Pyrophyllite clay for bacteriophage MS2 removal in the presence of fluoride
Jeong-Ann Park, Jae-Hyun Kim, Chang-Gu Lee and Song-Bae Kim

ABSTRACT
The aim of this study was to investigate the removal of the bacteriophage MS2 from aqueous solution using pyrophyllite. Batch experiments were conducted to examine MS2 sorption to pyrophyllite. The influence of fluoride, a groundwater contaminant, on the removal of MS2 was also observed. Column experiments were performed with pyrophyllite to examine MS2 removal in the absence and presence of fluoride. Batch results demonstrated that pyrophyllite was effective in MS2 removal. The percentage removal of MS2 increased from 5.26% to 99.99% (4.0 log removal) with increasing pyrophyllite concentrations from 0.2 to 20 g/L. At fluoride concentrations of 5 and 10 mg/L, the log removals of MS2 by pyrophyllite were 3.05 and 2.54, respectively, which were lower than that with no fluoride present. The results suggested that the removal of MS2 by pyrophyllite was influenced by fluoride ions because fluoride ions could compete with MS2 for sorption sites on the pyrophyllite surfaces. Column results showed that pyrophyllite was effective in MS2 removal under flow-through conditions, with a removal capacity of $8.17 \times 10^6$ pfu/g with no fluoride present and $4.70 \times 10^6$ pfu/g with 5 mg/L fluoride present.

Key words | adsorbent, bacteriophage MS2, competition, fluoride, pyrophyllite, virus removal

INTRODUCTION
Pyrophyllite is a 2.1 clay mineral having a dioctahedral layer structure with octahedrally coordinated Al ion sheets between two sheets of SiO$_4$ tetrahedra. It is a hydrous aluminosilicate clay with the chemical composition AlSi$_2$O$_5$(OH) (Bentayeb et al. 2003). The primary countries producing pyrophyllite are located in northeast Asia and include China, Korea, and Japan. Pyrophyllite has many industrial applications, including as a raw material in the ceramic, glass, and refractory industries (Singh 2011). Pyrophyllite has recently been investigated as a potential low-cost and environmental friendly adsorbent for removing various contaminants from water and wastewater (Gücek et al. 2005; Prasada & Saxena 2008; Gupta et al. 2009; Goswami & Purkait 2011; Kang et al. 2013; Kim et al. 2015).

Groundwater resources can be virally contaminated by septic tank effluents, wastewater discharge, and manure application on agricultural land. Such viral contamination results in a degradation of drinking water quality and is a threat to public health (Mawdsley et al. 1995). To provide safe drinking water and prevent water-borne viral diseases, water treatment alternatives using various adsorbents and filter media such as activated carbon, bituminous coal, and quartz sand have been considered (Gupta & Chaudhuri 1995; Powell et al. 2000; Elliott et al. 2011). Clays have also been tested for virus removal because of their large surface area and high ion exchange capacity (Lipson & Stotzky 1983; Schiffenbauer & Stotzky 1983). Sobsey et al. (1980) studied the adsorption of viruses (poliovirus, and reovirus) on different soil materials. The results showed that clays were more efficient in the removal of enteric viruses from wastewater than sand or organic soil. Chattopadhyay & Puls (1999) performed thermodynamic studies of the adsorption of bacteriophages (MS2, PhiX174, T2) on clay adsorbents including hectorite, kaolinite, and saponite. The authors reported that sorption was dependent on the surface hydrophobicity of both adsorbents and
bacteriophages. Jin et al. (2007) tested laboratory-synthesized layered double hydroxides (LDHs) for the removal of bacteriophages from aqueous solution. They demonstrated that the bacteriophages MS and PhiX174 were effectively removed by Mg/Al and Zn/Al LDHs with adsorption efficiencies ≥ 99%. To our knowledge, however, studies related to virus removal using pyrophyllite clay have never been reported.

The aim of this study was to investigate the removal of the bacteriophage MS2 from aqueous solution using pyrophyllite. The bacteriophage MS2 is a good surrogate for enteric viruses because its characteristics are similar to those of the enteric viruses and its detection is easy (Leclerc et al. 2000). In particular, MS2 is known as a poliovirus-like phage because it is the same type of positive-strand RNA virus as poliovirus and has a similar size (25–27 nm) (Madi- gan et al. 2009). Several researchers have demonstrated that MS2 was a good model virus for studying the adsorption and inactivation of enteric viruses such as hepatitis A virus, echovirus, and poliovirus in soil environments and water treatment systems (Sobsey et al. 1995; Arraj et al. 2005). Batch experiments were conducted to examine MS2 sorption to pyrophyllite. The influence of fluoride, a ground-water contaminant, on the removal of MS2 by pyrophyllite was observed. Column experiments were also performed with pyrophyllite to examine MS2 removal in the absence and presence of fluoride.

MATERIALS AND METHODS

Characterization of pyrophyllite

Pyrophyllite obtained from Sungsan Mining (Haenam, Korea) was used in the experiments. Before use, the pyrophyllite was washed twice using deionized water to remove surface impurities. Wet pyrophyllite was autoclaved for 15 min at 17.6 psi, cooled to room temperature, and oven-dried at 105 °C for 1 to 2 days. The characteristics of pyrophyllite have been described in detail elsewhere (Kang et al. 2013; Kim et al. 2013). Briefly, the X-ray fluorescence analysis indicated that pyrophyllite was mainly composed of Si (74.03%) and Al (21.20%). Also, the peaks for quartz (SiO2), dickite (Al2Si2O5(OH)4), and pyrophyllite (Al2Si4O10(OH)2) were observed from the X-ray diffraction pattern. Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen gas (N2) adsorption–desorption analysis using an ASAP 2010 instrument (Micromeritics, USA).

Virus and plaque assay

The bacteriophage MS2 (ATCC 15597-B1) was obtained from the American Type Culture Collection and was grown on Escherichia coli (E. coli) (ATCC 15597) using the double agar overlay method (Adams 1959). MS2 is an icosahedral single-stranded RNA phage (van Duin 1988). Enumeration of bacteriophages was performed by the plaque assay method (Adams 1959) using the aforementioned E. coli host. The host culture (0.2 mL) and 0.1 mL of the diluted virus sample were mixed with 5 mL of soft agar in a tube, and the mixture was then poured onto a trypticase soy agar plate to solidify. After solidifying, the plates were incubated at 37 °C for 18 h.

MS2 removal by pyrophyllite

Batch experiments were conducted in triplicate to examine the removal of bacteriophage MS2 by pyrophyllite. MS2 stock solution was diluted from a concentrated titer with artificial ground water (AGW) to the desired concentration. The virus stock concentration was ~ 10⁶ pfu/mL. The AGW included 0.075 mM CaCl₂, 0.082 mM MgCl₂, 0.051 mM KCl, and 1.5 mM NaHCO₃ at pH 7.6. The first set of batch experiments was performed to examine the removal of MS2 as a function of adsorbent (pyrophyllite) dosage. The batch experiment method consisted of adding 50 mL virus stock solution to 50 mL centrifuge tubes containing different concentrations of adsorbent (0.2–20 g/L). Pyrophyllite particles smaller than 0.149 mm (US Standard Sieves No. 100) in diameter with the BET surface area of 1.34 m²/g were used. After all tubes were properly prepared and sealed, they were shaken at 40 rpm for 300 min at 4 °C to avoid thermal inactivation of the virus. 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 by the plaque assay method. Control tubes were filled with only
bacteriophage solution and treated in the same manner as the experimental tubes. The second set of experiments was conducted to observe the removal of MS2 as a function of reaction time (pyrophyllite concentration = 20 g/L). Tubes were shaken for a set of desired reaction times ranging from 5 to 300 min.

The percent removal of bacteriophage (R) was calculated using the following formula:

$$ R = \left( \frac{C_0 - C}{C_0} \right) \times 100 $$

where $C_0$ and $C$ are the initial and final bacteriophage concentrations, respectively. The bacteriophage removal per unit mass of adsorbent ($S$) was calculated using the following formula:

$$ S = \left( \frac{C_0 - C}{M} \right) $$

where $M$ is the adsorbent concentration used in the experiment. The log removal of bacteriophage in the experiment was calculated using the following formula:

$$ \log \text{removal} = -\log \left( 1 - \frac{R}{100} \right) $$

**MS2 removal in the presence of fluoride**

Batch experiments were conducted to examine the removal of bacteriophage MS2 by pyrophyllite in the presence of fluoride (5 and 10 mg/L). The batch experiment method consisted of adding 50 mL virus stock solution to 50 mL centrifuge tubes containing different concentrations of pyrophyllite (2–20 g/L). In the experiments, MS2 stock solution was diluted with AGW to the desired concentration. The tubes were shaken at 40 rpm for 300 min at 4 °C. In addition, inactivation experiments for MS2 were conducted in fluoride solution where no pyrophyllite was present: 50 mL of virus stock solution was added to a 50 mL centrifuge tube containing two different concentrations of fluoride (5 and 10 mg/L). The tubes were shaken at 40 rpm for 300 min at 4 °C.

**Column experiments**

Pyrophyllite particles used in the column experiments were in the size range of 0.42 – 0.60 mm (US Standard Sieves No. 30 and No. 40). They had the BET surface area of 1.12 m²/g and particle density of 2.626 g/cm³. Column experiments were performed using a Plexiglas column (inner diameter = 2.5 cm, and column length = 10 cm) packed with pyrophyllite. Experimental conditions were as provided in Table 1. For each column experiment, a column was packed with pyrophyllite (mass of filter materials = 70.4 ± 0.4 g) by the tap-fill method to attain a bulk density of 1.442 ± 0.012 g cm⁻³ and a porosity of 0.452 ± 0.004.

Column experiments were conducted at 4 °C to minimize the inactivation of bacteriophage. The column was connected to a pump (QG400, FASCO, USA) operating at a rate of 0.5 mL/min (empty bed contact time, EBCT = 98.2 min). Prior to an experiment, the packed column was flushed upward with 20 bed volumes (1 bed volume = 26.8 cm³) of AGW until the column effluent was clear and a steady-state flow condition was established. Column experiments were performed in a downward flow mode with continuous injection of bacteriophage and/or fluoride in AGW at a flow rate of 0.5 mL/min. Effluent samples were collected at regular intervals (15 min) for 30 h using an

<table>
<thead>
<tr>
<th>Expt.</th>
<th>MS2 concentration (pfu/mL)</th>
<th>Fluoride concentration (mg/L)</th>
<th>Flow rate (mL/min)</th>
<th>EBCT (min)</th>
<th>$M_f$ (g)</th>
<th>MS (pfu)</th>
<th>Fluoride (mg)</th>
<th>$C_{cap}$</th>
<th>$q_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$5.98 \times 10^5$</td>
<td>-</td>
<td>0.5</td>
<td>98.2</td>
<td>70.2</td>
<td>$5.74 \times 10^8$</td>
<td>-</td>
<td>8.17 $\times 10^6$</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>$3.70 \times 10^5$</td>
<td>5.0</td>
<td>0.5</td>
<td>98.2</td>
<td>70.9</td>
<td>$3.33 \times 10^8$</td>
<td>1.61</td>
<td>4.70 $\times 10^6$</td>
<td>0.023</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>5.0</td>
<td>0.5</td>
<td>98.2</td>
<td>70.1</td>
<td>-</td>
<td>1.73</td>
<td>-</td>
<td>0.025</td>
</tr>
</tbody>
</table>
auto collector (Retriever 500, TELEDYNE, USA). The total injected solution volume was about 40 bed volumes. Effluent samples were analyzed to determine the bacteriophage concentration using the double agar overlay method. The fluoride concentration was measured using a fluoride ion selective electrode (9609BNWP, Thermo Scientific, USA).

In the fluoride measurement, a total ionic strength adjustment buffer solution (58 g of NaCl, 57 mL of CH₃COOH, and 150 mL of 6 M NaOH in 1,000 mL deionized water) was used to prevent interference by other ions.

RESULTS AND DISCUSSION

MS2 removal by pyrophyllite

Data for the removal of bacteriophage MS2 by pyrophyllite as a function of adsorbent dose are presented in Table 2. The percentage removal increased from 5.26% to 99.99% (4.0 log removal) as the pyrophyllite concentrations increased from 0.2 to 20 g/L. More than 99% of MS2 could be removed with a pyrophyllite concentration of ≥4 g/L. The removal of MS2 by pyrophyllite as a function of reaction time is presented in Table 3. The sorption of MS2 to pyrophyllite was rapid. Within 15 min, ~99.98% (=3.7 log removal) of MS2 was attained. More than 4.0 log removal was achieved after 180 min. The literature reports that virus sorption to clay particles is generally rapid. Sobsey et al. (1980) reported that the adsorption of poliovirus and reovirus on bentonite and kaolinite reached equilibrium within 15 min. Park et al. (2011) showed that sorption of bacteriophage MS2 on Mg/Fe LDH reached equilibrium within 60 min.

The experimental data for the effect of reaction time on MS2 removal were analyzed with kinetic sorption models (Figure 1). In the mode analysis, the following linear forms

<table>
<thead>
<tr>
<th>Pyrophyllite concentration (g/L)</th>
<th>MS2 concentration (pfu/mL)</th>
<th>Percentage removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>2.85 × 10⁶</td>
<td>5.26 ± 0.00</td>
</tr>
<tr>
<td>1</td>
<td>2.85 × 10⁶</td>
<td>41.23 ± 3.04</td>
</tr>
<tr>
<td>2</td>
<td>2.85 × 10⁶</td>
<td>92.81 ± 1.26</td>
</tr>
<tr>
<td>4</td>
<td>2.85 × 10⁶</td>
<td>99.23 ± 0.16</td>
</tr>
<tr>
<td>8</td>
<td>2.85 × 10⁶</td>
<td>99.78 ± 0.02</td>
</tr>
<tr>
<td>12</td>
<td>2.85 × 10⁶</td>
<td>99.84 ± 0.01</td>
</tr>
<tr>
<td>16</td>
<td>2.85 × 10⁶</td>
<td>99.99 ± 0.00</td>
</tr>
<tr>
<td>20</td>
<td>2.85 × 10⁶</td>
<td>99.99 ± 0.00</td>
</tr>
</tbody>
</table>

Table 3 | Removal of bacteriophage MS2 by pyrophyllite as a function of reaction time

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Initial</th>
<th>Final</th>
<th>Percentage removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4.62 × 10⁶</td>
<td>7.70 × 10³</td>
<td>99.835 ± 0.01</td>
</tr>
<tr>
<td>15</td>
<td>4.62 × 10⁶</td>
<td>4.35 × 10³</td>
<td>99.906 ± 0.00</td>
</tr>
<tr>
<td>30</td>
<td>4.62 × 10⁶</td>
<td>9.28 × 10²</td>
<td>99.980 ± 0.00</td>
</tr>
<tr>
<td>60</td>
<td>4.62 × 10⁶</td>
<td>1.26 × 10³</td>
<td>99.973 ± 0.00</td>
</tr>
<tr>
<td>120</td>
<td>4.62 × 10⁶</td>
<td>8.75 × 10²</td>
<td>99.981 ± 0.00</td>
</tr>
<tr>
<td>180</td>
<td>4.62 × 10⁶</td>
<td>1.50 × 10²</td>
<td>99.997 ± 0.00</td>
</tr>
<tr>
<td>240</td>
<td>4.62 × 10⁶</td>
<td>2.95 × 10²</td>
<td>99.994 ± 0.00</td>
</tr>
<tr>
<td>300</td>
<td>4.62 × 10⁶</td>
<td>2.10 × 10²</td>
<td>99.995 ± 0.00</td>
</tr>
</tbody>
</table>

Figure 1 | Kinetic model analyses: (a) pseudo first-order kinetic model; and (b) pseudo second-order kinetic model. Model parameters are provided in Table 4.
of pseudo first-order and pseudo second-order kinetic models were used:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]

(4)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e} + \frac{t}{q_e}
\]

(5)

where \(q_e\) is the amount of MS2 removed at equilibrium, \(q_t\) is the amount of MS2 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 4. The correlation coefficient showed that the pseudo second-order model was better than the pseudo first-order model at describing the kinetic data. The amount of MS2 removed at equilibrium \((q_e)\) was determined to be \(1.43 \times 10^8\) pfu/g from the pseudo second-order model.

The experimental data for the effect of adsorbent dose on MS2 removal were analyzed with equilibrium isotherm models (Figure 2, Table 5). In the mode analysis, the following linear forms of the Freundlich and Langmuir isotherm models were used:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

(6)

\[
\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}
\]

(7)

where \(C_e\) is the concentration of MS2 in the aqueous solution at equilibrium, \(K_F\) is the distribution coefficient, \(1/n\) is the Freundlich constant, \(Q_m\) is the maximum mass of MS2 removed per unit mass of pyrophyllite (removal capacity), and \(K_L\) is the Langmuir constant related to the binding energy. Values of \(K_F, Q_m, K_F,\) and \(n\) can be determined by fitting the Freundlich and Langmuir models to the observed data. The correlation coefficients showed that the Langmuir model was more suitable than the Freundlich model for MS2 sorption data. The maximum amount of MS2 removed per unit mass of pyrophyllite \((Q_m)\) was determined to be \(5.01 \times 10^8\) pfu/g. Pyrophyllite had a relatively high adsorption capacity compared to other materials. Jin et al. (2007) found that the adsorption capacities of Mg/Al and Ni/Al LDHs for MS2 and Phix174 were \(1.4 \times 10^7 - 2.1 \times 10^7\) pfu/g. Park et al. (2011) reported that adsorption capacity for MS2 by Mg/Fe LDH calcined at 300 °C was \(2.34 \times 10^8\) pfu/g.

**MS2 removal in the presence of fluoride in batch condition**

The effect of fluoride on MS2 removal by pyrophyllite is shown in Figure 3. At a pyrophyllite concentration of

| Kinetic sorption model parameters obtained from model fitting to experimental data |
|-----------------------------------|-----------------------------------|-----------------|-----------------|
| **Pseudo first-order model**      | **Pseudo second-order model**     |                  |
| \(q_e\) (pfu/g)                   | \(k_1\) (1/min)                   | \(R^2\)         |
| \(1.39 \times 10^8\)             | 1.17 \times 10^{-2}              | 0.74            |
| \(q_e\) (pfu/g)                   | \(k_2\) (g/pfu/min)              | \(R^2\)         |
| \(1.43 \times 10^8\)             | 6.13 \times 10^{-7}              | 1.00            |

**Equilibrium isotherm model parameters obtained from model fitting to experimental data**

<table>
<thead>
<tr>
<th>Freundlich model</th>
<th>Langmuir model</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_F) (L/g)</td>
<td>(Q_m) (pfu/g)                   \n</td>
</tr>
<tr>
<td>8.52 \times 10^5</td>
<td>5.01 \times 10^8</td>
</tr>
<tr>
<td>0.32</td>
<td>2.86 \times 10^{-5}</td>
</tr>
<tr>
<td>0.71</td>
<td>0.96</td>
</tr>
</tbody>
</table>
20 g/L, the log removal in the presence of 5 mg/L fluoride was 3.05, which was lower than for 0 mg/L fluoride. At the same concentration of pyrophyllite, the log removal in the presence of 10 mg/L fluoride was 2.54, which was lower than for 0 and 5 mg/L fluoride. The removal of MS2 by pyrophyllite was thus shown to be influenced by fluoride ions. The fluoride results could be attributed to fluoride ions competing with MS2 for sorption sites on the pyrophyllite surfaces (Kim et al. 2015). Separate batch experiments indicated that the fluoride adsorption capacity of pyrophyllite was 0.124 mg/g at the given conditions (pyrophyllite concentration = 20 g/L; initial fluoride concentration = 5 mg/L; and reaction time = 5 h), which indicated that fluoride could adsorb to pyrophyllite. In the inactivation tests, no inactivation of MS2 was observed at 5 mg/L fluoride, which meant that fluoride ions could only affect MS2 removal by pyrophyllite through occupation of sorption sites and thereby decrease MS2 adsorption to pyrophyllite. MS2 removal by pyrophyllite was lower at 10 mg/L fluoride than at 5 mg/L fluoride, even though MS2 inactivation by fluoride also contributed to MS2 removal at 10 mg/L fluoride. Note that 19.3% of the initial MS2 was inactivated at 10 mg/L fluoride in the inactivation tests. This result indicated that MS2 adhesion to pyrophyllite was further decreased at 10 mg/L fluoride because more sorption sites on pyrophyllite were occupied by fluoride ions.

The adsorption of fluoride to pyrophyllite could be described by a ligand exchange mechanism as fluoride ions could replace hydroxyl ions on the surfaces of pyrophyllite during adsorption (Goswami & Purkait 2011). Viruses have carboxyl (COOH) groups on their surfaces because they contain protein polypeptides, which are composed of amino acids (Gerba 1984). Thus, bacteriophage may adhere to the surfaces of pyrophyllite via replacement of hydroxyl ions by humic acids. It was reported that humic acids have carboxyl groups on their surfaces and adsorb to metal (aluminum and iron) oxides through replacement of hydroxyl ions on the surfaces of metal oxides (Chi & Amy 2004). However, the electrostatic attraction between MS2 and pyrophyllite is not favorable. It is known that MS2 has an isoelectric point of 3.9 (Zerda 1982); thus, it is negatively charged in our solution conditions (AGW = pH 7.6). The zeta potential of pyrophyllite in AGW was determined to be −22.8 mV, indicating that it was also negatively charged.

**MS2 removal in the presence of fluoride in flow-through conditions**

The breakthrough curves (BTCs) for MS2 and fluoride obtained from the column experiments are shown in Figure 4. The BTCs for MS2 are shown as bed volume versus log relative concentration, while the fluoride BTCs are presented as bed volume versus relative concentration. The column capacity for bacteriophage (or fluoride) removal
at a given flow rate and influent concentration \( C_{\text{cap}} \) was quantified as follows:

\[
C_{\text{cap}} = \frac{Q}{1000} \int_{t=0}^{t=\text{final}} (C_i - C_e)dt
\]  

(8)

where \( Q \) is the volumetric flow rate, \( C_i \) and \( C_e \) are the influent and effluent concentrations, respectively, of bacteriophage (or fluoride). The mass of bacteriophage (or fluoride) removed per unit mass of pyrophyllite in the column (removal capacity of pyrophyllite, \( q_a \)) was determined as follows:

\[
q_a = \frac{C_{\text{cap}}}{M_f}
\]  

(9)

where \( M_f \) is the mass of pyrophyllite in the column. The column experimental results are summarized in Table 1.

In Figure 4, the BTCs show that the log relative concentration of MS2 remained between −5.0 and −4.0 while the relative fluoride concentration at the effluent gradually increased with increasing bed volume. In the absence of fluoride (Expt. 1), the column capacity for MS2 removal \( C_{\text{cap}} \) was \( 5.74 \times 10^8 \) pfu, which was slightly higher than that \( (3.35 \times 10^8 \) pfu) in Expt. 2 when fluoride was present. In case of fluoride, the value of \( C_{\text{cap}} \) for fluoride in Expt. 2 was 1.61 mg, which was slightly lower than that \( (=1.73 \) mg) in Expt. 3 when MS2 was absent. The removal capacity \( q_a \) for MS2 was \( 8.17 \times 10^6 \) pfu/g in Expt. 1 and \( 4.70 \times 10^6 \) pfu/g in Expt. 2. For fluoride, the values of \( q_a \) in Expts 2 and 3 were 0.023 and 0.025 mg/g, respectively.

The column results indicated that pyrophyllite was effective in the removal of MS2 under flow-through conditions. Also, the effect of fluoride on MS2 removal in the column experiments was not as large as the fluoride effect in the batch experiments under the tested conditions (duration of column test = 30 h). This result indicates that the competition between fluoride ions and bacteriophages on the sorption sites of pyrophyllite was less in column experiments than in batch experiments, possibly due to the different experimental conditions (bacteriophage concentration, reaction (contact) time and adsorbent size/surface area etc.) between column and batch experiments.

**CONCLUSIONS**

Batch results demonstrated that pyrophyllite was effective in MS2 removal from aqueous solutions through the adhesion of the bacteriophage to pyrophyllite. The results also indicated that the removal of MS2 by pyrophyllite was influenced by fluoride ions. The log removal of MS2 in the presence of fluoride was lower than when no fluoride was present. This could be attributed to fluoride ions competing with MS2 for sorption sites on the pyrophyllite surfaces. Column results showed that pyrophyllite was also effective in MS2 removal under flow-through conditions. The effect of fluoride on MS2 removal in the column experiments was not substantial compared to the effect in batch experiments. Long-term column experiments will be necessary in order to examine the breakthrough of fluoride and bacteriophage and their competition for sorption sites on pyrophyllite during their transport through columns.

**ACKNOWLEDGEMENT**

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