PMMA-titania floating macrospheres for the photocatalytic remediation of agro-pharmaceutical wastewater

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ABSTRACT

Antibiotics such as tetracycline are used on a large scale in agriculture, and can become concentrated in wastewater lagoons that are used in conjunction with confined animal feeding operations. Solar-illuminated titanium dioxide can be used to photocatalytically degrade aqueous tetracycline, but its application in a lagoon environment requires that the photocatalyst be supported on a macroscopic support material to prevent loss of the nanoscale photocatalyst into the environment. In this work, titanium dioxide was deposited within a porous poly(methyl methacrylate) film on the surface of floating 7.0 cm diameter acrylic spheres. Six of these floating spheres removed over 96% of the tetracycline in 3.5 L of 60 mg/L tetracycline in natural pond water during 24 hours of solar illumination. The durability of these spheres under long-term solar exposure was also investigated along with the amount of photocatalyst lost from the sphere surface during use. These macroscale floating composite spheres provide a new method for removing tetracycline from wastewater lagoons with minimal risk of being displaced in the environment due to the large size of the spheres.

Key words | composite, floating, photocatalysis, polymer, tetracycline, titania

INTRODUCTION

Pharmaceutical waste is an increasingly significant environmental concern. Agricultural antibiotics such as tetracyclines are utilized in large quantities due to both therapeutic and continuous non-therapeutic application that aids in rapid and consistent growth of the livestock, and helps prevent epidemic disease in confined animal feeding operations (CAFOs) (Lindsey et al. 2007; Borghi & Palma 2014). Unfortunately, a large percentage of the applied antibiotic is excreted from the animal un-metabolized. Runoff from areas containing the affected animal waste then becomes a source of pharmaceutical contamination (Maroga Mboula et al. 2012; Borghi & Palma 2014). In a typical CAFO, runoff is collected in wastewater lagoons (Pei et al. 2007). Excess nutrients are eliminated from the lagoon water through biological action and through coagulation and precipitation as sludge on the lagoon bottom. Wastewater lagoons are not designed for the degradation of pharmaceutical waste, and much of the pharmaceutical compounds exit the lagoon in aqueous form to contaminate ground or surface water or within sludge that is broadcast on crop fields for fertilizer. Since antibiotics are bio-active in very low concentrations, agro-pharmaceutical waste has the capacity for significant environmental impact. The presence of tetracyclines in the environment has numerous negative impacts, most notably the promotion of pathogens with antibiotic resistance genes (Lindsey et al. 2001; Jiao et al. 2008; Zhang et al. 2014). Wastewater lagoons are an essential environmental protection component of most large livestock feeding operations, and any technique used for eliminating agro-pharmaceuticals from lagoon wastewater should be designed to work in concert with the primary function of the lagoon, nutrient control. Affecting water quality on a lagoon-scale is certainly nothing new. High-density polyethylene spheres with a diameter around 10 cm are commonly used as a UV-blocking, evaporation-slowing, and bird-deterring barrier on the surface of water reservoirs. Often referred to as ‘shade balls’, these large water-ballasted spheres cover the water...
surface and accomplish their intended task without themselves becoming a threat to aquatic or avian life due to their large size.

Titanium dioxide (titania) photocatalysis is a promising technique for removing aqueous contaminants when activated by UV-light. The reactive oxygen species, most notably hydroxyl and superoxide radicals, produced by UV-illuminated titania are capable of oxidizing a wide variety of aqueous contaminants, including pharmaceuticals such as tetracycline (Reyes et al. 2006; Maroga Mboula et al. 2012; Niu et al. 2013). Nanoscale titania maximizes photocatalytic activity, and thus it becomes practically necessary to deposit the photocatalyst on a macroscopic support material to avoid the post-use need to remove the nanoscale photocatalyst from the water. Many support materials have been used in laboratory and field studies, and floating photocatalytic supports have gained substantial attention due to the fact that they position the photocatalyst at the water surface – where the illumination and oxygenation are likely to be maximized (Machado et al. 2006; Magalhães & Lago 2009; Magalhães et al. 2011; Xing et al. 2013). Many different floating photocatalyst supports have been investigated, including perlite (Hosseini et al. 2007; Dlugosz et al. 2014), vermiculite (Machado et al. 2006), exfoliated graphite (Modestov et al. 1997), low density polyethylene (Magalhães et al. 2011), polystyrene (Magalhães & Lago 2009), and glass microbeads (Rosenberg et al. 1992; Shifu & Gengyu 2005). Titania-coated glass microbeads were proposed by Rosenberg, Brock and Heller for the photocatalytic degradation of oil slicks (Rosenberg et al. 1992). This very clever arrangement utilized floating glass microbeads with a portion of the sphere surface above the water level exposed to solar illumination. Although this approach and other floating composite photocatalysts have proven to be photocatalytically successful, it is doubtful that the widespread release of such small composites on a CAFO lagoon would be environmentally advisable. Larger composite structures are less likely to be ingested by wildlife or dispersed more widely in the environment than is intended, and are thus more amenable to release into an environment such as a CAFO wastewater lagoon. Larger floating photocatalyst supports would also facilitate retrieval and re-use which is necessary to coexist with periodic sludge-removal processes in a CAFO lagoon environment. Polymeric support materials, such as the poly(methyl methacrylate) (PMMA) used in this study, are advantageous as photocatalytic supports due to their high UV-transparency, low cost, mechanical ruggedness, and ease with which they can be used in a wide array of photocatalytic reactor designs (Carlson et al. 2007; Loetscher et al. 2009).

Stewart and coworkers recently developed a method for incorporating titania within porous PMMA. These porous composite materials have enhanced photocatalytic activity and better titania retention than comparable non-porous composites (Stewart et al. 2013). The application of a thin porous PMMA-titania layer to the exterior of a 7.0 cm diameter acrylic sphere provides a macroscale photocatalytically-active surface that is very amenable to the purification of shallow water bodies such as livestock wastewater lagoons. The large size of these floating spheres facilitates control over the titania deposition to leave the above-water portion of the sphere uncoated with titania, allowing it to serve as a solar collector for the titania surface below the water level. In this work, we report a simple method for producing these spheres, and evaluate their photocatalytic activity and durability for the degradation of aqueous tetracycline. These durable and effective macroscale composite structures provide a new vehicle for the removal of agro-pharmaceuticals from wastewater lagoons.

**METHODS**

**Materials**

All reagents were used as received without additional purification. Tetracycline hydrochloride (>95%) was obtained from Boston Bioproducts. Acetone (ACS grade) and Tween surfactant were purchased from Fisher Scientific. Granular PMMA with an average molar mass of 75,000 g/mol was manufactured by Polysciences Inc. The titania used was Degussa/Evonik P-25, with an average surface area of 50 m²/g and an average particle size of 30 nm. The 7.0 cm diameter hollow acrylic spheres were obtained from Factory Direct Craft. These spheres were utilized due to their low cost and UV-transparency down to 300 nm (75% at 365 nm, including reflection losses). The spheres are manufactured in the form of two watertight hemispheres in a clam-shell design which allowed for facile ballasting to ensure proper flotation depth. An ultraviolet light-emitting diode (UV-LED) lamp (XeLED-Ni1UV-R4-365-E27-SS) from Xenopus Electronix provided an irradiance of 26 mW/cm² at 365 nm on the surface of the photocatalytic sphere for the non-solar experiments.

**Floating sphere fabrication**

The PMMA-titania film was deposited on the surface of the 7.0 cm acrylic spheres using a method modified from Stewart et al. (2013). The sphere-coating solution was prepared from...
200 mL of acetone to which 3.0 mL of Tween surfactant, and varying amounts of a 44% (w/w) mixture of titania:PMMA were added. Each acrylic sphere was lowered into the acetone/PMMA/TiO2/Tween mixture, leaving the top 1.5 cm of the sphere unsubmerged. The sphere was then removed from the solution at a manually controlled rate of 3 cm/s, and immediately sprayed with distilled water over the entire sphere surface. The water coagulated the PMMA/acetone solution, leaving a high surface area, porous PMMA film within which the titania is firmly bound. The amount of PMMA in the acetone solution controls the viscosity of the solution, and thus directly impacts the resulting film thickness. In preliminary investigations, the PMMA mass was varied from 10 to 25 g in order to determine the film thickness that would provide the greatest photocatalytic activity. The results of these experiments are shown in the online supporting information. For the fabrication of all subsequent spheres, the coating solution was made with 20 g of PMMA, 16 g of titania, and 3 mL of Tween in 200 mL of acetone. This method provided a PMMA-titania film thickness of 0.35 mm. After the PMMA-titania coating had been applied, each sphere was illuminated with compact fluorescent blacklights (λ = 365 nm) with an irradiance of 2 mW/cm² for 24 h while submerged in water in order to maximize the exposed surface area of the titania within the PMMA matrix. This UV pre-treatment, inspired by the work of Ratova and Mills involving titania embedded within low density polyethylene films (Ratova & Mills 2015), significantly increased the photocatalytic activity of the composite as compared to un-treated surfaces. Following the UV pre-treatment, the spheres were fitted with a UV-transparent PMMA disk, with a 3.9 cm diameter and a thickness of 0.95 cm, glued to the interior bottom of the sphere to help maintain a vertical orientation while floating. Each sphere was then assembled from its component hemispheres in a distilled water bath to incorporate 125 mL of water in its interior for ballast, aligning the exterior water level with the top edge of the PMMA-titania film 1.5 cm from the top of the sphere. The surface of the sphere above the exterior water level served as a solar illumination collector, distributing the light to the lower surface of the sphere, while the upper sphere surface was primarily illuminated directly from above as shown in Figure 1.

Qualitative surface activity by Ag deposition

In an effort to visually evaluate the distribution of light to the entire titania-coated sphere surface, a sphere was placed in 250 mL of aqueous 0.1 M AgNO3 that also contained 0.3 M methanol. The sphere was exposed to early afternoon solar illumination in a 600 mL beaker, causing the Ag to be photocatalytically reduced on the titania surface as the methanol was sacrificially oxidized. A video was recorded from a side-on perspective to allow the visualization of the uniformity of the Ag deposition.

Photocatalytic evaluation

Solar photocatalytic tetracycline degradation experiments were performed in rectangular polypropylene tubs that were 25 × 18 cm across and contained 3.6 L of aqueous tetracycline. Each tub contained six acrylic floating spheres. Solar experiments were performed in Due West, South Carolina, USA (34.3334 N, 82.3879 W, altitude 213 m) from 8 a.m. to 8 p.m. during mostly sunny days in June and July of 2016. Afternoon high temperatures were around 32 °C each day. In each set of solar experiments, there were three tubs that were simultaneously investigated. The experimental tub contained six titania-coated spheres that were exposed to solar illumination for the duration of the experiment. The light control tub also had full sun exposure, but the acrylic spheres were not coated with titania. The dark control tub involved six titania-coated spheres, and the tub was kept covered with a corrugated cardboard box outdoors beside the experimental and light control tubs. There were three series of solar experiments, each beginning with a 30 min dark adsorption period prior to the initial
sampling. The first experiments began with 60 ppm tetracycline dissolved in distilled water. The second series involved 60 ppm tetracycline dissolved in water collected from a local pond. This pond has a surface area of 1.5 acres (6,070 m²), and a typical depth of 1–2 m and is fed by several springs and surface runoff. This size and depth is comparable to that of CAFO lagoons reported in previous tetracycline-related studies (Peak et al. 2007; Barkovskii et al. 2012), but is not directly impacted by agricultural activities and has no detectable tetracycline present. The water was collected from the pond surface 3 m from the pond edge from the vantage point of a floating dock. The pond water was used within an hour of collection and had a pH of 6.8. The initial concentration in the first two series of experiments was strategically high (60 mg/L) in order to facilitate the extraction of pseudo-first order rate constants as a metric for photocatalytic activity. One millilitre samples were periodically collected from each tub over a 2 day period. Each tub was magnetically stirred for 30 s prior to every sampling in order to obtain a representative water sample. The tubs were not mechanically stirred in between samplings in order to mimic unstirred lagoon environments. Initially, samples were collected at 1 h increments, with decreasing frequency as the reaction rates began to slow. Solutions began the day at 23°C, and the experimental and light control solutions peaked at 37°C before ending each day around 29°C. The dark control temperatures peaked at 34°C, and ended the day at 34°C due to the insulating effect of the corrugated cardboard box. During the overnight period of the 2-day experiments, each tub was covered and stored indoors at 23°C. The concentration of titania in the water samples after solar exposure was quantified using inductively coupled plasma mass spectroscopy (ICP-MS) (PerkinElmer Elan 9000).

Long-term durability

The long-term durability of these photocatalytic spheres was probed by testing a set of three titania-coated spheres for the degradation of 500 mL of 20 mg/L tetracycline using a UV-LED lamp with an irradiance of 26 mW/cm² measured at the surface of the sphere. After the photocatalytic pre-test was complete, the spheres were placed outdoors for 35 consecutive days. Following that long-term solar exposure, the spheres were returned to the laboratory for a photocatalytic post-test under identical conditions.

Low-concentration tetracycline degradation

Since feedlot lagoon water has been reported to typically have a much lower tetracycline concentration in the 0.01–16 µg/L range (Peak et al. 2007; Watanabe et al. 2010), the third set of solar experiments were carried out with 8 µg/L tetracycline dissolved in pond water. This experimental series is the most environmentally relevant evaluation of the ability of the titania-acrylic spheres to ameliorate tetracycline in wastewater lagoons. At the end of the low-concentration pond water experiments, 1.0 L of water was sampled from each tub for solid phase extraction (SPE) with high-performance liquid chromatography (HPLC) analysis.

Tetracycline detection

HPLC-UV (Agilent 1120) was used for tetracycline analysis. The mobile phase was 75% water (adjusted to a pH of 2.1 with sulfuric acid) and 25% acetonitrile with a flowrate of 0.7 mL/min. A C-18 column (Agilent Eclipse Plus 5 µm, 4.6×150 mm) was used with UV detection at 355 nm. The limit of quantitation was 1 ppm without the aid of SPE. Samples were syringe filtered with 0.45 µm PVDF filters, prior to the injection of a 20 µL sample. Triplicate analysis was used for all samples.

Analysis of the low-concentration samples required SPE prior to HPLC analysis. Oasis HLB cartridges (Waters, 6 mL/500 mg) were conditioned with 6 mL of methanol followed by 6 mL of water. 1.00 L samples with 4 mL of 7 mM EDTA were then drawn through the cartridge at a rate of 3 mL/min. The cartridge was washed with 2 mL of distilled water, and then extracted two times with 2 mL of methanol acidified with 0.9% (v/v) formic acid. The resulting sample was dried completely under vacuum and then re-dissolved in 1 mL of methanol prior to HPLC analysis. The limit of quantitation with SPE was 1 ppb with recovery of standard samples in excess of 91%.

RESULTS AND DISCUSSION

Qualitative surface activity by Ag deposition

Illumination is delivered to the photocatalytic surface of the sphere through two different routes. The upper portion of the sphere (above the sphere’s equator, but below the water level) is directly illuminated by light that travels through the water’s surface. Titania below the sphere’s equator is primarily illuminated by light that enters the sphere through the uncoated ‘tonsure’ and then exits the sphere through the acrylic walls. In order to provide visual confirmation that the entire sphere was photocatalytically
active, the deposition of Ag from the methanol-containing aqueous AgNO₃ solution was performed with solar illumination. The Ag deposition was rapid and uniform across the entire titania-coated surface of the sphere, with visual completion within 1 minute. The video record of this deposition process is available online at https://youtu.be/Ua5YGgZZKYU. The observation that the entire submerged sphere is active is extremely important in understanding the mechanism of photocatalytic action of the floating composite, and is visual confirmation of the floating sphere strategy devised by Rosenberg et al. (1992).

**Photocatalytic evaluation**

The solar photocatalytic degradation of tetracycline in distilled water proceeds rapidly with a pseudo-first order rate constant of 0.126 h⁻¹ as shown in Figure 2. The lack of significant tetracycline degradation of the light control experiment indicates that the tetracycline is not substantially degraded photolytically in distilled water, and the dark control results eliminate adsorption on the PMMA-titania surface as the culprit for the decreasing aqueous tetracycline concentration. The first order kinetic model is a very good fit to the experimental data, and the fact that the photocatalytic degradation rate is independent of the time of day (ranging from 8 a.m. to 8 p.m.) indicates that the solar irradiance is not the rate-limiting factor in the photocatalytic reaction, nor is the photocatalytic reaction highly temperature dependent.

In an actual wastewater lagoon environment, the aquatic matrix is far more complex and includes both dissolved species in solution and suspended solids such as biological matter which are known to affect the rate of pharmaceutical photolysis (Andreozzi et al. 2003; Jiao et al. 2008; Niu et al. 2013b).

The mechanism for photocatalytic degradation of tetracycline and the humic acid-sensitized photolytic degradation of tetracycline have been previously elucidated (Jiao et al. 2008; Maroga Mboula et al. 2012; Niu et al. 2013a, 2013b). The interaction of agro-pharmaceuticals with this matrix is not a simple one, and thus the evaluation of these spheres in such a matrix is extremely important in assessing the feasibility of these floating spheres in a wastewater lagoon. The pond used in this study is similar in size and depth to a typical CAFO lagoon, and provides a suitable model system without a tetracycline background concentration. The results of the solar pond water experiment are shown in Figure 3. The increased complexity of the pond water system is clearly indicated by the changes in behavior of the control experiments as compared to the distilled water experiments. Slight variability in daily temperature and cloud cover makes quantitative comparisons between Figures 2 and 3 of little use; however, a qualitative comparison between these data sets is informative. The tetracycline concentration slightly declined in the dark (k = 0.0115 h⁻¹), dropping by 12 mg/L over 2 days of solar exposure, likely due at least in part to adsorption on dispersed or precipitated solids alongside thermal degradation. The truly significant change from the distilled water, however, is in the light control data. The light control experiment in distilled water showed negligible tetracycline degradation, but in the pond water, the tetracycline degradation (rate constant k = 0.0814 h⁻¹) is quite significant compared to the rate constant
in the photocatalytic experiment ($k = 0.148 \text{ h}^{-1}$). Careful inspection of the light control results in pond water reveal that each day began with a comparably slower degradation rate than later in the day when the temperature was much warmer. The photolytic degradation of tetracycline in surface water has been shown to be substantial in shallow bodies of water such as high-rate algal ponds where the solar irradiance is large throughout the depth of the water column (de Godos et al. 2012). The magnitude of the difference between the experimental and light control would be expected to grow as the water temperature decreased. The water temperatures in these experiments was quite high – partly due to the location in balmy mid-summer South Carolina, and partly due to the small water volume (3.6 L) used in this experiment. The surface water temperature of the pond at midafternoon at the sampling location is 31°C, which is 6°C less than the mid-afternoon temperatures in the experimental and light control pond water experiments in the polypropylene tubs. In a CAFO wastewater lagoon, the average daily temperatures would favor the photocatalytic degradation of tetracycline to a greater extent than the results of Figure 3 would indicate, particularly in the non-summer months. It has been shown that complete photocatalytic mineralization of tetracycline by titania takes much longer than the preliminary degradation of the tetracycline, and that the toxicity of the photocatalytic degradation byproducts is considerably less as compared to those from photolytic degradation of tetracycline (Maroga Mboula et al. 2012; Niu et al. 2013a). Niu and coworkers showed that the toxicity of the photolytic tetracycline degradation byproducts under solar illumination exceeded that of tetracycline itself (Niu et al. 2013b).

Over the first few hours of solar exposure, the tetracycline-laden pond water changed from a green-tea hue to a very dark coffee-colored brown in both the light control and experimental tub. The dark control tub did not undergo this color change. By the end of the 2 days of the experiment, the light control sample was still dark black, but the titania-containing experimental tub had lightened significantly and had demonstrable turbidity that was not previously present. Over the next 10 days, these two tubs were placed outdoors for continued solar exposure. The content of the light control tub remained visually unchanged during that 10-day exposure, but the water in the photocatalyzed tub gradually cleared completely, leaving a tan precipitate on the floor of the tub. ICP-MS analysis showed that this precipitate was only 0.4% (w/w) titania, and was thus primarily comprised of the pond sediment and organic and biological detritus from the photocatalytic process. It has been previously noted that titania photocatalysis is capable of substantial mineralization of tetracycline, whereas the photolytic degradation in the presence of dissolved organic matter tends to incomplete oxidation with formation of potentially toxic degradation byproducts (Addamo et al. 2005; Reyes et al. 2006; Jiao et al. 2008; Yuan et al. 2011). In this way, photocatalytic floating spheres not only have the potential to reduce the aqueous tetracycline concentration in CAFO lagoons, but could also help avoid the negative implications of the dissolved organic material tetracycline photolysis. Another important environmental consideration for these floating composites is their ability to retain the titania photocatalyst. As mentioned above, a small amount of titania ended up in the post-photocatalytic sediment, and analysis of the water at the end of the photocatalytic experiment indicated a titania concentration of 169 μg/L, as compared to 104 μg/L in the dark control experiment, and 59 μg/L of background titania present in the water after the light control experiment. Observation of the post-use sphere surface shows that the predominant origin of the titania loss is sphere-on-sphere abrasion near the spheres’ equator during use and transport of the water-filled tubs. Nanotoxicology is inherently complicated by the impact of history, environment, surface functionalization, particle morphology and many other factors (Ren et al. 2016), and it is impossible at this time to fully determine the environmental impact of these titania levels on the environment. If ongoing nanotoxicology research indicates that aqueous titania concentrations in the ppb range present an environmental threat, the amount of titania loss in this application could be significantly decreased by leaving a titania-free band near the equatorial belt of each sphere at the expense of a lower photocatalytic activity.

**Long-term durability**

Significant titania loss from the sphere surface would lead to degradation of its photocatalytic performance, and the long-term durability of the spheres is of great importance for functional application in a CAFO lagoon. To investigate the effect of long-term solar exposure on the photocatalytic activity of the spheres, three spheres were photocatalytically pre-tested, exposed to the sun while floating in water for 35 days, and then post-tested as described in the experimental section. The average rate constant for the preliminary degradation of 500 mL of 20 mg/L tetracycline under UV-LED illumination was $1.88 \times 10^{-3} \text{ min}^{-1}$ with a standard deviation of $0.62 \times 10^{-3} \text{ min}^{-1}$. After 35 days in an unshaded exterior location, the rate constant was
observed to be $1.82 \times 10^{-3}$ min$^{-1}$ with a standard deviation of $0.29 \times 10^{-3}$ min$^{-1}$. The fact that the photocatalytic activity of these spheres was virtually unaffected by 35 days of solar exposure is an excellent indicator for the practicality of this solution in the field.

**Low-concentration tetracycline degradation**

Figure 4 shows the concentration of tetracycline remaining in solution after 8 h of solar exposure with an initial concentration of 8 µg/L in pond water. The photocatalytic kinetics was completely unaffected by the lower initial concentration. The final experimental concentration was 2.47 µg/L, as compared to the 2.45 µg/L predicted by the pond water photocatalytic kinetics at high concentration. The dark control experiment showed a predictably higher percentage of adsorption at lower concentration with a final tetracycline concentration of 6.33 µg/L. The tetracycline degradation kinetics in the light control experiment was unexpectedly slower, resulting in a final concentration of 5.80 µg/L. The fact that the pseudo-first order rate constant for the photocatalytic degradation of tetracycline was consistent at initial concentrations of 60 mg/L and 8 µg/L is an excellent indicator that this method is widely applicable in CAFO lagoon environments where the tetracycline concentrations are expected to vary.

**CONCLUSIONS**

The photocatalytic floating PMMA-titania spheres reported here provide a low-cost, effective, and durable option for the removal of tetracycline from surface water. Further investigation is needed in an actual CAFO lagoon with a sediment bottom and dispersed manure loading, since adsorption of tetracycline on these surfaces is known to be significant (Kim et al. 2005; Kim & Carlson 2007; Prado et al. 2009; Li & Zhang 2010; Watanabe et al. 2010), and would be expected to impact the rate of photocatalytic tetracycline oxidation. Furthermore, the polypropylene tubs used in this study do not reflect a realistic lagoon depth, and it remains to be determined if the presence of the photocatalytic floating spheres inhibits the nutrient-reduction function of the wastewater lagoon. This work does show, however, that this approach has the potential to significantly decrease aqueous tetracycline concentrations in CAFO lagoons without re-engineering the lagoon system.

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