Simultaneous removal of low concentrations of ammonium and humic acid from simulated groundwater by vermiculite/palygorskite columns

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A B S T R A C T
Vermiculite and palygorskite are common clay minerals having large surface area and high cation exchange capacities. They have different affinities for ammonium (NH4 +) and humic acid (HA), and hence were combined to remove NH4 + and HA simultaneously from simulated groundwater in column tests. Three columns were assembled by filling the columns with the same amount of vermiculite and palygorskite but in different arrangements. The simulated groundwater containing NH4 + and HA was pumped to the columns in an upward direction. The concentrations of N-NH4 + and HA at different height of the columns were measured over time. No significant differences on HA removal among the three column settings were observed. However, the NH4 + removal efficiencies were significantly different among the three column settings. For the column filled with separate vermiculite and palygorskite layers, NH4 + was mainly adsorbed on the vermiculite layer. In contrast, when mixture of vermiculite and palygorskite was packed at the ratio of 1:1, NH4 + was mainly accumulated at the bottom of the column.

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1. Introduction
Many studies were conducted to remove ammonium (NH4 +) from water (Karadag et al., 2005; Maranon et al., 2006; Wang et al., 2006). A search of ScienceDirect using the term “ammonium removal” resulted in over 100,000 returns. Among the most commonly used media zeolite resulted in a return of more than 7000 articles. Zeolite has large cation exchange capacity (CEC) and can be tailored into different particle sizes for wastewater and groundwater treatment. Tests on NH4 + removal using natural zeolite from New South Wales, Australia, via a cation exchange reaction at an optimum pH of 5.5, showed a NH4 + exchange capacity of 2 mg/g (Komarowski and Yu, 1997). With a CEC of 2.5 meq/g, the upload of NH4 + was as high as 4 mg/g (Cyrus and Reddy, 2011). Treatment of NH4 + containing wastewater using zeolite from Turkey resulted in a NH4 + removal of 1.6 meq/g, or 29 mg/g (Sarioglu, 2004). Zeolite was also studied for its applicability of simultaneous removal of ammonia and humic acid (HA) in batch tests (Mousavi et al., 2011). However, the application of zeolite as adsorbents for wastewater management could be limited by the facts that only synthetic zeolite had sufficient capacity and only natural zeolites could be manufactured in practical sizes for application, i.e. synthetic zeolite had too small grain size to be used and natural zeolite had low adsorption capacities (Johnson and Worrall, 2007). Moreover, as most natural zeolite contained a mixture of different exchangeable cations, pretreatment was commonly applied to convert the zeolite into homoionic and to increase the contaminant removal efficiency (Ingezakis et al., 2001).

In addition to zeolite, other clay minerals such as montmorillonite and vermiculite also have large CEC values, enabling them to be used for NH4 + removal. The overall capacity for NH4 + fixation may be greater for vermiculite compared to montmorillonite (Nieder et al., 2011). The NH4 + adsorbed on vermiculite could be slowly decomposed at normal humidity and more rapidly and completely at high humidity (Ahlrichs et al., 1972). The decomposition could be attributed to nitrification as a high rate of nitrification was found for ammonium vermiculite in comparison to ammonium sulfate (Stone and Wild, 1977).

Tests on NH4 + removal by sepiolite, a fibrous phyllosilicate, showed a NH4 + adsorption capacity up to 3.7 mmol/g, or 67 mg/g (Balci, 2004). However, attapulgite, another type of fibrous phyllosilicates and the synonym of palygorskite, had NH4 + adsorption capacity of only 8.5 mg/g, but the capacity increased to 21 mg/g when a chitosan-g-poly(acrylic acid)/attapulgite composite was used (Zheng et al., 2009).

Opposite to NH4 +, HAs have negative charges under ambient pH conditions. Thus, different strategies were needed to remove HA from water. Common methods include adsorption, membrane filtration, flocculation, ozonation, and biological and photoelectrochemical treatments (Imyim and Prapalimrungsi, 2010; Maghsoodloo et al., 2011; Wei et al., 2011). The HA adsorption capacity on activated carbon (AC)
could be as high as 80 mg/g (Rauthula and Srivastava, 2011). Granular activated carbon (GAC) achieved better removal of non-biodegradable organic matter compared to resins Amberlite XAD-4, XAD-8, and IR-120 (Rodriguez et al., 2004). Better HA removal was also achieved using anion exchange resins in comparison to flocculation (Bolto et al., 2004). In addition to using organic resins, inorganic minerals as adsorbent for the removal of HA were also tested. Sorption of HA by phillipsite- and chabazite-rich Neapolitan Yellow Tuff and a clinoptilolite-rich tuff from Turkey, both in the native and in Ca-enriched forms, also showed great promise with the amount of HA sorbed as much as 6 mg/g in comparison to 1.8 mg/g for GAC (Capasso et al., 2005). The percentages of HA and fulvic acid (FA) removal by xonotlite, a double chain inosilicate, reached up to 80% and 30%, respectively (Katsumata et al., 2003). Raw bentonite could also adsorb as much as 53 mg/g of HA (Salman et al., 2007). However, the swelling properties and small particle size prevented its applications in packed columns.

Raw vermiculite had negligible adsorption of FA. Maximum HA removal by vermiculite was found at pH 5 in medium of 0.020 mol/L KNO₃ and the removal was mainly due to precipitation (Abate and Masini, 2003). At the equilibrium solution concentration of 100 mg/L, the amount of FA and HA adsorbed on vermiculite was only 0.5 to 0.8 mg/g (Zhang et al., 2012). As most of the HA have negative charges, common earth materials such as zeolite and vermiculite were often modified by cationic surfactants to removed HA. Modification of vermiculite by a cationic surfactant hexadecyltrimethylammonium (HDTMA) increased FA adsorption to more than 20 mg/g (Abate et al., 2006). HDTMA-modified zeolite increased HA adsorption capacity from essential zero to over 120 mg/g (Li et al., 2011). Intercalation of poly (hydroxo aluminum) into bentonites raised the FA adsorption up to 70 mg/g (Vreysen and Maes, 2006).

Early studies showed that palygorskite could adsorb as much as 46 mg/g of humate (Singer and Huang, 1989). Sorption of HA from an initial concentration of 15 mg/L and a solid dose of 0.6 g/L on palygorskite decreased from 80% to 20% with increasing solution pH values from 4 to 6 (Niu et al., 2009).

As vermiculite and palygorskite have different affinities for NH₄⁺ and HA, it was anticipated that a synergist effect could be achieved when these two materials were used in combination. Thus, the goal of this study was to investigate the removal of NH₄⁺ and HA from simulated groundwater simultaneously in column tests under different experiment settings, which may provide a reference on material selection and structural design of permeable reactive walls.

2. Materials and methods

2.1. Materials

The vermiculite was obtained from Lingshou Xu-yang Mining Co., Ltd. in Hebei, China, with a particle size of 1.4–1.7 mm. It has a CEC of 0.92 meq/g. The palygorskite was obtained from Mingmei Minerals Co. Ltd., Anhui, China, with a particle size of 1.0–1.4 mm. It has a BET surface area of 213 m²/g and a CEC of 0.1 to 0.2 meq/g. The simulated ammonium solution was prepared by dissolving NH₄Cl in distilled water to achieve an N-NH₄⁺ concentration of 10 mg/L. The HA solution was supplied by Shanghai Huayang Chemical Reagent Co. Ltd. The simulated HA solution was prepared by dissolving 1 g HA in NaOH (0.025 M). After stirring for 30 min, distilled water was added to a final volume of 1 L and pH adjusted by 0.025 M HCl. After set aside over night, the solution was filtered through a filter paper with pore size between 30 and 50 μm before being used in adsorption experiments.

2.2. Batch tests

For the batch tests, 1.0 g of solid and 100 mL of solution containing different concentrations of NH₄⁺ and HA were placed in each 150 mL Erlenmeyer flask and shaken for 5 h at 200 rpm for vermiculite and 120 rpm for palygorskite. The mixture was centrifuged for 10 min at 6000 rpm for vermiculite and 9000 rpm for palygorskite. The supernatants were analyzed for residual NH₄⁺ or HA concentrations spectrophotometrically. The amount of NH₄⁺ or HA removed was calculated from the differences between the initial and equilibrium solution concentrations. Duplicate experiments were conducted for each test condition.

2.3. Column tests

Glass columns (4 cm in diameter and 50 cm in length) were used for the column experiments. Three column settings were assembled. The amount of vermiculite and palygorskite used was at 1:1 (v:v) ratio for all the three settings. In column 1, the bottom 20 cm was packed with palygorskite, while the top 20 cm with vermiculite. For column 2, the bottom 20 cm was packed with vermiculite, while the top 20 cm with palygorskite. Mixture of vermiculite and palygorskite at a ratio of 1:1 (v:v) was packed to 40 cm high for column 3 (Fig. 1). The parameters of the three column settings were listed in Table 1. A peristaltic pump was used for the delivery of simulated groundwater containing 10 mg/L N-NH₄⁺ and 20 mg/L HA in an upward direction. The flow rate was 0.91 cm³/min, resulting in a linear velocity of 2 m/d and a resident time of 5.4 h. The samples were taken every two days for a total of 55 days. The NH₄⁺ and HA concentrations were determined spectrophotometrically.

2.4. Methods of analyses

The NH₄⁺ was measured using a T6 Series UV/Vis Spectrophotometer (Beijing, Puxi Co.) at 420 nm by the Nessler’s reagent method, in which NH₄⁺ and mercury potassium iodide produced a yellow–brown complex in alkaline medium. The complex chrominance was proportional to the concentration of NH₄⁺. The HA concentration was determined using UV absorbance at 254 nm. Solution pH was measured with a pH meter (PHS-3C, Shanghai Leici Instrument Factory, China).

3. Results and discussion

3.1. Batch competitive adsorption

Overall, vermiculite was more effective in removing NH₄⁺ from water while palygorskite had higher affinity for HA. For vermiculite, the removal of NH₄⁺ from initial concentrations of 5 and 10 mg/L was about 55% in the absence of HA. In the presence of HA, the NH₄⁺ removal remained about the same or increased slightly to 58% (Fig. 2a). The values corresponded to NH₄⁺ adsorption of 0.57 mg/g. The removal of
HA by vermiculite was only 1–2% in the absence of NH$_4^+$. As the concentration of N-NH$_4^+$ increased to 40 mg/L, the HA removal increased to 8–9%, corresponding to 0.05 mg/g (Fig. 2b).

For palygorskite, the removal of NH$_4^+$ from initial concentrations of 5 and 10 mg/L was 12–13% in the absence of HA, corresponding to 0.05 and 0.1 mg/g. In the presence of HA, the NH$_4^+$ removal increased to 14–16% (Fig. 2c). The removal of HA by palygorskite was 38 and 31% from initial HA concentrations of 10 and 20 mg/L, in the absence of NH$_4^+$, corresponding to 0.4 and 0.6 mg/g. It increased to 70 and 58%, corresponding to 0.7 and 1.2 mg/g, when the initial N-NH$_4^+$ concentration was 20 mg/L (Fig. 2d).

Vermiculite had much higher CEC values and ammonium was adsorbed by ion exchange in the interlayer space. HA did not interfere with this adsorption. The removal efficiency of HA was low and increased with loading of ammonium. This may indicate that more edge sites became available for HA or A-adsorption. Palygorskite had much higher anion exchange capacity, resulting in higher P sorption. According to O. Owen et al. (2008), the removal of HA by palygorskite was attributed to the broken bond effects that possess positive charges to electrostatically attract HA or to the formation of complexation with Ca$^{2+}$ on palygorskite (Hering and Morel, 1988). These results indicate different mechanisms for NH$_4^+$ and HA removal by these two minerals, resulting in less competition but more cooperative adsorption. Similar to an early study in which co-adsorption was found for simultaneous removal of NH$_4^+$ and HA by zeolite (Moussavi et al., 2011).

### 3.2. Influence of packing and initial concentrations on NH$_4^+$ and HA removal

![Graphs](image)

![Graphs](image)

- **Fig. 2.** Batch studies on competitive adsorption between NH$_4^+$ and HA on vermiculite and palygorskite.

**Table 1**

<table>
<thead>
<tr>
<th>Columns</th>
<th>The mass (g) of vermiculite, palygorskite</th>
<th>Pore volume (cm$^3$)</th>
<th>Porosity (%)</th>
<th>Residence time (h)</th>
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</thead>
<tbody>
<tr>
<td>Column 1</td>
<td>242, 160</td>
<td>285</td>
<td>58.9</td>
<td>5.2</td>
</tr>
<tr>
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<td>243, 158</td>
<td>283</td>
<td>58.8</td>
<td>5.2</td>
</tr>
<tr>
<td>Column 3</td>
<td>243, 159</td>
<td>294</td>
<td>60.7</td>
<td>5.4</td>
</tr>
</tbody>
</table>
day 1 (Fig. 3c). For the 20 cm column, the residence time was 3.1 h, similar to 3 h to reach adsorption equilibrium from the batch study. It took 5 days before the effluent concentration exceeded the standard. At 30 cm high, the residence time was 4.6 h. It took 21 days before the effluent concentration exceeded the standard (Fig. 3c). These values corresponded to 0.07, 0.2, and 0.5 mg/g of HA uptake. With a packing height of 30 cm for palygorskite, at initial HA concentrations of 40, 20, and 10 mg/L, it took 4, 9, and 29 days before the effluent concentrations were higher than the standard (Fig. 3d). At the time when effluent concentrations exceeded the standard, the amounts of HA adsorbed were 0.63, 0.36, and 0.22 mg/g.

3.3. Contrast of NH4$^+$ and HA removal from a single solution to that from mixed solutions

When a column was packed with vermiculite to 30 cm high with a residence time of 4.6 h, the removal of NH4$^+$ from a single solution (10 mg/L N-NH4$^+$) or from a solution containing both solutes (10 mg/L N-NH4$^+$ and 20 mg/L HA) was compared. The removal of HA from a single solution (20 mg/L HA) and from a solution containing both solutes (20 mg/L HA and 20 mg/L N-NH4$^+$) was also compared.
of N-NH$_4^+$ and 20 mg/L of HA) was about the same (Fig. 4a). It took 13 and 15 days for the effluent NH$_4^+$ to exceed the standard from the single NH$_4^+$ solution and mixed solution, respectively, corresponding to an N-NH$_4^+$ adsorption of 0.22 mg/g. On the other hand, it took 2.5 and 3.5 days for the effluent HA concentrations to exceed the standard from the single solution (20 mg/L HA) and mixed solution (10 mg/L of N-NH$_4^+$ and 20 mg/L of HA), respectively (Fig. 4b), equivalent to HA adsorption of 0.15 and 0.2 mg/g.

In comparison to vermiculite, when the columns were packed with palygorskite to 30 cm high, a significant reduction in effluent HA concentration was achieved (Fig. 4c). It took about 20 and 40 days before the effluent HA concentration exceeded the standard from the single solution (20 mg/L HA) and mixed solution (10 mg/L of N-NH$_4^+$ and 20 mg/L of HA), respectively (Fig. 4b), equivalent to HA adsorption of 0.15 and 0.2 mg/g.

As the distance from the sampling port to the input port increased, NH$_4^+$ removal was observed when vermiculite was packed at the bottom half of the column. In contrast, the retention of NH$_4^+$ occurred mainly in the vermiculite layer. For the column packed with a mixture of palygorskite and vermiculite, retention of NH$_4^+$ happened mainly in the vermiculite layer. Its concentration decreased from 9.5 to 1.2 mg/L, accounting for more than 90% of NH$_4^+$ removal. For column 2, HA removal was mainly occurred in the vermiculite layer with a 50% removal (Fig. 6b). Extensive floc and precipitation were noticed. As vermiculite had weak adsorption for HA, the removal of HA from column 2 could be mainly attributed to precipitations. Removal of HA in column 3 was also achieved on the bottom part (Fig. 6c) mainly due to combination of precipitation and adsorption on palygorskite.

At a flow rate of 1 to 3 mL/min, it took about 93 to 98 PVs before full breakthrough of NH$_4^+$ occurred when a column was packed with zeolite at a diameter of 2.5 cm and a height of 37 cm (Cyrus and Reddy, 2011). In this study, after 55 days, corresponding to approximately 244–254 PVs of continuous input, the effluent N-NH$_4^+$ concentration was still less than 10% of the input concentration, demonstrating superior properties for NH$_4^+$ removal. Two adsorption sites were attributed to NH$_4^+$ retention on vermiculite – exchangeable and non-exchangeable with the capacity for the former site increased as solution pH decreased and that for the latter site not affected by solution pH (Shen et al., 1997).

Coating of clay minerals montmorillonite, illite, and kaolinite by HA significantly increased their cation sorption and especially for NH$_4^+$ (Zhang et al., 2013). The pKa value of HA was dependent on the size of HA molecules, varying from 3.67 with molecular weight of 1–10 kDa to 5.04 at 300 kDa (Shin et al., 1999). The pKa value of NH$_4^+$ was 9.2 (Bell et al., 2007). The solution pH in this study was 6–7. Under this pH condition, HA would bear negative charges while NH$_4^+$ would possess positive charges. They may form complex in solution or on solid surfaces.

Overall, the presence of one species may promote the adsorption of the other as demonstrated in this study. This cooperative adsorption mechanism may enhance mutual removal for wastewaters containing both contaminants at equal concentrations.

3.4. Influence of packing sequence on NH$_4^+$ and HA removal

For HA removal, negligible influence was observed with respect to different packing conditions (Fig. 5a). The concentrations of HA from each column were below the standard on day 55, corresponding to 244 to 254 PVs. The HA adsorption in these three columns was 2.89, 2.89, and 2.91 mg/g, respectively. On the other hand, packing vermiculite to the influent end achieved the best NH$_4^+$ removal, followed by packing the mixture of vermiculite/palygorskite (Fig. 5b). The worst NH$_4^+$ removal was observed when vermiculite was packed at the effluent end.

As the distance from the sampling port to the input port increased, both NH$_4^+$ and HA concentrations decreased at day 30 (Fig. 6). However, HA was mainly retained at Section 1, i.e. the bottom quarter of the packed materials, regardless of the packing methods. For column 1, HA removal was mainly concentrated in the palygorskite layer (Fig. 6a), which resulted in a decrease in HA concentration from 20 to below 10 mg/L. Retention of HA on vermiculite layer was low. In contrast, NH$_4^+$ removal happened mainly in the vermiculite layer. Its concentration decreased from 9.5 to 1.2 mg/L, accounting for more than 90% of NH$_4^+$ removal. For column 2, HA removal was mainly occurred in the vermiculite layer with a 50% removal (Fig. 6b). Extensive floc and precipitation were noticed. As vermiculite had weak adsorption for HA, the removal of HA from column 2 could be mainly attributed to precipitations. Removal of HA in column 3 was also achieved on the bottom part (Fig. 6c) mainly due to combination of precipitation and adsorption on palygorskite.

4. Conclusions

(1) Under dynamic flow through conditions, columns assembled with palygorskite and vermiculite in three different packing conditions all showed good HA removal. However, NH$_4^+$ removal was significantly affected by different packing conditions. The best NH$_4^+$ removal was achieved when vermiculite was packed at the bottom half of the column.

(2) Retention of HA under all three column packing conditions was mainly achieved at the bottom. In contrast, the retention of NH$_4^+$ occurred mainly in the vermiculite layer. For the column packed with mixture of palygorskite and vermiculite, retention of NH$_4^+$ occurred mainly at the bottom of the column.

![Fig. 5. Influence of packing sequence on the removal of HA (a) and NH$_4^+$ (b) at the effluent port. The horizontal line is the standard.](image-url)
(3) For NH$_4^+$ removal, the effluent concentration was less than 10% of the input concentration after a 10 mg/L N-NH$_4^+$ solution was fed for 55 days, corresponding to approximately 244–254 PVs of continuous input. Meanwhile, the effluent HA concentration was only 15% of the input concentration at day 55. The results demonstrated superior properties for both NH$_4^+$ and HA removal when vermiculite and palygorskite was packed in column setting combinatorically. Taking their particle sizes into consideration, the materials may serve as a good candidate to be used in permeable reactive barriers for groundwater remediation containing mixed types of contaminants, or to be used in fixed bed reactors for treatment of wastewater containing both NH$_4^+$ and HA.

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