Introduction

Functioning as a link between land and water bodies, wetlands purify polluted waters by removing nitrogen and phosphorus through a series of physicochemical processes [1-5]. However, such purification capacity is limited. If the optimal function of the wetland is to be maintained, precaution must be taken to prevent pollution and deterioration of wetland water quality [6-8]. Excessive amounts of nutrients, such as nitrogen and phosphorus, often overflow into natural wetlands, exerting a pollution load that seriously threatens wetland ecosystems. In recent years, non-point water pollution due to agricultural activities is causing increasing environmental and social concerns. Zhalong Nature Reserve has been included in the Directory of Important Wetlands in the World. Currently, large-scale inflows of waters with rich nutrient contents (such as nitrogen and phosphorus), pose the most serious threat to the wetland reserve and its ecosystem [9-12]. Therefore, it is an important issue to study the pollution procedure and degree caused by the migration...
of organic phosphorus in the wetland environment. As the wetland environment of different pH values produces different influence on the migration and conversion of organic phosphorus, the degradation process of wastewater containing organic phosphorus across the wetland is stipulated in this paper via organic phosphorus containing solutions of different pH values passing slowly by the wetland. Our study was conducted on the chemical kinetic characteristics of phosphorus migration in aqueous background in wetlands so as to explore the chemical kinetic characteristics of phosphorus migration in the aqueous background of different wetlands.

**Material and Methods**

**Study Area and Experimental Apparatus**

Zhalong Wetland is located in western Songnen Plain, along the lower Wuyuer River and Shuang Yang River basin (Fig. 1), a typical riverside wetland with a total area of 2,100 km². Reed marsh, which is the largest and most widely distributed landscape feature in the Wuyuer River basin, is an important feature of Zhalong Wetland. A typical swamp wetland was chosen as the prototype of simulation (Fig. 1), based on outdoor investigations and tests. This area was the main load-bearing area of drainage with geographical coordinates of 124°11′38″-124°14′14″ east longitude and 47°10′19″-47°13′16″ north latitude. Alongside water and reeds, soil samples (with depth reaching 45 cm) were collected from the wetland, which were used as the bottom material of pilot-scale wetlands in the experiment. Soil sample was enclosed in the pilot-scale wetlands with naturally packed density and original order (the disturbed samples were collected, bagged on site, and filled as its order in the laboratory because of large soil mass and distant range). The reeds were cut into small fragments of about 2-3 cm with each having a dormant bud. Each fragment with a dormant bud was planted per 10×20 cm area of the pilot-scale wetland, 2 cm below the surface land. The dormant buds were observed to sprout up under unsaturated conditions, then pouring water every other day to maintain the water level. Three months later, when the reeds were growing to maturity and roots were growing rapidly, the experiment began. Two pilot-scale wetlands, each 200 cm long and 50 cm wide, were installed and operated in the experiments for repetition and comparison. A photo of the experimental apparatus is shown in Fig. 2.

**Experimental Methods**

The test was designed to be conducted with the inflow water of six different pH values coded with the letters A, B, C, D, E, and F (refer to Table 1 for the pH values and inflow water concentrations). The water pH was adjusted by 1:20 HCl or 1% NaOH and measured with a pH meter (HP9807) and precise pH paper. The sample interval was 4 d and observing indexes were the concentration of organophosphorus in water samples and adsorbed in clay, total phosphorus, (TP), PO₄³⁻, and Ca²⁺. Organophosphorus pesticide is the bulk of the product that controls plant diseases and insect pests in agricultural production with characteristics of a broad-spectrum, efficiency, and speed. Among them, omethoate can be dissolved by many solvents, including water, ethanol, and hydrocarbons [13-16], and it is a material with high tonnage because the annual requirement for it will exceed 1×10⁵ tons [17-18]. So the organophosphorus contamination was prepared by omethoate 40 EC sold at market. Organophosphorus in water samples was extracted with Chloroform and detected by a nitrogen phosphorus detector (NPD). Adsorbed...
organophosphorus was extracted by acetone, water, and dichloromethane, and detected by gas chromatography of a nitrogen and phosphorus detector (GC/NPD).

Results and Discussion

Influence of pH Value on Migration Performance of Organic Phosphorus

Table 2 shows the values of organic phosphorus contents in the inflow water after the latter passes by the clay pan. The data of six groups observed in test conditions shows that the content of organic phosphorus in the inflow water decreases while pH value increases, and the content of organic phosphorus in the inflow water on day 24 is less than 0.2mg/L when pH = 9.0. We analyzed the organic phosphorus being converted into PO$_4^{3-}$ at higher speeds in the condition of high pH value, and the phosphate radical is easy to absorb on the surface of the soil particles, which results in a great increase of the PO$_4^{3-}$ absorbed in the clay soil when pH = 9.0 (see Table 3). It can be seen that pH value plays a significant role in the migration and conversion of organic phosphorus, that is, the migration performance of organic phosphorus in the clay pan declines while pH increases.

Influence of pH Value on Mineralization Rate of Organic Phosphorus

The mineralization of organic phosphorus refers to its degradation and conversion process and the mineralization rate is used to indicate the extent of degradation and conversion. Organic phosphorus first produces PO$_4^{3-}$, which is migrated or converted in the mineralization process. The mineralization degree can be expressed by the ratio of reduced organic phosphorus to the original content (Table 4).

The content of organic phosphorus in the inflow water of Groups B-F in the test conditions on day 16 was about 0.4mg/L, and the mineralization rate reached 74% or above while the mineralization rate of inflow water in Group F reached 90%. Only the mineralization rate of inflow water in Group A was 39.44% on day 16 and exceeded 75% on day 24.

Part of the PO$_4^{3-}$ produced in the mineralization of organic phosphorus flows out with water and the other is absorbed by the clay pan and left in the clay (Table 3). Fig. 3 shows the variation of PO$_4^{3-}$ in the effluent of the six groups: the content of PO$_4^{3-}$ in Groups A-F declines gradually and the gradient of the content of PO$_4^{3-}$ rises with the increase of the pH value as a whole.

Chemical Kinetic Characteristics of Migration of Organic Phosphorus

The test studied the chemical kinetic equitation between PO$_4^{3-}$ and Ca$^{2+}$ in water and the standard Gibbs free energy change of reaction ($\Delta G_f^{\circ}$) of chemical reaction that may take place between PO$_4^{3-}$ and Ca$^{2+}$ was calculated, and the K value was obtained through the relationship between the $\Delta G_f^{\circ}$ and equilibrium constant, and then the dominant chemical reaction between PO$_4^{3-}$ and Ca$^{2+}$ was determined. The $\Delta G_f^{\circ}$ of ions and compounds can be found in Environmental Aquatic Chemistry [19].

Kinetic Relationship of c-pH

The following chemical reactions may take place between PO$_4^{3-}$ and Ca$^{2+}$:

<table>
<thead>
<tr>
<th>Test</th>
<th>Ca$^{2+}$ absorbed in the clay soil (mg/g)</th>
<th>PO$_4^{3-}$ absorbed in the clay soil (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.31±0.03</td>
<td>0.0014±0.0002</td>
</tr>
<tr>
<td>B</td>
<td>0.28±0.01</td>
<td>0.0032±0.0007</td>
</tr>
<tr>
<td>C</td>
<td>0.32±0.06</td>
<td>0.0025±0.0003</td>
</tr>
<tr>
<td>D</td>
<td>0.36±0.05</td>
<td>0.0027±0.0004</td>
</tr>
<tr>
<td>E</td>
<td>0.40±0.02</td>
<td>0.0049±0.0003</td>
</tr>
<tr>
<td>F</td>
<td>0.27±0.03</td>
<td>0.0068±0.0004</td>
</tr>
</tbody>
</table>
\[
\Delta G_r^0 = \Delta G_f^{production} - \Delta G_f^{reactant}
\]

In Formula (5), \(\Delta G_r^0\) is the standard Gibbs free energy change of reaction and \(\Delta G_f^0\) is the standard Gibbs free energy change of formation.

According to the calculation of \(\Delta G_r^0\) of the above chemical equation, the test determined that equations (1) and (2) are the dominant reaction equations between PO\(_4^{3-}\) and Ca\(^{2+}\). \(\Delta G_r^0\) of equations (3) and (4) can be neglected because they are too small. In standard conditions, the temperature is 298.15K.

Calculation with Reaction Equation (1):

\[
\log K = -0.175 \Delta G_r^0
\]

By checking the numerical table of \(\Delta G_f^0\), \(\Delta G_r^0 = 1301.5\) kJ/mol, we can know that \(\log K = 227.26\).

\[
\Delta G_r^0 = \sum(\Delta G_f^{production}) - \sum(\Delta G_f^{reactant})
\]

Calculation with Reaction Equation (2):

\[
\Delta G_r^0 = -356.9\text{kJ/mol}, \log K = 62.46.
\]

Combining (1) and (2):

\[
6\text{Ca}^{2+} + 5\text{PO}_4^{3-} + \text{OH}^- = \text{Ca}_3(\text{PO}_4)_2(\alpha) + \text{Ca}_5(\text{PO}_4)_3(\text{OH})
\]

From \(K = \frac{1}{[\text{Ca}^{2+}]^6[\text{PO}_4^{3-}]^5[\text{OH}^-]}\) we can see that

\[
\log[\text{PO}_4^{3-}] = \frac{14 - \text{pH} - 6\log[\text{Ca}^{2+}] - \log K}{5}
\]

\[
[\text{PO}_4^{3-}] = 10^\frac{\text{pH} - \text{pH} + \log K}{5}.
\]

\[
\log[\text{Ca}^{2+}]\ and \log K\ are \ both\ state,
\]

\[
\log c = -\frac{\text{pH}}{5} + M, M = \log D_i
\]

Refer to Fig. 4 for the data observed in the variation of log\(c\) with the pH value of the inflow water. When pH value is between 6.5 and 9.0 (PO\(_4^{3-}\) content of inflow water is 0.39 mg/L), the log\(c\) declines with the increase of pH value with the gradient \(-0.1729\).

**Kinetic relationship of c-t**

The test analyzed the first-order equation between \(c\) and \(t\) of types of ion:

\[
\frac{dc}{dt} = k_1 c,
\]

We get \(
\frac{dc}{c} = k_1 dt,
\)

\[c = e^{k_1 t + A_1}\]

So \(c = A_2 e^{k_2 t}\) \((A_2 = e^{A_1})\)

![Fig. 3. Relationships between PO\(_4^{3-}\)influent concentration and time with different pH.](image)

![Fig. 4. Relationships between pH and log\(c\) of PO\(_4^{3-}\).](image)

Table 4. Mineralization rate of organophosphor in the experiment.

<table>
<thead>
<tr>
<th>Test</th>
<th>Time/d</th>
<th>Precipitate</th>
<th>PH</th>
<th>pH</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4</td>
<td>52.047</td>
<td>63.743</td>
<td>55.962</td>
<td>39.441</td>
</tr>
<tr>
<td>B</td>
<td>8</td>
<td>60.819</td>
<td>60.234</td>
<td>68.772</td>
<td>75.906</td>
</tr>
<tr>
<td>C</td>
<td>12</td>
<td>58.340</td>
<td>54.330</td>
<td>62.963</td>
<td>74.492</td>
</tr>
<tr>
<td>D</td>
<td>16</td>
<td>49.123</td>
<td>65.497</td>
<td>67.836</td>
<td>75.906</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>60.702</td>
<td>65.497</td>
<td>76.023</td>
<td>77.778</td>
</tr>
<tr>
<td>F</td>
<td>24</td>
<td>70.760</td>
<td>81.287</td>
<td>84.211</td>
<td>90.643</td>
</tr>
</tbody>
</table>

![Fig. 3. Relationships between PO\(_4^{3-}\)influent concentration and time with different pH.](image)

![Fig. 4. Relationships between pH and log\(c\) of PO\(_4^{3-}\).](image)
\[
\ln c = k_1 t + N, \quad N = \ln A_2 \quad (9)
\]

Refer to Fig. 5 for the data observed in the variation of \(\ln c\) with the time. It can be seen that the \(\ln c\) of the six groups of pH value declines with time passing, and the gradient is between -0.0417 and -0.0746. Therefore, the \(\ln c\) declines continuously with the time passing in the condition of six groups of pH values, and its gradient is between -0.0417 and -0.0746.

Conclusions

1) For this paper we simulated wastewater containing organic phosphorus degradation process across the wetland via organic phosphorus containing solutions of different pH values slowly passing the simulation groove so as to explore the chemical kinetic characteristics of phosphorus migration in the aqueous backgrounds of different wetlands.

2) Our study shows that the migration performance of organic phosphorus in the wetland declines while pH value increases, and that the mineralization of organic phosphorus in clay pan increases with enhanced pH value. The mineralization rate of organic phosphorus in the eighth day may reach over 74% (\(\text{pH} \geq 7\)) or above 90% when \(\text{pH} = 9.0\).

30 The ionic concentration of \(\text{PO}_4^{3-}\), which is the direct product of mineralization of organic phosphorus, decreases somewhat when the pH value increases or with the passage of time. When pH value is between 6.5 and 9.0 (\(\text{PO}_4^{3-}\) content of inflow water is 0.39 mg/L), the \(\ln c\) declines with the increase of pH value with the gradient of -0.1729, and the \(\ln c\) declines continuously over time, and its gradient is between -0.0417 and -0.0746.

4) Our study provides the parameter basis to explore the chemical kinetic characteristics of phosphorus migration in the aqueous backgrounds of different wetlands.
the purification mechanism and determine chemical kinetic mode of organic phosphorus migration in the aqueous background of wetlands.

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References