Effects of Reclaimed Water on the Characteristics of Dimethyl Phthalate Adsorption on Sediments

Zigong Ning¹,², Pengxiang Li², Shuang Zhou³, Yunkai Li¹,*, Munehide Ishiguro⁴, Wei Zhao¹, Meie Wang⁵

ABSTRACT: Adsorptions of Dimethyl Phthalate (DMP) on three sediments in both reclaimed and ultrapure water were studied using the batch technique and the effects of reclaimed water on it were clarified. The data were interpreted by using Freundlich and Dubinin-Radushkevich models. The values of $1/n$ were among 0.207 to 0.766, showing the presence of multiple adsorption sites on sediments. Compared with the ultrapure water as the background solution, the adsorption capacities of sediments for DMP were reduced in case of reclaimed water due to the competition of substances in reclaimed water. The mean adsorption energy, $E$, is smaller in the reclaimed water than that in ultrapure water. Water Environ. Res., 89, 274 (2017).

KEYWORDS: DMP, sediment, reclaimed water, adsorption.

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Introduction

Dimethyl phthalate (DMP) is widely used as a plasticizer to improve the flexibility and durability of polyvinyl chloride (PVC)-based plastics (Osman et al., 2013). The DMP is not chemically bound to the PVC polymer. Therefore, DMP is easily released into the environment (Staples et al., 1997). DMP has been detected in the natural water and soil (Gledhill et al., 1980). 0.36 µg/L of DMP was detected in the underground water near the Homestead Wastewater Treatment Plant in Florida (Foster et al., 2012). Because DMP causes the functional disturbances of nervous system of animals, it is ecologically toxic and a hazardous material (Douglas et al., 1986).

Adsorption is the main method responsible for extracting the toxic compounds from the water phase, which strongly influences the fate, behavior, bioavailability and the transport of toxic compounds in the environment. Besides, water solubility also is a determining factor controlling the environmental distribution and behaviors of DMP (Abdel daim et al., 2012; Staples et al., 1997). Many previous works have reported about sorption behaviors of DMP on soils (Yang et al., 2013; Li et al., 2010), sediments (Gao et al., 2011; Xia et al., 2012), beads (Osman et al., 2012; Chen et al., 2007), polymer resins (Zhang et al., 2007) and carbon nanotubes (Den et al., 2006) by applying the Langmuir, Freundlich, and Dubinin-Radushkevich adsorption equations. The reclaimed water has been regarded as one of the water resources to solve water shortage problem and recover water ecosystems in big cities all over the world, such as Santee Project in Sycamore Valley (California Santee Town, United States), Nobidome River in Tokyo (Japan), Olympic Lake (Chaoyang District, Beijing), Lianshi Lake (LSL) and Xiaoyue Lake (XYL) in Yongding River (Mentougou District, Beijing) and so on. The reclaimed water is an extremely complicated multi-material coexisting system, which contains various inorganic and organic substances and microorganisms (Li, 2012). The reclaimed water is supposed to strongly influence the fates of DMP in the water ecosystem. However, the research of DMP adsorption influenced by the reclaimed water is rare.

The DMP adsorbed on sediments was studied by the batch method. The effects of reclaimed water on adsorption characteristics of DMP on sediments were analyzed. The aim of the present study is to elucidate the adsorption phenomena of DMP on sediments of urban lakes especially under the influence of reclaimed water—a multi-material coexisting system.
Table 1—The basic physicochemical properties and particle composition of sediments.

<table>
<thead>
<tr>
<th>Sediments</th>
<th>Organic matter (g/kg)</th>
<th>CEC (mmol/kg)</th>
<th>pH</th>
<th>Sand 1.0–0.05</th>
<th>Silt 0.05–0.002</th>
<th>Clay &lt; 0.002 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSL</td>
<td>83.4</td>
<td>174</td>
<td>7.68</td>
<td>38</td>
<td>56</td>
<td>6</td>
</tr>
<tr>
<td>DXL</td>
<td>10.4</td>
<td>207</td>
<td>8.18</td>
<td>22</td>
<td>46</td>
<td>32</td>
</tr>
<tr>
<td>XYL</td>
<td>67.7</td>
<td>10.7</td>
<td>7.8</td>
<td>64.4</td>
<td>30.6</td>
<td>5</td>
</tr>
</tbody>
</table>


Materials and Methods

Materials. Reclaimed Water. The reclaimed water used in the present study was obtained from a reclaimed water plant located in Qinghe Town, Haidian District of Beijing. The wastewaters from the around areas in Beijing, such as Zhongguancun Science Park, Qinghe River Industrial Park, Residential Quarter and so on, are collected as the wastewater sources of the sewage water plant of Qinghe, which are treated by the Anaerobic Anoxic Oxic technology (A²/O) to remove nitrogen and phosphorus. The A²/O process consists of an anaerobic tank followed by an anoxic anaerobic tank. Its effluents are regarded as the sources of reclaimed water plant of Qinghe. The membrane treatment and process of ozone are used to make the reclaimed water. The qualities of reclaimed water used in this research were as follows: the total organic carbon (TOC) (combustion oxidation non-dispersive infrared absorption method) was 6.06 mg/L, CODCr (Dichromate Method) 28.5 mg/L and BOD₅ (Dilution and Seeding method) 3.6 mg/L.

Sediments. The sediments were selected from top fresh sediments (0–10 cm) of Lianshi Lake (LSL), Xiaoyue Lake (XYL), and Daoxiang Lake (DXL) in Beijing city in September in 2011. LSL and XYL are located in Mentougou District of Beijing. The reclaimed water from the plant of Qinghe is directly discharged into LSL and XYL. DXL is located in Haidian District of Beijing. The sediment samples were air-dried in a laboratory. The sordries (such as stones and roots) were removed. The dry samples were ground and passed through a 1 mm screen. The basic physicochemical properties and particle composition of the sediments are shown in Table 1. The content of organic matter in sediments were measured according to Soil—Determination of Organic Carbon—Potassium Dichromate Oxidation Spectrophotometric Method. The Ammonium Acetate Method was applied to measure the cation exchange capacity of sediments. The distribution of particles diameter was measured according to the method of Hydrometer. According to soil texture triangle of the USDA classification system, the sediments from LSL, DXL and XYL were the silty clay, silty clay loam and sandy loam, respectively.

Chemical Agent. The Dimethyl Phthalate is 99% analytical grade (bought from Dr. Hielscher Company, Germany). Acetone, hexane, methylene chloride, and methanol are chromatographic pure. CaCl₂ and other chemical reagents are analytical pure. The ultrapure water was obtained by Mili-Q ultrapure water instrument.

Adsorption Experiment. The experiments of DMP adsorption on the sediments were conducted by the batch method. The procedures of the experiment were as follows: Adsorption Experiments. The sediments of 2 g were placed into the 50 mL centrifuge tube. Twenty mL solutions at 5, 10, 20, 50, 100 or 200 mg/L DMP (These concentrations were selected according to the result of pre-experiments, which were not shown in this text) with 1.1 g/L CaCl₂ (increasing the solubility of DMP) in the ultrapure water were added into the tube. They were shaken for 6 hours at 25 ± 2 °C. The suspensions were centrifuged for 10 min at 4000 r/min. The DMP concentrations in the supernatant solutions were detected by a HPLC system (1200, Agilent, USA) with UV detection. The amount of DMP adsorbed by the sediment was calculated by subtracting the amount of DMP in equilibrium solution from the total amount of initially added DMP as the following equation:

\[ q = \frac{C_0V - CV}{W_S} \]

where \( q \) is the adsorption amount per gram of the solid phase, \( C_0 \) is the initial DMP concentration of input solution, \( C \) is the final DMP concentration in the solution, \( V \) is the volume of the input = equilibrium solution.

Experiments on the Effects of Reclaimed Water on DMP Adsorption on Sediments. Two grams of each sediment was placed into the 50 mL centrifuge tube. Twenty mL solution at different DMP concentration with 1.1 g/L CaCl₂ was prepared using the reclaimed water. It was added into the centrifuge tube. The tube was shaken for 24 hours at 25 ± 2 °C. The suspension was centrifuged and the DMP concentration in the supernatant was measured by a HPLC system (1200, Agilent, USA) with UV detection. The amount of DMP adsorbed by the sediments was calculated by subtracting the amount of DMP in equilibrium solution from the total amount of initially added DMP as described above in the equation.

Kinetics of Adsorption Experiments. A series of 2 g sediment samples were placed into 50 mL centrifuge tube, and 20 mL of 100 mg/L DMP solutions with 1.1 g/L CaCl₂ in ultrapure water was added. The tubes were shaken for 0.5 h, 1.0 h, 2.0 h, 4.0 h, 8.0 h, 12.0 h, and 24.0 h, respectively. The amount of DMP adsorbed by sediment was obtained as written before.

Results and Discussion

The Kinetics of DMP Adsorbed by Sediments. The effect of connect time on the DMP adsorbed on sediments is shown in
Figure 1. As can be seen from the Figure, the amount of DMP adsorption on three sediments increased with the contact time increasing, indicating that the rates of DMP adsorbed on sediments were rapid initially and slowed down progressively. The participation of specific functional groups and active surface sites perhaps made the initial rapid DMP adsorption. After 6 h approximately, the rate of DMP adsorbed on sediments was almost zero, and one can find that beyond 6 h there was almost no further increase in the adsorption amount even though the contact time continued to 24 h, which indicates that the equilibrium was reached within 6 h. Therefore, the equilibrium contact time for the experiment was fixed to 6 h.

**Adsorption Isotherms of DMP on Sediments.** Figure 2 shows the adsorption amount of DMP on three sediments against the equilibrium concentration. As can be seen from the Figure, the amount of DMP adsorbed on three sediments increased with the increase of its concentration in solution because the adsorption site on sediments became progressively occupied by DMP. There were almost no differences of the amount of DMP adsorbed among three sediments at low DMP concentration. However, the difference progressively increased with the increase of DMP concentration because of the difference of adsorption capacity of sediments for DMP.

**Freundlich Isotherm Model.** The Freundlich isotherm model is usually applied for solid surfaces, which possess multiple kinds of adsorption sites where adsorption energies are different. Theoretically, the model can be derived from the following Langmuir-Freundlich equation, which is derived analytically by integrating many local Langmuir equations for different adsorption sites (Van Riemsdijk et al., 1986).

\[
\theta = \frac{(kC)^m}{1 + (kC)^m}
\]

where \(\theta\) is the adsorption ratio, \(C\) is the concentration and \(k\) and \(m\) are constants. When \((kC)^m<<1\), we obtain the Freundlich equation.

The Freundlich equation was applied to fit the isotherm of DMP adsorbed on three sediments (Freundlich et al., 1926). The linearized equation is:

\[
\log(S) = \log(K_F) + \frac{1}{n} \log(C_e)
\]

where \(S\) is the DMP adsorption amount per g of sediments, mg/g, \(C_e\) is the equilibrium solution concentration, mg/L, and \(K_F\) and \(1/n\) are the empirical constants of the Freundlich equation. The plots of \(\log(S)\) against \(\log(C_e)\) for DMP adsorption on three sediments are shown in Figure 3a. From the slope and the intercept of the plots, one can get the values of empirical constants \(1/n\) and \(K_F\), respectively, which are shown in Table 2.

As it can be seen from the Figure and Table, the logarithm of adsorption amount increases in proportion to the logarithm of equilibrium concentration with the high correlation coefficients (\(r^2: 0.829–0.923\)). Meanwhile, the values of \(1/n\) for DMP adsorbed on three sediments were smaller than 1, which showed that the process of DMP adsorbed by sediment was not a simple partition process which interacts with only one similar adsorption site, but a process of nonlinear adsorption which interacts with different multiple sites. Gao et al. (2011) reported that the DMP adsorption isotherm could adequately be fitted well to the Freundlich model (\(R^2 > 0.981\)) and the DMP adsorption isotherm was nonlinear with \(1/n\) values ranging from 0.691 to 0.759. Yang et al. (2013) reported that the values of \(1/n\) were close to 1 indicating that the partition was the main sorption mechanism for DMP adsorbed by soils. \(K_F\) is the Freundlich sorption coefficient characterizing the sorption capacity. The different values of \(K_F\) for different sediments are different, revealing the different sediment sorption capacity. The order of sediment sorption affinity in three sediments charac-
characterized by $K_F$ values are LSL > DXL > XYL, which is related to the type of organic matter and sediment mineral structure (Mitra et al., 1999; Yang et al., 2013). The values of $K_F$ were among 0.079 to 0.188 for the three sediments, and were smaller than that reported by Yang et al. (2013) and Gao et al. (2011) because of the difference of organic matter and clay contained.

**Langmuir Isotherm Model.** Langmuir (1918) firstly proposed the Langmuir adsorption isotherm model for the gases adsorption on solid phase, which is derived assuming a finite number of identical adsorption sites and the absence of lateral interaction between adsorbed species. Up to now, it has been widely used to describe the adsorption phenomena in solution (Gao et al., 2011; Osman et al., 2012; Khan et al., 1995). Its linearized form is as follows:

$$\frac{C_e}{S} = \frac{1}{S_{ml} K_L} + \frac{C_e}{S_m}$$

Where $S$ is the amount of DMP adsorbed by per unit mass of sediments, $C_e$ is the equilibrium concentration of DMP in the equilibrium solution. $S_{ml}$ is the adsorption capacity, $K_L$ is the binding constant related to the free energy of adsorption $\Delta G^0 = -RT \ln (K_L)$, ($R = 8.3145 \text{J/(mol.K)}$ is the gas constant; $T$ is the temperature (K)) (Khan et al., 1995; El-Kamash et al., 2005). The fitted isotherm data by Langmuir model at 298K was shown in Figure 3b, which was obtained by plotting $C_e/S$ against $C_e$. Gao et al. (2011) successfully applied the Langmuir model to describe DMP adsorbed by sediments from the Jiamusi region of the Songhua River ($R^2 = 0.991$). Osman et al. (2012) published the good fitting result ($R^2 > 0.99$) of Langmuir model for DMP adsorbed by the poly macro beads, and showed that DMP adsorbed by beads was a favorable process. Den et al. (2006) researched the DMP adsorbed by carbon nanotubes, and also found that the Langmuir model could fit adsorption isotherm well ($R^2 > 0.98$), and pointed out that Langmuir isotherm model was more suitable than Freundlich isotherm model to characterize the DMP adsorption isotherm curves. However, in the present research, the fitted results by the Langmuir model was not good for DMP adsorbed by the three sediments, while those by Freundlich model was good, which indicates that the DMP adsorption sites on sediments were highly heterogeneous.

**Dubinin-Radushkviech Isotherm Model.** In order to investigate the nature of the DMP sorption processes on three sediments, Dubinin-Radushkviech isotherm (Dubinin et al., 1947; Foo et al., 2010; Osman et al., 2012; Osman et al., 2013) was also verified in the linear form:

$$\ln (S) = \ln (S_{mD}) - K_{D-R} e^2$$

Where $S$ is the amount of DMP adsorbed by per mass of sediments (mg/g), $S_{mD}$ is the maximum adsorption capacity (mg/g), $K_{D-R}$ is the Dubinin-Radushkviech isotherm constant (mol$^2$/J$^2$), and $e$ is the Polany potential (J/mol), which can be calculated as: $e = RT \ln \left(1 + 1/C_e\right)$ (Osman et al., 2012; Osman et al., 2013).
Linear regression analysis was conducted using ln(S) and $e^2$ and $SmD/R\_K_D/C_0\_R$ and $E$ were obtained as shown in Figure 3c and Table 2. The mean adsorption energy $E$ (kJ/mol) is defined as the free energy changing when one mole of DMP is transferred to the surface of the solid from infinity in the solution. One can calculate it by equation of $E = (-2K_{D,R})^{-0.5}$ (Laus et al., 2010). The values of mean adsorption energy $E$ for DMP adsorbed on three sediments are larger than 8 kJ/mol (Osman et al. 2012; Osman et al. 2013; El-Kamash et al., 2005), which indicates the chemical ion exchange. The sediment matrix containing adsorption sites with different adsorption energies (Chen et al., 2007; Gao et al., 2011) caused the difference of the mean adsorption energy $E$ of DMP adsorbed by three sediments.

Effect of Reclaimed Water on DMP Adsorbed by Sediments. The adsorption amount of DMP adsorbed by three sediments in the reclaimed water against the equilibrium concentration ($C_{eq}$) is shown in Figure 4. One can find from the figure that the amount of DMP adsorbed by three sediments increases with the DMP concentration increasing in range of this experimental concentration (0 to 200 mg/L). For the same initial DMP concentration, the adsorption amount of DMP in reclaimed water was smaller than that in the ultrapure water, because the reclaimed water was a multi-material coexisting system, containing amounts of organic matters (the concentrations of TOC, CODCr and BOD$_5$ were 6.06 mg/L, 28.5 mg/L and 3.6 mg/L, respectively) and other ions (Gan et al., 2010; Hu et al., 2011), which would compete for the adsorption sites on the sediments matrix with DMP.

As it can be seen in the Figure 5, Freundlich, Langmuir and Dubinin-Radushkviech adsorption isotherm models also were applied to describe the DMP adsorbed by three sediments in reclaimed water. As it can be observed from the figure, the Langmuir model is not yet suitable for DMP adsorbed by sediments. Meanwhile, the models of Freundlich and Dubinin-Radushkviech were applied successfully. The parameters of Freundlich and Dubinin-Radushkviech isotherm models for DMP adsorbed by three sediments are presented in Table 3.

The value of parameter 1/n between 0 and 1 represents the adsorption intensity and surface heterogeneity. The closer to zero the value is, the more heterogeneous the adsorption is. The value below unity implies chemical sorption process (Haghseresh et al., 1998; Foo et al., 2010). In the condition of reclaimed water, one can find that the range of value 1/n are between 0 and 1, but their values are larger than that obtained in the ultrapure water. The result indicates that chemical adsorption process is still the dominant mechanism for DMP adsorbed by sediments in reclaimed water. The larger values of 1/n indicate the adsorption sites on sediments for DMP become less heterogeneous. The sorption sites of sediments for DMP occupied by the organic matters or ions originally remaining in reclaimed water made the values of parameters $K_F$ be smaller than those in ultrapure water. The DMP combining with the organic matter in

<table>
<thead>
<tr>
<th>Sediments</th>
<th>$1/n$</th>
<th>$K_F$</th>
<th>$R^2$</th>
<th>$K_{D,R}$</th>
<th>$S_{mD,R}$ (10$^{-6}$mol/g)</th>
<th>$R^2$</th>
<th>$E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSL-R</td>
<td>0.207</td>
<td>0.188</td>
<td>0.829</td>
<td>0.0017</td>
<td>5.070</td>
<td>0.786</td>
<td>17.150</td>
</tr>
<tr>
<td>DXL-R</td>
<td>0.213</td>
<td>0.098</td>
<td>0.912</td>
<td>0.004</td>
<td>20.624</td>
<td>0.865</td>
<td>11.180</td>
</tr>
<tr>
<td>XYL-R</td>
<td>0.688</td>
<td>0.079</td>
<td>0.932</td>
<td>0.0061</td>
<td>94.062</td>
<td>0.941</td>
<td>9.054</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sediments</th>
<th>$1/n$</th>
<th>$K_F$</th>
<th>$R^2$</th>
<th>$K_{D,R}$</th>
<th>$S_{mD,R}$ (10$^{-6}$mol/g)</th>
<th>$R^2$</th>
<th>$E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSL-R</td>
<td>0.342</td>
<td>0.133</td>
<td>0.870</td>
<td>0.0024</td>
<td>6.702</td>
<td>0.833</td>
<td>14.434</td>
</tr>
<tr>
<td>DXL-R</td>
<td>0.546</td>
<td>0.072</td>
<td>0.839</td>
<td>0.0044</td>
<td>19.423</td>
<td>0.795</td>
<td>10.660</td>
</tr>
<tr>
<td>XYL-R</td>
<td>0.766</td>
<td>0.051</td>
<td>0.954</td>
<td>0.0066</td>
<td>84.508</td>
<td>0.960</td>
<td>8.704</td>
</tr>
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</table>
reclaimed water was more easily to be in reclaimed water rather than adsorbed on sediments, which indicates that the reclaimed water would inhibit the DMP adsorbed by sediments. The values of mean adsorption energy in the condition of reclaimed water were smaller than that of in condition of pure water, it is supposed to be the reason that the substances in reclaimed water adsorbed on sediments change the sites.

**Conclusions**

In this study, the adsorption behavior of DMP on three sediments from urban lakes and the effects of reclaimed water on it were investigated by using batch experiment. The model experiment results are limited to one-component system because of the given condition in this experiment. The Freundlich and Dubinin-Radushkevich models are more suitable to describe DMP adsorption on sediments than Langmuir model. The reclaimed water reduced the DMP maximum adsorption capacity because of the competition of the components in reclaimed water. The organic matters in reclaimed water were likely to combine with DMP to make DMP more readily existing in reclaimed water, and inhibiting the DMP adsorbed on sediments.

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