iron-oxide forms a complex with arsenic in aqueous stream [10]. Various modified processes of iron-oxide to treat arsenic has been applied and reported.

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Slag is a major by-product in steel-making industries and a waste material reused widely for their useful properties. Slag consists of calcium oxide, magnesium oxide and other metal oxides. It is well known that slag is an alternative adsorbent for heavy metals because of high capacity in neutralization of acid. Major mechanism of the metal removal is precipitation as a form of metal hydroxide. However, few researches have focused on the removal of arsenic using slags [11,12]. The removal efficiency of arsenic by steel making slag was controlled by the lime (CaO) and iron oxide (Fe_2O_3) contents. Arsenic was removed by Ca-As precipitation such as a form of $Ca_3(AsO_4)_2$ and was removed by adsorption on iron oxide. Iron oxide provides arsenic with favorable adsorption site.

In this study, we investigated the removal characteristics of arsenic using three different types of slag in points of kinetics and isotherms.

2. Materials and methods

2.1. Materials

The 3 types slag (SlagY, SlagJ and SlagK) were obtained from POSCO (Pohang, Korea) and each slag comes from different steel making process. Slag was sieved to less than 2.0 mm and slag with the diameter less than 2.0 mm was used in this study. The composition of slag was summarized in Table 1 [13]. The calcium oxide was major component of slags and the contents were 65.8 for Y, 44.6 for J and 54.2 wt% for K, respectively. Stock solution of arsenic was prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ (Sigma, USA) in deionized water.

2.2. Batch experiments

2.2.1. Effect of the contact time

A mass of 3 g of slag and 30 ml of arsenic solution with a concentration of 18.93 mg/l were mixed by over-head shaker for 24 h. At the desired time interval, the samples were taken and centrifuged at 3000 rpm for 10 min. To determine solution pH and residual concentration of arsenic, supernatant was analyzed by pH/ISE meter (735P, Istek, Korea) and Anodic Stripping Voltammetry (ASV, PDV6000, MTI, Australia).

2.2.2. Effect of initial arsenic concentration

A mass of 0.3 g of slag was mixed with arsenic solution (30 ml) of various concentrations by over-head shaker for 24 h. The ratio of slag and arsenic solution was 1:100. To determine the effect of initial pH on the removal of arsenic, these experiments were carried out at initial pH 4.0, 7.0 and 10.0. The samples were taken and centrifuged, then the pH and arsenic concentration in supernatant were analyzed by pH/ISE meter and ASV.

2.2.3. The effect of the slag dose

In order to determine the effect of the slag dose on arsenic removal, slag of various doses was mixed with arsenic solution of pH 3.0 for 24 h. The initial arsenic concentration was 20 mg/l, and the dose of slag was from 16.7 g/l–100 g/l. After 24 h, the samples were taken and centrifuged, residual arsenic concentration was measured by ASV.

2.2.4. The concentration of calcium

To measure the amount of calcium dissolved from slag into aqueous phase, 3 g of slag and 30 ml of deionized water at the initial pH 2.0, 4.0, 7.0 and 10.0 were mixed by over-head shaker. After 24 h, the mixture was centrifuged at 3000 rpm for 10 min, concentration of calcium in solution was analyzed by AAS (AA-6300, Shimadzu, Japan).

3. Results and discussion

3.1. Effect of the contact time

Fig. 1 shows the effect of contact time on the removal of arsenic and equilibrium pH after 24 h. As shown in Fig. 1a, the concentration of arsenic was rapidly reduced during 30 min, then arsenic was completely removed by Slag Y and Slag J within 12 h. In case of Slag K, removal rate of arsenic was slower and removal efficiency was lower compared to Slag J and Y. It was because the content of calcium oxide of Slag Y was higher than that of others. Also, iron oxide can provide adsorption site for arsenic [10,14]. In case of Slag J, the total iron content was the highest compared to others. That was the reason for faster and higher removal of arsenic compared to Salg K. After 24 h, the increase of pH in the solution was observed as shown in Fig. 1d. Equilibrium pH for Slag J and Y was greater than 12.0 immediately, but the pH for Slag K was

Table 1
The chemical composition of the Slag Y, J and K

Oxide (wt%)	CaO	SiO_2	Al_2O_3	MgO	MnO	Total Fe
SlagY	65.8	10.8	1.6	3.5	—	13.4
SlagJ	44.6	6.1	3.9	2.7	1.0	28.3
SlagK	54.2	23.3	7.3	5.1	—	2.0

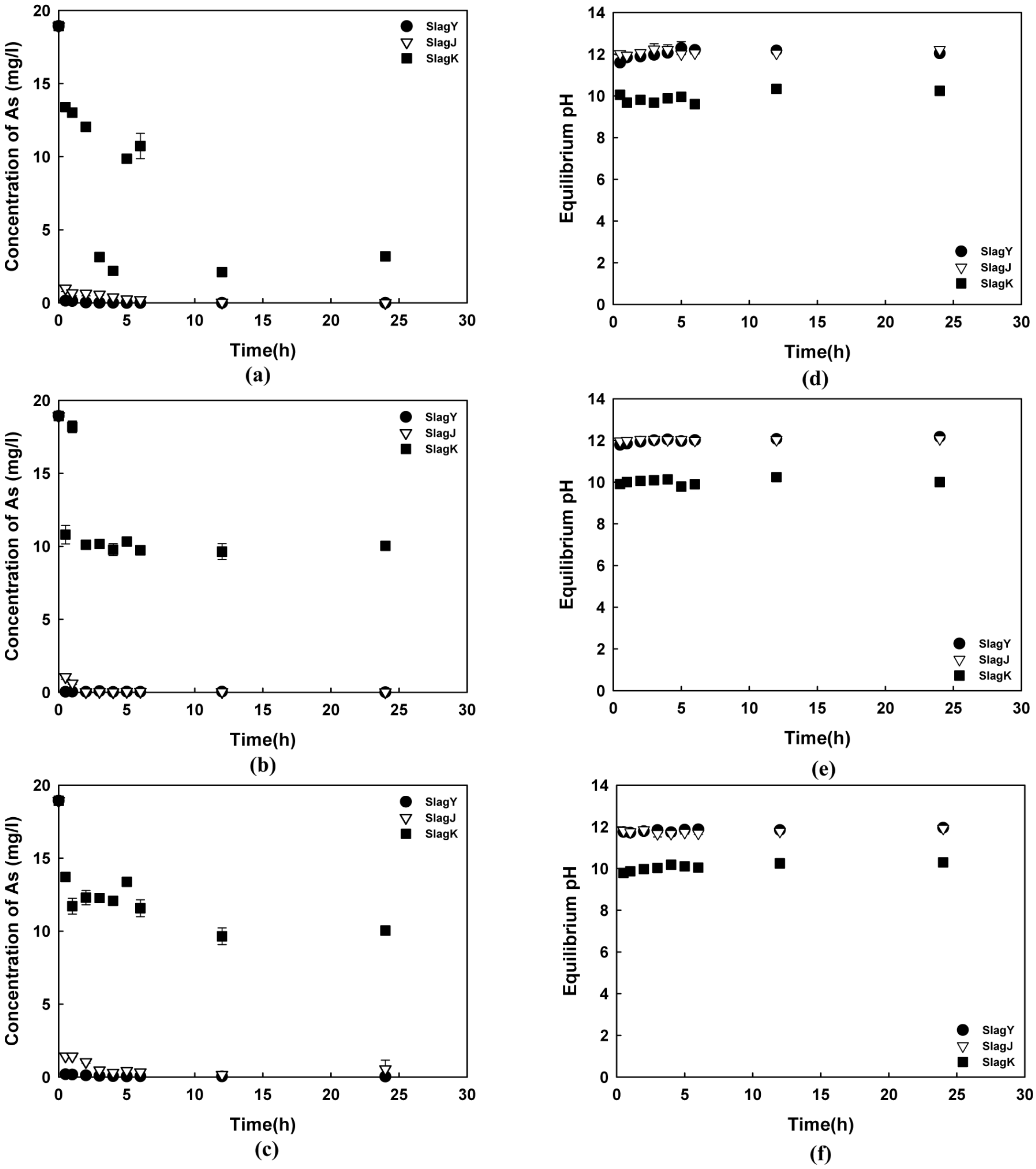

Fig. 1. Effect of the contact time on arsenic removal at pH 4.0, 7.0 and 10.0. (a), (b) and (c) are concentrations of arsenic with the time, (d), (e) and (f) are equilibrium pH, initial arsenic concentration — 18.93 mg/l, dose of slag — 100 g/l.

10.0. Increase in pH and removal of arsenic might be explained by the following mechanisms [15]:

$$2AsO^{3-} + CaO + H^{+} \rightarrow Ca_3(AsO_4)_2 + OH^{-} \quad (1)$$

The higher equilibrium pH in solution, the more arsenic was removed (Fig. 1a and d) because dissolution of the lime (CaO) caused to produce more hydroxide ion and calcium ion. The calcium and arsenic formed calcium arsenate precipitates. In the case of Slag Y and J, arsenic removal efficiency and equilibrium pH at the initial pH 7.0 and 10.0 showed similar results at the initial pH 4.0 (Fig. 1a, b and c). In the case of Slag K, the removal of arsenic decreased as the initial pH increased (Fig. 1a, b and c) because the solubility of calcium oxide increased with pH. To investigate the adsorption characteristics of arsenic on slag, the experimental results were fitted into pseudo-first-order and second-order model. The two adsorption kinetic models are expressed as follows [16–18]:

Pseudo-first-order model:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (2)$$

Pseudo-second-order model:

$$\frac{t}{q_t}=\frac{1}{K_2 q_e^{\,2}}+\frac{1}{q_e}t \qquad (3)$$

where q_e and q_t (mmol/g) are the amount of adsorbed heavy metals at equilibrium and at time t, respectively. K_1 and K_2 are the first-order rate constant (h^{-1}) and second-order rate constant (h g/mmol), respectively. The parameters and linear plots of pseudo-second-order model are shown in Table 2 and Fig. 2 (pseudo-first-order not shown). The pseudo-second-order model was more appropriate to explain adsorption characteristics of arsenic on slag compared to pseudo-first-order model.

3.2. *Effect of initial arsenic concentration*

Fig. 3 shows the effect of the initial arsenic concentration on the removal of arsenic and equilibrium pH. As the initial concentration of arsenic increased, the removal efficiency of arsenic decreased dramatically (Fig. 3). Arsenic was mainly removed by precipitation such as form of $Ca_3(AsO_4)_2$. In the thermo-dynamical simulation using Mineql, arsenic forms calcium arsenate at pH 7.0 and most arsenate forms the precipitates above pH 9.0 at the presence of excess calcium ion (Fig. 5). The simulation results are consistent with the experimental results. As shown in Table 1, the content of CaO was the highest in Slag Y, and calcium dissolved into the aqueous phase played the important role in the removal of arsenic. Even though CaO content in Slag J was lower than that in Slag K, the content of iron oxide in Slag J was rather higher than Slag K, as a result, the removal efficiency in Slag J was higher than that in Slag K. Iron oxide is a favorable adsorption site for arsenic. At the case of initial pH 4.0 (Fig. 2d), the equilibrium pH decreased gradually as the initial concentration of arsenic increased. The major form of arsenic at pH 4.0 is $H_2AsO_4^-$,arsenic was deprotonated and released the hydrogen ions, and the hydrogen ions released from arsenic reduced the equilibrium pH. The higher concentration of arsenic produced more hydrogen ions, the

Table 2
Pseudo-second-order parameters for the adsorption of arsenic onto slag

	pH 4		pH 7		pH 10	
	K_2	R^2	K_2	R^2	K_2	R^2
Slag Y	1.6×103	0.99	12.2×103	0.99	11.7×103	0.99
Slag J	2.2×103	0.99	16.7×103	0.99	15.9×103	0.99
Slag K	1.9×103	0.92	7.3×103	0.99	7.9×103	0.99

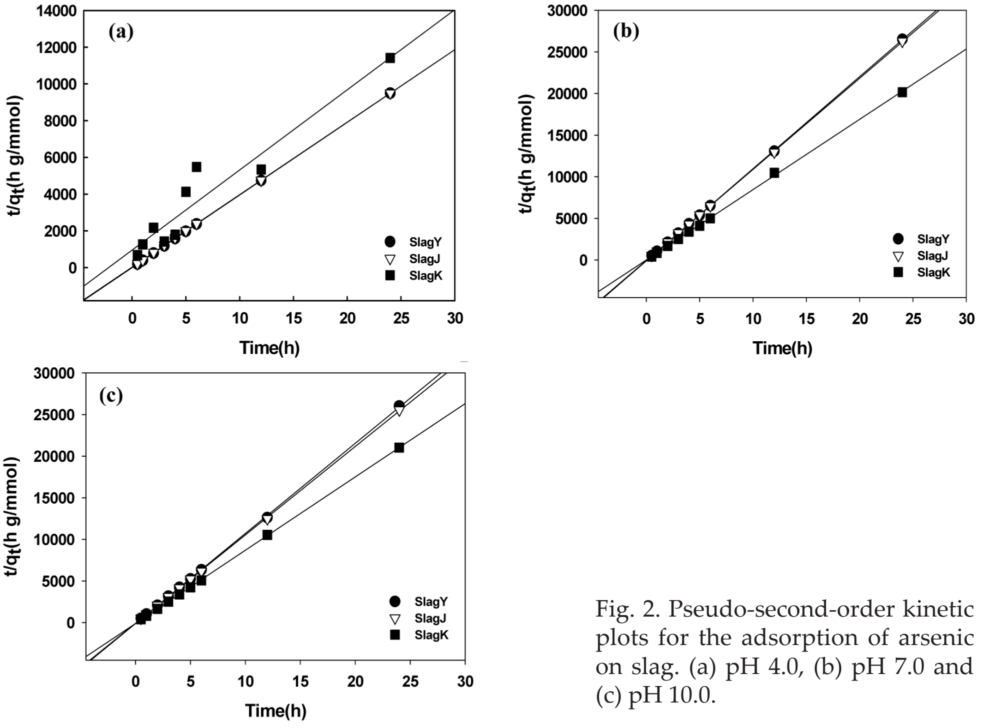

Fig. 2. Pseudo-second-order kinetic plots for the adsorption of arsenic on slag. (a) pH 4.0, (b) pH 7.0 and (c) pH 10.0.

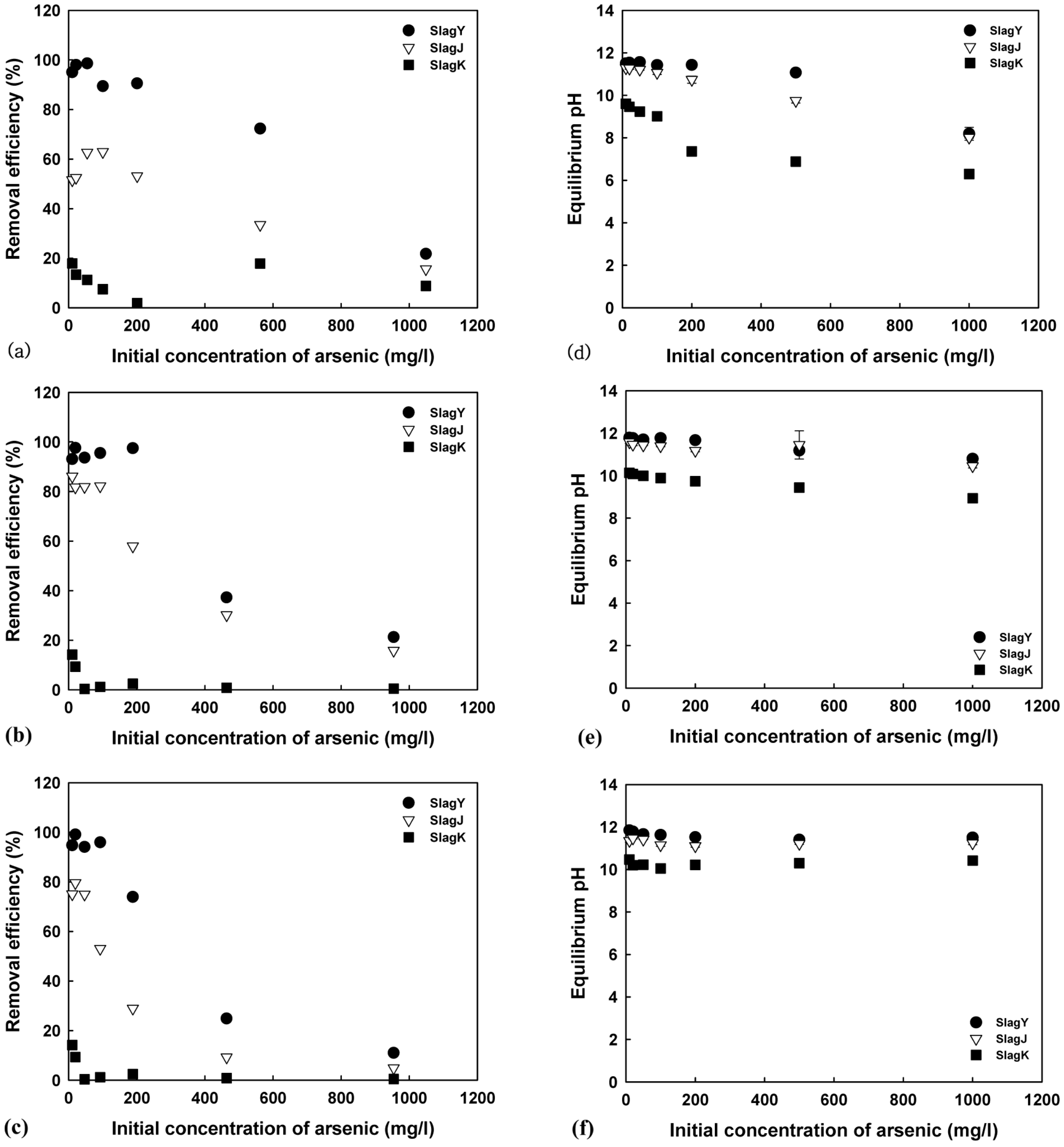

Fig. 3. Effect of initial arsenic concentration on arsenic removal at pH 4.0, 7.0 and 10.0. (a), (b) and (c) are removal efficiencies of arsenic, (d), (e) and (f) equilibrium pH, initial arsenic concentration — 10.84–1049 mg/l, dose of slag — 10 g/l, contact time — 24 h.

decrease in solution pH was significant. Although the similar phenomena occurred at pH 7.0 and pH 10.0, the amount of hydrogen ions released from arsenic was much less than that at pH 4.0. As the initial pH decreased, the decrease in equilibrium pH was more significant. In order to determine the adsorption capacity of arsenic on slag, the experimental results were applied to Langmuir and Freundlich isotherm models. The Langmuir and Freundlich isotherm models can be expressed as follows [19]:

Langmuir isotherm model:

$$q_e = \frac{Q_{\max} K_a C_e}{1 + K_a C_e} \tag{4}$$

Freundlich isotherm model:

$$q_e = K_F C_e^{1/n} \tag{5}$$

q_e (mg/g) is the adsorbed amount of heavy metals and C_e (mg/l) is equilibrium concentration of heavy metals. $Q_{\max}$ and K_a are maximum adsorbed amount and Langmuir Isotherm constant, respectively. K_F (mg/g) and n are Freundlich constants. The parameters of Langmuir and Freundlich isotherm models are summarized in Table 3. Fig. 4 shows the Langmuir isotherm of each slag at various initial pH. The Langmuir isotherm model fitted well compared to Freundlich isotherm model. The parameters

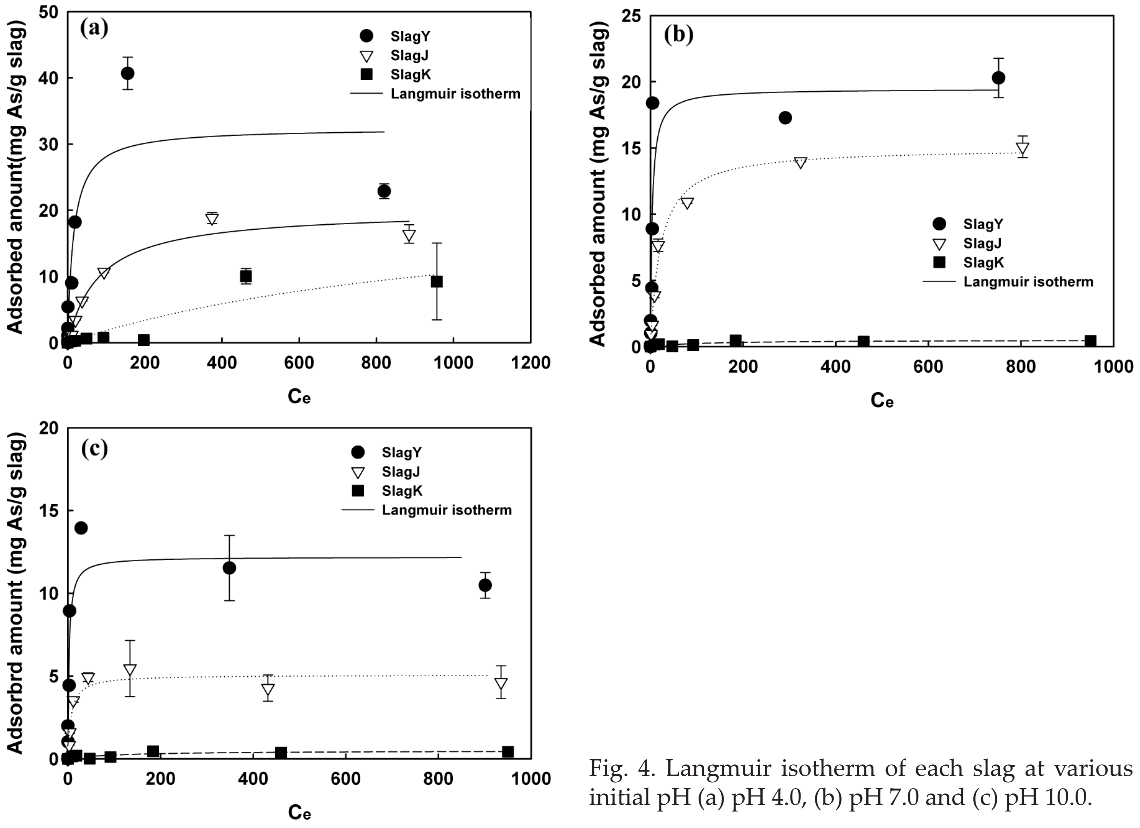

Fig. 4. Langmuir isotherm of each slag at various initial pH (a) pH 4.0, (b) pH 7.0 and (c) pH 10.0.

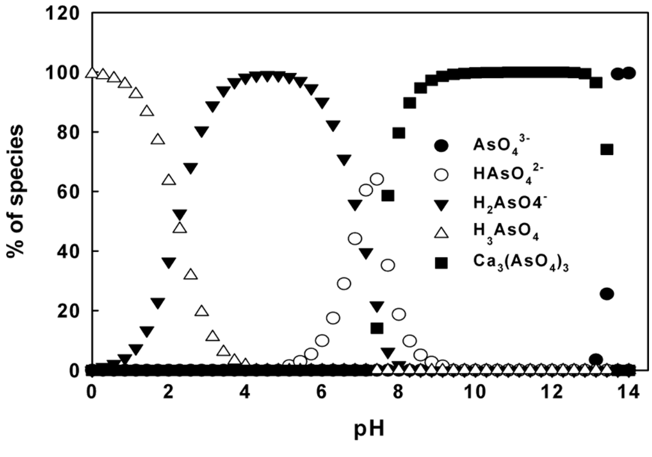

Fig. 5. The simulation results using Mineql.

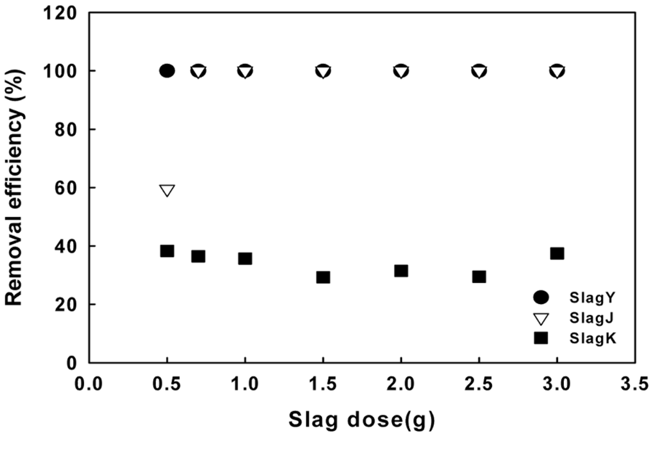

Fig. 6. Effect of the slag dose on arsenic removal at initial pH 3.0. Initial arsenic concentration — 20.24 mg/l, dose of slag — 16.7–100 g/l.

of Langmuir and Freundlich isotherm models are summarized in Table 3.

3.3. *Effect of the slag dose*

Fig. 6 shows the effect of the slag dose on the removal of arsenic. At an initial arsenic concentration of 20.24 mg/l and a slag mass of 16.7 g/l, the removal efficiency of arsenic was 100%, 59.5% and 38.3 % for Slag Y, J and K, respectively. Above 23.3 g/l of Slag J and Y, arsenic of 20.24 mg/l was removed completely. In the case of Slag K, we could not find any trends on removal efficiency with the dose of slag and the removal efficiency was ranged 29.3–38.3% even though the dose increased.

3.4. *Concentration of calcium*

Fig. 7 shows the amount of calcium dissolved from slag into the aqueous streams at various initial pHs. The amount of calcium in the aqueous phase decreased with

Table 3
Parameters of Langmuir and Freundlich isotherms models

Langmuir isotherm model						
	pH 4		pH 7		pH 10	
	Q_{max}	R^2	Q_{max}	R^2	Q_{max}	R^2
Slag Y	32.4	0.91	19.5	0.93	12.2	0.97
Slag J	20.0	0.99	15.0	0.99	5.1	0.98
Slag K	9.2	0.88	0.5	0.87	0.5	0.87

Freundlich isotherm model									
	pH 4			pH 7			pH 10		
	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2
Slag Y	7.93	4.8	0.81	6.12	5.56	0.87	4.97	7.02	0.89
Slag J	1.6	2.7	0.94	2.63	3.57	0.97	2.01	6.90	0.92
Slag K	0.05	1.27	0.86	0.05	3.13	0.87	0.05	3.11	0.87

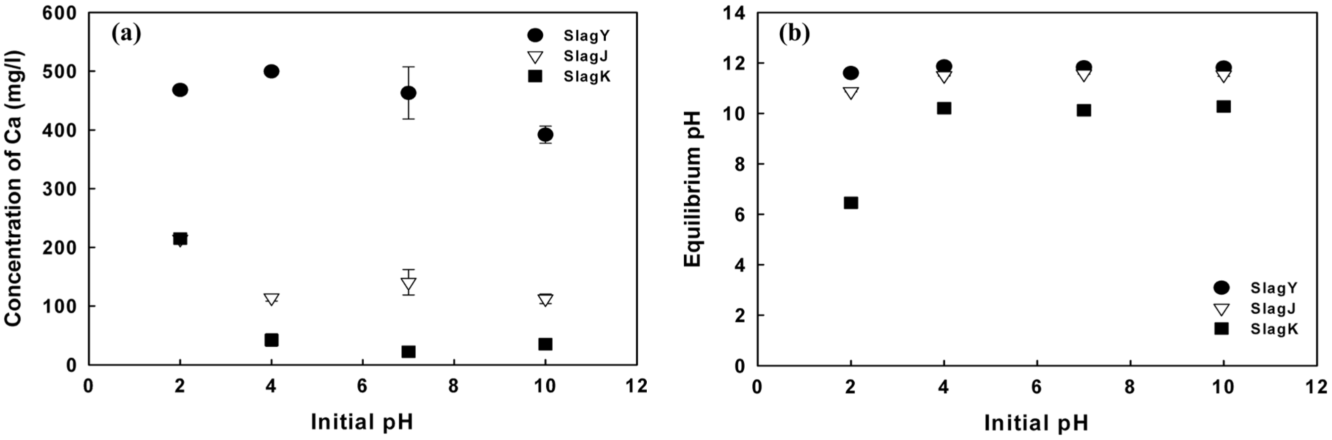

Fig. 7. Concentration of calcium and equilibrium pH at various initial pHs: (a) calcium concentration, (b) equilibrium pH. Dose of slag — 100 g/l, contact time — 24 h.

the increase in the initial solution pH because the solubility of the CaO increased at acidic conditions. The order of calcium concentration is consistent with the removal efficiency of arsenic. This result means that arsenic is mainly removed by Ca-As precipitation. Even though too acidic condition (pH 2.0) enhanced the dissolution of CaO in Slag K, Ca-As precipitation was inhibited by neutral or slightly acidic equilibrium pH.

4. Conclusion

Batch experiments were carried out to investigate the removal characteristics of As(V) using steel-making slags. Arsenic was removed by Ca-As precipitation in the form of $Ca_3(AsO_4)_2$, and calcium came from dissolution of CaO. The removal efficiency of arsenic on slag was affected by the content of iron oxide because iron oxide provided arsenic with favorable adsorption sites. The experimental results were fitted into two kinetic and isotherm models, and pseudo-second-order and Langmuir isotherm model fitted well compared to other models. Arsenic was removed by Slag Y and Slag J within 30 min, however Slag K was not effective to remove arsenic with a longer contact time. Removal of arsenic increased with the decrease in the initial pH because of enhancement in dissolution of CaO. Calcium concentration decreased with the increase in the initial pH because the solubility of lime (CaO) increased at acidic conditions. After the reaction, the equilibrium pH sharply increased because dissolution of the CaO caused the production of hydroxide ions.

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