Removal of Off-Flavor Compounds in Aquaculture Water by Spray-Coated TiO₂ Photocatalysis

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Abstract
A major challenge for aquaculturists using recirculating aquaculture systems is the accumulation of off-flavor compounds, such as geosmin and 2-methylisoborneol (MIB), in the farmed fish. This work investigates the removal of off-flavor compounds in aquaculture systems using titanium dioxide (TiO₂) photocatalysis. Due to concerns of TiO₂ nanoparticles on fish, TiO₂ was immobilized onto glass plates. A photodegradation reactor that incorporated the TiO₂ coated plates was designed and operated as a recirculating system. Methyl orange was used as a surrogate compound for geosmin and MIB. In parameter optimization experiments, a flow rate of 2.5 mL/s, a water depth of 2 mm and a TiO₂ dosage of 0.25 mg/cm² were found to provide a high methyl orange removal rate constant of 0.77/h, when the compound was supplied in a solution made in deionized (DI) water. Due to the presence of natural organic matter (NOM) in the RAS water, the methyl orange removal rate constant decreased to 0.44/h. The results indicate that although NOM interferes with the photocatalysis process, if an extended reaction time is applied acceptable removal efficiencies can be achieved. This work is currently being applied in a photocatalysis study on removal of off-flavor compounds in RAS.

Keywords: off-flavor compounds, photodegradation, recirculating aquaculture systems, titania, titanium dioxide

Introduction
The collapse of wild fish stocks and increased global demand for seafood has led to the rapid expansion of the aquaculture industry. However, negative environmental impacts of the aquaculture industry include high energy and fresh water consumption, and release of nutrients, solids and organic matter into the environment. The use of recirculating aquaculture systems (RAS) has the potential to reduce the impacts of aquaculture on the environment. However, the accumulation of off-flavor compounds, such as geosmin and 2-methylisoborneol (MIB), in RAS and can reduce the quality and marketability of the fish products. Traditional wastewater treatment methods, such as coagulation, flocculation, and sedimentation, are ineffective for removing off-flavor compounds [1]. Advanced oxidation processes (AOPs) are a class of treatment techniques that has potential to remove many persistent contaminants in water [2]. Photocatalysis is a promising technology for the removal of geosmin, MIB and other contaminants in water [3]. Degussa P-25 is a nano-size titanium dioxide (e.g., TiO₂, titania) photocatalyst that has been used in a number of photocatalysis applications due to its relatively high activity [4]. It has a 3.08eV band gap [5] and can absorb light at wavelengths below 400nm to form the e/h⁻ pair, which induces the photocatalysis reaction [6]. In a conventional photocatalysis process, TiO₂ powder is suspended in water as slurry [7]. Centrifugation is subsequently applied to remove the TiO₂ powder from treated water. However, the effectiveness of centrifugation is low. In addition, some suspended particles can aggregate, especially at high concentrations, which may reduce the oxidation effectiveness. Particulate suspensions are also not easily adapted for use in continuous flow systems [8]. Another concern with using suspended TiO₂ in RAS applications is that carry-over of TiO₂ powder into fish tanks might negatively affect fish health. To avoid these problems, immobilized TiO₂ methods are needed.

In a prior study by our group, Zhang, Stefanakos, et al. developed a reactor that incorporated glass plates spray-coated with TiO₂. The overall goal of this research was to investigate the potential for using this novel TiO₂ photocatalytic reactor for the removal of off flavor compounds from RAS systems. A surrogate compound, methyl orange (MO), was used to test the reaction efficiency due to its stability under ultraviolet (UV) illumination in the absence of a catalyst [7]. Prior studies have been performed to test MO degradation efficiency in deionized (DI) water [9]. However, no prior research on MO degradation in aquaculture water has been conducted. In this study, optimal conditions for reactor operation, including catalyst loading rate, liquid flow rate, and water depth, were investigated.

Materials and Methods
Reactor Design
A bench scale close-loop aluminum sheet reactor was designed and constructed in two sections. The bottom section consisted of an aluminum plate with a length of 38.1 cm, a width of 5.08 cm, and a height of 2.54 cm and included three sections - a water inlet, a reaction section, and a water outlet (Figure 1). Both the inlet and outlet ducts were smooth. Two TiO₂ coated glass plates (the coating process is described below) with dimensions of 17.78 cm length and 5.08 cm width were placed at the bottom of the reaction section. A UVA-transparent glass plate (95% transparent) was placed above the bottom section, which was designed as a lid to decrease the influence of water evaporation due to heat generation from the UV lamps. Two UV lamps (Rayonet RPR 8139748009; E-mail: norma@usf.edu)

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3500) were placed above the UVA-transparent glass plate as the light source. The wavelength of the lamps is between 300 and 420 nm [10].

Photocatalyst preparation included four steps (Figure 2). P-25 was dissolved in ethanol (95% pure) with ultrasonic (Branson 3510, Danbury, CT) mixing to maintain a constant ratio of 1 g of P-25 per 20 mL of ethanol. Depending on the target concentration of TiO2 onto the glass plate, either 0.25 or 0.5 mg/cm², the initial weight of the P-25 was adjusted to 43 mg or 86 mg, respectively. The well-mixed P-25 solution was then sprayed onto heat-resistant glass plates (McMaster-Carr, Atlanta, GA) using an air brush (Paasche HAPK H#3, Chicago, IL). The spray area was calculated based on the number glass plates to be coated in each experimental run. The estimated thickness for the TiO2 layer was calculated to be 0.06 mm for measured surface area coverage of 77.42 cm²/plate, based on the initial volume and concentration of TiO2 that was sprayed onto each plate and considering a 10% loss in material. Heat-resistant glass plates were ultrasonically cleaned for 1 hour before spraying. These substrates were selected because part of the preparation process for the photocatalytic reactor involved a high temperature calcination process and these plates remain dimensionally stable even when exposed to high temperatures. The coated glass plates were dried at room temperature for 1 hour and then placed in a muffle furnace to calcine at 100°C for 1.5 hours, 200°C for 0.5 hours, and 350°C for 2 hours. These conditions were chosen based on the work of Wang et al. (2012), who reported that a slow annealing process followed by a high temperature calcine process significantly increased the reaction activity of the TiO2 coating layers [11,12].

Methyl Orange Degradation Kinetic Study

Table 1 includes a series of experiments that was conducted to evaluate the effectiveness of TiO2 photocatalysis using spray-coated glass plates on the photo-degradation of MO. Each parameter was tested once. The first-order reaction model was found to be best fit the MO degradation kinetics, and the experimental data was analyzed by least-square method.

Chemicals and Analysis

Degussa P-25 was obtained from Sigma-Aldrich (St. Louis, MO). Both MO (0.1% w/v) and ethanol (95%) were obtained from Fisher Scientific (Pittsburgh, PA). All chemicals were used as received without further purification. Aquaculture wastewater was collected from Mote Aquaculture Research Park (MAP, Sarasota, FL), a RAS facility which produces six metric tonnes of Siberian sturgeon (Acipenser baerii). Aquaculture wastewater was collected from Mote Aquaculture Research Park (MAP, Sarasota, FL), a RAS facility which produces six metric tonnes of Siberian sturgeon (Acipenser baerii). Aquaculture wastewater was collected from Mote Aquaculture Research Park (MAP, Sarasota, FL), a RAS facility which produces six metric tonnes of Siberian sturgeon (Acipenser baerii).

As mentioned previously, suspended TiO2 is difficult to remove from treated water [8]. Although it is unknown whether TiO2 nanoparticles have the potential to influence fish health, particles less than a certain size are known to affect fish health [14], thus it is important to keep TiO2 stable in the reactor system. Thus, spray-coating TiO2 onto glass plates was used in this study. To verify whether the TiO2 nanoparticles adhered to the glass surfaces, TiO2-coated glass plates were flushed by recirculating deionized water through the reactor at 2.5 mL/s for seven days. Water samples were collected daily, and titanium concentrations were measured by ICP-MS.

The titanium concentration in water flushed from the reactor over time is shown in Figure 3. Some random variations were observed, which were always were below the system error of 1.98 µg/L. Based on these results, the removal of titanium dioxide from the glass plates was insignificant.

Methyl Orange Degradation Kinetics Study

Effect of flow rate on photo-degrading methyl orange

A photocatalytic reaction on a TiO2 surface can be expressed using the Langmuir–Hinshelwood model [9]. The reaction rate is calculated by:

$$\ln \left( \frac{C_t}{C_0} \right) = -Kt$$  

where $C_t$ is the concentration of MO over time (mg/L), $C_o$ is the initial concentration of MO (mg/L), $K$ is the reaction rate constant (h⁻¹), and $t$ is the illumination time (h). $K$ can be determined from the slope of a plot of $-\ln(C/C_o)$ vs. $t$. The value of $K$ was obtained directly from the regression analysis of the linearized plot. The effect of flow rate on MO removal in deionized water is shown in Figure 4.
This research was conducted for degradation of MO at an initial concentration of 20 mg/L at flow rates of 1.0 mL/s, 2.5 mL/s, and 5.0 mL/s. The water depth was 2 mm. During the 4-hour experiment, the rate constants of different flow rates and their linear relationship were measured and are shown in Table 2. The results indicate that higher flow rates result in a higher rate constant. In consideration that higher flow rates would have higher energy costs, a flow rate of 2.5 mL/s was used in the following study with RAS water.

**Effect of water depth on photo-degradation of methyl orange**

Water depth influences the penetration of UV light into the TiO\(_2\) layer. It has been reported that the effect of water depth in photo-degradation of trichloroethylene (TCE) in water using a sand TiO\(_2\) catalyst was better when water depth was maintained within a range of 16 mm to 45 mm; with higher or lower water levels decreasing the TCE degradation efficiency [15]. In this study, the water depth was controlled at 2.0 mm and 4.5 mm and the MO concentration was maintained at 20 mg/L. The results are shown in Figure 5.

Table 3 shows the rate constants of different water depths and their linear relationship. The rate constant for 2 mm water depth is 1.15/h, which is almost two times higher than for a water depth of 4.5 mm. A high water depth above the catalyst increased the required catalytic reaction time most likely because the color of the MO prevented UV photons from penetrating into the water to the TiO\(_2\) catalyst, which reduced the amount of activated TiO\(_2\) atoms. To get the best photo-degradation results, a water depth of 2 mm was used in subsequent experiments.

**Effect of TiO\(_2\) concentration on photo-degradation of methyl orange**

It has been reported that TiO\(_2\) dosage influences photo-degradation efficiency [15]. At higher TiO\(_2\) concentrations, more TiO\(_2\) molecules are activated, which results in more electron pairs available in the water to degrade contaminants in water. However, higher TiO\(_2\) concentrations are difficult to immobilize onto glass plates, which increases the potential for flushing TiO\(_2\) into the water. In this study, the effect of TiO\(_2\) concentration on the degradation of MO was tested. The results are shown in Figure 6.

The catalyst loading rates were 0.25 mg/cm\(^2\) and 0.50 mg/cm\(^2\). The photo-degradation rate was only slightly different between these two values (Table 4) because more TiO\(_2\) was fixed onto the glass plate so that more photons were activated by UV light [16]. From the results above, and also taking into consideration the coating fixation study results mentioned previously, a catalyst concentration of 0.25 mg/cm\(^2\) was used in subsequent experiments. The effect of roughness on reactor effectiveness was reported by Zhang et al. but it is beyond the scope of this paper.

**Removal of methyl orange dissolved in aquaculture wastewater**

Aquaculture water has a complex composition, which gives it a light brown color and a turbid appearance compared with deionized water. In this study, aquaculture water was collected from a sturgeon RAS. Water quality characteristics of the sturgeon RAS water are shown in Table 5.

Natural organic matter (NOM) gives the water its brown color [17]. UV-vis is a method to quantitatively measure all the compounds in a sample that absorb UV-light. It is simple and fast; however, not all NOM can be detected [17]. Different wavelengths can be used to detect different chromophores of NOM. UV\(_{254}\) typically is used to detect the aromatic groups [18], as they contain double-bonded carbon atoms,
was 10 mg/L for this experiment. We can see that MO had almost 99% removal after 6 hours in deionized water, which was reduced to 85% in sturgeon RAS wastewater.

The reaction rate constants for all three groups are shown in Table 6. The overall reaction rate constants of photo-degrading MO, NOM, and both MO and NOM were 0.53/h, 0.09/h, and 0.33/h, respectively. This result indicates that NOM will interfere with the photocatalysis process when treating RAS waters. If we separate the overall reaction time into two parts—the first 1.5 hours and the later 4.5 hours—we found that in the first 1.5 hours, the photo-degrading rate of NOM and NOM+MO was almost the same (0.14/h and 0.18/h). After that, the photo-degradation rate started to change dramatically—the rate of degrading NOM started to slow down, but the rate of degrading NOM and MO had greater than a 2x increase. It is likely NOM has a closer affinity with UV-TiO2 photoreaction compared with MO, in the first 1.5 hours; NOM was

### Table 3: Rate constant ($K$) and linear regression coefficients of degrading methyl orange (MO) at different water depths.

<table>
<thead>
<tr>
<th>Water depth (mm)</th>
<th>$K$ (h$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.1504</td>
<td>0.9927</td>
</tr>
<tr>
<td>4.5</td>
<td>0.6676</td>
<td>0.9894</td>
</tr>
</tbody>
</table>

### Table 4: Rate constant ($K$) and linear regression coefficients of degrading methyl orange (MO) at different TiO2 concentrations.

<table>
<thead>
<tr>
<th>TiO2 concentration (mg/cm$^2$)</th>
<th>$K$ (h$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>1.1504</td>
<td>0.9927</td>
</tr>
<tr>
<td>0.50</td>
<td>1.2875</td>
<td>0.9917</td>
</tr>
</tbody>
</table>

### Table 5: Water quality of sturgeon recirculating aquaculture systems (RAS) wastewater.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.59±0.1</td>
</tr>
<tr>
<td>Turbidity</td>
<td>6.04±1.9 (NTU)</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1.62±0.16 (mS/cm)</td>
</tr>
<tr>
<td>Color</td>
<td>Light brown</td>
</tr>
</tbody>
</table>

which have the strong absorption properties of UV light. However, UV$_{254}$ was the wavelength found in this study to have the highest intensity when scanning the sturgeon RAS wastewater (Figure 7), which showed that some specific organic compounds instead of aromatic groups were dominant in the sturgeon RAS wastewater. According to a prior study, UV$_{254}$ can be used to examine alkyl bromides [19]. It is known that bromides are mainly disinfection by-products of ozonation [20]. At MAP, ozonation is one of the water treatment processes used to purify water.

The influence of TiO2 photodegradation of NOM was studied. The degradation efficiency at two different wavelengths, UV$_{254}$ and UV$_{234}$, is shown in Figure 8. After 6.5 hours of irradiation, 47% of the NOM was removed by UV-TiO2 radiation based on the 254 nm wavelength. However, only 10% of bromides (UV$_{254}$) were removed after 6.5 hours. The results indicate that bromides cannot be removed by TiO2 photocatalysis efficiently. At the same time, half of the activated aromatic groups in the aquaculture water could be oxidized. Thus, we can predict that the presence of NOM in RAS water may influence MO removal efficiency.

A comparison of the MO degradation efficiency for MO-contaminated deionized water (MO), sturgeon RAS wastewater (NOM), and MO-contaminated sturgeon RAS wastewater (NOM+MO) is shown in Figure 9. The hydraulic retention time (HRT) was maintained at 10s, the flow rate was 2.5 mL/s, and the methyl orange concentration...
probably physically removed from the water by absorption onto the titanium dioxide surface. Later, some intermediate oxidation products started to release from the TiO$_2$ surface. These intermediate products cannot absorb as strongly as NOM on the TiO$_2$ surface [21].

**Table 6:** Rate constant ($k$) and linear regression coefficients of photo-degrading methyl orange (MO), natural organic matter (NOM), and MO-contaminated NOM.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Overall</th>
<th>0-1.5 h</th>
<th>1.5-6 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$ (h$^{-1}$)</td>
<td>$R^2$</td>
<td>$k$ (h$^{-1}$)</td>
</tr>
<tr>
<td>MO</td>
<td>0.53</td>
<td>0.99</td>
<td>0.46</td>
</tr>
<tr>
<td>NOM</td>
<td>0.09</td>
<td>0.97</td>
<td>0.14</td>
</tr>
<tr>
<td>NOM+MO</td>
<td>0.33</td>
<td>0.97</td>
<td>0.18</td>
</tr>
</tbody>
</table>

**Conclusions**

The finding of this study indicates the spray-coated TiO$_2$ photocatalysis can mineralize MO and intermediate oxidation products due to hydroxyl oxidation. From our data, we can predict that the desired removal of degrading MO-contaminated sturgeon RAS wastewater can be achieved by extending the reaction time. This work is currently being applied in a photocatalysis study on removal of off-flavor compounds in RAS in MAP, and it has been experimentally proved to remove geosmin and MIB in the aquaculture wastewater efficiently.

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