Sorption of Arsenic and Fluoride in Neutral Mine Drainage Using Fe-Based Sorbents

Myoung-Soo Ko[1], Su-Jin Kim[1], Oh-Hun Kwon[2]

[1]Kangwon National University, Korea, Republic of (South Korea)

[2]Korea Mine Rehabilitation and Mineral Resources Corporation (South Korea)
msko@kangwon.ac.kr, ORCID 0000-0002-7404-7958

Abstract

Arsenic (As) and fluoride (F) are persistent contaminants in mine drainage that pose substantial environmental and health risks even at low concentrations. Unlike trace metals, As and F remain in dissolved ion under neutral pH conditions, making their removal challenging with conventional treatment methods. Adsorption is a promising alternative due to its space efficiency, operational simplicity, and cost-effectiveness. This study investigates the sorption mechanisms of As and F using two iron (Fe)-based adsorbents: AMDS (MIRESORB, E&Chem Solution) and GFH (GEH 102, Wasserchemie GmbH & Co. KG). AMDS contains 50.2 wt% of Fe, while GFH contains 73.1 wt% of Fe, with specific surface areas of 274.9 m^2/g and 316.5 m^2/g, respectively. Kinetic and isotherm sorption experiments were conducted at pH 7.4 to simulate neutral mine drainage conditions. The results showed that As sorption onto both AMDS and GFH followed the pseudo-second-order kinetic model and the Langmuir isotherm model, indicating monolayer adsorption through a chemisorption mechanism. While GFH exhibited a slightly higher maximum adsorption capacity (q_m = 42.4 mg/g) than AMDS (q_m = 32.3 mg/g), AMDS demonstrated excellent sorption efficiency relative to Fe content. The F sorption followed the pseudo-second-order kinetic model and followed the Freundlich isotherm model, suggesting multilayer adsorption via chemical interactions. The Freundlich sorption coefficient (K_F) was 0.21 for AMDS ($R^2 > 0.99$) and 0.43 for GFH ($R^2 > 0.98$), indicating that GFH had a higher fluoride adsorption capacity. Both AMDS and GFH exhibited adequate sorption performance for As and F removal. However, considering cost-effectiveness and removal efficiency, AMDS emerged as a promising sorbent for neutral mine drainage treatment. Since As and F are negatively charged ions, they would compete for adsorption sites, influencing removal efficiency. To validate the competitive sorption behavior of As and F, further research is being conducted to assess how their co-existence affects sorption mechanisms and capacity. Understanding competitive sorption dynamics is essential for developing effective mine water treatment strategies in areas where both contaminants are present.

Keywords: Arsenic, fluoride, sorption, mine drainage, iron-based sorbents

Introduction

Mine drainage, originating from abandoned mine, contains various toxic elements, including metals, metalloids, and nonmetals. Common metallic elements such as Fe, Al, and Mn in mine drainage precipitate by neutralization, however, arsenic (As) and fluoride (F) remain as dissolved anionic species under neutral pH. Thus, distinct treatment methods are required to remove As and F from mine drainage. Precipitation, coagulation, ion exchange, and electrodialysis are potential candidate methods. These methods need high operational costs and extensive areas. Sorption process is considered an applicable method for As and F removal due to operational simplicity and low energy requirement. Iron (hydr)oxides has focused notable attention as an effective sorbent for As and F, because of high reactive surface area and geochemical affinity. This study investigates the sorption behaviors of As and F under neutral pH using iron-based materials. furthermore, competitive desorption process evaluated in the presence of both As and F to simulate the complex chemical environment of actual mine drainage.

Methods

Characterization of Adsorbents

Two iron-based adsorbents were used: MIRESORB (AMDS, E&C Solution, Korea), derived from mine drainage sludge, and granular ferric hydroxide (GFH, Wasserchemie GmbH & Co., Germany). Mineralogical properties and major element composition were determined by XRD (D2 PHASER, Bruker, Germany) and XRF (ZSX Primus II, Rigaku, Japan). Surface morphology was observed using SEM–EDS (JSM-7900F, JEOL, Japan). Specific surface area and pore structures were analyzed using BET (BELSORP MAX X, MicrotracBEL, USA). The point of zero charge (pH_{pzc}) was determined following Balistrieri LS, Murray JW (1981).

Adsorption Isotherms and Kinetics

Batch experiments were conducted in duplicate to evaluate As and F adsorption. For isotherms, initial concentrations

***Table 1** Surface area and major elements compositions of adsorbents.*

Adsorbent	Surface Area (m^2/g)	Elements composition (wt%)								
		O	Fe	Mg	Al	P	S	Mn	As	F
AMDS	274.9	36.4	50.3	2.5	8.3	0.2	1.7	0.7	-	-
GFH	316.5	26.2	73.1	-	0.2	0.1	0.3	0.2	-	-

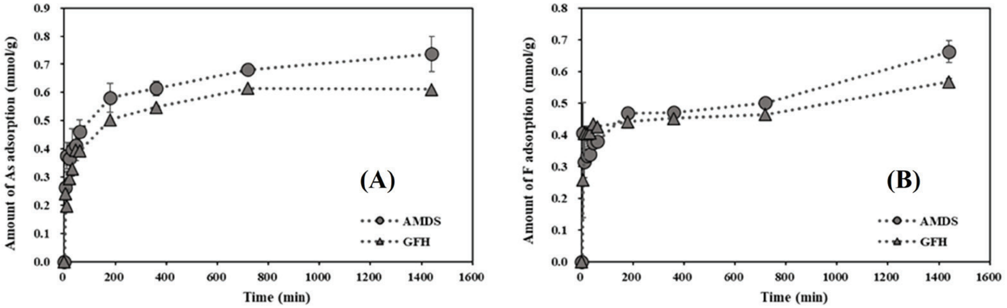

***Figure 1** Adsorption kinetics of (A) As and (B) F onto AMDS and GFH.*

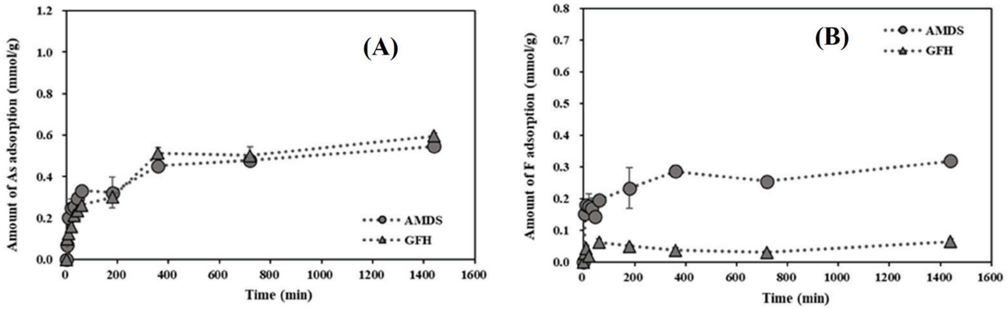

***Figure 2** Adsorption capacity of (A) As and (B) F with competitive conditions.*

(0.02–1.0 mM) were prepared in 0.1 M HEPES buffer. Adsorbent (0.01 g) was reacted with 10 mL of solution for 24 h. Kinetic studies used an initial concentration of 1.5 mM, with samples collected at intervals from 5 to 1440 min. Langmuir, Freundlich, pseudo-first order (PFO), and pseudo-second order (PSO) models were applied to describe the adsorption behavior.

Competitive Desorption

A three-step procedure, which are saturation, washing, and desorption, was performed at 25 °C and pH 7.4. Adsorbents were saturated with 10 mM As or F for 24 h, then recovered by centrifugation. Saturated adsorbent samples were washed three times with 10 mL of ethanol (99.5%) for 5 min each. Finally, desorption was induced by adding a counter-ion solution (10 mM) for 24 h, followed by filtration (0.45 µm) to assess competitive behavior.

Results and Discussion

Adsorbent Characterization

The GFH exhibited a higher Fe content (73.1 wt%) and a larger specific surface area (316.51 m^2/g) compared to AMDS (Table 1). Despite the lower Fe content in AMDS, its specific surface area remains comparable to that of GFH, suggesting a highly porous structure suitable for the sorption of dissolved ions.

Adsorption Kinetics of As and F

The adsorption of both As and F onto AMDS and GFH followed the pseudo-second order (PSO) kinetic model ($R^2 > 0.99$) (Figure 1). The kinetics indicate that the rate-limiting step for As and F presence during chemisorption process involving valence forces. The rapid initial sorption process observed in the first 180 min suggests that the active surface sites of the iron (hydr) oxides are readily accessible at pH 7.4.

Adsorption Isotherms and Capacity

The equilibrium results for As were described by the Langmuir isotherm model, implying monolayer adsorption on a surface with a finite number of identical sites. GFH showed a higher maximum adsorption capacity (q_m = 42.4 mg/g) than AMDS (q_m = 32.3 mg/g). However, sorption efficiency of AMDS showed higher by normalized to Fe content. Fluoride adsorption results followed the Freundlich isotherm model (R^2 0.98–0.99), indicating multilayer adsorption on heterogeneous surfaces. The Freundlich constant (K_F), representing the adsorption capacity, was 0.43 for GFH and 0.21 for AMDS. The higher K_F and q_m values for GFH can be attributed to abundant of Fe content and surface area. Both adsorbents achieved sufficient removal performance under neutral conditions.

Sorption Mechanisms and Competitive Behavior

Because As and F are negatively charged at neutral pH, the competitive reaction would occur at the same reactive sites on the adsorbent surface (Figure 2). This behavior is attributed to the formation of inner-sphere complexes with hydroxyl groups on the iron (hydr)oxide surface. The presence of As influence the F desorption from the adsorbents due to the geochemical affinity. Further investigation into the competitive sorption dynamics is currently being conducted to assess the performance of AMDS in complex mine water matrices.

Conclusions

This study evaluated the efficacy of two iron-based adsorbents, AMDS and GFH, for the removal of As and F from neutral mine drainage. Both materials demonstrated rapid adsorption kinetics, following the pseudo-second-order model, that implied rate limiting chemisorption. The equilibrium data revealed that As adsorption followed the Langmuir isotherm, indicating monolayer coverage, while F adsorption was better described by the Freundlich model, suggesting multilayer adsorption on heterogeneous surface sites. Although GFH exhibited higher maximum adsorption capacities, AMDS showed outstanding removal efficiency relative to Fe content and specific surface area. Both As and F removal were driven by the formation of inner-sphere complexes with surface hydroxyl groups. However, since both contaminants exist as anionic species at neutral pH, competitive adsorption occurs, which may influence overall treatment performance in complex mine water matrices. In conclusion, AMDS emerged as a promising and cost-effective alternative for treating mine drainage containing both As and F.

Acknowledgements

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References

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