



Reactive ceramic pellets incorporated iron for removing As(III), As(V), and Cr(VI) from aqueous solutions

Sunwon Rha, Yun Sik Gong, Ho Young Jo*

Department of Earth and Environmental Sciences, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea, Tel. +82-2-3290-3179; Fax: +82-2-3290-3189; emails: hyjo@korea.ac.kr (H.Y. Jo), sunwon671@korea.ac.kr (S. Rha), kongys278@korea.ac.kr (Y.S. Gong)

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ABSTRACT

A ceramic filter coated with a reactive material has a high thermal and chemical stability and can be used to treat wastewater under extreme conditions. With the aim of enhancing the reactivity of conventional ceramic materials, the feasibility of incorporating an iron material as the reactive material into conventional ceramic materials was evaluated. Reactive ceramic pellets were synthesized by mixing zero-valent iron (ZVI) with conventional ceramic materials composed of primarily alumina in order to enhance the reactivity of the conventional ceramic materials. To evaluate the removal of As(III), As(V), and Cr(VI) from aqueous solutions, batch sorption tests were conducted under various conditions (i.e., pH and solid-to-liquid ratio) using synthesized ceramic pellets incorporating various iron contents and ZVI and aluminum oxide (Al_2O_3) as reference materials. Results show that ZVI had a higher sorption capacity than Al_2O_3 under acidic conditions, and the adsorption capacity of synthesized ceramic pellets for As and Cr increased when the iron content of the synthesized ceramic pellets increased. These results indicate that the addition of iron materials into conventional ceramic materials can enhance the reactivity of the conventional ceramic material for removal of As and Cr from aqueous solutions.

Keywords: Ceramic material; Zero-valent iron; Alumina; Arsenic; Chromium

1. Introduction

Water pollution has increased in relation to the development of various industrial processes, and the need to provide effective water treatment is thus imperative to ameliorate environmental pollution. Although toxic chemicals such as arsenic (As) and chromium (Cr) can occur as natural phenomena, the pollution of groundwater by such substances mainly occurs in relation to anthropogenic activities [1–4]. As and Cr are carcinogenic substances with high toxicities and environmental risks; therefore, water treatment techniques are urgently required for their removal [3,5,6].

As and Cr exist as oxyanions with various oxidation states that depend on the oxidation potential (Eh) and pH of natural water [1,7,8], and their mobility in the environment depends on their chemical species. As(III) is more mobile and toxic than As(V); however, As(V) is dominant in surface waters under oxidizing conditions, such as those in industrial wastewater. As(V) is thus more of a focus than As(III) in wastewater treatment studies, and its adsorption efficiency is generally higher than that of As(III) during water treatment due to its high stability. In contrast, Cr(VI) is more mobile than Cr(III), and thus Cr(III) is generally removed more easily through adsorption than Cr(VI). Therefore, oxidation/reduction methods are used together

* Corresponding author.

with adsorption methods for the treatment of wastewater contaminated with Cr.

Many methods have been used to treat As- and Cr-contaminated water, such as precipitation [9,10], coagulation [10], oxidation/reduction [6,11,12], membrane treatment [13,14], ion exchange [5,15], and adsorption [4,16,17]. Filtration technology provides certain advantages as follows: low energy requirements, environmentally friendly, and simple process compared with others [18]. Ceramic filters can remove contaminants (e.g., suspended solids) from wastewater through a membrane process via the fine pores in a filter, and they are effective for use in precision filtration processes under extreme conditions such as at high temperatures and/or in acidic conditions, due to their high thermal and chemical stability and high mechanical strength [18]. There is currently a demand for the development of reactive ceramic filters with enhanced wastewater treatment capacities that can be used in heavy metal contaminated wastewater treatment under extreme conditions [18–20].

Zero-valent iron (ZVI), iron (oxy)hydroxides, activated alumina, activated carbon, and zeolites are increasingly used as reactive sorbent materials to remove As and Cr from wastewater [21–24]. ZVI and iron (oxy)hydroxides containing ferrous iron can reduce Cr(VI) to Cr(III), while hydrogen peroxide (or the hydroxyl groups formed during oxidation of iron) can oxidize As(III) to As(V), resulting in an increased adsorption capacity [16,21]. In addition, oxidized iron precipitates as ferric iron (oxy)hydroxides, which exhibit a high adsorption capacity. As and Cr can be removed through co-precipitation with iron(oxy)hydroxides or by electrostatic adsorption [25,26]. Aluminum (oxy)hydroxide, which is generally used as a base material for ceramics, also has the capacity to adsorb metals. Aluminum hydroxide has a high adsorption capacity for As(V), but its desorption capacity for As through reduction is lower than that of iron hydroxide [16,27]. Activated alumina also has a high adsorption capacity for heavy metals because it has a high specific surface area with a large number of pores [16,23,24].

Reactive ceramic filters have recently been the focus of wastewater treatment studies, as they exhibit a heightened heavy metal treatment capacity in relation to their enhanced reactivity, which is achieved by coating the filters with reactive substances [19,20,28]. However, these filters currently have a limitation for use: when the reactive material is applied as a coating on the ceramic filter, the reactive material can be peeled from the filter's surface. Therefore, this study evaluates the feasibility of incorporating iron materials (which have a high capacity for removing As and Cr) as the reactive material into ceramic materials, with the aim of resolving the peeling problem associated with coated ceramic filters. It is of note that although the functions of a reactive ceramic filters are filtration and reactivity, only the reactivity of the reactive ceramic material was evaluated in this study. Batch sorption tests for As and Cr were conducted under different conditions (i.e., pH and solid-to-liquid ratio) using synthesized ceramic pellets containing varying amounts of iron. In addition, batch sorption tests for As and Cr were conducted under different

conditions using aluminum oxide (Al_2O_3) powder as a base material for ceramic pellets and ZVI powder as a reactive material. The removal capacities of the synthesized ceramic pellets were then compared with those of the ZVI and Al_2O_3 powders.

2. Materials and methods

2.1. Materials

As(III), As(V), and Cr(VI) were the target contaminants in wastewater treatment, and analytical grade NaAsO_2 (Sigma-Aldrich Co., USA), $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich Co., USA), and $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ (Junsei Chemical Co. Ltd., Japan) were used in this respect. Initial As and Cr solutions were prepared by dissolving the chemicals in deionized (DI) water at three concentrations of 5, 10, and 100 mg L^{-1} ; and 0.1 and 0.01 M solutions of HNO_3 (Sigma-Aldrich Co., USA) and 0.1 M and 0.01 M NaOH (Sigma-Aldrich Co., USA) were used to adjust the initial pH of the solutions.

ZVI was employed as the reactive material and alumina (Al_2O_3) as the main component of the ceramic pellets employed as adsorbents to remove As and Cr oxyanions present in wastewater. ZVI and Al_2O_3 powders passing through a #200 US sieve ($<75 \mu\text{m}$) were used as sorbents. X-ray fluorescence (XRF, PW2404, Philips, Netherlands), X-ray diffractometry (XRD, Smartlab, Rigaku, Japan), and an accelerated surface area and porosimetry system (ASAP2020, Micromeritics, USA) were employed to investigate the basic material properties of the sorbents. XRF results were quantified by assuming that all elements were present as oxides and indicated that ZVI consisted primarily of Fe (99.2%) with a trace amount of Si (0.8%; Table 1). Furthermore, aluminum oxide was primarily composed of Al (93.3%) with a small amount of Si (6.1%) and Ca (0.2%; Table 1). The XRD results shown in Fig. 1 suggest that the Fe in ZVI and Al in alumina were present as Fe^0 and Al_2O_3 , respectively.

Synthesized ceramic pellets were prepared by mixing ZVI with a conventional ceramic material composed of primarily alumina with trace amounts of clay minerals, feldspar, silica, and methyl cellulose type binders. An amount of ZVI equivalent to 10% or 30% of the ceramic materials was added to evaluate the effect of iron addition on the removal capacity, and the actual ZVI contents of the synthesized ceramic pellets were 0%, 9.1%, and 23.1% (Table 2). Materials were mixed using a blender in a sludge state that contained a mixture of water and glycerin, and the resulting material was then placed into an extruder with a diameter of approximately 4–5 mm to create spherical pellets; the

Table 1
Chemical composition of the ZVI and alumina determined by XRF analysis

Material	Chemical composition (wt.%)			
	Fe_2O_3	SiO_2	Al_2O_3	CaO
ZVI	99.2	0.8	–	–
Alumina	–	6.1	93.3	0.2

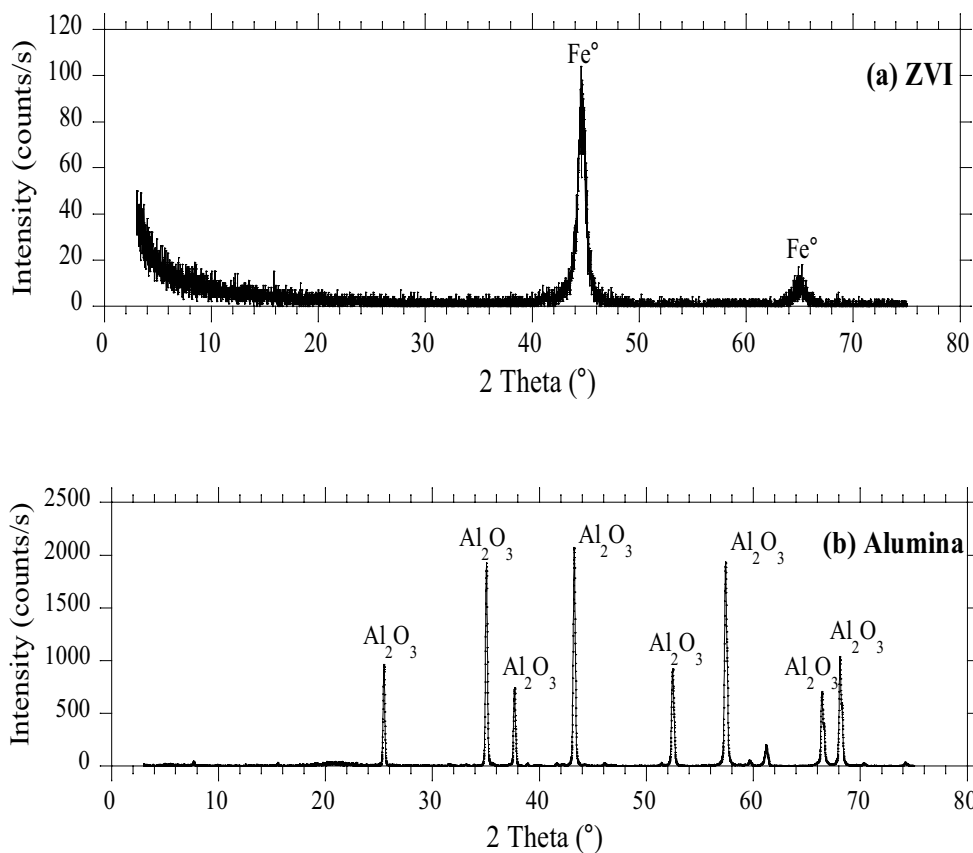


Fig. 1. XRD analysis results for (a) ZVI and (b) alumina.

Table 2
Synthesis conditions for ceramic pellets

Pellet	Ceramic material (g)	ZVI (g)	Total (g)
0% ZVI	2,160	0	2,160
9% ZVI	2,160	216	2,376
23% ZVI	2,160	648	2,808

pellets were subsequently dried at 80°C for 12 h in an oven and sintered at 1,250°C for 2 h in a furnace without controlling air flow, which could cause oxidic conditions.

2.2. Methods

Batch sorption tests were conducted using ZVI and Al_2O_3 powders at initial concentrations of 10 and 100 mg L^{-1} to investigate their capabilities of removing the target contaminants, As(III), As(V), and Cr(VI). The initial pH of solutions was adjusted to 3, 5, or 7 using 0.1 M and 0.01 M HNO_3 and 0.1 M and 0.01 M NaOH solutions. 40 mL of the solution and 0, 0.5, 1, 2, or 5 g of sorbent (i.e., 0, 12.5, 25, 50, and 125 g L^{-1} , respectively) were placed in a 50-mL centrifuge tube and stirred at a rate of 160 revolutions per minute (rpm) for 24 h at 25°C, using a precise shaking incubator (WIS-10RL, DAIHAN Scientific Co. Ltd., Korea).

Batch sorption tests were also conducted using synthesized ceramic pellets with various ZVI contents (0%, 9%, and 23%) to determine the removal of As(III), As(V), and Cr(VI) from aqueous solutions with initial concentrations of 5 or 10 mg L^{-1} , and the initial pH of the solutions was adjusted to 3 or 5. 30 mL of the solution and 0, 10, 20, 30, 40, or 50 pellets were placed in a 50-mL centrifuge tube, and the mixture was shaken at a rate of 160 rpm at 25°C for 24 or 48 h in a precise shaking incubator. The solid-to-liquid ratio was calculated based on the weight of the pellets.

After the batch sorption tests, the solutions were centrifuged at 5,000 rpm in a table-top centrifuge (VS-5500i, Vision Scientific Co. Ltd., Korea) for 10 min to separate the solids from the liquid. The supernatant was filtered through a 0.2- μm syringe filter (Whatman™), and the pH was immediately measured with a pH electrode. A control solution without sorbents and the filtered solutions were placed in 50-mL centrifuge tubes, sealed with parafilm, and stored at 4°C for chemical analysis.

Cation concentrations in the solutions were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 7200, Thermo scientific, USA). The solid samples remaining after centrifugation were dried at 60°C for 48 h in an oven, and dried solid samples were then analyzed by XRD, XRF, and field-emission scanning microscopy (FE-SEM, Quanta 250FEG, FEI™) with energy dispersive X-ray spectroscopy (EDX). FE-SEM analyses were conducted

in SE mode at 15 kV, and EDX analyses were conducted in 2D image-mapping mode at 15 kV.

2.3. Calculation of removal efficiency and sorbed amount

For the various sorbents, the removal efficiencies for As(III), As(V), and Cr(VI) were calculated using the concentrations determined by ICP–OES analyses both before and after the batch sorption tests according to Eq. (1) as follows:

$$\text{Removal efficiency (\%)} = \frac{C_i (\text{mgL}^{-1}) - C_f (\text{mgL}^{-1})}{C_i (\text{mgL}^{-1})} \times 100 \quad (1)$$

where C_i represents the concentration of As or Cr in the control solution without sorbents, and C_f represents the As or Cr concentration in the filtered solution after the batch test. The removal efficiency calculated with Eq. (1) does not consider the amount of sorbent used, and to evaluate the removal efficiency for a given mass of sorbent, the sorbed amount per unit mass of sorbent (q_e) was calculated by assuming that all the contaminants removed from the liquid phase were adsorbed to the sorbent as Eq. (2) as follows:

$$\text{Sorbed amount, } q_e (\text{mg g}^{-1}) = \frac{[C_i (\text{mg L}^{-1}) - C_f (\text{mg L}^{-1})] \times V (\text{L})}{m_{\text{sorbent}} (\text{g})} \quad (2)$$

where V is the volume of the solution and m_{sorbent} is the mass of the sorbent used.

3. Results and discussion

3.1. Characteristics of sorbents

Before conducting the batch sorption tests, the specific surface area and pore volumes of the raw sorbent materials were determined using N_2 gas adsorption analysis (Table 3). Results show that Al_2O_3 exhibited a higher Brunauer–Emmett–Teller (BET) specific surface area ($0.88 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($2.15 \times 10^{-3} \text{ m}^3 \text{ g}^{-1}$) than ZVI ($0.37 \text{ m}^2 \text{ g}^{-1}$ and $0.86 \times 10^{-3} \text{ m}^3 \text{ g}^{-1}$, respectively), which suggests that Al_2O_3 contains more pores than ZVI.

A significant decrease in the BET specific surface area and total pore volume was noted when ZVI was added to the synthesized pellets, although there was almost no change in BET specific surface area and total pore volume when the ZVI content was increased from 9% to 23%: the BET specific surface area of synthesized ceramic pellets without ZVI was $1.31 \text{ m}^2 \text{ g}^{-1}$, whereas the BET specific surface areas of synthesized ceramic pellets with 9% and 23% ZVI were

0.47 and $0.42 \text{ m}^2 \text{ g}^{-1}$, respectively (Table 3). This significant decrease in surface area could be attributed to the increased weight of the pellet with the addition of ZVI, which has lower BET specific surface area and total pore volume.

SEM–EDX analyses were conducted on the synthesized ceramic pellets after sintering to investigate the effect of ZVI addition on the surface characteristics of the ceramic pellets. The surface roughness and grain size of the ceramic pellets were found to increase with an increase in the ZVI content, as shown in Fig. 2. For the ceramic pellets with 23% ZVI, aggregation of Al- and Fe-containing particles was observed, suggesting that aggregation may cause the observed increase in surface roughness and grain size.

Both Fe and Al were relatively evenly distributed on the surface of the ceramic pellets, which implies that Al_2O_3 and ZVI were well mixed during synthesis (Fig. 2). With an increase in the ZVI content from 9% to 23%, the Fe content increased from 19.54% to 45.90% whereas the Al content decreased from 37.73% to 23.87% (Table 4). The higher Fe content determined by EDX analysis (compared with the amount of Fe added into the ceramic pellet) could be related to surface enrichment of Fe during the mixing process and/or vaporization of light elements (e.g., O) during the sintering process. As sintering was conducted in a furnace without controlling air flow, the Fe on the surface of the ceramic pellets may have been oxidized and thus present in oxide forms (e.g., Fe_2O_3 and Fe_3O_4) [19].

3.2. Removal characteristics of ZVI

Figs. 3 and 4 show the removal efficiencies and sorbed amounts of As(III), As(V), and Cr(VI) with pH changes ($\Delta\text{pH} = \text{pH}_f - \text{pH}_i$), respectively, during sorption batch tests for 24 h using ZVI. In general, the removal efficiency increased with an increase in the amount of ZVI, regardless of the element type. This effect is due to the increased number of adsorption sites with the increased amount of reactive material employed. However, the sorbed amounts decreased with an increasing amount of ZVI because of the reduced amounts of sorbates (i.e., As and Cr) in the solution. The removal efficiency and sorbed amounts with ZVI at a given test condition increased in the following order: As(V) > As(III) > Cr(VI) (Fig. 3). The results also showed that the removal efficiency was higher when the initial pH and concentration were lower, but the final solution pH increased relative to the initial pH for all test conditions. The increase in pH for a given test condition increased in the following order: As(V) > As(III) > Cr(VI) (Fig. 4), and the degree of change in the solution pH was proportional to the removal efficiency (Figs. 3 and 4).

As(III) can be oxidized to As(V) by hydrogen peroxide, oxygen, and the hydroxyl group formed during oxidation

Table 3
Specific surface area and total pore volume of sorbents (powder and pellets) determined by N_2 gas adsorption analysis

Properties	Powder		Synthesized ceramic pellet		
	ZVI	Al_2O_3	0% ZVI	9% ZVI	23% ZVI
BET specific surface area ($\text{m}^2 \text{ g}^{-1}$)	0.37	0.88	1.31	0.47	0.42
Total pore volume ($\times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$)	0.86	2.15	3.74	0.87	1.00

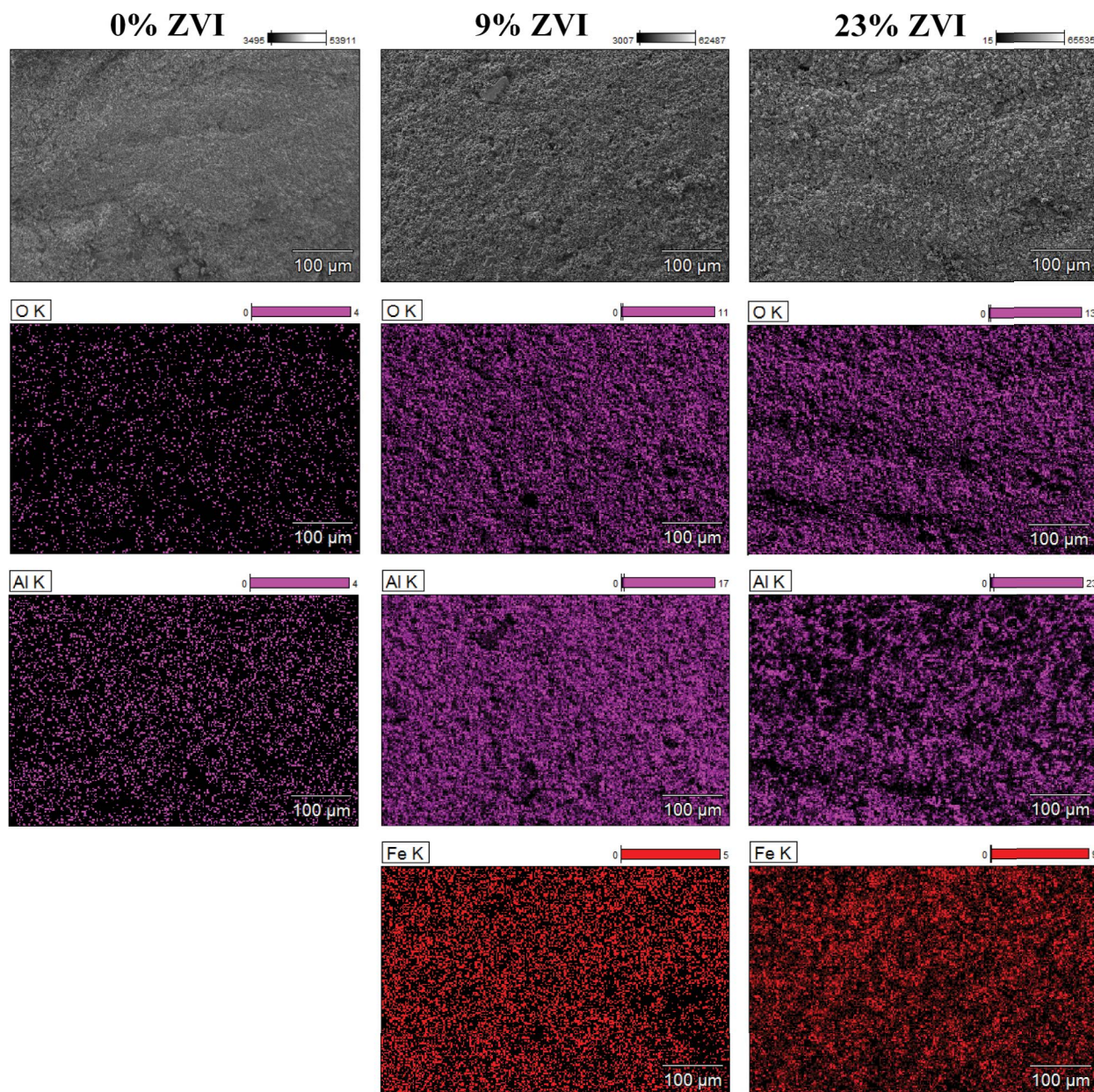


Fig. 2. SEM–EDX mapping images of synthesized ceramic pellets with 0%, 9%, and 23% ZVI.

Table 4
Elemental content of ceramic pellets determined by EDX analysis

Element	0% ZVI (wt.%)	9% ZVI (wt.%)	23% ZVI (wt.%)
Al	40.60 ± 0.47	37.73 ± 0.17	23.87 ± 0.11
Si	7.61 ± 0.38	5.94 ± 0.08	3.55 ± 0.06
Fe	–	19.54 ± 0.33	45.90 ± 0.36

of ZVI in the presence of dissolved oxygen [3], and oxidized ferrous iron forms ferric iron (oxy) hydroxides, which can remove As(III) and As(V) through adsorption or co-precipitation [16,29]. The degree of change in the pH was found to be proportional to the sorbed amounts of As(III) and

As(V), which suggests that As(III) and As(V) were adsorbed by the iron (oxy)hydroxides formed during oxidation of ZVI. As(III) exists as $H_3AsO_3^0$ at $pH < 7$ and as $H_2AsO_3^-$ at $pH > 7$, whereas As(V) exists as $H_2AsO_4^-$ at $pH < 7$ and as $HAsO_4^{2-}$ at $pH > 7$.

The sorption capacity of iron (oxy)hydroxides increased with a decrease in the pH, resulting in the greater removal efficiency of As(V) than As(III). In addition, As(III) can be oxidized to As(V); however, the degree of As(III) oxidation is likely to be low. Similar to As(V), Cr(VI) can be reduced to Cr(III) during ZVI oxidation in an aqueous solution. Therefore, Cr(III) can be adsorbed onto the newly formed iron (oxy)hydroxides, removed by the co-precipitation with iron (oxy)hydroxides, or precipitated as chromium hydroxide at

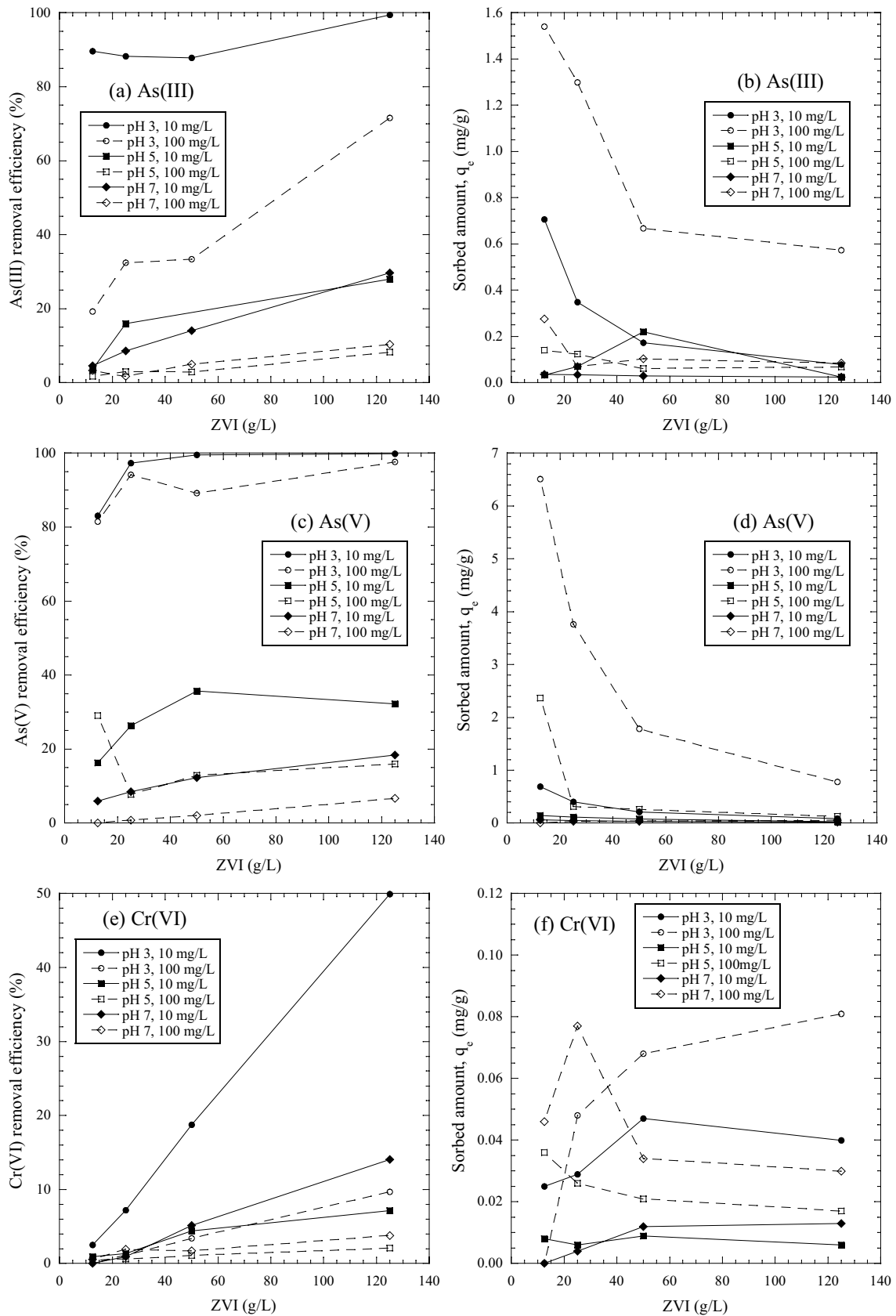


Fig. 3. Removal efficiencies of (a) As(III), (c) As(V), and (e) Cr(VI) and sorbed amounts of (b) As(III), (d) As(V), and (f) Cr(VI) using ZVI, as a function of the solid-to-liquid ratio at various initial pH and concentration conditions.

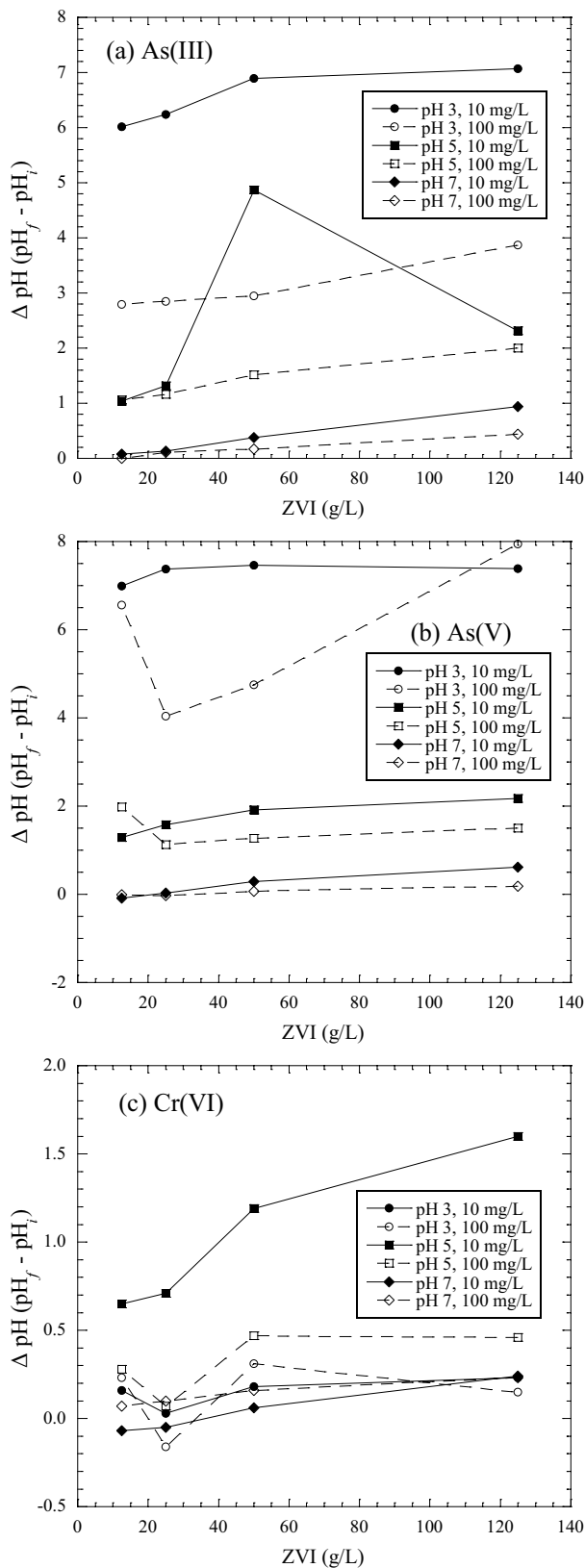


Fig. 4. Difference between initial and final pH (ΔpH) for (a) As(III), (b) As(V), and (c) Cr(VI) using ZVI, as a function of the solid-to-liquid ratio at various initial pH and concentration conditions.

a high pH [21,26,30]. Cr(VI) exists as HCrO_4^- at $\text{pH} < 6$ and as CrO_4^{2-} at $\text{pH} > 6$, and the sorbed amount of Cr(VI) thus increased at low initial pH conditions, which promoted the oxidation of ZVI.

3.3. Removal characteristics of Al_2O_3

Figs. 5 and 6 show the removal efficiencies and sorbed amounts of As(III), As(V), and Cr(VI) and the pH changes ($\Delta \text{pH} = \text{pH}_f - \text{pH}_i$), respectively, during sorption batch tests with Al_2O_3 for 24 h. The removal characteristics of Al_2O_3 were seen to be similar to those of ZVI. However, the removal efficiency and sorbed amounts with Al_2O_3 were lower than those with ZVI for a given test condition. Greater sorbed amounts were generally obtained at a lower initial pH and at higher initial concentrations. The removal efficiency and sorbed amounts with Al_2O_3 at a given test condition increased in the following order: As(V) > As(III) > Cr(VI) (Fig. 5). Although the final solution pH increased relative to the initial pH for all test conditions (Fig. 6), the increase in pH at a given test condition was lower than in tests conducted with ZVI (Figs. 4 and 6). However, the degree of change in the pH was proportional to the removal efficiency for tests with Al_2O_3 .

The removal of As(III), As(V), and Cr(VI) by Al_2O_3 is likely attributed to adsorption by electrostatic attraction. The surface of Al_2O_3 can be protonated in acidic conditions (the point of zero charge of Al_2O_3 is 8.7–9), which increases its anion capacity [17,31]. The greater increases in the final solution pH observed with ZVI compared with Al_2O_3 likely occurred because H^+ ions are significantly consumed by the oxidation of ZVI but are consumed to a lesser extent during adsorption by complexation on the surface of Al_2O_3 .

3.4. Comparison between ZVI and Al_2O_3

Fig. 7 shows the sorbed amounts of As(III), As(V), and Cr(VI) resulting from sorption batch tests with ZVI and Al_2O_3 under specific conditions (initial concentration = 100 mg L^{-1} and solid-to-liquid ratio = 25 g L^{-1}) for 24 h. Tests with ZVI provided significantly higher sorbed amounts of As(III), As(V), and Cr(VI) than those with Al_2O_3 at an initial $\text{pH} = 3$; however, tests with Al_2O_3 provided higher sorbed amounts than those with ZVI at an initial $\text{pH} = 7$ (Fig. 7). These results indicate that the removal capacity of ZVI increased with a decreasing initial pH, whereas that of Al_2O_3 increased with an increasing initial pH.

The sorbed amounts of As(III) (1.3 mg g^{-1}) and As(V) (3.8 mg g^{-1}) with ZVI at $\text{pH} = 3$ were much higher than those with Al_2O_3 (0.18 and 0.10 mg g^{-1} , respectively) at $\text{pH} = 7$. These lower sorbed amounts of As(III) and As(V) with Al_2O_3 than with ZVI can be attributed to the lower surface charge potential of Al_2O_3 than the iron (oxy)hydroxides formed during ZVI oxidation. In addition, As(III) and As(V) can be co-precipitated with iron (oxy)hydroxides during ZVI oxidation.

However, the sorbed amounts of Cr(VI) with ZVI (0.03 – 0.08 mg g^{-1}) were slightly lower than those with Al_2O_3 (0.11 – 0.15 mg g^{-1}), regardless of the initial pH (initial concentration = 100 mg L^{-1} and solid-to-liquid ratio = 25 g L^{-1})

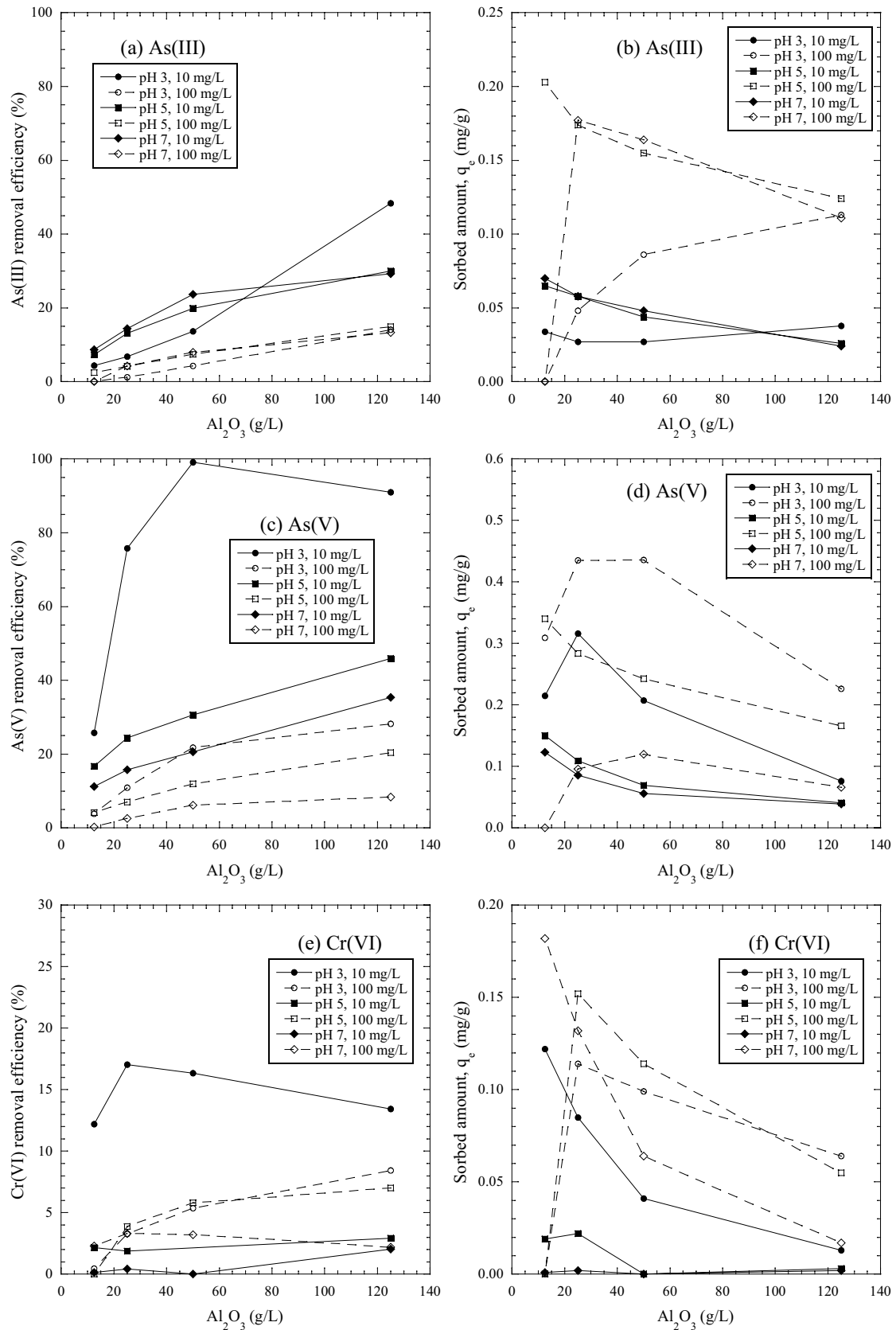


Fig. 5. Removal efficiencies for (a) As(III), (c) As(V), and (e) Cr(VI) and sorbed amounts of (b) As(III), (d) As(V), and (f) Cr(VI) using Al₂O₃ as a function of the solid-to-liquid ratio at various initial pH and concentration conditions.

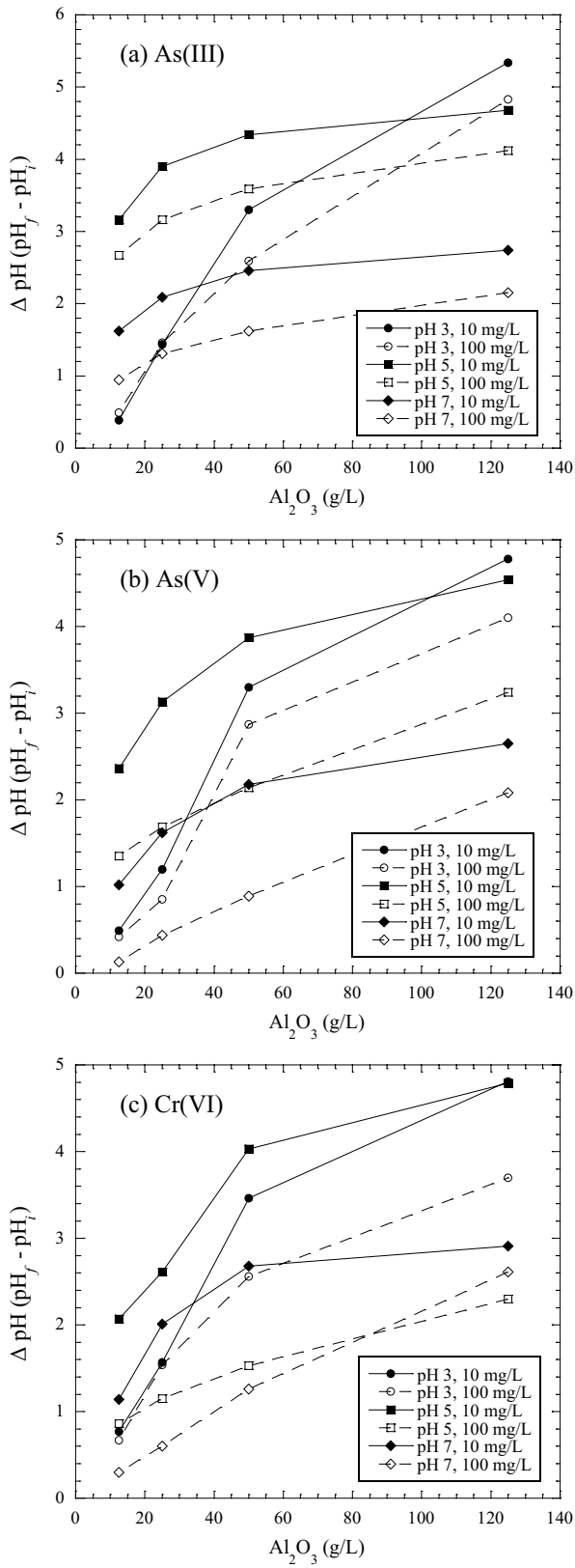


Fig. 6. Difference between initial and final pH (ΔpH) for (a) As(III), (b) As(V), and (c) Cr(VI) using Al_2O_3 as a function of the solid-to-liquid ratio at various initial pH and concentration conditions.

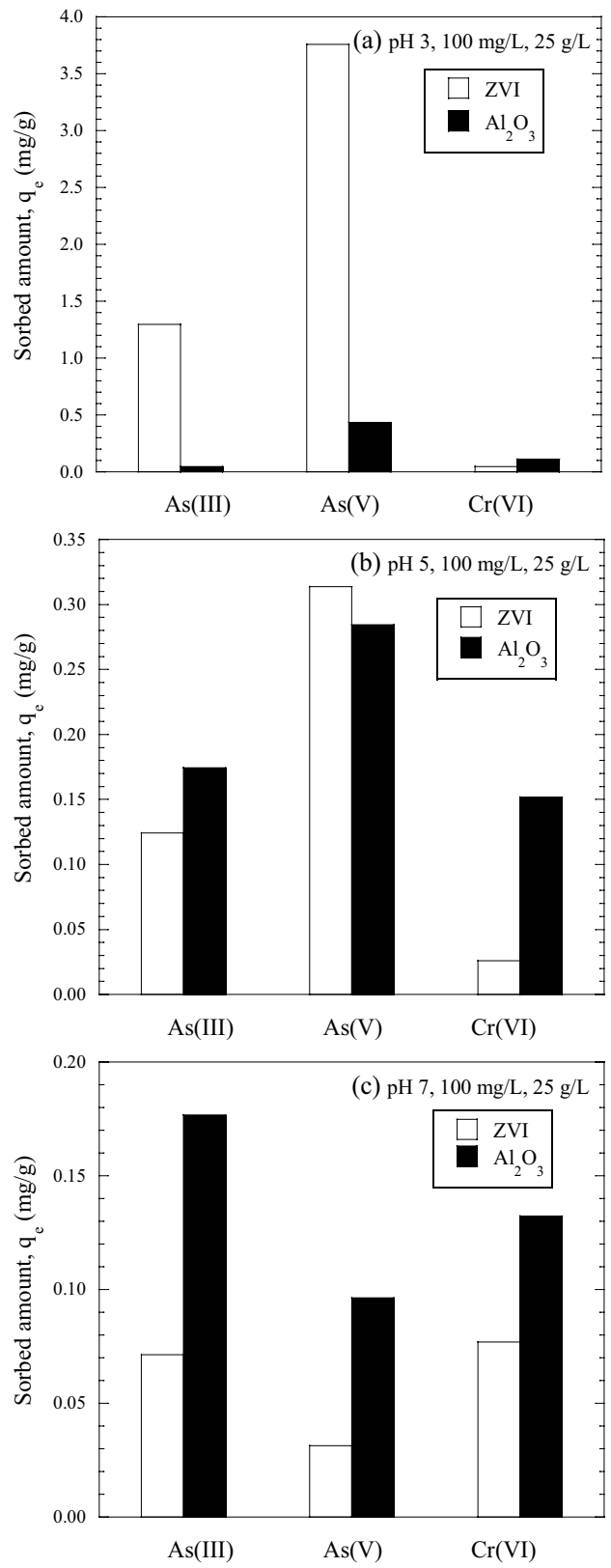


Fig. 7. Sorbed amount per unit mass of As(III), As(V), and Cr(VI) using ZVI and Al_2O_3 at initial conditions of (a) pH 3, (b) pH 5, and (c) pH 7 (initial concentration: 100 mg L⁻¹, solid-to-liquid ratio: 25 g L⁻¹).

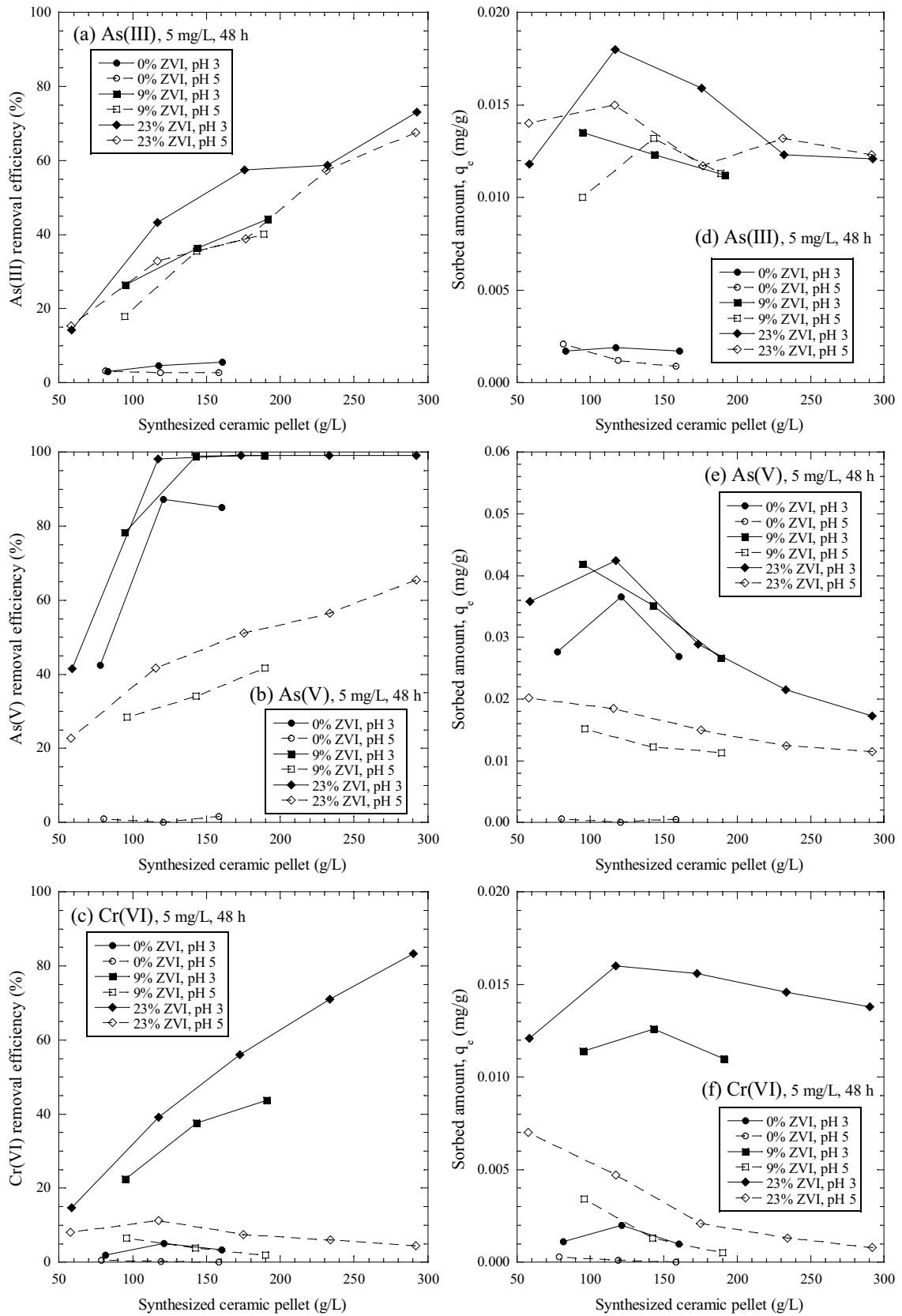


Fig. 8. Removal efficiencies for (a) As(III), (b) As(V), and (c) Cr(VI) and sorbed amounts of (d) As(III), (e) As(V), and (f) Cr(VI) using synthesized ceramic pellets, as a function of the solid-to-liquid ratio at various initial pH and ZVI contents.

(Fig. 7). These results indicate that ZVI and Al_2O_3 are more effective at removing As(III), As(V), and Cr(VI), respectively, suggesting that incorporation of ZVI and Al_2O_3 may be effective for removing As(III), As(V), and Cr(VI) from aqueous solutions.

3.5. Removal characteristics of synthesized ceramic pellets

Figs. 8 and 9 show the removal efficiencies and sorbed amounts of As(III), As(V), and Cr(VI) and pH changes ($\Delta\text{pH} = \text{pH}_f - \text{pH}_i$), respectively, for sorption batch tests using the synthesized ceramic pellets conducted for a 48-h period. The removal efficiencies increased with an increase in the number of pellets added; this is because the number of adsorption sites increased with the increased amount of sorbent employed. In addition, the removal efficiencies and sorbed amounts increased with an increase in the iron contents of the pellets, due to the increased amount of reactive material employed. However, the sorbed amounts decreased with an increase in the number of pellets added; this result is comparable with those obtained using ZVI and Al_2O_3 powder. Furthermore, similar to the results with ZVI, the removal efficiencies and sorbed amounts increased with a decrease in the initial pH. However, changes in pH were more significant in the tests with ZVI (Figs. 4 and 9), which indicates that removal with the synthesized ceramic pellets can be attributed mainly to electrostatic attraction and partially to redox reactions.

Fig. 10 shows the sorbed amounts of As(III), As(V), and Cr(VI) for tests using synthesized ceramic pellets with various added ZVI contents under different adsorption conditions while employing a constant number of pellets (solid-to-liquid ratio = 117 g L^{-1}). Sorbed amounts with the synthesized ceramic pellets were found to be inversely proportional to the initial pH and directly proportional to the reaction time (Fig. 10). The maximum sorbed amounts of As(III), As(V), and Cr(VI) with synthesized ceramic pellets containing 23% ZVI were 0.018 , 0.042 , and 0.016 mg g^{-1} , respectively, and these maximum amounts occurred at $\text{pH} = 3$ (Fig. 10). As the reaction time increased from 24 to 48 h, the sorbed amounts of As(III) and As(V) increased by a factor of approximately 2, from 0.009 to 0.018 mg g^{-1} and from 0.026 to 0.042 mg g^{-1} , respectively. Although the reaction with the synthesized ceramic pellets proceeded more slowly than with the powdered samples, these longer reaction times correspond with the higher probability of As(III), As(VI), or Cr(VI) diffusing into the pellets from the pellet surface.

The sorbed amounts of As(III), As(V), and Cr(VI) increased with an increase in the iron content of the synthesized ceramic pellets (Figs. 8 and 10). The sorbed amount of As(III) by ceramic pellets with 23% ZVI was 0.018 mg g^{-1} , which is approximately 1.5 times greater than that for ceramic pellets with 9% ZVI. The maximum sorbed amounts of As(V) by ceramic pellets with 0% ZVI and 23% ZVI were 0.032 and 0.042 mg g^{-1} , respectively, whereas the maximum sorbed amounts of As(V) by ZVI and Al_2O_3 powders were 6.45 and 0.30 mg g^{-1} , respectively (Figs. 3, 5, and 8). The ZVI of the ceramic pellet may be converted to iron oxides during synthesis; therefore, the removal properties of ZVI-incorporated ceramic pellets are related to the adsorption characteristics of iron and aluminum oxides. In addition,

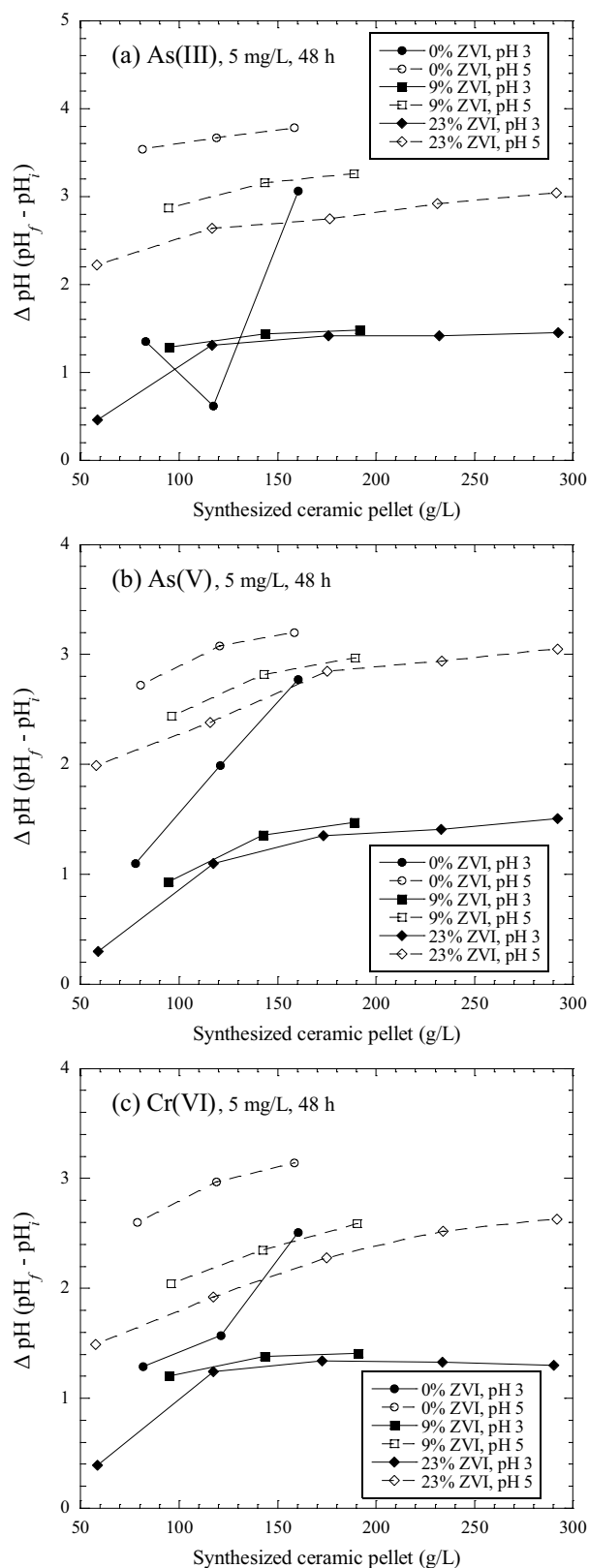


Fig. 9. Differences between initial and final pH (ΔpH) for (a) As(III), (b) As(V), and (c) Cr(VI) using synthesized ceramic pellets, as a function of the solid-to-liquid ratio at various initial pH and ZVI contents.

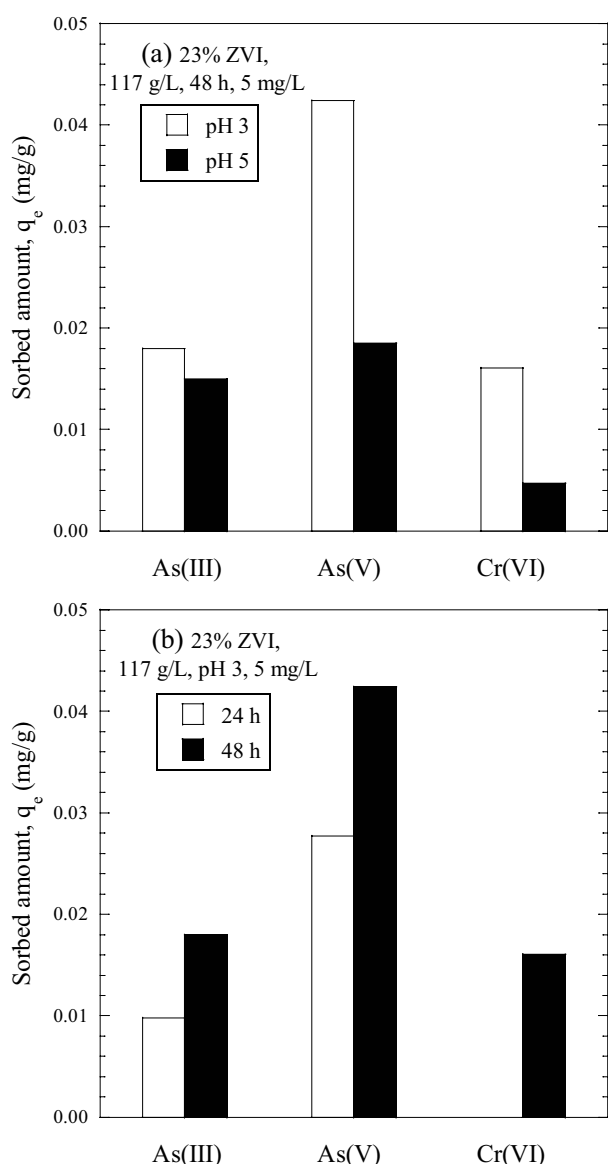


Fig. 10. Sorbed amounts of (a) As(III), As(V), and Cr(VI) using synthesized ceramic pellets with 23% ZVI at varying initial pH (initial concentration: 5 mg L⁻¹, solid-to-liquid ratio: 117 g L⁻¹, and reaction time: 48 h); and (b) As(III), As(V), and Cr(VI) using synthesized ceramic pellets with 23% ZVI at different reaction times (initial pH = 3, initial concentration: 5 mg L⁻¹, and solid-to-liquid ratio: 117 g L⁻¹).

because the adsorption capacity of iron oxides is generally higher than that of aluminum oxides, the removal capacity increases with an increase in the iron content of the ceramic pellets.

4. Conclusions

The feasibility of incorporating iron into a ceramic material to enhance reactivity with the aim of removing As(III), As(V), and Cr(VI) from wastewater was evaluated. Batch tests were conducted for the removal of As(III), As(V), and Cr(VI) from aqueous solutions under different conditions

using ZVI and Al₂O₃ powders, respectively, and synthesized ceramic pellets with various added ZVI contents.

Results showed that ZVI provided a higher removal capacity than Al₂O₃ under the same conditions: the sorbed amounts with ZVI were approximately 3–7 times greater than those with Al₂O₃. The maximum sorbed amounts with ZVI were 6.45, 1.55, and 0.08 mg g⁻¹ for As(V), As(III), and Cr(VI), respectively, at an initial pH of 3, whereas those for Al₂O₃ were 0.44, 0.20, and 0.11 mg g⁻¹, respectively. These results suggest that ZVI has a higher sorption capacity than Al₂O₃ for As(V), As(III), and Cr(VI) under acidic conditions, and could thus be employed as a potential additive to improve the adsorption capacity of ceramic materials under acidic conditions.

ZVI oxidized quickly under low pH conditions to form iron (oxy)hydroxides that can adsorb metal oxyanions. During oxidation of ZVI, As(III) is oxidized to As(V) and Cr(VI) is reduced to Cr(III). As a result, the removal efficiency of metals with the addition of ZVI varied in accordance with changes in the initial pH of the solution and the types of species within the solution. Al₂O₃ exhibits a positive surface charge at a low pH, leading to the adsorption of metal oxyanions through electrostatic attraction. Therefore, the maximum amount sorbed with respect to the addition of Al₂O₃ occurred within a pH range where metals exist as monovalent anions with the lowest adsorption energies.

When using the synthesized ceramic pellets, the sorbed amounts of As(III), As(V), and Cr(VI) were proportional to the reaction time and iron content of the ceramic pellets but were inversely proportional to the initial pH. The maximum sorbed amounts for ceramic pellets in the absence of iron were lower than those for the Al₂O₃ powder because of the lower surface area of the ceramic pellets, whereas the surfaces of synthesized ceramic pellets containing iron were characterized by Al and Fe oxides that adsorbed metal oxyanions from the aqueous solution through electrostatic attraction.

The results of this study suggest that the incorporation of ZVI into basic ceramic materials (primarily Al₂O₃) improves the reactivity. However, when ZVI is added to basic ceramic materials, ZVI can be oxidized to form iron oxides during sintering, which provides a lower removal capacity than ZVI powder. Therefore, to enable an increase in the reactivity, ceramic pellets with ZVI should be synthesized (e.g., mixing and sintering) in a reducing environment, or a reducing agent (e.g., carbon) should be added during sintering to prevent ZVI oxidation. In addition, the ceramic pellets with ZVI should be evaluated at various time and concentration conditions to investigate their sorption characteristics.

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