

# Column Adsorption Experiments for the Removal of Arsenic and Fluoride Ions in Mine Drainage using Adsorbents

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## Abstract

Alum sludge-based adsorbent (ASBA) and granular ferric hydroxide (GFH) were applied in mine drainage and synthetic solutions to investigate the adsorption efficiencies of arsenate (As(V)) and fluoride (F). Whereas the adsorption capacity of ASBA for F decreased rapidly after 513–761 bed volumes (BVs), As(V) could be treated for 930–1,145 BVs. The higher concentration of F than As(V) in the influent may be one of the factors that shortened the breakthrough for F. As(V) for GFH was maintained below 50  $\mu\text{g L}^{-1}$  for 8,212 BVs. These adsorbents could be used to remove As(V) and F under field conditions.

**Keywords:** Adsorption, arsenate, fluoride, mine drainage, alum sludge-based adsorbent

## Introduction

that causes death as well as peripheral neuropathy and skin cancer if the body is exposed to inorganic arsenic for a long time (Jomova et al. 2011). Also, it has been reported that an excessive supply of F in the body results in F deposition, neurological problems, and immune system disorders (Streat et al. 2008; Kim et al. 2013).

In general, the geological features of the area are closely related to the pollutants dissolved in mine drainage. According to Nicolli et al. (2008), F is mainly found in groundwater at high concentrations in granite-rich areas and frequently occurs with arsenic in an alkaline environment. The geology of the Suri (Sujung) abandoned metal mine in the Republic of Korea is a location where biotite

granite penetrated at the end of the Cretaceous period along the Ordovician limestone layer in the late Paleozoic era. As(V) and F are present at an average concentration of 79.5  $\mu\text{g L}^{-1}$  and 3.26  $\text{mg L}^{-1}$  in alkaline mine water discharged from the waste metal mine, exceeding 50  $\mu\text{g L}^{-1}$  and 3  $\text{mg L}^{-1}$  as the maximum contamination level (MCL). Therefore, As(V) and F above a specific concentration flowing out of this abandoned mine area must be removed for the conservation of the aquatic ecosystem and the health of residents living in nearby areas.

The purpose of this study was to investigate the adsorption efficiencies of As(V) and F in abandoned metal mine drainage and synthetic solutions using ASBA produced by wastewater treatment facilities in the Republic of Korea (KOMIR 2021) and

GFH by a cost-saving and easy-to-manage adsorption treatment technique (MIRECO 2017; Kumar et al. 2020). Following X-ray diffraction (XRD), wavelength dispersive X-ray fluorescence (WD-XRF), and extreme high resolution scanning electron microscope (FE-SEM) observations, the crystalline structure and mineralogical composition of ASBA and GFH were examined. Also, laboratory-scale column experiments for 503 days were conducted on ASBA and GFH using mine drainage and synthetic solutions with dissolved As(V) and F.

## Materials and methods

Two alum-based adsorbents (ASBA-3 and ASBA-G) of different sizes and shapes and granular ferric hydroxide (GFH) were used in the experiment. ASBA was prepared by the following procedure using sludge obtained from the sedimentation tank of the water treatment facilities: water treatment sludge, water, and dissociation reagents were put into a hydrothermal synthesizer in a certain amount, stirred at 100 rpm under 100 °C control, and the reaction was carried out for 1 d and left for 2 d. Thereafter, the reactant obtained by washing several times with distilled water until the pH of the filtrate became neutral was dried until the moisture content was less than 5 wt.%. An amorphous specimen of 0.2–2.0 mm was selected from the produced dry materials, placed in an electric furnace under air supply conditions, and thermally treated at 500 °C for 1 h to prepare ASBA-G. ASBA-3 was prepared by mixing it properly, injecting it into a mold, shaping it into a sphere, and being thermally treated. GFH purchased and used GEH102 products from GEH Wasserchemie GmbH & Co. KG in Germany. The particle diameter of GFH was 0.2–2.0 mm, and it was sealed to preserve moisture on the surface of the adsorbent and stored in a darkened place.

By using XRD (D8 ADVANCE, Bruker, Germany) and WD-XRF (ZSA PrimusIV, Rigaku, Japan), the mineral properties and constituent elements of the adsorbent samples were examined. Samples were prepared in homogeneous powder using an agate mortar and 100 mesh standards for those analyses. A Brunauer-Emmett-Teller (BET) surface

area analyzer (3Flex, Micromeritics, USA) was used to determine the surface area of adsorbents. Also, the pore structure and size distribution of the adsorbent were examined by FE-SEM (Verios G4 UC, FEI, USA). To remove moisture and other impurities present on the adsorbent surface before specific surface area (SSA) measurement, N<sub>2</sub> gas was adsorbed and analyzed in an analysis bath of -195.85 °C for 12 h under a nitrogen atmosphere (Badruzaman et al. 2004), and a specimen was observed with a silver paste (Dotite D500) to obtain a high-resolution surface image. The solid addition method (Oladoja and Aliu 2009) was used to determine the point of zero charge (pHPZC) of adsorbent samples.

Laboratory-scale column experiments were performed for 503 days using synthetic solutions containing As(V) and F and mine drainage collected from the waste metal mine Suri (Sujung). Each volume of water was injected through a peristaltic pump at flow rates of 0.28, 0.1665, and 0.0535 mL min<sup>-1</sup>. Empty bed contact time (EBCT) was set to 88.2 (ASBA-3, ASBA-G, and GFH), 150.9 (ASBA-G2), and 469.7 (ASBA-G3) min, respectively. In the case of ASBA-3, ASBA-G, and GFH, it was treated with mine drainage up to 5,502 BVs, and synthetic solutions spiked with As(V) and F after 5,502 BVs were used because of the difficulties of collecting water samples from this mine site. Also, ASBA-2 and ASBA-3 used synthetic solutions after 2,128 and 683 BVs, respectively. Synthetic solutions simulating mine drainage contaminated with As(V) and F were prepared by diluting a standard solution, in which disodium hydrogen arsenate heptahydrate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, Sigma-Aldrich, USA) and sodium fluoride (NaF, 99.9%, Sigma-Aldrich, USA) were dissolved at a concentration of 1,000 mg L<sup>-1</sup> in deionized water. The prepared standard solution was used after being refrigerated. 0.1 N of hydrochloric acid (HCl, DAEJUNG, Republic of Korea) and sodium hydroxide (NaOH, DAEJUNG, Republic of Korea) were used for pH titration of the experimental solution. They were set up for a bottom-up flow.

## Results and discussion

### Characteristics of ASBA and GFH

As a result of FE-SEM analysis, ASBA had a bumpy shape, while GFH showed a shape in which small grains were attached to the surface (Figure 1). ASBA was mostly composed of  $\text{Al}_2\text{O}_3$  (57.32%) and  $\text{SiO}_2$  (18.21%), while GFH was most composed of  $\text{Fe}_2\text{O}_3$  (89.58%) through WD-XRF analysis (Table 1). GFH and ASBA-G (0.2–2 mm) were granular, and ASBA-3 (3 mm) was spherical. As a result of comparative analysis of the XRD pattern with ICDD's database, ASBA displayed various diffraction peaks, and the main crystal phases were quartz, muscovite, albite, and orthoclase. Iron oxide and akaganeite were detected in GFH as a diffraction pattern close to amorphous (Figure 2). As a result of BET analysis, the SSAs of powdered ASBA-3, ASBA-G, and GFH were 136.34, 126.07, and 257.02  $\text{m}^2\text{g}^{-1}$ , respectively. According to IUPAC classification, it was classified as IV(a) type adsorption and desorption isotherms, which indicated that mesopores were developed in adsorbents and caused high

SSA, porosity, and capillary condensation (Figure 3; Thommes et al. 2015).

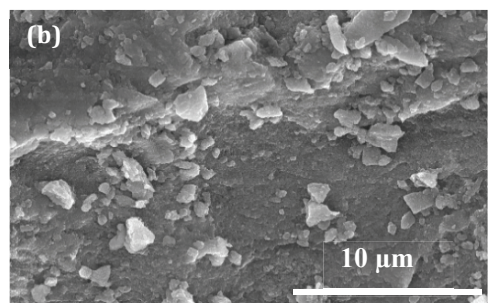
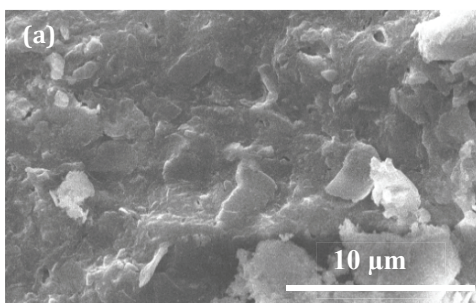
As a result of measuring the zero charge point of the adsorbent surface using the solid addition method, ASBA-3 and ASBA-G had pHPZC at value of 5.25 and 5.29, respectively, while GFH had zero charge on the particle surface at a pH of 6.72 (Figure 4). Therefore, ASBA is expected to be negatively charged in a neutral aqueous solution, so it is estimated that the adsorption of As(V) is slightly lower than that of GFH. Meanwhile, GFH has a positive charge on the surface of an acidic or neutral aqueous solution, so it is easy to adsorb As(V) ( $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ) present in the form of anions.

### As(V) and F treatment efficiencies in laboratory-scale column experiments

To evaluate the adsorption efficiencies of these adsorbents, laboratory-scale column experiments were conducted by changing from mine drainage to synthetic solutions injected into the column at 79.5  $\mu\text{g L}^{-1}$  and 3.26  $\text{mg L}^{-1}$  using ASBA and GFH. When mine drainage and synthetic solutions were passed through these adsorbents, breakthrough for As(V) occurred after 1,145 (ASBA-3), 930 (ASBA-G), 949 (ASBA-G2), 1,066 (ASBA-G3), and 8,212 (GFH) BVs granules were packed. As(V) concentration was maintained below 10  $\mu\text{g L}^{-1}$  until GFH reacted with 8,212 BVs (Figure 5). It represented that As(V) had a high affinity for iron compounds, which were the main ingredient in GFH. As the EBCT became shorter, the contact time between As(V) and the adsorption site decreased, indicating that the time to adsorb and remove As(V) below the MCL (50  $\mu\text{g L}^{-1}$ ) of discharged water was

**Table 1** Major element composition of adsorbents analyzed by WD-XRF.

Composition (wt.%)	ASBA	GFH
$\text{Al}_2\text{O}_3$	57.32	0.69
$\text{SiO}_2$	18.21	0.31
$\text{P}_2\text{O}_5$	5.58	0.02
$\text{Fe}_2\text{O}_3$	2.94	89.58
MnO	1.26	–
$\text{Cr}_2\text{O}_3$	0.01	0.87
$\text{CO}_2$	11.53	5.77
Cl	0.05	2.33



**Figure 1** FE-SEM images of adsorbents (a) ASBA and (b) GFH.

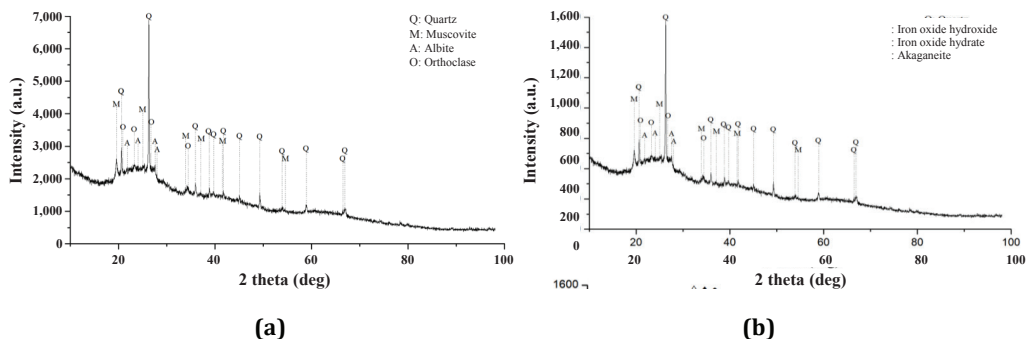


Figure 2 XRD patterns of adsorbents; (a) ASBA and (b) GFH.

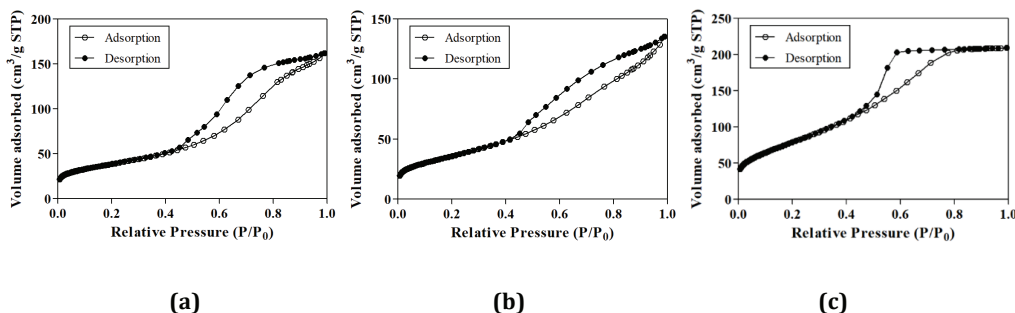


Figure 3  $N_2$  adsorption-desorption isotherm of adsorbents; (a) ASBA-3, (b) ASBA-G, and (c) GFH.

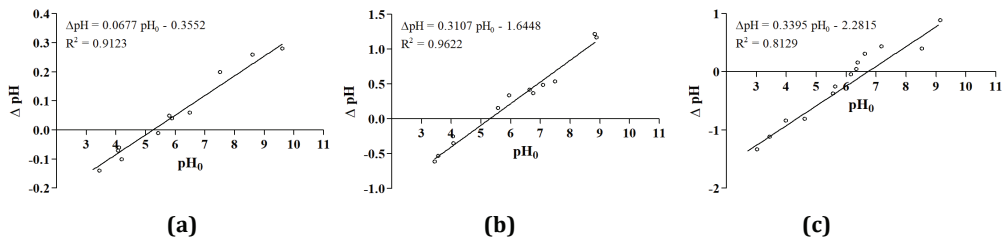


Figure 4 Determination of  $pH_{pzc}$  (point of zero charge) of adsorbents; (a) ASBA-3, (b) ASBA-G, and (c) GFH.

insufficient. ASBA-G reached the MCL earlier than ASBA-3. However, ASBA-3 showed a higher As(V) concentration in effluent than ASBA-G, indicating that ASBA-G had a better adsorption capacity than ASBA-3 (Figure 6).

In the case of F in ASBA-G2 and ASBA-G3, the F concentration of effluent increased faster than that of As(V). Thus, breakthrough occurred after 513 (ASBA-G2) and 761 (ASBA-G3) BVs, respectively (Figure 7). In the case of As(V), the breakthrough was

reached after treatment with 930 to 1,145 BVs. Meanwhile, the adsorption capacity for F decreased rapidly after treatment with 513 to 761 BVs and the breakthrough then happened. One of the causes that may have reduced the breakthrough time for F was the higher concentration of F than As(V) in the influent, and then F was adsorbed more in ASBA-G2 and ASBA-G3 granules. In addition, because F and hydroxide ions were competitively adsorbed under a pH condition

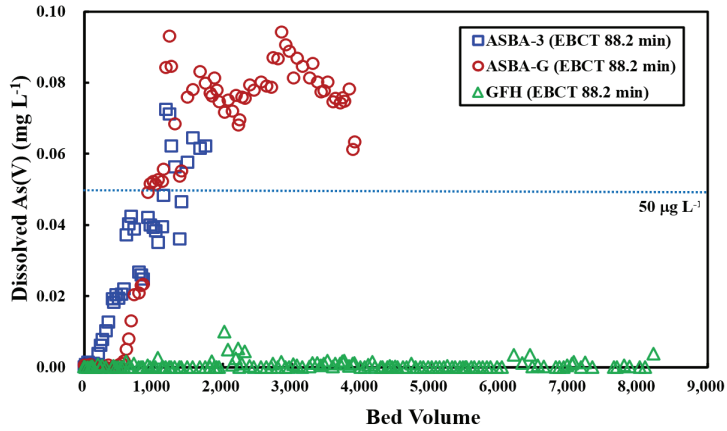


Figure 5 Changes in As(V) concentration of column effluent at EBCT 88.2 min of adsorbents.

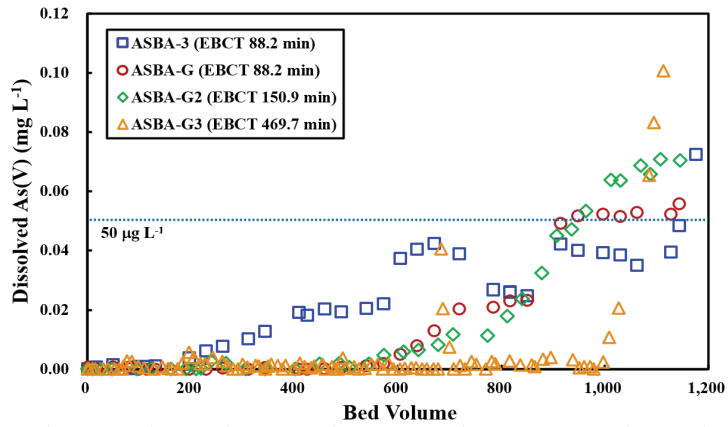


Figure 6 Changes in As(V) concentration of column effluent according to EBCT of ASBA.

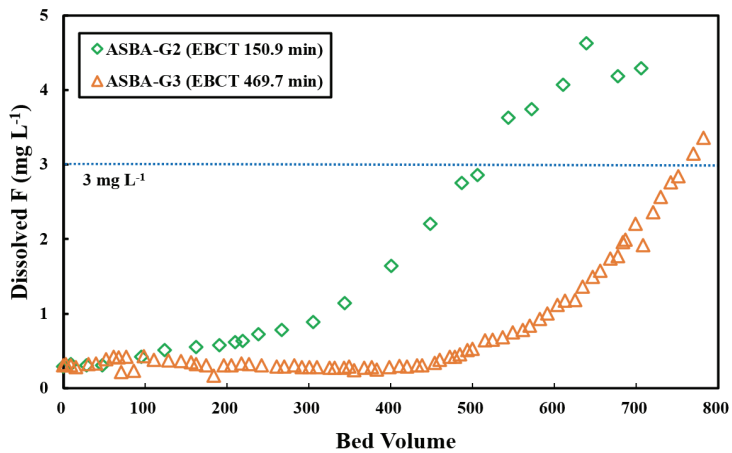


Figure 7 Changes in F concentration of column effluent according to EBCT of ASBA.



close to neutral, the adsorption amount of F would have been relatively reduced (Streat et al. 2008). Therefore, ASBA and GFH have the potential to be used under field conditions for the remediation of As(V) and F.

## Conclusions

Laboratory-scale column experiments were executed on ASBA and GFH using mine drainage and synthetic solutions for a duration of 503 days. GFH removed As(V) from 79.5  $\mu\text{g L}^{-1}$  to 10  $\mu\text{g L}^{-1}$  while processing 8,212 BVs. Also, ASBA treated 930–1,145 BVs to eliminate As(V) and 513–761 BVs for the removal of F. Thus, it was found that the length of the EBCT and the breakthrough BV had a proportional relationship. Because the F concentration in the influent was higher than that of As(V), the breakthrough for F was shorter than that of As(V). Therefore, at field sites contaminated with As(V) and F, these adsorbents may contribute to the removal of As(V) and F.

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## References

- Badruzzaman M, Westerhoff P, Knappe DR (2004) Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH). *Water Res* 38(18):4002–4012. <https://doi.org/10.1016/j.watres.2004.07.007>
- Jomova K, Jenisova Z, Feszterova M, Baros S, Liska J, Hudecova D, Rhodes CJ, Valko M (2011) Arsenic: toxicity, oxidative stress and human disease. *J Appl Toxicol* 31(2):95–107. <https://doi.org/10.1002/jat.1649>
- Kim JH, Song YM, Kim SB (2013) Fluoride sorption property of lanthanum hydroxide. *J Korean Soc Environ Eng* 32(7): 714–721 (in Korean)

- KOMIR (2021) Development of site-specific sorption processes to remove heavy metals in low-flow mine drainage. Technology Report 2021-041, Korea Mine Rehabilitation and Mineral Resources Corporation (KOMIR), Republic of Korea (in Korean)
- Kumar R, Kang CU, Mohan D, Khan MA, Lee JH, Lee SS, Jeon BH (2020) Waste sludge derived adsorbents for arsenate removal from water. *Chemosphere* 239:124–832. <https://doi.org/10.1016/j.chemosphere.2019.124832>
- MIRECO (2017) Media evaluation and on-site demonstration to remove arsenic adsorption in mine drainage, Technology Report, Korea Mine Reclamation Corporation (MIRECO), Republic of Korea (in Korean)
- Nicolli HB, Tujchneider OC, Paris MDC, Blanco MDC, Barros AJ (2008) Sources and mobility of arsenic in groundwater from centre-north plain of Santa Fe Province, Argentina. In: *Proceedings of the 2nd International congress: arsenic in the environment: arsenic from nature to humans*, p 21–23
- Oladoja NA, Aliu YD (2009) Snail shell as coagulant aid in the alum precipitation of malachite green from aqua system. *J Hazard Mater* 164(2-3):1496–1502. <https://doi.org/10.1016/j.jhazmat.2008.09.114>
- Streat M, Hellgardt K, Newton NLR (2008) Hydrous ferric oxide as an adsorbent in water treatment: Part 3: Batch and mini-column adsorption of arsenic, phosphorous, fluorine and cadmium ions. *Process safety and environmental protection* 86(1):21–30. <https://doi.org/10.1016/j.psep.2007.10.009>
- Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, Sing KS (2015) Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution IUPAC technical report). *Pure Appl Chem* 87(9–10):1051–1069. <https://doi.org/10.1515/pac-2014-1117>