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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/cm³ 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.

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.

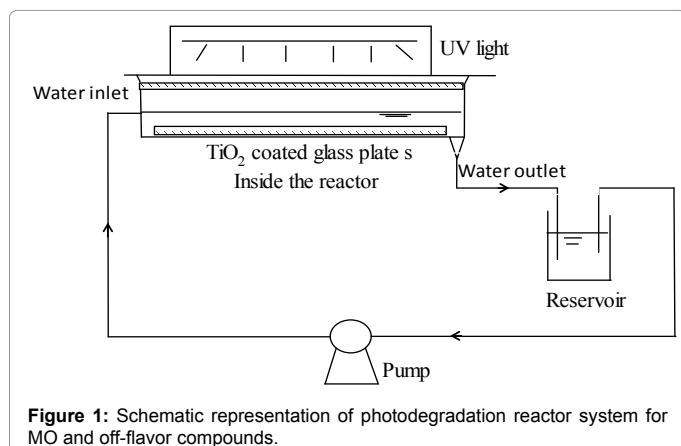## Materials and Methods

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 sectionA 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

Figure 1: Schematic representation of photodegradation reactor system for MO and off-flavor compounds.

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 1g 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 adjust 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 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 then 500°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 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 baeri*). Wastewater samples were stored in a refrigerator for no more than 3 days before use. MO concentrations were measured using a Genesys

10uv scanning spectrophotometer. The concentrations of titanium were detected by using a Perkin Elmer (Waltham, MA) inductively-coupled plasma mass spectrometer (ICP-MS). The method detection limit (MDL) for titanium was determined using EPA [13] methods and was found to be 0.364 µg/L. UV-vis was used to characterize the presence of natural organic matter (NOM) in the aquaculture wastewater (Ocean Optics Spectrophotometer, Winter Park, FL). The pH and conductivity of wastewater is measured by Orion 5 Star meter and probe (Fisher Scientific, Pittsburgh, PA). The turbidity is measured by Orbeco TB200 portable turbidity meter (Sarasota, FL).

Results and Discussion

Coating Fixation Study

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 heath [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.
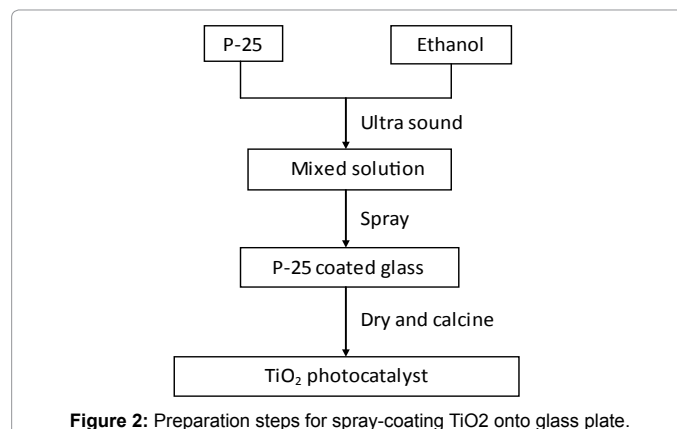
Methyl Orange Degradation Kinetics Study

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:

$$\ln\left(\frac{C}{C_o}\right) = -Kt \quad (2)$$

where C is the concentration of MO over time (mg/L), C_0 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 $-\ln(C/C_0)$ 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.

Figure 2: Preparation steps for spray-coating TiO2 onto glass plate.

Parameters	Variable
Flow rate (mL/s)	1.0-5.0
Water depth (mm)	2.0-4.5
TiO₂ concentration (mg/cm²)	0.25-0.50
Water quality	DI water, RAS wastewater

Table 1: Experimental design of methyl orange degradation kinetic study.
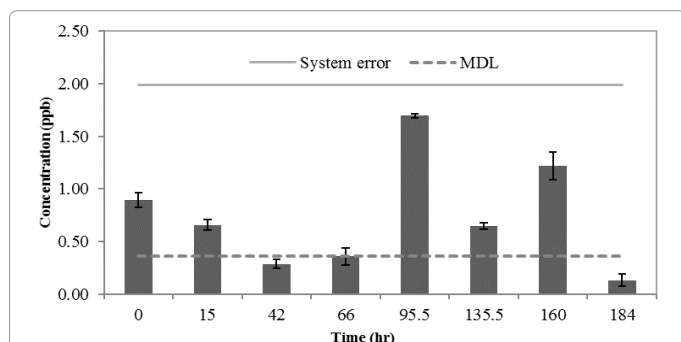

Figure 3: Detected titanium concentration in water (ppb) vs. time (hr). System error calculated to be 1.98 ppb; method detection limit was 0.36 ppb.

This research was conducted for degradation of MO at an inital 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 TiO₂ layer. It has been reported that the effect of water depth in photo-degradation of trichloroethylene (TCE) in water using a sand TiO₂ catalyst was better when water depth was maintained within a range of 16mm 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 TiO₂ catalyst, which reduced the amount of activated TiO₂ atoms. To get the best photo-degradation results, a water depth of 2 mm was used in subsequent experiments.

Effect of TiO₂ concentration on photo-degradation of methyl orange

It has been reported that TiO₂ dosage influences photo-degradation efficiency [15]. At higher TiO₂ concentrations, more TiO₂ molecules are activated, which results in more electron pairs available in the water to degrade contaminants in water. However, higher TiO₂ concentrations are difficult to immobilize onto glass plates, which increases the potential for flushing TiO₂ into the water. In this study, the effect of TiO₂ concentration on the degradation of MO was tested. The results are shown in Figure 6.

The catalyst loading rates were 0.25 mg/cm² and 0.50 mg/cm². The photo-degradation rate was only slightly different between these two values (Table 4) because more TiO₂ 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/cm² 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. UV₂₅₄ typically is used to detect the aromatic groups [18], as they contain double-bonded carbon atoms,
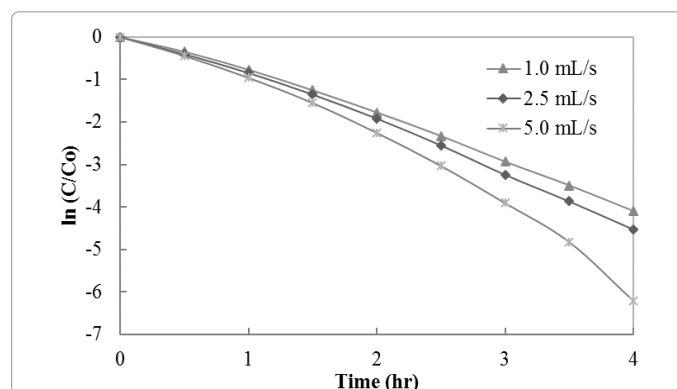

Figure 4: Effect of flow rate on methyl orange (MO) degradation kinetics (initial MO concentration =20 mg/L).

Flow rate (mL/s)	K (h⁻¹)	R²
1	1.1017	0.9932
2.5	1.1504	0.9927
5	1.5125	0.9744

Table 2: Rate constant (K) and linear regression coefficients of degrading methyl orange (MO) at different flow rate.
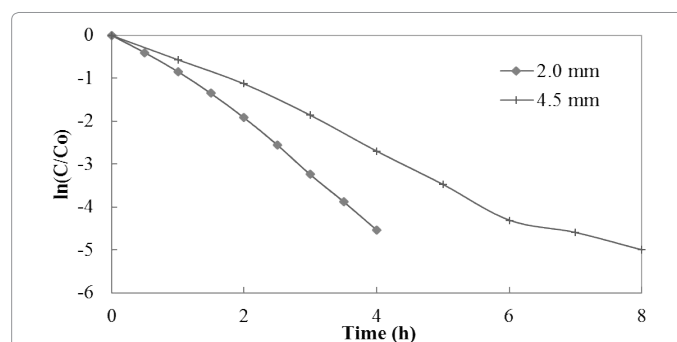

Figure 5: Effect of water depth on methyl orange (MO) degradation kinetics (initial MO concentration =20 ppm).

Water depth(mm)	K (h^{-1})	R^2
2	1.1504	0.9927
4.5	0.6676	0.9894

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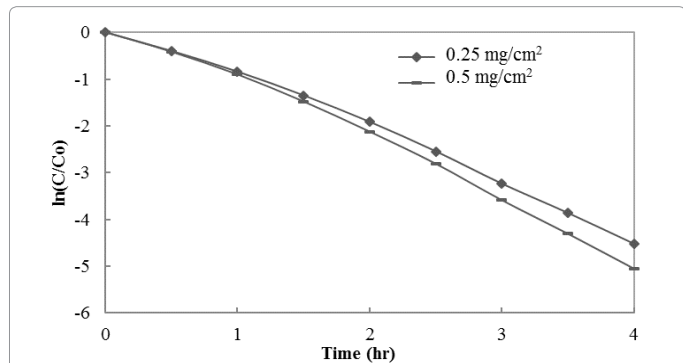

Figure 6: Effect of TiO$_2$ concentrations on methyl orange (MO) degradation kinetics (initial MO concentration=20 ppm).

TiO$_2$ concentration (mg/cm^2)	K (h^{-1})	R^2
0.25	1.1504	0.9927
0.50	1.2875	0.9917

Table 4: Rate constant (K) and linear regression coefficients of degrading methyl orange (MO) at different TiO$_2$ concentrations.

Parameter	Value
pH	6.59±0.1
Turbidity	6.04±1.9 (NTU)
Conductivity	1.62±0.16 (mS/cm)
Color	Light brown

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

which have the strong absorption properties of UV light. However, UV$_{234}$ 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$_{234}$ 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 TiO$_2$ 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-TiO$_2$ radiation based on the 254 nm wavelength. However, only 10% of bromides (UV$_{234}$) were removed after 6.5 hours. The results indicate that bromides cannot be removed by TiO$_2$ 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

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-TiO$_2$ photoreaction compared with MO, in the first 1.5 hours; NOM was
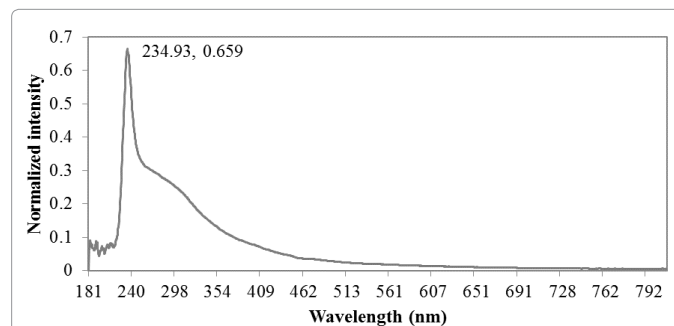

Figure 7: Spectrum of sturgeon recirculating aquaculture systems (RAS) wastewater; highest intensity found for wavelength UV$_{234}$.
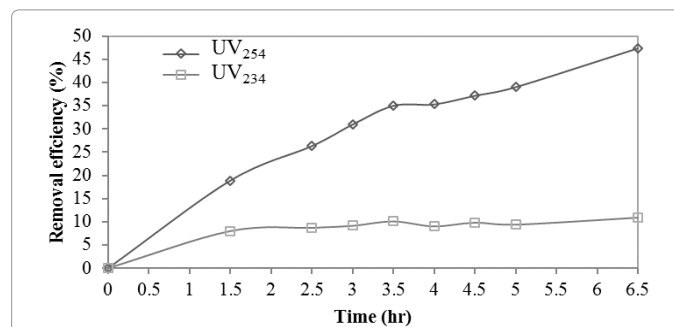

Figure 8: Natural organic matter (NOM) removal efficiency by photo-degradation of sturgeon recirculating aquaculture systems (RAS) wastewater vs. time under UV$_{254}$ and UV$_{234}$.
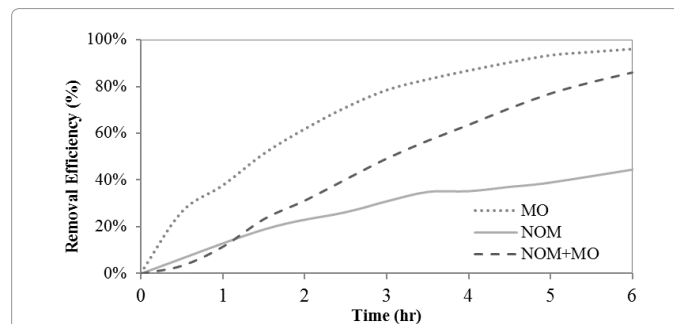

Figure 9: Photodegradation efficiency comparison for methyl orange (MO) contaminated deionized water, sturgeon recirculating aquaculture systems wastewater (NOM), and methyl orange contaminated sturgeon recirculating aquaculture systems wastewater (NOM+MO).

	Overall		0-1.5 h		1.5-6 h	
	K (h^{-1})	R^2	K (h^{-1})	R^2	K (h^{-1})	R^2
MO	0.53	0.99	0.46	0.99	0.57	0.99
NOM	0.09	0.97	0.14	0.99	0.08	0.97
NOM+MO	0.33	0.97	0.18	0.93	0.40	0.99

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

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].

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.

Acknowledgments

References

1. Song W, O'Shea K (2007) Ultrasonically induced degradation of 2-methylisoborneol and geosmin. Water Res 41:2672–2678.

2. Crittenden J, Trussell R, Hand D, Howe K, Tchobanoglous G (2005) Water Treatment: Principles and Design, John Wesley& Sons, Inc., New Jersey.

3. Pestana C, Robertson P, Edwards C, Wilhelm W, McKenzie C, et al. (2014) A continuous flow packed bed photocatalytic reactor for the destruction of 2-methylisoborneol and geosmin utilising pelletised TiO$_2$. Chem Eng J 235: 293–298.

4. Ohtani B, Prieto-Mahaney O, Li D, Abe R (2010) What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test. J Photochem Photobiol A Chem 216: 179–182.

5. Sojić D, Despotović V, Abramović B, Todorova N, Giannakopoulou T, et al. (2010) Photocatalytic degradation of mecoprop and clopyralid in aqueous suspensions of nanostructured N-doped TiO$_2$. Molecules 15:2994–3009.

6. Al-qaradawi S, Salman S (2002) Photocatalytic degradation of methyl orange as a model compound. J Photochem Photobiol A Chem 148: 161–168.

7. Wang C, Zhao J, Wang X, Mai B, Sheng G, et al. (2002) Preparation, characterization and photocatalytic activity of nano-sized ZnO/SnO$_2$ coupled photocatalysts. Appl Catal B Environ 39: 269–279.

8. Sopyan I, Watanabe M, Murasawa S, Hashimoto K, Fujishima A (1996) An efficient TiO$_2$ thin-film photocatalyst: photocatalytic properties in gas-phase acetaldehyde degradation. J Photochem Photobiol A Chem 98: 79–86.

9. Liao D, Badour C, Liao B (2008) Preparation of nanosized TiO$_2$/ZnO composite catalyst and its photocatalytic activity for degradation of methyl orange. J Photochem Photobiol A Chem 194: 11–19.

10. Zhang Y, Stefanakos E, Goswami D (2013) Effect of photocatalytic surface roughness on reactors effectiveness for indoor air cleaning. Build Environ 61:188–196.

11. Wang G, Xu L, Zhang J, Yin T, Han D (2012) Enhanced photocatalytic activity of TiO$_2$ powders (P25) via calcination treatment. Int. J. Photoenergy 2012:1-9.

12. Zhang Y (2013) Modeling and design of photocatalytic reactors for air purification, Grad. Sch. Theses Diss

13. U.S. Environmental Protection Agency (2011) A Laboratory Study of Procedures Evaluated by the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs.

14. Federici G, Shaw B, Handy R (2007) Toxicity of titanium dioxide nanoparticles to rainbow trout (Oncorhynchus mykiss): Gill injury, oxidative stress, and other physiological effects. Aquat Toxicol 84: 415–430.

15. Farooq M, Raja I, Pervez A (2009) Photocatalytic degradation of TCE in water using TiO$_2$ catalyst. Sol Energy 83: 1527–1533.

16. Pettit S, Gonzalez L, Michaels J, Alcantar N, Ergas S, et al. (2014) Parameters influencing the photocatalytic degradation of geosmin and 2-methylisoborneol utilizing immobilized TiO$_2$. Catal Letters 144: 1460–1465.

17. Matilainen A, Sillanpää M (2010) Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere 80: 351–65.

18. Korshin G, Chow C, Fabris R, Drikas M (2009) Absorbance spectroscopy-based examination of effects of coagulation on the reactivity of fractions of natural organic matter with varying apparent molecular weights. Water Res 43: 1541–1548.

19. Tang Y, Ji L, Tang B, Zhu R, Zhang S, et al. (2004) Studies on photodissociation of alkyl bromides at 234 and 267 nm. Chem Phys Lett 392:493–497.

20. Gunten U (2003) Ozonation of drinking water: part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Res 37: 1469–1487.

21. Huang X, Leal M, Li Q (2008) Degradation of natural organic matter by TiO$_2$ photocatalytic oxidation and its effect on fouling of low-pressure membranes. Water Res 42: 1142–1150