Re-evaluation and reconstruction of water purification system using soil I. Assessment of soil as a sorbent of humic substances and phosphate ion


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Abstract The purpose of our study is to develop a treatment procedure for humic substances (HS hereafter) and phosphate ion in wastewater and environmental water by percolation of the water through a constructed soil layer at the hydraulic loading of a few metres per day. In the present work, batch sorption tests were conducted for more than 80 samples of soil, sludge, mineral and organic materials in order to find good sorbents for fulvic acid (FA hereafter) and phosphate ion. The results showed that the sorption of FA was high for some charcoal, and apatite and goethite minerals. Comparatively high sorption of FA was found for some Andosols and volcanic ash soil. Significant sorption of phosphate ion, on the other hand, was found for various types of soil, sludge from water treatment plants and some waste materials. The linear isotherm was obtained for the sorption of FA to a charcoal, apatite and goethite minerals, and Andosols.

Keywords Batch sorption test; fulvic acid; soil filtration; sorption isotherm

Introduction

Recently the water purification systems using soil (Kunimatsu and Sugahara, 1988; Wakatsuki et al., 1993; Hamasaki et al., 2004) were applied to on-site treatment of river water and secondary treatment effluent from toilets in a few locations in Japan. The concept of the Japanese system was originated from the land treatment (Loehr and Overcash, 1985) in which wastewater was applied to soil, and the percolate, purified by physical-chemical-biological processes in soil, was discharged to the aquifer or to the surface water body. The system applied in Japan featured high infiltration rate of wastewater per unit area of land (ca. 1,500 m/yr) compared to the conventional system (maximum 125 m/yr), as constructed horizons of soil and additives with high permeability were used in place of natural soil horizons. Because of the high infiltration rate, the mechanisms that contribute to the removal of pollutant in the Japanese system could have been different from those working in the conventional systems (Reed et al., 1995).

The purpose of our study is to develop a treatment procedure for HS and phosphate ion in wastewater and environmental water using soil. As HS are precursors of disinfection by-products, their presence in environmental water can have adverse effect on the quality of drinking water. Among the techniques such as oxidation/biofiltration, and activated carbon sorption and coagulation to remove HS (Weber et al., 1983; Edzwald, 1993; Graham, 1999), our approach has some advantages over the other techniques because it can be used on-site at low operational cost, and does not generate the sludge that requires subsequent treatments.
In the present work, we evaluated the sorption of HS and PO$_4^{3-}$ to various soil and additives by batch sorption experiment, in order to find promising materials for the high infiltration rate – water purification system using soil.

**Materials and methods**

**Preparation of FA solution**

The FA used in the present experiment was the one contained as an impurity in commercial humic acid purchased from Aldrich (Milwaukee, WI). The FA stock solution was prepared by dissolving 10 g of the humic acid to 200 mL of 0.4 w/v% NaOH solution followed by the titration to pH 1 to precipitate the humic acid fraction. The precipitate was eliminated by centrifugation and filtration through GF/F filter. The liquid phase that contained FA was back-titrated to pH 7, stood still overnight to precipitate the iron oxides and was filtered again to obtain the clear brown solution of FA. The FA obtained by this procedure was shown to be ca. 70% humic by fractionation using XAD-8 resin (Thurman and Malcolm, 1981), and ca. 30% of its organic carbon was biodegradable when measured by the method developed by Servais *et al.* (1987).

**Batch sorption experiment for screening purposes**

Batch experiments were conducted to investigate the sorption of FA and phosphate ion to 23 volcanic ash soil, 13 alluvium soil, 12 mineral, 5 charcoal, 5 sediment, 2 sand, 12 sludge, 4 waste and 7 organic additive samples, all collected from various places from Japan. The sorption experiment was started by weighing the air-dried samples (pulverized to pass 2 mm sieve) and water from Hayama River, Shiga, Japan (filtered with 0.7 µm pore diameter glass fiber filter, GF/F from Whatman plc, Kent, UK) in a glass Erlenmeyer flask. Each flask was kept at 25°C in a dark place for one week, and then the FA stock solution and river water were added so that the concentration of the added FA was ca. 30 mg/L as the concentration of DOC (dissolved organic carbon) in the liquid phase. The solid (g) to liquid (mL) ratio was 1:2.5 (ratio 1:10 or 1:100 was applied to some of the samples). The sorption of added FA was monitored by measurement of DOC concentration in the filtered liquid phase, 1 hr, 24 hrs, 72 hrs and 168 hrs after the addition of FA. The batch sorption experiment of phosphate ion was conducted likewise, and its sorption was monitored by measurement of total phosphorus (T-P hereafter) in the filtered liquid phase 168 hrs after its addition. Blank samples were prepared by adding river water to the solid phase at the same solid to liquid ratio as the sorption experiment.

The sorption of each sorbate was evaluated by the apparent $K_d$ value, calculated from the following equation assuming the linear sorption isotherm:

$$K_d = (V/m) ((C_b + C_0)/C - 1)$$

where $C_0$ (mg/L) and $C$ (mg/L) are the respective added and measured DOC (or T-P) concentrations in the liquid phase; $C_b$ (mg/L) is the DOC (or T-P) concentration in the liquid phase of the sample blank, and $m$ (g) and $V$ (L) respectively are the mass of sorbent and the volume of the solution in each flask.

**Sorption isotherm experiment**

A further experiment was conducted to obtain the sorption isotherm for sorbents that showed significant sorption of FA. The experiment was conducted by adding varying concentrations of FA to the liquid phase in each flask of the batch experiment, while maintaining the constant solid to liquid ratio. The solid phase was pulverized to pass a 60 mesh sieve. In order to minimize the variation in the salinity and pH among the flasks to which different concentrations of FA was added, the FA used in this experiment was desalinated.
prior to use. The desalination was done by gel filtration using ca. 100 mL of Sephadex G-25 resin (Pharmacia and Pfizer Co., NY) packed in a glass column. The desalinated FA was shown to be almost 100% humic by the fractionation using XAD-8 resin.

Nodvin et al. (1986) showed that the partitioning of DOC in a closed system is best described by linear initial mass isotherm (i.e., linear correlation between $C_0$ and DOC sorbed per unit amount of sorbent) when:

1. the sorption of DOC follows the conventional linear sorption isotherm (linear correlation between the equilibrium concentration of the organic matter added in the liquid phase and the amount of the organic matter sorbed per unit amount of the sorbent);
2. the exchangeable organic carbon was present in the system before the organic material of interest was added.

The initial mass sorption isotherm is obtained by plotting $C_0$ in horizontal axis and $q$ in the vertical axis, where $q$ is estimated by the following equation:

$$q = V(C_b + C_0 - C)/m$$

(2)

The solid to liquid distribution coefficient $K_d$ can be estimated using the following equation:

$$K_d = aV/(V-am)$$

(3)

where $a$ is the slope obtained by the regression analysis of the initial mass isotherm.

**Results and discussion**

**The batch sorption experiment for screening purposes**

Samples that showed high sorption of FA and phosphate ion are listed in Tables 1 and 2. Apparently, soil samples that have high affinity toward FA were rather rare. Some volcanic ash soil and Andosols showed comparatively high sorption of FA among the soil samples tested. Usage of materials such as charcoal, goethite and apatite minerals in addition to soil may be necessary to facilitate the removal of FA in the actual treatment system. Sorption of phosphate ion, on the other hand, was high for many soil and sludge samples.

**The sorption isotherm**

Examples of the sorption isotherm obtained in this study are shown in Figure 1 for limonite.

**Table 1** Samples that showed high $K_d$ values of FA in batch experiment (listed in higher orders of $K_d$ 168 hrs after the addition of FA)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Apparent $K_d$ (mL/g) of FA</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1.0</td>
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<tr>
<td>Apatite (reagent)</td>
<td>76.0</td>
</tr>
<tr>
<td>Calcium phosphate (reagent)</td>
<td>47.4</td>
</tr>
<tr>
<td>Andosols (Koga, Shiga)</td>
<td>9.0</td>
</tr>
<tr>
<td>Charcoal made out of wood</td>
<td>7.9</td>
</tr>
<tr>
<td>Volcanic ash soil (“Akadama soil” from Tochigi)</td>
<td>3.6</td>
</tr>
<tr>
<td>Andosols (Santo, Shiga)</td>
<td>4.8</td>
</tr>
<tr>
<td>Sludge from a WTP in Shiga</td>
<td>3.4</td>
</tr>
<tr>
<td>Limonite (goethite from Akamizu, Kumamoto)</td>
<td>8.8</td>
</tr>
<tr>
<td>Goethite (Gifu)</td>
<td>4.2</td>
</tr>
<tr>
<td>Charcoal made out of bamboo</td>
<td>6.8</td>
</tr>
<tr>
<td>Volcanic ash soil (Andosols from Ibaragi)</td>
<td>3.0</td>
</tr>
<tr>
<td>Bentonite</td>
<td>13.9</td>
</tr>
</tbody>
</table>
Goethite mineral from Akamizu, Kumamoto prefecture, Japan, produced by iron bacteria and Andosols from Sando, Shiga prefecture, Japan. Kaiser et al. (1996) reported that the linear sorption isotherm can describe the sorption of DOC to various types of soil. Figure 1 shows that the linear initial mass isotherm (and consequently linear sorption isotherm) also describes the sorption of FA to soil and mineral samples well. The \( K_d \) values obtained by Eq. (3) for the initial mass isotherm \((C_0 \text{ vs. } q)\) shown in Figure 1(a) were almost identical to the slope of the regression equation of the conventional \( C \text{ vs. } q \) isotherm (shown in Figure 1(b)). The relationship between DOC concentration at equilibrium \( (C) \) and the amount of DOC sorbed \( (q) \) therefore is described as:

\[
q = K_d C + b
\]

where \( b \) is the intercept.

The \( K_d \) values obtained using Eq. (1) in the simple batch sorption test, and those obtained using Eq. (3) in the sorption isotherm experiment are compared in Table 3. The two \( K_d \) values differed within a factor of 1. The difference was probably caused by the exchangeable organic carbon that was present in the system before the FA was added, because the effect of such organic carbon could not be considered for in the simple batch experiment conducted by adding only one kind of concentration of FA. Also the difference in FA used for the sorption test could have contributed to the difference in obtained \( K_d \) values (i.e., desalinated FA was used for isotherm experiment, but FA before desalination was used for the simple batch sorption test for screening purposes).

Figure 1 Sorption isotherm plot. (a) initial mass sorption isotherm, (b) conventional isotherm

Table 2 Samples that showed high \( K_d \) values for \( PO_4^{3-} \) in batch experiment (listed in higher orders of \( K_d \) 168 hrs after the addition of \( PO_4^{3-} \))

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Apparent ( K_d ) (mL/g) of ( PO_4^{3-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volcanic ash soil (subsoil from Amagase, Oita)</td>
<td>5,000</td>
</tr>
<tr>
<td>Volcanic ash soil (&quot;Akadama soil&quot; from deeper layer)</td>
<td>5,000</td>
</tr>
<tr>
<td>Volcanic ash soil (fine grained &quot;Kanuma soil&quot;, from Tochigi)</td>
<td>5,000</td>
</tr>
<tr>
<td>Silt from Sakishima, Osaka</td>
<td>5,000</td>
</tr>
<tr>
<td>Volcanic ash soil (&quot;Shirasu&quot; from Kagoshima)</td>
<td>5,000</td>
</tr>
<tr>
<td>Sludge from water treatment plant in Shiga</td>
<td>3,323</td>
</tr>
<tr>
<td>Calcium phosphate (reagent)</td>
<td>3,348</td>
</tr>
<tr>
<td>Limonite (goethite from Akamizu, Kumamoto)</td>
<td>1,810</td>
</tr>
<tr>
<td>Andosols from Santo, Shiga</td>
<td>1,700</td>
</tr>
<tr>
<td>Sludge from water treatment plant in Shiga</td>
<td>1,554</td>
</tr>
<tr>
<td>Coal fly ash mixed with gypsum</td>
<td>1,293</td>
</tr>
<tr>
<td>Andosols from Mt. Sanbe, Shimane</td>
<td>1,200</td>
</tr>
</tbody>
</table>
**Conclusions**

Through batch sorption experiment, FA was found to be removable by limited numbers of soil, goethite and apatite minerals, and certain kind of charcoal, whereas phosphate ion could be removed by various types of soil and sludge. Addition of these materials as sorbents in water purification systems using soil was considered effective. The isotherm of the sorption of FA to charcoal, apatite, limonite and Andosols was linear.

**References**


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*Table 3* Comparison between $K_d$ values (mL/g) of FA obtained by different procedures

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_d$ from sorption isotherm Eq. (3) (mL/g)</th>
<th>Apparent $K_d$ obtained using Eq. (1) (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limonite</td>
<td>53.8</td>
<td>23.7</td>
</tr>
<tr>
<td>Andosols (Santo, Shiga)</td>
<td>14.7</td>
<td>77.8</td>
</tr>
<tr>
<td>Charcoal made out of wood</td>
<td>443.9</td>
<td>117.8</td>
</tr>
<tr>
<td>Apatite</td>
<td>54.8</td>
<td>145.1</td>
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