EFFECT OF A PHOTOCATALYTIC COMPOSITE COUPLED WITH POTAMOGETOR CRISPUS ON CONTROL SEDIMENT PHOSPHORUS

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The treatment efficiency of phosphorus (P) in a sediment with the joint action of a new photocatalytic composite Sr-TiO2/PCFM and submerged macrophyte was studied for the first time in Donghu Lake, Wuhan, China. The results showed that Sr-TiO2/PCFM prepared by the sol–gel process exhibited a strong photocatalytic capacity. The dosage of Sr-TiO2/PCFM, irradiation, operation temperature, reaction time and pH were the principal factors affecting the removal of each sediment P forms by Sr-TiO2/PCFM. The synergistic effect of Sr-TiO2/PCFM and submerged macrophyte Potamogetor crispus on the sediment P under irradiation and control conditions showed that the removal rates of each P form have been further enhanced after irradiation. The unity of Sr-TiO2/PCFM and Potamogetor crispus plays a more important role in removing the sedimental P than the summation of Sr-TiO2/PCFM and Potamogetor crispus used separately under the irradiation conditions. The results suggested that the united technology of Sr-TiO2/PCFM and submerged macrophyte could be further applied to the treatment of endogenous P pollution in eutrophic lakes.

Keywords: Sr-TiO2/PCFM, submerged macrophyte, synergistic effect, sediment P in all fractions, P removal

1 INTRODUCTION

Phosphorus (P) in lakes comes from two sources, i.e., the internal release of sediment and the external load.1,2 The accumulation of endogenous P in sediment can bring great potential risk to eutrophication. Lake sediments are considered to be the reservoir of P, and the release of endogenous P in sediments is the main source of eutrophication, especially in shallow lakes.3,4

In nutrient-rich shallow lakes, the inputs of exogenous P will be brought under control through a variety of technologies. The internal P load becomes the decisive resource of overburden water P supply after controlling the input of external phosphorus load.5 Thus, it is very important to decrease the content of endogenous P and inhibit the release of endogenous P in sediments.

Various endogenous pollution-control strategies have been developed, such as dredging,6 oxidation treatment, physicochemical sedimentation,7,8 phytoremediation9 and in-situ sediment capping10,11 to reduce the release flux of P from sediment in eutrophic lakes. Submerged plants have certain inhibitory effects on sediment resuspension and P release, and uptake and absorb P from interstitial water and sediment, which is an applicable way to restore the eutrophic water ecosystem.12,13 However, the restoration process of P by plants is often affected by the growing period and surroundings, and single ecological technologies cannot be applied effect-
ively. At present, a synergistic technology for control sediment P is urgently needed.5

Nano-titanium dioxide (nano-TiO$_2$) has the advantages of high stability, low toxicity, large specific surface area and high catalytic efficiency, and is considered as one of the most practical candidate materials for environmental pollution control.15–18 Nano-TiO$_2$ thin films have become a hotspot because of their ease of recycling and separation.

In our previous studies, porous ceramic filter media (PCFM) was adopted as the carrier of the TiO$_2$ film, and we found that the photocatalytic composite has a great potential to control the internal P pollution. While little is known about the remediation effect of sediment P in all fractions with the synergistic effect of nano-TiO$_2$ and submerged macrophytes. To further enhance the single action of submerged macrophytes and nano-TiO$_2$ on sediment P remediation, a Sr-TiO$_2$/PCFM (Sr doped into TiO$_2$) photocatalyst capable of responding to visible light was developed, and the removal effect of each sediment P forms with the joint effects of Sr-TiO$_2$/PCFM and submerged macrophyte were studied for the first time.

2 EXPERIMENTAL PART

2.1 Study sites and sampling

Donghu Lake is located to the northeast of Wuhan city, Hubei province, China. The sampling site (30°33’04.9”N, 114°21’07.1”E) is located on the west side of Shuiguo Lake (one sub-lake of Donghu Lake), which is a serious eutrophication area. Surface sediment samples (0–10cm) and PCFM were collected and obtained.5, 19

2.2 P fractions

P fractions were employed with the SMT harmonized protocol, containing five P forms: Fe/Al-P, Ca-P, OP, IP and TP.20 The operationally defined scheme was composed of five phosphorus forms: Fe/Al-P (NaOH-extractable P, P bound to Al, Fe and Mn oxides and hydroxides), Ca-P (HCl-extractable P, P associated with Ca), organic P (OP), inorganic P (IP) and total P (TP). In a separate extraction, HCl-extracted inorganic P (IP) and the residual were treated at 450 °C to decompose the organic matter and to release the P bound to organic matter (OP). TP concentration in sediments was determined by treating the sample at 450 °C, followed by HCl extraction.

2.3 Batch experiments

2.3.1 Adsorption experiments

A certain amount of Sr/TiO$_2$-PCFM and 5 g of sediment samples were added and shaken for a period of time at different pH and temperatures for a stirring experiment. Chloroform (0.1 %) was added to inhibit the bacterial activity.

2.3.2 Photocatalytic experiments

The photoreactor system was made up of a quartz beaker reactor (500 mL), a nitrogen pump and a 125-W high-pressure mercury lamp. Sr/TiO$_2$-PCFM and the sediment were put into a 250-mL KCl solution (0.02 M). The suspension was irradiated under the high-pressure mercury lamp for 0.5 h. The visible light was shone vertically into the solution and the distance between the illuminant and liquid level was 40cm, and the luminous flux was 1500 Lm.

2.3.3 Phytoremediation experiments

*Potamogeton crispus* was sampled from the Donghu Lake in Wuhan, China. *Potamogeton crispus* (approximately 20 cm in length) were planted in the polythene buckets with a layer of sediment on the bottom.5

2.3.4 Combined experiments

*Potamogeton crispus* (approximately 20 cm in length) was planted into the polythene buckets (diameter 45 cm, height 60 cm). A sediment sample of 8 cm in thickness and Sr-TiO$_2$/PCFM with a certain thickness were placed in each bucket after the *Potamogeton crispus* grew stable. The visible light was shone vertically into the solution and the distance between the illuminant and the liquid level was 50 cm, the irradiation frequency was 2 h/d, and the control group was under outdoor conditions.

3 RESULTS AND DISCUSSION

3.1 Sediment characteristics

The characteristics and compositions of sediments in Donghu Lake are shown in Table 1.19 The grain size of the samples was almost less than 63 mm, and the silt fraction (4–63 mm) was the main one (79.76 %).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (%)</td>
<td></td>
</tr>
<tr>
<td>&lt;4 μm</td>
<td>9.26±0.05</td>
</tr>
<tr>
<td>4–63 μm</td>
<td>79.76±0.62</td>
</tr>
<tr>
<td>63–400 μm</td>
<td>6.89±0.02</td>
</tr>
<tr>
<td>Major element (w/%)</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>49.58±0.56</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>11.46±0.21</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>23.57±0.38</td>
</tr>
<tr>
<td>CaO</td>
<td>12.64±0.16</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>5.14±0.05</td>
</tr>
<tr>
<td>pH</td>
<td>7.39±0.20</td>
</tr>
<tr>
<td>TOC (%)</td>
<td>5.22±0.06</td>
</tr>
<tr>
<td>P fractions (mg kg$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>Fe/Al-P</td>
<td>462±13</td>
</tr>
<tr>
<td>Ca-P</td>
<td>105±5</td>
</tr>
<tr>
<td>IP</td>
<td>553±14</td>
</tr>
<tr>
<td>OP</td>
<td>173±6</td>
</tr>
<tr>
<td>TP</td>
<td>771±15</td>
</tr>
</tbody>
</table>

Table 1: Properties and chemical compositions of the sediment
3.2 Preparation of Sr/TiO₂-PCFM

PCFM coated with a nano-Sr/TiO₂ film (Sr/TiO₂-PCFM) with a TiO₂ content 11.5 % (w/w) was obtained as referred to in our previous research. TEM micrographs of the nano-TiO₂ film (Figure 1a) shows that the film had good surface properties with an average particle size of 10–20 nm. SEM photographs of the Sr-TiO₂/PCFM (fracture surface) (Figure 1b) show that the compact nano-TiO₂ film was firmly loaded on the surface of the PCFM.

3.3 Removal of sediment P with Sr/TiO₂-PCFM in stirring tests

3.3.1 Effect of dosage of Sr/TiO₂-PCFM

In order to study the effect of the amount on the removal of P in the sediments by Sr/TiO₂-PCFM, tests were conducted under adsorption (no irradiation) and photocatalytic (irradiation) conditions. The related results are shown in Figure 2. The increase of the Sr/TiO₂-PCFM dosage increased the removal rate of the sediment P both under adsorption and photocatalytic conditions (P < 0.05). When the amount of Sr/TiO₂-PCFM was 4–6 g, the increased trend of the removal quantity of sediment P flattens out. The removal quantity of each P forms (Ca-P, Fe/Al-P, IP, OP and TP) was 16 mg/kg, 188 mg/kg, 218 mg/kg, 70 mg/kg and 305 mg/kg, respectively, as the dosage was 4 g. Under photocatalytic conditions, the removal quantity of each P forms was 17 mg/kg, 229 mg/kg, 262 mg/kg, 86 mg/kg and 360 mg/kg, respectively, correspondingly, the removal rate was 16.2 %, 49.6 %, 47.4 %, 49.7 % and 46.7 %, respectively. It is clear that the removal amounts of each P form were increased after irradiating with a high-pressure mercury lamp (P < 0.05).

3.3.2 Effects of reaction time

The effects of reaction time on the P removal from the sediment by Sr/TiO₂-PCFM at 20±2 °C under adsorption (no irradiation) and photocatalytic (irradiation) conditions are presented in Figure 3. In Figure 3, under adsorption conditions, the removal quantities of each P form were increased rapidly within 4 h, then continued to increase at a slow rate (P < 0.05). The removal quantity of each P forms was 16 mg/kg, 190 mg/kg, 218 mg/kg, 72 mg/kg and 303 mg/kg /kg, respectively, as the reaction time was 8 h.

Under photocatalytic conditions, the removal quantities of each P form were increased significantly in a short time and achieved the equilibrium within 4 h. The removal quantity of each P form was 17 mg/kg, 229 mg/kg, 262 mg/kg, 86 mg/kg and 360 mg/kg, respectively, correspondingly, the removal rate was 16.2 %, 49.6 %, 47.4 %, 49.7 % and 46.7 %, respectively.

3.3.3 Effects of pH on P removal

The operation pH not only influences adsorption performance, it also influences the photocatalytic effect. The solution pH affects the adsorption effect by changing the surface properties of the adsorbents. Meanwhile, the stepwise reduction potential of the phosphate, and the valence band and conduction band of TiO₂ change as the pH changes. Thus, the pH was viewed as an important factor in the process of Sr-TiO₂/PCFM treating sediment P.
The related results are presented in Figure 4. The adsorption efficiency of sediment P in all fractions was the highest under the conditions of adsorption with strong acid. The adsorption amount of each P form from the sediment at pH 2 was 19 mg/kg, 207 mg/kg, 243 mg/kg, 78 mg/kg and 340 mg/kg, respectively. The corresponding adsorption rate was up to 18.1 %, 44.8 %, 43.9 %, 45.1 % and 44.1 %, respectively. The adsorption amount of each P form decreased at different levels as the pH increased from 2 to 12 ($P < 0.05$). The possible reason was that the isoelectric point pH of the nano TiO$_2$ was 6.25, the lower pH induced an increase of the surface positive charge on Sr-TiO$_2$/PCFM, which was beneficial to the adsorption of phosphate ions in sediments.

Under photocatalytic conditions, the removal effect of the sediment P in all fractions was influenced more obviously by pH ($P < 0.05$). When pH = 2, the removal quantity of each P form was 20 mg/kg, 256 mg/kg, 292 mg/kg, 93 mg/kg and 403 mg/kg, respectively, correspondingly, the removal rate was 19.0 %, 55.4 %, 52.8 %, 53.8 % and 52.3 %, respectively. The removal quantities of each P form were 3 mg/kg, 28 mg/kg, 32 mg/kg, 9 mg/kg and 43 mg/kg, respectively, higher than in the neutral condition. The possible reason was that the stepwise reduction potential of phosphate in acidic conditions was higher than that in neutral and alkaline, which was relatively easy to be reduced through photodegradation. While the in-depth mechanisms need to be further studied and explored.

3.3.4 Influence of operation temperature

Temperature is generally regarded to be an important factor in adsorption and photocatalytic processes.$^{23, 25}$ The removal of sediment P by Sr/TiO$_2$-PCFM was studied at different temperatures, ranging from 5 °C to an extreme high temperature 70 °C under adsorption and photocatalytic conditions (Figure 5). As seen from Figure 5, the temperature has an impact on the removal of sediment P in the both conditions ($P < 0.05$). The removal amounts of each P form increased as the temperature rises (5–30 °C). Under the adsorption conditions, the removal quantity of each P forms at 5 °C was 13 mg/kg, 163 mg/kg, 183 mg/kg, 54 mg/kg and 276 mg/kg, respectively. And the removal amount of each P forms on PCFM at 30 °C was 16 mg/kg, 189 mg/kg, 220 mg/kg, 71 mg/kg and 308 mg/kg, respectively. The adsorption amount of sediment P was decreased in different degrees as the operation temperature rose ($P < 0.05$). The removal quantity of each P form at 70 °C was decreased 5 mg/kg, 55 mg/kg, 55 mg/kg, 18 mg/kg and 75 mg/kg, respectively.

Under photocatalytic conditions, the removal amount of each P form at 5 °C was 13 mg/kg, 203 mg/kg, 220 mg/kg, 68 mg/kg and 296 mg/kg, respectively, the corresponding removal rate was 12.4 %, 43.9 %, 39.8 %, 39.3 % and 38.4 %, respectively. When the temperature rose to 30 °C, the removal quantity of each P form was increased to 17 mg/kg, 236 mg/kg, 263 mg/kg, 85 mg/kg and 364 mg/kg, respectively, correspondingly, the removal rate was 16.2 %, 49.8 %, 47.6 %, 49.1 % and 47.2 %, respectively. Under the adsorption conditions, the removal amounts of all P forms (except Ca-P) were decreased in varying degrees as the operation temperature rose. It was speculated that the high temperature promotes the desorption process and Brownian motion, thus reducing the efficiency of the photocatalytic reaction.

3.4 Static adsorption tests

For further applying to treat the actual lake with Sr-TiO$_2$/PCFM, static adsorption tests were carried out with reaction times from 0 d to 22 d. The related results are shown in Figure 6. The removal amount of each P form was not apparent after 18 d ($P < 0.05$). The adsorption quantity of each P form on 18d was 11 mg/kg, 136 mg/kg, 154 mg/kg, 52 mg/kg and 218 mg/kg, respectively. Correspondingly, the adsorption rate was 10.5 %, 29.4 %, 27.8 %, 30.1 % and 28.3 %, respectively.

Figure 4: Effect of overlying water pH on P removal

Figure 5: Effect of temperature on P adsorption
The change trends of each P form under photocatalytic conditions were similar to that under adsorption conditions, the reaction equilibrium was achieved at 16 d. The removal quantity of each P forms on 16 d was 13 mg/kg, 159 mg/kg, 181 mg/kg, 63 mg/kg and 254 mg/kg, respectively. The corresponding adsorption rate reached 12.4 %, 34.4 %, 32.7 %, 36.4 % and 32.9 %, respectively. The sediment P were reduced efficiently by Sr-TiO₂/PCFM.

3.5 The combined effect of Sr-TiO₂/PCFM and submerged plants

3.5.1 Effects of thickness of Sr-TiO₂/PCFM on the removal of TP

Tests were carried out with different thickness (1 cm, 2 cm, 4 cm and 6 cm) to investigate the effects of the thickness of Sr-TiO₂/PCFM on sediment P removal under irradiation and outdoor (control group) conditions. The results are presented in Figure 7. In outdoor conditions, the removal amount of TP on 120 d was 176 mg/kg as the thickness was 4 cm, correspondingly, the removal rate was 22.8 %. The removal amount of TP at 120 d added just 16 mg/kg when the thickness increased to 6 cm. Under irradiation conditions, the removal amount of TP at 120 d was 192 mg/kg and 202 mg/kg as the thickness was 4 cm and 6 cm, correspondingly, the removal rate was 24.9 % and 26.2 %, respectively. It is thus clear that the removal quantity of TP was further improved after irradiation, especially the first 45 d. The Sr-TiO₂/PCFM thickness of 4 cm was selected as the optimal dosage to study the synergistic effect of Sr-TiO₂/PCFM and submerged plants on sediment P removal.

3.5.2 The combined effect of Sr-TiO₂/PCFM and Potamogeton crispus

The removal quantity of sediment P is presented in Figure 8. The removing rate of Fe/Al-P and IP increased rapidly within 45 d and then slowly and later flattened at 75 d. The removal quantity of Fe/Al-P, IP, OP and TP by

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Potamogeton crispus on 75 d was 141 mg/kg, 151 mg/kg, 35 mg/kg and 19 3mg/kg, respectively.

The synergistic effects of Sr-TiO2/PCFM (thickness 4 cm) and Potamogeton crispus on sediment P under irradiation and control conditions are presented in Figure 9. The removal quantity of each P form was 23 mg/kg, 240 mg/kg, 256 mg/kg, 67 mg/kg and 336 mg/kg, respectively, correspondingly, the removing rate was 21.9 %, 51.9 %, 46.3 %, 38.7 % and 43.6 % in the control group. Under the irradiation conditions, the removal quantity of each P form reached 28 mg/kg, 282 mg/kg, 306 mg/kg, 81 mg/kg and 403 mg/kg, respectively. Correspondingly, the removal rate reached 26.7 %, 61.0 %, 55.3 %, 46.8 % and 52.3 %, respectively. It was observed that the removal rates of the sediment P were further enhanced after irradiation, and the removal amount of each P forms (except Ca-P) increased obviously more than the control group especially within 60 d.

Through comparing the removal effects of each method, we found that the unity of Sr-TiO2/PCFM and Potamogeton crispus have more remarkable effects on sediment P removal than the summation of the effect of Sr-TiO2/PCFM and Potamogeton crispus applied separately under the irradiation conditions. The probable reasons were that:

1) the irradiation of high-pressure mercury lamp not only enhanced the photocatalytic efficiency, but also increased the biomass of the submerged macrophyte;

2) the residual P forms in the sediment that did not adsorb on the Sr-TiO2/PCFM were changed by Potamogeton crispus through nutrition partitioning and root oxygenation, and then the adsorption of residual P on Sr-TiO2/PCFM was promoted;26

3) the growth of Potamogeton crispus was also accelerated owing to the trace elements contained in Sr-TiO2/PCFM;

4) the mineralization process of the sediment was promoted with the help of micro-organisms on Sr-TiO2/PCFM, thus the bioavailability by Potamogeton crispus was further enhanced.

4 CONCLUSIONS

The control effect of each P form in an eutrophic lake with the synergistic effect of Sr-TiO2/PCFM and Potamogeton crispus was studied for the first time. The main contributions of this work are as follows:

1) The compact nano-Sr-TiO2 film firmly loaded on the surface of the PCFM, and the average particle size of TiO2 was10–20nm;

2) Sr-TiO2/PCFM dosage, reaction time, irradiation, operation temperature and pH were the principal factors affect the removal of sediment P by Sr-TiO2/PCFM.

3) The removal amount of each P form in the sediment under the optimal photocatalytic conditions was 20 mg/kg, 256 mg/kg, 292 mg/kg, 93 mg/kg and 403 mg/kg, respectively. Under the optimal photocatalytic conditions of static tests, the removal amount at 16 d was 13 mg/kg, 159 mg/kg, 181 mg/kg, 63 mg/kg and 254 mg/kg, respectively.

4) The effect of the combination of Sr-TiO2/PCFM and Potamogeton crispus on sediment P in all fractions under irradiation and control conditions showed that the removal rates of each P form were further enhanced after irradiation. The combination of Sr-TiO2/PCFM and Potamogeton crispus demonstrated the higher removal effect of sedimental P than the summation of Sr-TiO2/PCFM and Potamogeton crispus applied separately under the irradiation conditions.

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