Degradation of Residual Dyes through Photocatalysis after Hydrolysis of PETE Plastic

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Marine plastic pollution remains a problem, with over 170 trillion pieces of plastic in the world's oceans. A process that can efficiently degrade PETE plastic is hydrolysis, where the PETE is broken into its terephthalic acid and ethylene glycol monomers, which are the fundamental chemical building blocks that form plastics. TPA serves a commercial purpose in paints, pharmaceuticals, and environmental industries. While this useful, oftentimes harmful dyes remain in the obtained TPA. Green PETE plastics were degraded under neutral-hydrolysis conditions for 2 hours, after which TPA was produced. It was found that the UV degradation of the remaining dyes within the obtained TPA in the presence of TiO2 could be performed in a timely manner. The process produced statistically significant results, showing that TiO2 has a rate order of 1 in the kinetics of dye degradation. In addition, the degradation proceeded the fastest in acidic conditions.

Keywords: Dye degradation, Photocatalysis, PETE Degradation, TPA, Hydrolysis

Introduction

The world's oceans are incredibly polluted with plastics. As of 2023, with a growing plastic smog covering the global environment, an increasing amount of it has found its way into marine ecosystems. There are now estimated to be over 170 trillion particles of plastic in the world's oceans, and the number is only projected to continue increasing, with the rate expected to soar by 2.6 times between now and 2040[1]. Microplastics are devastating to marine life, and are widely known to inhibit growth and development, feeding and behavioral activity, reproduction, immune systems, and genetic health[2]. Recent studies of Pacific oysters and zebrafish larvae also correlate that animals in plastic-contaminated water have decreased fertility rates[3] and lowered survivability[4].

To solve the problem of contaminated water, it is crucial to develop technology to prevent plastic from entering waterways which flow into the ocean, cutting off the issue from the root source rather than attempting to remove plastic after contamination has occurred. However, current plastic disposal problems have a plethora of drawbacks, including high costs associated with the implementation of technology[5]. Despite the need for improved technology, infrastructure remains lacking and disposal systems remain poor, contributing to the influx of plastic into water-based ecosystems.

Though recycling has been proposed as a solution to plastic pollution, it has proven to be an ineffective solution due to its small scope, with only 9% of plastics being recycled worldwide[6]. Furthermore, the recycling process can release microplastics into the resulting wash water, which may be less than 10μm in size, and therefore environmentally relevant[7]. Thus, it is vital to study the processes of alternative methods of plastic disposal, such as breaking down plastics into terephthalic acids, henceforth known as TPAs. The prevalent plastic polyethylene terephthalate (PETE), with resin code 1, can be broken down into TPA through a process known as hydrolysis when in neutral conditions. During this process, polymerization is reversed, giving products terephthalic acid (TPA), a monomer with various chemical uses, and ethylene glycol, an easy to remove by-product[8]. The TPA produced can then be reused in pharmaceuticals, paints, and even metal complexes that can be used to absorb PFAS, through hydrogen bonding, electrostatic forces, and additional intermolecular forces[9].

While the literature on PETE hydrolysis is already comprehensive, many PETEs contain pigments—for example, titanium dioxide is a pigment frequently used to give plastic a white or opaque color[10]. The impact of pigments on the formation of TPA from PETE remains a research gap. If pigments are not properly removed from recycled plastic, their presence in bodies of water could be toxic, further damaging the health of both humans and animals. Dyes have been shown to cause or exacerbate widespread illnesses such as asthma, skin allergies, and respiratory illnesses[11]. Therefore, this study aims to research how the presence of titanium dioxide in various amounts impacts the rate of production and purity of product in the production of terephthalic acid from PETE plastic. A key objective is to develop a streamlined process for degrading both plastic and the pigment by optimizing the pH and titanium dioxide catalyst

Conditions	Methylene Blue	TPA, no TiO2, pH 3	TPA, 2.5% TiO2, pH 3	TPA, 5% TiO2, pH 3	TPA, 5% TiO2, pH 11
Absorbance (0 min)	1.431	0.017	0.344	0.043	0.120
Absorbance (5 min)	0.011	0.008	0.0299	0.011	0.044
Absorbance (10 min)	0.032	0.002	0.020	0.0028	0.038
Absorbance (15 min)	0	0.002	0.020	0	0
Absorbance (20 min)	0	0.001	0.162	0	0
Absorbance (25 min)	0	0.001	0	0	0
Absorbance (30 min)	0	0	0	0	0

Table 1 Absorbance over time vs conditions of degradation

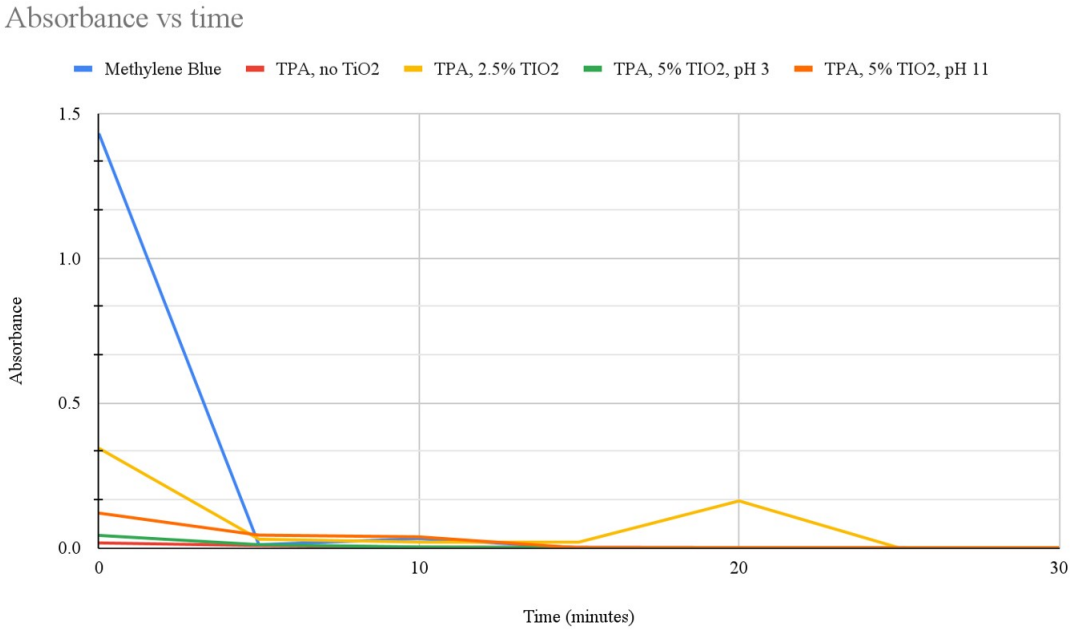

Fig. 1 TPA and TiO2 Absorbance vs Time

during heterogeneous photocatalysis. In addition to this, the study will cover the kinetics of pigment degradation from pigmented plastics. This impactful research could fill the research gap on pigment degradation; the final dye degradation process is expected to be cross-applicable to pigments as pigments have lower stability and therefore likely a lower threshold for decomposition using the same processes [12]. This is due to the fact that dyes are soluble and chemically bind to a medium, whereas pigments are insoluble and are physically painted onto a medium. Furthermore, the use of titanium dioxide would mean that a cheap and readily available catalyst can be used, as opposed to traditional organo-metallic catalysts, which can be expensive [13]. The independent variables of this experiment are the amount of titanium dioxide added (0%, 2.5%, 5% w/w), and the pH of the solution (3, 7, 11). The levels of titanium dioxide were chosen, as plastics can contain up to 5% titanium dioxide as additives, and varying within the 0-5% range would allow insight as to whether industrial photocatalysis can be achieved without additives. Methylene Blue, while not used often in plastics, was offered as an additional comparison, as methylene blue exhibits ideal and quick degradation [14]. In response, the kinetics and efficiency of the photodegradation will be measured as dependent variables. During the experiment, the controls will include the color and brand of plastic being used, the hydrolysis conditions for PETE degradation, and the time and environment of pigment photodegradation.

The hypothesis of this experiment is as follows: If the amount of hydrogen ions and titanium dioxide is increased for all three reaction processes, the reaction time will decrease and the efficiency will increase. This should be due to catalyzing the reaction or leading to more efficient pathways.

Results

The TPA with 2.5% TiO2 had the highest measured absorbance, while the TPA with 5% TiO2 and pH 11 had the lowest measured absorbance. Both the TPA without TiO2 and the TPA with 5% TiO2 and pH 3 had a relatively small absorbance. In comparison to the methylene blue, the TiO2 had a much lower initial absorbance, often being as much as 140 times lower. A notable exception is the TPA with 2.5% TiO2, which had an initial absorbance that was only around 4 times lower. The unexpected peak at 20 minutes was likely due to improper calibration, or unclean cuvettes, as the peak quickly disappeared by the next measurement of the solution.

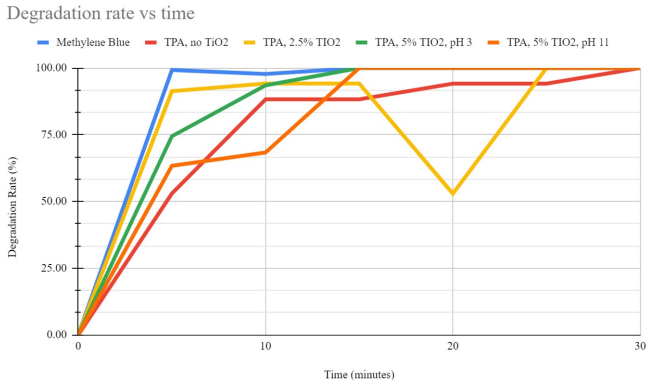

Fig. 2 Absorbance at all conditions vs time

Percent degradation was calculated as the percent of absorbance that was lost, as absorbance is directly correlated with concentration.The degradation rate of methylene blue was the first to level off quickly around 100%. Of all the experimental conditions, both of the TPAs with 5% TiO2 were the first to reach 100% degradation. Furthermore, between the TPAs with 5% TiO2, the photospectroscopy that took place in pH 3 had a higher degradation rate than the one that took place in pH 11. Ultimately, all the TPAs were found to have a degradation rate that was lesser on average than the control of methylene blue. Overall, the TPA without TiO2 was observed to have the lowest trendline, though the TPA with 5% TiO2 in pH 11 had a lower degradation rate at one point at 10 minutes. The TPA with 2.5% TiO2 also had a lower degradation rate at one point at 20 minutes. However, every experimental photospectroscopy ended with an approximately 100% degradation rate.

Table 3 refers to the rate constants, calculated according to the first-order degradation of dyes ((N. T. Hoang, V. T. Nguyen, N. D. M. Tuan, T. D. Manh, P. Le, D. V. Tac, F. M. Mwazighe, Degradation of dyes by UV/Persulfate and comparison with other UV-based advanced oxidation processes: Kinetics and role of radicals. Chemosphere, 298, 134197 (2022).)). TPA1 refers to the TPA with 0% TiO2, TPA2 refers to the TPA with 2.5% TiO2, TPA3 refers to the TPA with 5% TiO2 and pH3, and TPA4 refers to the TPA with 5% TiO2 and pH 11. From the data, it is clear that a 5% ratio of TiO2 results in the fastest degradation of plastic dyes, with the acidic conditions being slightly favored. Because the rate constant of TPA3 is approximately twice as much as TPA1, we can deduce that the reaction order with respect to TiO2 is 1.

Tables 4 and 5 show the data and p-values outputted for the t-tests conducted. Blue refers to methylene blue. TPA1 refers to the TPA with 0% TiO2, TPA2 refers to the TPA with 2.5% TiO2, TPA3 refers to the TPA with 5% TiO2 and pH3, and TPA4 refers to the TPA with 5% TiO2 and pH 11. The suffix _ab indicates a t-test run between the absorbance of the indicated experimental conditions and the control conditions containing methylene blue. The suffix _de indicates a t-test run between the degradation rate of the indicated experimental conditions and the control conditions. The p-values are shown in the bottom row. All values represent percent degradation or absorbance. The required significance level to be considered statistically significant was established to be 0.05. All of the null hypotheses were rejected, indicating that the differences in both degradation rate and absorbance between the methylene blue and the various TiO2 experimental conditions were statistically significant.

Discussion

As the data shows, the degradation of plastic dyes and pigments is possible, with all samples reaching 100% degradation. The degradation of green 7Up dyes has been shown to be able to degrade at efficient rates comparable to more studied dyes such as Methylene Blue. This is most likely due to the similar structures of many dyes—often conjugated pi systems. Because the structure of common dyes such as the ones used in the experiment are not available to the public, studying them will be difficult. However, studying the effects of photocatalysis will nonetheless provide valuable insights into possible degradation methods. Titanium Dioxide has been shown to degrade dyes through radical production caused by electron-hole recombination [15].

Combined with the neutral-state hydrolysis of TPA, an efficient and well-established process, dyed plastics could be environmentally degraded into ethylene glycol, terephthalic acid, and degraded dyes. As seen, the role of TiO2 is significant, with an increased amount of TiO2 added being directly proportional to the rate of degradation. This effect could level-off at higher TiO2 levels, but percentages up to 5.0% TiO2 have shown to be successful, with greater concentrations of photocatalyst leading to greater degradation rates. Because of this, a required TiO2 percentage in dyed plastics could aid the degradation processes. In addition, acidic conditions were found to foster faster dye degradation than basic conditions. Both of these findings support the hypothesis that TiO2 and acidic conditions would lead to the fastest dye degradation. These results work to streamline the

Conditions	Methylene Blue	TPA, no TiO2, pH 3	TPA, 2.5% TiO2, pH 3	TPA, 5% TiO2, pH 3	TPA, 5% TiO2, pH 11
Degradation % (0 min)	0.00	0.00	0.00	0.00	0.00
Degradation % (5 min)	99.2	52.9	91.3	74.4	63.3
Degradation % (10 min)	97.8	88.2	94.2	93.5	68.3
Degradation % (15 min)	100.	88.2	94.2	100.	100.
Degradation % (20 min)	100.	94.1	52.9	100.	100.
Degradation % (25 min)	100.000	94.118	100.	100.	100.
Degradation % (30 min)	100.000	100.000	100.	100.	100.

Table 2 Degradation rate over time vs conditions of degradation

	TPA1_ab	TPA2_ab	TPA3_ab	TPA4_ab
Degradation Rate Constant (k min-1)	0.151	0.0804	0.273	0.200

Table 3 Rate constants

Time	TPA1_ab (%)	TPA2_ab (%)	TPA3_ab (%)	TPA4_ab (%)
0 min	0.017	0.344	0.043	0.120
5 min	0.008	0.030	0.011	0.044
10 min	0.002	0.020	0.003	0.038
15 min	0.002	0.020	0.000	0.000
20 min	0.001	0.162	0.000	0.000
25 min	0.001	0.000	0.000	0.000
30 min	0.000	0.000	0.000	0.000
	P value	0.031	0.000	0.001

Table 4 Absorbance T-test

Time	TPA1_de (%)	TPA2_de (%)	TPA3_de (%)	TPA4_de (%)
0 min	0.00	0.00	0.00	0.00
5 min	52.9	91.3	74.4	63.3
10 min	88.2	94.2	93.5	68.3
15 min	88.2	94.2	100.	100.
20 min	94.1	52.9	100.	100.
25 min	94.1	100.	100.	100.
30 min	100.	100.	100.	100.
	P value	0.031	0.000	0.001

Table 5 Degradation T-test

degradation process, as the terephthalic acid monomer is weakly acidic. However, it must also be acknowledged that other factors could influence reaction rate. For example, a finer version of the TiO2 powder could result in a faster reaction rate due to the increased surface area of the catalyst. The impact of crystalline structure on reaction rate remains ambiguous in the literature, yet is a variable that also likely influences reaction rate [16]. Furthermore, since the rate of reaction is also directly proportional to the square root of the intensity of light, light intensity is also a factor contributing to the calculated reaction rate [17]. Testing an expanded sample size could help cement this effect, and further increase the statistical significance of the process. Testing a greater range of pHs would create a greater understanding of the correlation between pH and degradation rate. In addition, testing different colored plastics could determine whether this process stays consistent for all colors, and even a mixture of colors. Both of these are important for the future of recycling. Lastly, a concerted process, where PETE and dye degradation could occur in a singular vessel, could make this process an even simpler and time-efficient process, encouraging companies to implement it into their plastic disposal processes.

Methods

This project required 7-Up PETE bottles, distilled water, ethylene glycol, a Porr reactor, titanium dioxide (henceforth referred to as TiO2), a UV light chamber, and a spectrometer. The Porr reactor was used in order to maintain a high temperature and pressure environment. The UV light chamber was used for dye photocatalytic degradation, and the spectrometer was used to monitor dye degradation.

The procedure was divided into two stages: plastic degrada-

tion and dye degradation. In the initial plastic degradation stage, the colored 7-Up bottles, which contain PETE, were collected. The plastics were cut into squares of approximately 0.2 cm x 0.2 cm[18]. It was necessary to cut them into small pieces, as the reaction could only continue at a practical rate when the pieces had a large surface area. Samples were then created, each with 2.5 grams of plastic, 2.5 milliliters of ethylene glycol, and 40 milliliters of distilled water. This allowed for a neutral state hydrolysis reaction, in which ethylene glycol was both a catalyst and a product of the reaction[16]. The reaction took place for 2 hours at 210 degrees celsius and 115 PSI, as high temperatures and pressures were required for the reaction to occur. After the reaction was finished, the samples were centrifuged 3 times at 8,000 rotations per minute for 6 minutes, for a total of 18 minutes. Resultantly, the water and ethylene glycol were separated from the terephthalic acid, which was the main product due to its chemical applications[19]. After overnight drying, the terephthalic acid, which remained impure due to the dye contamination, was weighed. Samples were covered during overnight drying in order to prevent contamination.

In the dye degradation stage, methylene blue was degraded first as a comparison, as the degradation of dyes such as methylene blue has been well studied[14]. The required components for the degradation were 25 milliliters of solution, consisting of 10 parts per million of methylene blue and 10 milligrams of TiO2 P25. All of the produced TPA was used to create one solution, which was split into 25 milliliters each. This ensures that each solution had the same concentration of TPA. 6 4-watt UVC lamps, each with a wavelength of 256 nanometers, were required. 2 mL of the solution were sampled every 5 minutes, and the samples' absorbances were measured using a spectrophotometer that had a wavelength of 665 nanometers. Then, separate samples were created using 0.6 grams of TPA diluted to 50 milliliters. Samples were either created with 0% (0 milligrams), 2.5% (15 milligrams), or 5% (30 milligrams) of TiO2 P25, as these are the common concentrations of TiO2 in plastics. The samples were then placed under UV lights, and their dye concentrations were measured using a spectrophotometer for 5 hours[20]. A wavelength of less than 387.5 nanometers was required to overcome titanium's band gap and activate the photocatalyst[21]. The degradation was conducted at 25 degrees Celsius, as temperature was shown not to be a major factor in photocatalysis[22]. Once the optimal amount of TiO2 was determined, the dye degradation was conducted again at a pH of 3 and a pH of 11 in order to find the optimal pH of the green pigment, which occurs at different pH in commercially available plastics.

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