Removal Efficiency of Arsenic by Adsorbents having Different Type of Metal Oxides

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Abstract

In this study, oxidation of As (III) as well as removal of total arsenic by adsorbents coated with single oxides or multi-oxides (Fe (III), Mn (IV), Al (III)) was investigated. In addition, multi-functional properties of adsorbents coated with multi-oxides were evaluated. Finally, application of activated carbon impregnated with Fe or Mn-oxides on the treatment of As (III) or As (V) was studied. As (V) adsorption results with adsorbents containing Fe and Al shows that adsorbents containing Fe show a greater removal of As (V) at pH 4 than at pH 7. In contrast adsorbents containing Al shows a favorable removal of As (V) at pH 7 than at pH 4. In case of iron sand, it has a negligible adsorption capacity for As (V) although it contains 217.9 g-Fe/kg-adsorbent. Oxidation result shows that manganese coated sand (MCS) has the greatest As (III) oxidation capacity among all metal oxides at pH 4. Oxidation efficiency of As (III) by IMCS (iron and manganese coated sand) was less than that by MCS. However the total removed amount of arsenic by IMCS was greater than that by MCS.

Keywords: Arsenic, Adsorption, Metal-oxide, Oxidation

1. Introduction

Arsenic is not an abundant element in the earth's crust, and the average crustal concentration is approximately 1.8 mg/kg. However through geogenic processing of crustal materials, arsenic can be concentrated in soil to a typical range of 2 to 20 mg/kg, in some cases with concentrations as high as 70 mg/kg.[1] Unlike many other contaminants that are anthropogenic, arsenic contamination in water systems also comes from natural sources, through the erosion of rocks, minerals and soils.[2] Industrialization and urbanization have been promoted exposure of arsenic to human. While mining or treating of mineral, sulphuric mineral on soil surface is oxidized by oxygen and water and form the acid mine drainage (AMD) entering into the ground or surface water. AMD originated from abandoned mine increase the continual mobility of heavy-metals including arsenic and causes widespread contamination of heavy metals in nearby soils, surface and ground waters.[3]

In Korea, arsenic contamination is serious near in abandoned mines. There are above 2,000 places of mines including 936 ab-

andoned metal mines and 338 abandoned coal mines. Approximately 80% of mines are abandoned without a proper environmental remediation.[4] From the results of soil contamination research for 168 places, many abandoned mines have serious contamination. 62% of mines go over soil contamination warning standard and 52% of mine over run soil contamination counter measure standard. Contaminants in excess of soil contamination counter measure standard are founded As for 55 places, Cd for 39 places, Cu for 28 places, Pb for 30 places, Hg for 7 places, cyanide for 6 places, Cr (VI) for 23 place and Ni for 1 place.[5]

Arsenic is commonly present in environment like semi metallic element (As^0), arsenate (As^{5+}), arsenite (As^{3+}) and arsine (As^{3-}). Among them, in water systems, most arsenics are present as trivalent arsenite (As (III)) and pentavalent arsenate as shown in Fig. 1. One important characteristic of arsenic is easy of change in oxidation state through chemical and biological reaction. The important influencing factors for the mobility of arsenic are known as pH, redox condition, biological activity and adsorption-desorption reaction.[1,6]

Generally, ground water is exposed to anoxic condition, so arsenic is commonly exist as arsenite. In surface water exposed to aerobic condition, arsenic is predominantly presents as arsenate. Fig. 2 shows the speciation of arsenite and arsenate depending on the pH and redox potential.[7] Arsenate species present as

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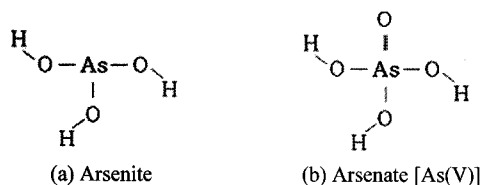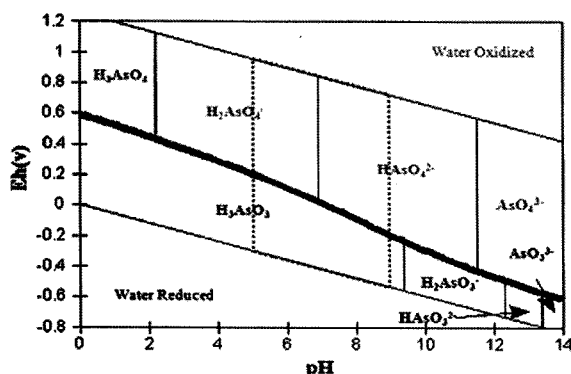E-mail: jkyang@kw.ac.kr
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(a) Arsenite   (b) Arsenate [As(V)]

Fig. 1. Difference in molecular configuration of arsenite and arsenate.

Fig. 2. Arsenic speciation by Eh and pH conditions.[7]

H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} are stable in strongly oxidized conditions irrespective of specific pH. Meanwhile arsenite species such as H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} are stable in reduction condition.

Arsenic treatment depends on the changes of arsenic speciation caused by solution pHs. When arsenic is present as an anion, it is easily removed by adsorption, anion exchange and co-precipitation processes.[8] According to arsenic speciation calculated by MINEQL software, As (V) is generally present as anions (89% as $H_2AsO_4^-$ and 11% as $HAsO_4^{2-}$) in natural pH range. Arsenic adsorption in soil is generally affected by pH.[9,10] When pH is higher than pH$_{PZC}$ (point of zero charge) of adsorbent, metal-oxides in soil surface have negative charges and arsenics are also present as anion. Therefore arsenic adsorption onto the soil surface is inhibited by repulsive forces. While the pH is lower than pH$_{PZC}$ of adsorbent, adsorption reaction is favorable due to the attractive forces between the soil surface having positive charges and arsenic present as anion.[11,12]

From the adsorption studies with minerals like Fe/Mn/Al-oxides and soils, various arsenic adsorption mechanisms are suggested as shown in below;

< Monodentate Complex Formation >

■-OH + HAsO₄²⁻ ⟶ ■-OAsO₃H⁻ + OH⁻   (1)

< Bidentate Mononuclear Complex Formation >

          (2)
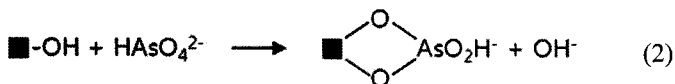
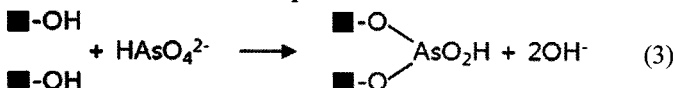< Bidentate Binuclear Complex Formation >

          (3)

Generally, reactions expressed in Eq. (1)~ (3) are commonly

occur in low pH condition. Because OH groups in surface of metal-oxides obtain protons and changed to OH_2 groups which is easily replaceable.[12,13] Adsorption is widely used process in the removal of arsenic. Therefore removal of arsenic in ground and surface water near abandoned mines was investigated by using metal-oxide coated sands in order to use them as filter material because these media are environmentally friendly and requires an economical cost in the preparation and operation process.

In this study several metal-oxide coated sands were prepared with coating of single-oxide or multi-oxides on the sand or impregnation of single oxide on activated carbon.[14] In addition, oxidation of As (III) as well as removal of total arsenic by adsorbents coated with single oxides or multi-oxides (Fe (III), Mn (IV), Al (III)) was investigated. Finally, multi-functional properties of adsorbents coated with multi-oxides were evaluated.

2. Methods

Iron sand (IS) was used as a natural metal-oxide. As synthetic metal-oxides, naturally prepared manganese coated sand (N-MCS) in a filtration plant, Birm (used to remove Fe and Mn), Activated alumina (AA), Iron coated sand (ICS), manganese coated sand (MCS), aluminium coated sand (ACS), iron and manganese coated sand (IMCS), iron and aluminium coated sand (AICS), manganese and aluminium coated sand (AMCS), iron, manganese and aluminium coated sand (XCS), iron impregnated activated carbon (Fe-AC) and manganese impregnated activated carbon (Mn-AC) were used. Iron sand, a major composition was Fe (III), was obtained from an iron mine in Indonesia. Activated alumina (AA) was obtained from Sigma-Aldrich Company. N-MCS obtained from six months operation in a filtration plant has particle size as 12-14 mesh. Joomoonjin sand, widely used sands in Korea, having particle size ranging from 0.5 to 1.0 mm was used as the supporting material for the preparation of ICS, MCS, ACS, IMCS, AICS, AMCS and XCS. Prior to coating iron and manganese onto the sand, the Joomoonjin sand was pre-washed with 0.1 N HCl for 2 hrs and rinsed three times with deionized water to remove any impurities. All chemicals were analytical grade. FeCl₃, Mn (NO₃)₂ and AlCl₃ was purchased from Aldrich Chemicals. The NaNO₃ used to fix ionic strength was obtained from Fisher Scientific. All solutions were prepared with deionized water (18 MΩ-cm) prepared using a Hydro-Service reverse osmosis/ion exchange apparatus (Model LPRO-20). All bottles and glassware were acid washed and rinsed with deionized water before use.

2.1. Preparation of Metal-coated Sand

In order to prepare ACS, IMCS, AICS, AMCS, XCS a Fe/Mn/Al solutions (100 mL of (IMCS - 0.05 M FeCl₃ + 0.05 M Mn (NO₃)₂ · 6H₂O, AMCS - 0.05 M AlCl₃ + 0.05 M Mn (NO₃)₂ · 6H₂O, AICS - 0.05 M AlCl₃ + 0.05 M FeCl₃, AICS - 0.05 M AlCl₃ + 0.05 M FeCl₃, ACS - 0.1 M AlCl₃, XCS - 0.05 M AlCl₃ + 0.05 M FeCl₃ + 0.05 M Mn (NO₃)₂ · 6H₂O), previously adjusted to pH 7 with NaOH solution, was mixed with Joomoonjin

sand (80 g) in a rotary evaporator. By rotating the rotary evapo-
rator at 30 rpm in water bath maintained at 70°C, the water in
the suspension was continuously removed by applying vacuum
until approximately only 10% of the water remained in the sus-
pension. After then the sand was dried at 150°C for 1-hr to allow
stabilization of the coating process. In order to remove traces of
uncoated (soluble) manganese and iron on the sand, the dried
sand was rinsed several times with distilled water and then dried
again at 105°C. Preparation of ICS and MCS was followed the
previous study.[15]

2.2. Preparation of Metal-impregnated Activated Carbon

In the preparation of Mn-AC and Fe-AC, 1000 mL of 0.5 M
Mn $(NO_3)_2$ and 0.125 M $FeCl_3$ solution, adjusted to pH 6 and 4,
was mixed with GAC (200 g) in a flask. By rotating the flask at
70°C, the water in the suspension was continuously removed,
until approximately 10% of the water remained, and the sample
then baked at 150°C for 1 hr. To remove any soluble manga-
nese and iron, the dried Mn-AC and Fe-AC was rinsed several
times with distilled water and again dried at 105°C for 24 hrs.

2.3. Solution Preparation

Typical concentrations of arsenic and other contaminants
found in abandoned Jeonju mines are summarized in Table 1.
[16] In this study, artificial wastewater mimic to the typical con-
centrations found in the abandoned Jeonju mines was prepared
and used. pHs of artificial wastewater were adjusted to pH 4 or 7.

Table 1. Concentrations of cations and anions found in AMD from
Jeonju abandoned mines[16]

Contaminant	As	Mn	Ca	Mg	SO₄	HCO₃
Concentration (mg/L)	1.27	2.05	205	21.8	410	177

2.4. Surface Properties of Adsorbents

In order to measure the total amounts of metals in each metal-
oxide, an acid digestion method (USEPA 3050B) was used to
dissolve all the metals included in each metal-oxide. After filt-
ration, the dissolved metal concentrations were measured using
an inductively coupled plasma (ICP, Perkin-Elmer Model Optima
2000 DV). To analyze combined types of metal-oxides, X-ray
diffraction analysis was carried out on a Powder X-Ray Diffr-
actometer (PXRD, model D5005, Bruker). The point of zero
charge (PZC) of each solid sample is estimated using by acid-
base titration method. The pH_{PZC} of adsorbents are summarized
in Table 2.

2.5. Batch Adsorption Tests

Each adsorbent (2 g/L) was mixed with prepared artificial
contaminated water in plastic bottles. All experiments were
accomplished at ambient temperature (22-25°C). The initial pH
of suspensions for each adsorbent was adjusted to 4 or 7 using

Table 2. pH_{PZC} of adsorbents

	pK_{a1}	pK_{a2}	pH_{pzc}
Iron Sand	4.67	9.15	6.91
Fe-AC	4.84	10.52	7.68
Mn-AC	4.46	9.00	6.73
AA	6.78	9.52	8.15
N-MCS	4.58	8.00	6.29
ACS	4.86	8.22	6.54
MCS	4.73	8.70	6.71
ICS	4.46	9.10	6.78
AMCS	4.87	9.30	7.09
IMCS	4.63	9.15	6.89
AICS	4.62	8.70	6.66
XCS	4.64	8.52	6.58

diluted 1 N HNO_3 and 1 N NaOH solutions. The plastic bottles
were shaken for at least 24 hours to ensure sufficient adsorption
time. After the suspensions were filtered using 0.45 μm filters
(Gelman), the dissolved arsenic concentrations in the filtrate were
measured using the ICP. The adsorbed amounts of arsenic were
calculated from the difference between the total initial arsenic
concentration and the total dissolved arsenic concentration.

3. Result and Discussion

3.1. Metal Content of Adsorbents

Metal contents on each adsorbent measured by USEPA 3050B
are summarized in Table. 3. AA contains the most amount of
Al, Birm has the greatest amount of Mn. Iron Sand has 217 g of
Fe (III) per 1 kg of Iron Sand. Birm has also a great amount of
Fe and Al in addition to Mn. N-MCS has a great amount of Al
and Mn, but Fe content was negligible. Total amount of metals
coated on synthetic adsorbents was quite similar (3,000~4,000
mg/kg-soil).

As (V) adsorption results with adsorbents containing Fe and
Al are shown in Fig. 3, respectively. Adsorbents containing Fe
show a greater removal amount of As (V) at pH 4 than at pH 7.
In contrast adsorbents containing Al shows a favorable removal
of As (V) at pH 7 than at pH 4. It is generally known that As (V)
adsorption onto Al-oxides is maximum around neutral pH.[17,18]
However adsorbents containing both Fe and Al, removal trend
of As (V) depends on the ratio of Fe/Al on the surface of adsor-
bents. This result suggests that As (V) adsorption is strongly
affected by Fe than Al. Adsorption of As (V) onto a certain
metal oxide is controlled by the surface characteristics such as
pHzpc and speciation of As (V) which is depending on the solu-
tion pH. As mentioned in previous section, pH is higher than
pH_{PZC} of an adsorbent, the surface of metal-oxide as well as
arsenic have negative charges. Therefore arsenic adsorption
onto the adsorbent can be inhibited by repulsive forces. While
the pH is lower than pH_{PZC} of adsorbent, adsorption reaction is
favorable due to the attractive forces between the mineral sur-
face having positive charges and arsenic present as anion.[11,12]
Generally, surface complexation reactions expressed in Eq. (1)~

Table 3. Amount of metal-oxides as metal in adsorbents

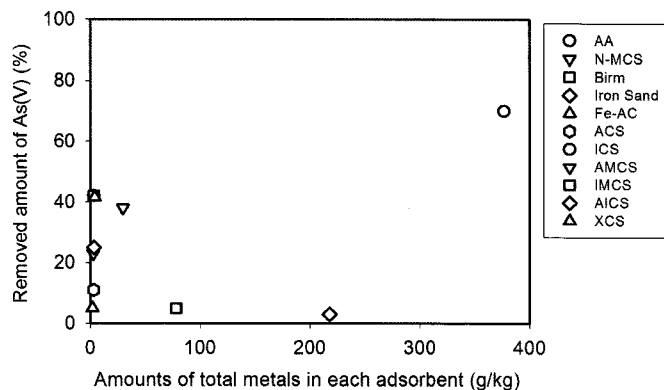|	Al (mg/kg)	Fe (mg/kg)	Mn (mg/kg)
AA	376,700	-	-
N-MCS	19,480	-	10,300
Birm	10,300	4,824	63,120
Iron Sand	-	217,900	-
Fe-AC	-	2,014	-
Mn-AC	-	-	1,724
ACS	3,115	-	-
ICS	-	3,360	-
MCS	-	-	2,518
AMCS	1,225	-	1,595
IMCS	-	2,513	968
AICS	1,711	1,752	-
XCS	1,522	2,018	601

Fig. 4. Removal trends of As (V) by amounts of total metals in each adsorbent after 24 hrs at pH 4.

amount Al but also depends on the mineral types. The major mineral type of Al in AA and N-MCS was identified as Al_2O_3. Mn-oxides have shows different adsorption capacity depending on the minerals types. According to the previous reports, a-MnO_2 has 80 times greater adsorbing capacity for As (V) than β-MnO_2, and γ-MnO_2.[19] N-MCS shows a greater removal of As (V), because the type of Mn is α-MnO_2. The mineral type in Mn-AC was identified as Mn_2O_3 type from XRD measurement.

Generally, Fe-oxides are known as a good adsorbent for As (V).[20] However, in case of Iron Sand, it shows a negligible adsorption capacity for As (V) although it contains 217.9 g-Fe/kg-soil. From the previous investigation of As (V) removal by iron-coated sand, As (V) adsorption was little affected by the presence of background electrolytes except trivalent anions such as PO_4^{3-}. Therefore, it is assumed that divalent anions such as SO_4^{2-} and CO_3^{2-} has negligible effect on the adsorption of As (V) onto the surface of metal-oxides. Therefore different adsorption capacity of As (V) by Iron Sand, ICS, and IMCS could be explained by the different mineral types of Fe (III) on adsorbents. In case of IMCS, the mineral type of Fe (III) was mixture of goethite and hematite.[15]

To identify effects of the amounts of all metals as well as type of metal oxides on the removal of As (V), the removed amounts of As (V), as percent, by several adsorbents were compared in Fig. 4. As shown in Fig. 4, it was difficult to find any correlation between the removed amount of As (V) and contents of all metals in each adsorbent. Therefore this result clearly suggests that adsorption capacity of As (V) by metal oxides is controlled by mineral type as well as amounts of total metals in adsorbents.

(a)

(b)

Fig. 3. Arsenic removal by (a) Fe-containing and (b) Al containing adsorbents after 24 hrs at two different pHs.

(3) are commonly occur in low pH condition.

After 24 hrs, AA shows the the most removal of As (V) among all metal-oxides. N-MCS also adsorbs a great deal of As (V). However Birm, containing a great amount of Al, shows negligible adsorption capacity for As (V). This result mighty be explained by that As (V) adsorption is not only controlled by the
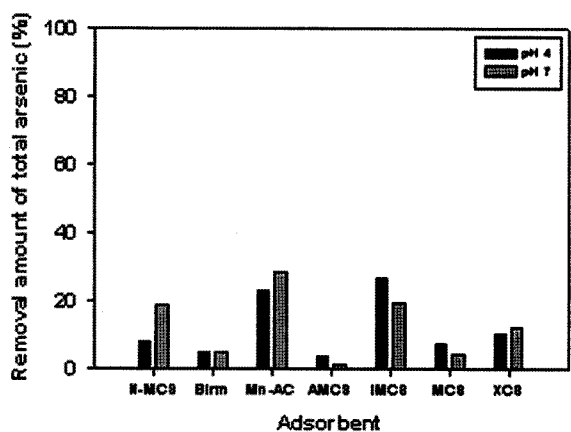
3.2. As (III) Oxidation

As (III) oxidation was performed by adsorbents containing Mn. As shown in Fig. 5, MCS and IMCS shows the greatest oxidation efficiency for As (III) at pH 4. Although MCS has a good oxidation capacity for As (III), the total removal of arsenic was less than that IMCS. This result could be explained by the presence of Iron-oxides that shows a good adsorption capacity for As (III).

MCS is not an efficient media to remove total arsenic, but it shows a good oxidizing capacity for As (III). And adsorbents
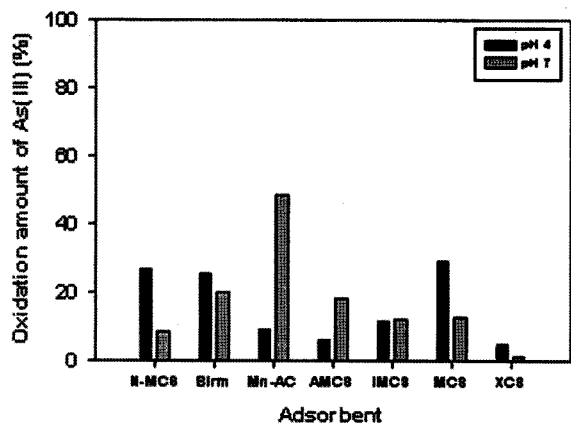
(a)

(b)

Fig. 5. Percent oxidation of (a) As (III) and (b) removal of total arsenic by adsorbents containing Mn after 24 hrs at two different pHs.

containing Al is not a good material for As (III) oxidation. Different As (III) oxidation efficiency was observed with the MCS and Mn-AC. MCS has the most As (III) oxidation capacity at pH 4, but As (III) oxidation by Mn-AC was favorable at pH 7. N-MCS, containing Mn and Al, shows a gradual increase of the removed amounts of total arsenic as pH increases. This trend was explained by the decrease of As (III) oxidation by Mn-oxides and increase of arsenic adsorption by Al-oxides as pH increased. Mn-AC shows a god As (III) oxidation at pH 7 than pH 4.

4. Conclusions

From this research, adsorption capacity of As (V) by Fe-oxides decreased as the crystallinity of Fe-oxides increased. When both Fe (III) and Al (III) are coated on a supporting material, arsenic adsorption was more influenced by the fraction of Fe (III) than that of Al (III). From the oxidation of As (III) and subsequent removal of total arsenic by IMCS, it was possible to suggest that IMCS acts as an multi-functional media. Therefore it is possible to reduce several operating steps when IMCS was used as filter material. And activated carbon impregnated with manganese showed a good oxidation capacity for As (III) at pH 7, and could be used as another multi-functional material.

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