

56 (2015) 760–769 October



# Influence of As(V) on bacteriophage MS2 removal by hematite in aqueous solutions

Jeong-Ann Park<sup>a</sup>, Chang-Gu Lee<sup>a</sup>, Song-Bae Kim<sup>a,b,\*</sup>

<sup>a</sup>Environmental Functional Materials & Biocolloids Laboratory, Seoul National University, Seoul 151-921, Korea, Tel. +82 2 880 4595; emails: pjaan720@snu.ac.kr (J.-A. Park), changgu@snu.ac.kr (C.-G. Lee), Tel. +82 2 880 4587; Fax: +82 2 873 2087; email: songbkim@snu.ac.kr (S.-B. Kim)

<sup>b</sup>Department of Rural Systems Engineering, Research Institute of Agriculture and Life Sciences, Seoul National University, Seoul 151-921, Korea

Received 7 January 2014; Accepted 21 June 2014

#### ABSTRACT

In this study, the removal of MS2 by hematite in the absence and presence of As(V) was examined in batch experiments. The sorption tests demonstrate that As(V) could have a negative effect on MS2 removal by occupying sorption sites on hematite through competition with MS2, causing a decrease in MS2 removal. In the experiments (hematite dosages = 0.5–4.0 g L<sup>-1</sup>; reaction time = 4 h; MS2 concentration =  $6.01 \times 10^5$  pfu mL<sup>-1</sup>), the percent removals of MS2 by hematite were in the range of 95.0–99.8%. In the presence of As (V) (=0.2 mg  $L^{-1}$ ), the percent removals of MS2 by hematite were 55–88% lower compared to removal in the absence of As(V). The inactivation of MS2 in an As(V) solution where no hematite was present was observed, showing that As(V) could have a positive effect on MS2 removal through the inactivation of MS2, resulting in an increase of MS2 removal. In the inactivation tests (reaction time = 4 h; As(V) concentration = 0.1-1.0 mg L<sup>-1</sup>; MS2 concentration =  $3.68 \times 10^5$  pfu mL<sup>-1</sup>), the percent removals of MS2 were in the range of 4.1–11.1%. In another tests (reaction time = 6 h; As(V) concentration =  $0.1-10 \text{ mg L}^{-1}$ ; MS2 concentration =  $4.10 \times 10^5$  pfu mL<sup>-1</sup>), the percent removals were in the range of 2.2–20.1%. This study demonstrates that As(V) mainly has a negative effect on MS2 removal by hematite through the competitive sorption, but a positive effect of As(V) via the inactivation of MS2 cannot be neglected.

Keywords: Arsenic; Bacteriophage MS2; Hematite; Inactivation; Sorption

#### 1. Introduction

The interactions between iron oxides and viruses are of great interest for researchers in the environmental disciplines. Some researchers have investigated the adhesion of viruses during their transport through geochemically heterogeneous aquifers because viral contamination of groundwater is a serious environmental problem [1–3]. For example, Ryan et al. [4] investigated the transport of bacteriophage PRD1 in an iron oxide-coated sand aquifer. Foppen et al. [5] performed column experiments to examine the transport of PRD1 in goethite ( $\alpha$ -FeOOH)-coated sand. In aquifers, iron (hydr)oxides provide surface charge heterogeneities because they carry positive surface

<sup>\*</sup>Corresponding author.

<sup>1944-3994/1944-3986 © 2014</sup> Balaban Desalination Publications. All rights reserved.

charges at groundwater pH conditions. Thus, negatively charged viruses can favorably adhere to the positively charged surfaces of aquifer sediments.

Other researchers have also been interested in the removal of viruses in granular media, filters, and membranes amended with iron (hydr)oxides [6–8]. For instance, Brown and Sobsey [9] used ceramic filter materials amended with iron oxides such as goethite, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), and magnetite (Fe<sub>3</sub>O<sub>4</sub>) to remove the bacteriophages MS2 and PhiX174 from drinking water. Gutierrez et al. [10] investigated the adsorption of bacteriophage MS2 and rotavirus to hematite coated on glass fiber. Raciny et al. [11] examined the removal of MS2 using magnetite coated on polysulfone membranes. Virus removal in water treatment systems can be enhanced through surface modification with iron (hydr)oxides.

Researchers have reported that oxyanions (phosphate, (bi)carbonate) and cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>) can interfere with the adhesion of viruses to iron (hydr) oxides [5,11–13]. To our knowledge, however, studies related to virus removal by iron (hydr)oxides in aqueous solutions containing arsenic (As), a major groundwater contaminant, are scarce. In many countries such as Bangladesh, Chile, and India, As occurs naturally in groundwater at concentrations ranging from 0.01 to 5 mg  $L^{-1}$  and exceeds the guideline of the World Health Organization (0.01 mg  $L^{-1}$ ), causing serious health-related problems and human mortality [14]. The aim of this study was to investigate the influence of As(V) on the removal of bacteriophage MS2 by hematite in aqueous solutions. The removal of MS2 or As(V) by hematite was observed separately in batch experiments. Also, the simultaneous removal of MS2 and As(V) by hematite was examined. Finally, the inactivation of MS2 in an As(V) solution where no hematite was present was observed at various concentrations of As(V).

#### 2. Materials and methods

# 2.1. Synthesis and characterization of hematite particles

All chemicals used for the experiments were purchased from Sigma-Aldrich. Hematite particles were prepared by precipitation method. An alkali solution of sodium hydroxide (NaOH) was added dropwise into a 500 mL solution of 0.25 M iron chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O) at room temperature with intensive stirring until pH 8.0. The resulting precipitates were aged at 60 °C for 18 h and then washed thoroughly with deionized water to remove excess sodium. The washed precipitates were oven-dried again at 150 °C for 18 h and then pulverized in a ball mill.

A transmission electron microscope (TEM, JEM-1010, JEOL, Tokyo, Japan) was used to obtain images of the hematite. The particle size of hematite was determined by the TEM image analysis (number of particles = 119) using ImageJ 1.43u software (National Institutes of Health, Bethesda, MD, USA). Nitrogen gas (N<sub>2</sub>) adsorption-desorption experiments were performed for hematite using a surface area analyzer (BELSORP-max, BEL Japan Inc., Japan) after the sample was pretreated at 120°C. From the N2 adsorptiondesorption isotherms, the specific surface area, average pore diameter, total pore volume, and mesopore volume were determined using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses. The mineralogical and crystalline structural properties were examined using X-ray diffractometry ([XRD], D8 Advance, Bruker, Germany) with Cu Kα radiation of 1.5406 Å at a scanning speed of 0.6°/s. Infrared spectra were obtained in attenuated total reflectance mode using a Nicolet 6700 (Thermo scientific, USA) Fourier transform infrared (FTIR) spectrometer.

#### 2.2. Virus and plaque assays

The bacteriophage MS2 (ATCC 15597-B1), obtained from the American Type Culture Collection, was grown on *Escherichia coli* (ATCC 15597) using the double-agar overlay method [15]. Bacteriophages were enumerated by the plaque assay method using the aforementioned host. Host culture (0.2 mL) and 0.1 mL of diluted virus sample with 5 mL of soft agar were added to tubes, and then, the mixture was poured onto trypticase soy agar plates to solidify. After solidifying, the plates were incubated at 37 °C for 18 h.

#### 2.3. Batch experiments

# 2.3.1. Bacteriophage MS2 removal by hematite

Batch experiments were conducted to examine the removal of bacteriophage MS2 by hematite as a function of hematite dosage (0.5–4.0 g L<sup>-1</sup>) with a reaction time of 4 h and MS2 concentration of  $6.01 \times 10^5$  pfu mL<sup>-1</sup>. MS2 stock solution was diluted from a concentrated titer to the desired concentration. The batch experiment method consisted of adding virus stock solution to 50-mL centrifuge tubes containing hematite particles. After all tubes were properly prepared and sealed, they were shaken at 200 rpm and 4°C. The suspensions were then centrifuged at 9,000 × g and 4°C for 15 min (Combi-514R; Hanil Science Industrial, Incheon, Korea). The viable bacteriophage concentration was determined using the plaque

assay method. Control tubes were filled with only bacteriophage solution and treated in the same manner as the experimental tubes. Another set of tests was conducted to examine the removal of MS2 as a function of reaction time with a hematite dose of 2 g L<sup>-1</sup> and MS2 concentration of  $2.94 \times 10^5$  pfu mL<sup>-1</sup>.

The bacteriophage removal was calculated using the following formula:

$$R = \left[\frac{C_0 - C}{C_0}\right] \times 100\tag{1}$$

where *R* is the percent removal of bacteriophage, and  $C_0$  and *C* are the initial and final bacteriophage concentrations, respectively. The bacteriophage removal per unit mass of adsorbent was calculated using the following formula:

$$S = \left[\frac{(C_0 - C)}{M}\right] \tag{2}$$

where S is the amount of bacteriophage removed per 1 g of hematite, and M is the adsorbent concentration used in the experiment. All the experiments were performed in triplicate.

#### 2.3.2. As(V) removal by hematite

Batch experiments were performed to examine As(V) sorption to hematite as a function of hematite dosage  $(0.5-4.0 \text{ g L}^{-1})$  with a reaction time of 4 h and As(V) concentration of 0.2 mg  $L^{-1}$ . A stock solution of As(V) was prepared by dissolving reagent-grade sodium arsenate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, 98–102%, Sigma-Aldrich, USA) in deionized water. An As(V) solution was added to 50-mL tubes containing hematite. After all tubes were sealed, they were shaken at 200 rpm and 4°C. After the reaction, a sample was taken, centrifuged, and filtered through a 0.45-µm membrane filter. Arsenic concentrations were measured by inductively coupled plasmaatomic emission spectroscopy (ICP-AES) (ICP-1000 IV, Shimadzu Co., Japan). Another set of tests was conducted to observe As(V) sorption to hematite as a function of reaction time with a hematite dose of 2.0 g  $L^{-1}$  and As(V) concentration of 0.2 mg  $L^{-1}$ . All the experiments were performed in triplicate.

# 2.3.3. Simultaneous removal of bacteriophage MS2 and $A_{S}(V)$ by hematite

Batch experiments were conducted to examine the simultaneous removal of MS2 and As(V) by hematite as a function of hematite dosage (reaction time = 4 h). MS2 solution  $(6.01 \times 10^5 \text{ pfu mL}^{-1})$  and As(V) solution  $(0.2 \text{ mg L}^{-1})$  were added to 50-mL tubes containing various concentrations of hematite  $(0.5-4.0 \text{ g L}^{-1})$ . The tubes were shaken at 200 rpm at 4°C. Another tests were performed to observe the simultaneous removal of MS2 and As(V) by hematite as a function of reaction time with a hematite dose of 2.0 g L<sup>-1</sup>, As(V) concentration of 0.2 mg L<sup>-1</sup>, and MS2 concentration of 2.94 × 10<sup>5</sup> pfu mL<sup>-1</sup>. All the experiments were performed in triplicate.

# 2.3.4. Bacteriophage MS2 inactivation tests in As(V) solution

Inactivation tests were performed to examine the MS2 removal in an As(V) solution where no hematite was present. The first tests were conducted to observe the MS2 inactivation in an As(V) solution as a function of reaction time. Virus stock solution was added to 50-mL centrifuge tubes containing an As(V) solution (As(V) concentration =  $0.2 \text{ mg L}^{-1}$ ; MS2 concentration =  $1.55 \times 10^5 \text{ pfu mL}^{-1}$ ). The tubes were shaken at 200 rpm and 4°C to avoid thermal inactivation of the virus. The control tubes were filled with only bacteriophage solution and treated in the same manner as the experimental tubes.

Further inactivation tests were conducted to observe the effect of As(V) concentrations on MS2 removal in the absence of hematite. The tests were conducted with a reaction time of 4 h and MS2 concentration of  $3.68 \times 10^5$  pfu mL<sup>-1</sup>. Virus stock solution was added to 50-mL centrifuge tubes containing various concentrations of As(V) (0.1–1.0 mg L<sup>-1</sup>). Another set of tests was performed with a reaction time of 6 h, As(V) concentrations of 0.1–10 mg L<sup>-1</sup>, MS2 concentration of  $4.10 \times 10^5$  pfu mL<sup>-1</sup>. All the experiments were performed in triplicate.

### 3. Results and discussion

# 3.1. Characteristics of hematite particles

The hematite particles synthesized in the laboratory are shown in Fig. 1. The hematite particles were spherical, with a particle size ranging from 112 to 262 nm (average =  $167 \pm 35$  nm), which was determined from the TEM image (Fig. 1(a)). The N<sub>2</sub> adsorption and desorption isotherms of hematite are provided in Fig. 1(b). According to the BET analysis, hematite had a specific surface area of 98.0 m<sup>2</sup> g<sup>-1</sup>, average pore diameter of 8.25 nm, and total pore volume of 0.2022 cm<sup>3</sup> g<sup>-1</sup>. The BJH analysis determined the mesopore volume of hematite to be 0.1996 cm<sup>3</sup> g<sup>-1</sup>.



Fig. 1. Hematite particles synthesized in the laboratory: (a) TEM image (bar = 500 nm); (b) nitrogen gas (N<sub>2</sub>) adsorption–desorption isotherm.

The XRD pattern and FTIR spectra of hematite are presented in Fig. 2. The XRD pattern (Fig. 2(a)) indicates that the peaks at  $2\theta = 24.180$ , 33.198, 35.682, 40.917, 49.529, 54.137, 62.527, and 64.100 were attributed to (012), (104), (110), (113), (024), (116), (01 8), (214), and (300) crystal planes of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS 79-007), respectively. The FTIR data (Fig. 2(b)) indicate that the band around 3,423 cm<sup>-1</sup> corresponded to the stretching vibration of OH groups, and the band around 1,628 cm<sup>-1</sup> was assigned to the bending vibration of H<sub>2</sub>O molecules. The peak at 891 cm<sup>-1</sup> was attributed to a Fe–OH vibration. In addition, the prominent peaks at 458 and 559 cm<sup>-1</sup> corresponded to Fe–O vibrations [16,17].

#### 3.2. Removal of MS2 or As(V) by hematite

The removal of bacteriophage MS2 or As(V) by hematite is presented in Fig. 3. The effect of hematite



Fig. 2. XRD pattern (a) and FTIR spectrometer (b) of hematite particles.

dose on MS2 removal in the absence of As(V) is shown in Fig. 3(a). The percent removals of MS2 increased from 95.0 to 99.8% with an increasing hematite dose from 0.5 to 4.0 g L<sup>-1</sup>, indicating that hematite was effective in the removal of MS2. The effect of reaction time on MS2 removal in the absence of As(V) is shown in Fig. 3(b), demonstrating that the sorption of MS2 to hematite was very fast. The percent removal of MS2 was 99.8% at 5 min and reached >99.9% at 15 min.

The effect of hematite dose on As(V) removal in the absence of MS2 is presented in Fig. 3(c). The percent removal of As(V) was 96.5% at a hematite dose of  $0.5 \text{ g L}^{-1}$ . The percent removal increased slightly with increases of the hematite dose. At 4.0 g L<sup>-1</sup>, the percent removal reached 99.8%. The effect of reaction time on the removal of As(V) in the absence of MS2 is shown in Fig. 3(d), indicating that the sorption of As



Fig. 3. Removal of bacteriophage MS2 and As(V) by hematite particles: (a) effect of hematite dose on MS2 removal; (b) effect of reaction time on MS2 removal; (c) effect of hematite dose on As(V) removal; and (d) effect of reaction time on As(V) removal.

(V) to hematite was very rapid. The percent removal of As(V) was 94.5% at 5 min and reached >99% at 1 h.

#### 3.3. Simultaneous removal of MS2 and As(V) by hematite

The removal of bacteriophage MS2 by hematite in the presence of As(V) is presented in Fig. 3. With an increasing hematite dose from 0.5 to 4.0 g L<sup>-1</sup>, the percent removals of MS2 increased from 7.4 to 44.4% (Fig. 3(a)). In the presence of As(V), the percent removals of MS2 were 55–88% lower compared to removal in the absence of As(V). Fig. 3(b) showed that in the presence of As(V), the percent removal of MS2 was 47.7% at 1 h. These results demonstrate that the level of MS2 removal in the presence of As(V) was far lower than in the absence of As(V).

The removal of As(V) by hematite in the presence of MS2 is also shown in Fig. 3. In the presence of MS2, the percent removals of As(V) were 60.0% at 0.5 g  $L^{-1}$  and 98.7% at 4.0 g  $L^{-1}$  (Fig. 3(c)). At low

doses of hematite, the difference of As(V) percent removal between the absence of MS2 and the presence of MS2 conditions was noticeable. However, the difference decreased as hematite dose increased because the number of sorption sites on the hematite surfaces increased with increasing hematite dose. Fig. 3(d) showed that in the presence of MS2, the As(V) sorption to hematite was slightly reduced. The percent removal of As(V) was 86.4% at 5 min and reached >95% at 4 h.

### 3.4. Kinetic sorption model analysis

Kinetic model analyses for the MS2 data are shown in Fig. 4. In the model analysis, the following linear forms of pseudo-first-order and pseudo-second-order kinetic models can be used [18,19]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \frac{t}{q_{\rm e}} \tag{4}$$

where  $q_e$  is the amount of contaminant removed at equilibrium,  $q_t$  is the amount of contaminant removed at time t,  $k_1$  is the pseudo-first-order rate constant, and  $k_2$  is the pseudo-second-order rate constant. The kinetic model parameters are provided in Table 1. In the pseudo-first-order model (Fig. 4(a)), the value of  $q_e$  $(1.28 \times 10^8 \text{ pfu g}^{-1})$  in the absence of As(V) was one order of magnitude larger than that  $(2.25 \times 10^7 \text{ pfu g}^{-1})$ in the presence of As(V). In the pseudo-second-order model (Fig. 4(b)), the value of  $q_e$  (1.52 × 10<sup>9</sup> pfu g<sup>-1</sup>) in the absence of As(V) was two orders of magnitude greater than that  $(6.25 \times 10^7 \text{ pfu g}^{-1})$  in the presence As(V). In addition, the value of of k2  $(1.82\,\times\,10^{-6}~g~pfu^{-1}~h^{-1})$  in the absence of As(V) was one order of magnitude larger than the value



Fig. 4. Kinetic model analysis for bacteriophage MS2 data: (a) pseudo-first-order model; (b) pseudo-second-order model. Model parameters are provided in Table 1.

 $(1.02 \times 10^{-7} \text{ g pfu}^{-1} \text{ h}^{-1})$  in the presence of As(V) (Table 1). The correlation coefficients ( $R^2$ ) indicate that the kinetic data were well described by the pseudo-second-order kinetic model.

Kinetic model analyses for the As(V) data are shown in Fig. 5. The kinetic model parameters are provided in Table 2. In the pseudo-first-order kinetic model (Fig. 5(a)), the values of  $q_e$  in the absence and presence of MS2 were  $9.96 \times 10^{-2}$  and  $9.54 \times 10^{-2}$  mg g<sup>-1</sup>, respectively. In the pseudo-second-order kinetic model (Fig. 5(b)), the values of  $q_e$  were 9.90 × 10<sup>-2</sup> mg g<sup>-1</sup> in the absence of MS2 and  $9.52 \times 10^{-2}$  mg g<sup>-1</sup> in the presence of MS2. The amount of As(V) removed  $(q_e)$  in the presence of MS2 was slightly lower than the amount removed in the absence of MS2. In addition, the value of  $k_2$  (1.67 × 10<sup>3</sup> g mg<sup>-1</sup> h<sup>-1</sup>) in the absence of MS2 was three times larger than that  $(5.49 \times 10^2 \text{ g mg}^{-1} \text{ h}^{-1})$ in the presence of MS2 (Table 2). The correlation coefficients  $(R^2)$  indicate that the pseudo-second-order model was better at describing the kinetic data than the pseudo-first-order model.

#### 3.5. Inactivation of MS2 in As(V) solution

Parallel to the experiment for the MS2 removal by hematite in an As(V) solution as a function of reaction time (Fig. 3(b)), the inactivation of MS2 was observed as a function of reaction time at the same concentration of an As(V) solution (As(V) concentration = 0.2 mg L<sup>-1</sup>) where no hematite was present. The inactivation data can be analyzed with the following expressions [20–21]:

$$\ln\left[\frac{C(t)}{C_0}\right] = \frac{\lambda_0}{\alpha} [\exp(-\alpha t) - 1]$$
(5)

$$\ln\left[\frac{C(t)}{C_0}\right] = \lambda t \tag{6}$$

where  $\lambda_0$  is the initial inactivation rate coefficient,  $\alpha$  is the resistivity coefficient, and  $\lambda$  is the constant inactivation rate coefficient. Eq. (5) is the time-dependent rate inactivation model, whereas Eq. (6) is the constant rate inactivation model, which can be reduced from Eq. (5) when the inactivation rate coefficient is considered constant [21].

In the inactivation data, the percent removal of MS2 was very low (<2%) at an initial time period (0–2 h) and increased slowly to 5% at 4 h and 9% at 6 h. Therefore, the constant rate inactivation model Eq. (6) was used to analyze the data (Fig. 6). The constant inactivation rate coefficient  $\lambda$  was determined to be 1.36 × 10<sup>-2</sup> h<sup>-1</sup>. During the MS2 inactivation

	Pseudo-first-order model			Pseudo-second-order model		
	$q_{\rm e}$ (pfu g <sup>-1</sup> )	$k_1 (h^{-1})$	$R^2$	$q_{\rm e}$ (pfu g <sup>-1</sup> )	$k_2$ (g pfu <sup>-1</sup> h <sup>-1</sup> )	$R^2$
MS2 w/o As(V) MS2 w/As(V)	$1.28 \times 10^{8}$ $2.25 \times 10^{7}$	$\begin{array}{c} 3.45 \times 10^{-3} \\ 4.01 \times 10^{-1} \end{array}$	0.36 0.38	$1.52 \times 10^9 \\ 6.25 \times 10^7$	$1.82 \times 10^{-6}$ $1.02 \times 10^{-7}$	1.00 0.99

Table 1 Kinetic model parameters from the experimental data of bacteriophage MS2



Fig. 5. Kinetic model analysis for As(V) data: (a) pseudofirst-order model; (b) pseudo-second-order model. Model parameters are provided in Table 2.

experiment in an As(V) solution, the As(V) concentrations were also monitored as a function of reaction time (Fig. 7), indicating that the adsorption of As(V) to the surfaces of MS2 was negligible. Compared to the percent removal of MS2 due to the sorption to hematite in the absence of As(V) (>99%, Fig. 3(b)), the percent removal due to the inactivation in an As(V) solution (=0.2 mg L<sup>-1</sup>) was low.

Further experiments were performed to examine the MS2 inactivation in various concentrations of As(V) solutions where no hematite was present (Fig. 8). In the inactivation tests (reaction time = 4 h; As(V) concentration = 0.1–1.0 mg L<sup>-1</sup>), the percent removals were in the range of 4.1-11.1% with an average removal of 7.5  $\pm$  3.1%. In another tests (reaction time = 6 h; As(V) concentration =  $0.1-10 \text{ mg } \text{L}^{-1}$ ), the percent removals were in the range of 2.2-20.1% with an average removal of  $10.1 \pm 5.5\%$ . The inactivation of MS2 was not linearly dependent on the As(V) concentration under the given experimental conditions, but the MS2 inactivation generally increased with increasing As(V) concentration from 0.1 to 10 mg  $L^{-1}$ . These results demonstrate that the contribution of As(V) on the removal of MS2 via the inactivation could not be neglected at the As(V) concentration of  $\geq 0.5 \text{ mg L}^{-1}$ .

#### 3.6. Effect of As(V) on MS2 removal

The experiments demonstrate that As(V) could play important roles in MS2 removal in two respects. The first concerns the negative effect of As(V) on the removal of MS2 in aqueous solutions via a hindrance effect on bacteriophage adhesion to hematite. Results indicate that the removal of MS2 in hematite was greatly reduced in the presence of As(V). Although As(V) could contribute to the removal of MS2 through inactivation, overall MS2 removal was decreased considerably in the solution containing both As(V) and hematite. This phenomenon could be attributed to the competition between MS2 and As(V) for the sorption sites on the surfaces of hematite particles. It is well known that As(V) adsorbs strongly to iron (hydr)oxides via inner-sphere and outer-sphere complexes [22-24]. In the experiments, all the sorption sites on the hematite surfaces were available for MS2 adsorption in the absence of As(V). In the presence of As(V), however, As(V) occupied many sorption sites through competition with MS2, causing a decrease in the MS2 adhesion. Similar findings have been reported in the literature for competitive sorption between oxyanions and viruses to iron (hydr)oxides [4,11,13]. Gutierrez et al. [10] reported a decrease of MS2 and rotavirus

Table 2	
Kinetic model parameters	from the experimental data of As(V)

	Pseudo-first-order model			Pseudo-second-order model		
	$q_{\rm e} \ ({\rm mg \ g}^{-1})$	$k_1 \ \mathrm{h}^{-1}$	$R^2$	$q_{\rm e} \ ({\rm mg \ g}^{-1})$	$k_2 (g mg^{-1} h^{-1})$	$R^2$
As(V) w/o MS2	$9.96 \times 10^{-2}$	1.28	0.96	$9.90 \times 10^{-2}$	$1.67 \times 10^{3}$	1.00
As(V) w/MS2	$9.54 \times 10^{-2}$	1.08	0.96	$9.52 \times 10^{-2}$	$5.49 \times 10^{2}$	1.00



Fig. 6. The constant rate inactivation model fit to MS2 inactivation data.



Fig. 7. As(V) concentration as a function of time during the inactivation experiment of bacteriophage MS2 in an As (V) solution.

removal by hematite nanoparticles in the presence of bicarbonate ions. Zhuang and Jin [12] also reported that the adsorption of MS2 and Phix174 goethite was reduced in the presence of phosphate ions, resulting in enhanced transport in goethite-coated sand columns.



Fig. 8. Inactivation of bacteriophage MS2 in various concentrations of an As(V) solution where no hematite was present.



Fig. 9. TEM image of bacteriophage MS2 (bar = 20 nm).

The second is related to the positive effect of As(V) on the removal of MS2 in aqueous solutions via inactivation of MS2. MS2 (Fig. 9) consists of single-stranded

RNA (nucleic acid) encapsulated within a capsid (protein coat) [25]. MS2 has a particle size of 24–26 nm [26]. MS2 is called a naked virus because it has no envelope, which is a lipid layer around the nucleocapsid (nucleic acid + protein coat). The mechanisms of the bacteriophage inactivation by arsenic are not known. Reports in the literature indicate that arsenic can generate reactive oxygen species (ROS) to induce oxidative stress in human and animal cells [27,28]. ROS can react with cellular constituents such as thiols, resulting in the denaturation of proteins and enzymes [29,30]. Therefore, bacteriophage may be inactivated in the arsenic solution due to denaturation of the capsid.

# 4. Conclusions

Bacteriophage MS2 removal by synthetic hematite particles in the absence and presence of As(V) was investigated in batch experiments. As(V) could have a negative effect on the removal of MS2 via the hindrance on MS2 adhesion to hematite. Sorption tests show that As(V) could occupy sorption sites on hematite through the competition with MS2, causing a decrease in the removal of MS2. In addition, As(V) could have a positive effect on the removal of MS2 through the inactivation of MS2, resulting in an increase of MS2 removal. Inactivation tests demonstrate that MS2 could be inactivated in As(V) solution, perhaps due to the denaturation of the viral capsid. This study demonstrates that As(V) mainly has a negative effect on the MS2 removal by hematite through the competitive sorption, but a positive effect of As(V) via the MS2 inactivation cannot be neglected. Currently, viral contamination and arsenic poisoning of groundwater are widespread environmental problems around the world. Iron (hydr)oxides and iron (hydr) oxide-coated filter media (sand, granular activated carbon, etc.) can be used to remove both viruses and arsenic in adsorptive filtration technology. This study helps improving our knowledge of applying iron oxides for the simultaneous removal of virus and arsenic from groundwater.

#### Acknowledgements

This research was supported by the Korea Ministry of Environment as GAIA project.

### References

[1] R.A. Abudalo, Y.G. Bogatsu, J.N. Ryan, R.W. Harvey, D.W. Metge, M. Elimelech, Effect of ferric oxyhydroxide grain coatings on the transport of bacteriophage PRD1 and *Cryptosporidium parvum* oocysts in saturated porous media, Environ. Sci. Technol. 39 (2005) 6412–6419.

- [2] J.N. Ryan, R.W. Harvey, D.W. Metge, M. Elimelech, T. Navigato, A.P. Pieper, Field and laboratory investigations of inactivation of viruses (PRD1 and MS2) attached to iron oxide-coated quartz sand, Environ. Sci. Technol. 36 (2002) 2403–2413.
- [3] J.P. Loveland, J.N. Ryan, G.L. Amy, R.W. Harvey, The reversibility of virus attachment to mineral surfaces, Colloids Surf., A 107 (1996) 205–221.
- [4] J.N. Ryan, M. Elimelech, R.A. Ard, R.W. Harvey, P.R. Johnson, Bacteriophage PRD1 and silica colloid transport and recovery in an iron oxide coated sand aquifer, Environ. Sci. Technol. 33 (1999) 63–73.
- [5] J.W.A. Foppen, S. Okletey, J.F. Schijven, Effect of goethite coating and humic acid on the transport of bacteriophage PRD1 in columns of saturated sand, J. Contam. Hydrol. 85 (2006) 287–301.
- [6] I. Bradley, A. Straub, P. Maraccini, S. Markazi, T.H. Nguyen, Iron oxide amended biosand filters for virus removal, Water Res. 45 (2011) 4501–4510.
  [7] Y. You, J. Han, P.C. Chiu, Y. Jin, Removal and inacti-
- [7] Y. You, J. Han, P.C. Chiu, Y. Jin, Removal and inactivation of waterborne viruses using zerovalent iron, Environ. Sci. Technol. 39 (2005) 9263–9269.
- [8] J. Lukasik, Y.F. Cheng, F. Lu, M. Tamplin, S.R. Farrah, Removal of microorganisms from water by columns containing sand coated with ferric and aluminum hydroxides, Water Res. 33 (1999) 769–777.
- [9] J. Brown, M.D. Sobsey, Ceramic media amended with metal oxide for the capture of viruses in drinking water, Environ. Technol. 30 (2009) 379–391.
- [10] L. Gutierrez, X. Li, J. Wang, G. Nangmenyi, J. Economy, T.B. Kuhlenschmidt, M.S. Kuhlenschmidt, T.H. Nguyen, Adsorption of rotavirus and bacteriophage MS2 using glass fiber coated with hematite nanoparticles, Water Res. 43 (2009) 5198–5208.
- [11] I. Raciny, K.R. Zodrow, D. Li, Q. Li, P.J.J. Alvarez, Addition of a magnetite layer onto a polysulfone water treatment membrane to enhance virus removal, Water Sci. Technol. 63 (2011) 2346–2352.
- [12] J. Zhuang, Y. Jin, Interactions between viruses and goethite during saturated flow: Effects of solution pH, carbonate, and phosphate, J. Contam. Hydrol. 98 (2008) 15–21.
- [13] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem. 17 (2002) 517–568.
- [14] M.H. Adams, Bacteriophages, Interscience Publishers, New York, NY, 1959.
- [15] Z. Jing, S. Wu, Synthesis and characterization of monodisperse hematite nanoparticles modified by surfactants via hydrothermal approach, Mater. Lett. 58 (2004) 3637–3640.
- [16] S.J. Parikh, J. Chorover, ATR-FTIR spectroscopy reveals bond formation during bacterial adhesion to iron oxide, Langmuir 22 (2006) 8492–8500.
- [17] Y.S. Ho, G. Mckay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
- [18] T. Mathialagan, T. Viraraghavan, Adsorption of cadmium from aqueous solutions by vermiculite, Sep. Sci. Technol. 38 (2003) 57–76.

- [19] Y. Sim, C.V. Chrysikopoulos, One-dimensional virus transport in porous media with time-dependent inactivation rate coefficients, Water Resour. Res. 32 (1996) 2607–2611.
- [20] R. Anders, C.V. Chrysikopoulos, Evaluation of the factors controlling the time-dependent inactivation rate coefficients of bacteriophage MS2 and PRD1, Environ. Sci. Technol. 40 (2006) 3237–3242.
- [21] C.V. Chrysikopoulos, A.F. Aravantinou, Virus inactivation in the presence of quartz sand under static and dynamic batch conditions at different temperatures, J. Hazard. Mater. 233–234 (2012) 148–157.
- [22] Y. Brechbühl, I. Christl, E.J. Elzinga, R. Kretzschmar, Competitive sorption of carbonate and arsenic to hematite: Combined ATR-FTIR and batch experiments, J. Colloid Interface Sci. 377 (2012) 313–321.
- [23] J.G. Catalano, C. Park, P. Fenter, Z. Zhang, Simultaneous inner and outer sphere arsenate adsorption on corundum and hematite, Geochim. Cosmochim. Acta 72 (2008) 1986–2004.
- [24] D.M. Sherman, S.R. Randall, Surface complexation of arsenic(V) to iron(III) (hydr)oxides: Structural

mechanism from ab initio molecular geometries and EXAFS spectroscopy, Geochim. Cosmochim. Acta 67 (2003) 4223–4230.

- [25] M.T. Madigan, J.M. Martinko, P.V. Dunlap, D.P. Clark, Brock Biology of Microorganisms, twelveth ed., Benjamin Cumming, Menlo Park, CA, 2010.
- [26] K.S. Zerda, Adsorption of Viruses to Charge-Modified Silica, Ph.D. dissertation, Baylor College of Medicine, Houston, TX, 1982.
- [27] T.C. Lee, I.C. Ho, Modulation of cellular antioxidant defense activities by sodium arsenite in human fibroblasts, Arch. Toxicol. 69 (1995) 498–504.
- [28] G.R. Schinella, H.A. Tournier, H.O. Buschiazzo, P.M. Buschiazzo, Effect of arsenic (V) on the antioxidant defense system: In vitro oxidation of rat plasma lipoprotein, Pharmacol. Toxicol. 79 (1996) 293–296.
- [29] T.C. Lee, I.C. Ho, Differential cytotoxic effects of arsenic on human and animal cells, Environ. Health Perspect. 102 (1994) 101–105.
- [30] M.F. Hughes, Arsenic toxicity and potential mechanisms of action, Toxicol. Lett. 133 (2002) 1–16.