



## Application of photochemical technologies for treatment of landfill leachate

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### ABSTRACT

Because of widely varying practices in solid waste management, an all-inclusive solution to long-term management of landfill leachate is currently not available. There is a major technological need for sustainable, economical options for safe discharge of leachate to the environment. Two potential on-site pretreatment technologies, photochemical iron-mediated aeration (PIMA) and TiO<sub>2</sub> photocatalysis were compared for treatment of landfill leachate at laboratory scale. Results of bench scale testing of real landfill leachate with PIMA and TiO<sub>2</sub> photocatalysis showed up to 86% conversion of refractory COD to complete mineralization, up to 91% removal of lead, up to 71% removal of ammonia without pH adjustment, and up to 90% effective color removal with detention times between 4 and 6 h, in field samples. The estimated contact times for 90% removal of COD, ammonia, lead, and color were found to be on the order of 10–200 h for PIMA and 3–37 h for TiO<sub>2</sub> photocatalysis. Testing with actual leachate samples showed 85% TiO<sub>2</sub> photocatalyst recovery efficiency with no loss in performance after multiple ( $n > 4$ ) uses. Pre-filtration was not found to be necessary for effective treatment using either process.

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### 1. Introduction

A rising concern with landfill facilities is the collection and safe disposal of leachate. The difficulties in dealing with municipal landfill leachate are related to its highly variable composition and high concentrations of recalcitrant organic compounds, ammonia and heavy metals [1–9]. These characteristics make the material difficult to treat by either biological or chemical means. The ideal leachate management approach must be sustainable, economical, adaptable to site-specific conditions, and capable of dealing with evolving regulations. After evaluating different engineering alternatives for long-term leachate management [10], the most effective and sustainable strategies for the future involve technologies that can destroy different classes of harmful contaminants in one reactor without producing adverse byproducts and residuals. One acceptable approach would be to discharge the leachate to the sanitary sewer system, after on-site pretreatment to reduce the toxicity of the leachate to the receiving facility. The technologies that can meet these on-site pretreatment requirements include advanced oxidation treatment processes that: (1) are easy to operate because they just require sufficient contact time, (2) do not rely on complex precipitation reactions, chemical additions, or biochemical processes, (3) are not subject to biological upsets because they are physico-chemical processes that create broad

spectrum oxidants to remove aqueous contaminants, and (4) are designed to avoid merely transferring the pollutant to another medium (i.e. air, sludge, concentrates, etc.). Two such processes with these characteristics include: photochemical iron-mediated aeration (PIMA) and TiO<sub>2</sub> photocatalysis.

#### 1.1. Photochemical iron-mediated aeration (PIMA)

PIMA is a novel photochemically assisted iron-mediated aeration process for oxidizing organics and co-precipitating inorganics in wastewater, which was co-developed by the University of Miami and Florida Atlantic University [11,12]. PIMA has been demonstrated in laboratory tests to simultaneously remove certain metal oxyanions (arsenite, arsenate, vanadate, and chromate), heavy metals (Hg, Ni, Pb, and Cd), radionuclides (Sr), and environmentally relevant organic constituents, such as 17 $\beta$ -estradiol, di-*n*-butyl phthalate, nonylphenol, and ethylenediamine tetraacetic acid (EDTA). Furthermore, lab scale demonstrations have shown the capability for inactivation of *E. coli*, coliform, and heterotrophic bacteria as well as color/odor removal. The effect of added ultraviolet energy increased the reaction rate by a factor of 4 at neutral pH in comparison to dark iron-mediated aeration controls [11]. This was unexpected since Fenton-like chemical reaction rates are known to be unfavorable at ambient pH (i.e. 6–8). Another result of preliminary testing was that oxidation byproducts were identified as readily biodegradable oxidation intermediates. Only 10% of the original carbon content was accounted for from by-products analysis, indicating the possibility of near complete (>90%) mineralization to

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**Table 1**  
Review of COD removal using photochemical technologies.

Water type	Reagent dose	UV lamp (intensity)	Reactor	COD <sub>o</sub> (mg/L)	pH	Removal (%)	Time (min)	Reference
Grey water	2.0–5.0 g/L TiO <sub>2</sub>	nr (TQ 150z1)	Batch	3940	10.3	44	150	[39]
Simulated wastewater	1% Pt–TiO <sub>2</sub> immobilized on silica gel	88 W (1.8 mW/cm <sup>2</sup> )	Fixed bed	62	6.5	86	30	[40]
Simulated wastewater	0.3–1.0 g/L TiO <sub>2</sub>	8 W	Batch	10	nr	82	120	[41]
Lagoon wastewater	2.0 g/L TiO <sub>2</sub>	Solar radiation	Batch	660	8.0 (315 alk)	42	120	[42]
Reactive red 120 dye	1.9 g/L TiO <sub>2</sub>	8 W (21 W/cm <sup>2</sup> )	Batch	50	7.0	67	720	[43]
Industrial wastewater	0.6 g/L TiO <sub>2</sub>	6 × 18 W	Batch	3.2	6.0	62	60	[44]
Industrial wastewater	4 plates immobilized TiO <sub>2</sub>	4 × 4 W	Batch	120 (TOC)	9.0	34	30	[45]
Industrial wastewater	1.0 g/L TiO <sub>2</sub>	415 W	Batch	135	8.0	22 (diluted 1:100 + filtered)	1440	[46]
Industrial wastewater	0.5 g/L TiO <sub>2</sub>	400 W	Batch	404	3.0	40	240	[47]
Landfill leachate	5.0 (batch) immobilized	16 × 40 W (10 W/cm <sup>2</sup> )	Thin-film fixed bed	985	5.0	70	480	[48]
Landfill leachate	3.0 g/L TiO <sub>2</sub>	8 W (21 W/cm <sup>2</sup> )	Batch	1673	8.7	30	720	[22]
Landfill leachate	1.0–2.0 g/L TiO <sub>2</sub>	150 W (0.5 mW/cm <sup>2</sup> )	Batch	1200	7.5	35–57	60	[36]
Simulated leachate	40 g/L Fe	450 W	Fibrous fixed bed	990	7.5	5	1440	[11]
Simulated leachate	40 g/L Fe	450 W (19 μW/cm <sup>2</sup> )	Fibrous fixed bed	740	7.0	40	960	[12]
Landfill leachate	10–40 g/L Fe	450 W (19 μW/cm <sup>2</sup> )	Fibrous fixed bed	4220	7.5	5	960	[12]

nr = not reported.

carbon dioxide [11]. These findings imply the potential to completely destroy environmentally stable and persistent organic compounds, without pH adjustment or chemical addition.

Although the PIMA reaction mechanism is not completely understood, evidence suggests oxidation via hydroxyl radical and/or ferryl species, implying indiscriminate oxidation of organics. Essentially, the process is thought to begin with a stepwise oxidation of Fe(0) → Fe(II) → Fe(III) enhanced by ultraviolet light. In the presence of complexed ferric iron, the photo-assisted Fenton reaction ( $\lambda < 360$  nm) can accelerate the rate of hydroxyl radical formation by two orders of magnitude, while regenerating ferrous iron to propagate a Fenton cycle [13]. The ferric iron acts as a photosensitizer and may also participate in the formation of oxidants, such as hydroxyl radical, through photo-Fenton chemistry. The combined action of the oxidative power of hydroxyl radicals, coprecipitation via insoluble Fe(III) precipitates, the stripping power of aeration, and the photolytic effect of ultraviolet energy work to decrease the concentrations of pollutants and impurities. Under aerobic conditions, some ferric chelates are known to be rapidly photodegraded by solar radiation with a half-life on the order of 2 h [14–17]. The rate of photodegradation is thought to be pH-dependent (optimized at pH < 3.1) [18]. A particularly surprising result was that radical scavenging was not observed to terminate the reaction, even with 200 mg/L bicarbonate and 33% more TOC than raw sewage [11,12], which suggests that the reaction involves a self-regenerative, reactive surface area associated with the soluble Fe(II).

### 1.2. TiO<sub>2</sub> photocatalysis

Photocatalysis on titanium dioxide (TiO<sub>2</sub>) is a sustainable process for the treatment of water and wastewater. Li Puma et al. [29] note that, “the application of photocatalytic oxidation for wastewater treatment on an industrial scale is currently hindered by a lack of simple mathematical models that can be readily applied to reactor design.” Photocatalysis involves the use of ultraviolet (UV) light to excite a semiconductor catalyst and generate a mixture of indiscriminate oxidants including hydroxyl radical and superoxide radical. Photocatalytic processes for destruction of organics are well known (refer to Table 1). However, recently, certain nitrogen-containing organic pollutants have been treated with photocatalysts through a reductive pathway [19], and Vohra and Davis [20] measured nearly 70% removal of lead (in the form

of organic intermediate complexes) at neutral pH after 50–70 min of treatment. Furthermore, photocatalysis has also been demonstrated for pH 3–8 at millimolar concentrations of organically bound trace metal contamination [21] as well as the destruction of certain other heavy metals [22]. In experiments by Hilmi et al. [23], glass plates coated with immobilized TiO<sub>2</sub> were used in a photocatalytic process to collect mercury, lead, copper, and cadmium from aqueous solutions containing individual metals and mixtures. In those tests, individual metals at concentrations of 1.0–5.2 mg/L were reduced to undetectable levels in less than 1 h of treatment. Since suspended TiO<sub>2</sub> catalysts enjoy free contact with UV irradiation in a photoreactor, they are expected to achieve better efficiency than immobilized TiO<sub>2</sub> catalysts. However, the separation and reuse of suspended catalyst powders from treated water often limits its application in practice.

### 1.3. Objective

PIMA and TiO<sub>2</sub> photocatalysis have been researched for COD removal in the literature (see Table 1), but not for other components found in landfill leachate (i.e. BOD<sub>5</sub>, color, ammonia, trace metals, etc.). These emerging technologies work by using ultraviolet light to activate the surface of a semi-conductor (i.e. titanium dioxide or iron oxide coating of metallic iron) to produce highly reactive species derived from water that can rapidly destroy man-made organic chemicals, breaking them down into carbon dioxide, water, and innocuous salts. The objective of this project is to evaluate the process removal efficiency of PIMA and photocatalysis with TiO<sub>2</sub> on typical landfill leachate constituents of COD, BOD<sub>5</sub>, color, ammonia, and lead at the concentrations commonly found in landfill leachate.

## 2. Methods

Collection of process performance data was conducted in two phases. The first set of experiments involved initial screening tests with synthetic leachates [24,25] to determine the magnitude of residual generation and oxidation kinetics. The next set of experiments utilized field samples of real leachate.

### 2.1. Simulated leachate

Simulated leachates were prepared to allow testing of individual contaminants and mixtures. All samples of simulated leachates

**Table 2**  
Initial water quality of simulated leachate samples.

Constituent	Model compound	Source	Range	Units
COD	KHP	Fisher Scientific (Pittsburgh, PA)	1050–10,900	mg/L
BOD <sub>5</sub>	Glucose/glutamic Acid	Hach Company (Loveland, CO)	55–425	mg/L
Lead	Pb(NO <sub>3</sub> ) <sub>2</sub>	Hach Company (Loveland, CO)	0.03–0.30	mg/L
Ammonia	NH <sub>4</sub> Cl	Fisher Scientific (Pittsburgh, PA)	110–930	mg/L as NH <sub>3</sub> -N
Alkalinity	NaHCO <sub>3</sub>	Carolina Biological Supply Company (Burlington, NC)	200–4330	mg/L as CaCO <sub>3</sub>

were created from dry stock or standards of individual or mixed components of leachate dissolved in sterile buffered reagent water [26]. For each constituent, the range of concentrations tested is listed in Table 2. These levels were determined according to the leachate water quality data collected from various sources [1–9]. The minimum, maximum and a level in between were tested to determine concentration dependence. Prior to testing, samples were mixed vigorously overnight and were initially buffered to pH 7.5 using sodium bicarbonate and hydrochloric acid. Color and odors are not present in synthetic leachate and were not evaluated until the processes were tested with real leachate.

## 2.2. Real leachate

Synthetic leachate provides the substrate for bacteria, but does not contain a significant microbial population. Actual field samples of leachate were also collected from a variety of landfill sites located in Florida, USA. Actual leachate samples were collected on site in plastic containers and stored at 4 °C until use. Samples were collected from the following locations:

1. Solid Waste Authority of Palm Beach County in West Palm Beach, FL.
2. North Polk County Landfill Site 201 (bioreactor landfill) in Lakeland, FL.
3. Broward County Central Disposal Sanitary Landfill in Deerfield Beach, FL.

The leachate collected from the Solid Waste Authority of Palm Beach County is a composite sample from municipal solid waste, waste-to-energy ash, wastewater sludge, yard waste, and construction and demolition waste, combined with leachate from a separate closed landfill, plus condensate water from a refuse-derived fuel waste-to-energy plant. This facility was sampled from the wet well prior to deep well injection disposal. The North Polk County Landfill was sampled directly from the leachate storage tank. The Broward County Central District Sanitary Landfill facility has leachate from

**Table 4**  
First order kinetics analysis for PIMA experiments.

Parameter	Leachate Type	Co (mg/L)	Fe (g/L)	UV intensity (μW/cm <sup>2</sup> )	$I_{(\eta,R),z^*}$ (μW/cm <sup>2</sup> )	Time (min)	Removal (%)	$k$ (h <sup>-1</sup> )	$r^2$	Theta* (h)
COD	Simulated individual	1050	16	8	125	1440	44%	0.020	0.81	230
COD	Simulated individual	1050	16	19	238	1440	51%	0.024	0.77	200
COD	Simulated individual	1050	16	49	502	1440	54%	0.026	0.82	180
COD	Simulated mixture	740	16	19	238	960	38%	0.029	0.77	158
COD	Simulated mixture	11,600	16	19	238	960	33%	0.024	0.96	190
COD	Real leachate (Solid Waste Authority)	2950	16	19	238	960	10%	0.004	0.44	1220
BOD <sub>5</sub>	Simulated individual	200	16	19	238	960	39–44%	0.034	0.99	135
BOD <sub>5</sub>	Simulated mixture	470	16	19	238	960	52–89%	0.100	0.99	45
BOD <sub>5</sub>	Real leachate (Solid Waste Authority)	666	16	19	238	960	20%	0.014	0.99	322
Ammonia	Simulated Individual	930	16	8	125	960	13%	0.006	0.99	813
Ammonia	Real leachate (Solid Waste Authority)	930	4.1	19	238	960	21%	0.010	0.61	464
Lead	Simulated individual	0.30	16	19	238	960	>99.97%	0.484	0.99	9.5
Lead	Simulated mixture	0.35	16	19	238	960	77–99.95%	0.477	0.99	10
Lead	Real leachate (Solid Waste Authority)	0.0029	8.1	19	238	960	91%	0.149	0.99	31
Color	Real leachate (Solid Waste Authority)	>500 PCU	8.1	19	238	240	88–98%	0.188	0.79	27

\* The value of theta is the estimated time required to achieve 99% removal.

**Table 3**  
Initial water quality of real leachate samples.

Constituent	Range	Units
COD	140–5200	mg/L
BOD <sub>5</sub>	290–720	mg/L
Lead	BDL–0.0054	mg/L
Ammonia	800–2500	mg/L as NH <sub>3</sub> -N
Color	>500	PCU
Alkalinity	200–4330	mg/L as CaCO <sub>3</sub>

active municipal solid waste cells and waste-to-energy ash combined with condensate water. A summary of the constituent levels from the real leachate samples is reported in Table 3. Specific concentration levels used in selected experiments are found in Table 4 for PIMA experiments and Table 5 for TiO<sub>2</sub> experiments.

## 2.3. PIMA bench reactor

The bench scale pilot reactor for PIMA consisted of a photochemical safety cabinet, a sample tube holding chamber, quartz immersion well, plug flow water cooling system for the lamp, humidified aeration system, and quartz test tube PIMA reactors (2.8 cm ID × 20 cm tall, volume = 123 mL), as described in [11,26,27]. The ultraviolet source was an axially mounted 450 W medium pressure mercury vapor lamp and power supply from Ace Glass Incorporated (Vineland, NJ). The bulb length was 0.244 m and diameter was 0.025 m with a radiation zone of 0.13 m in height. Of the total energy radiated, 40–48 percent is in the ultraviolet portion of the spectrum (from 220 nm to 400 nm), 40–43 percent in the visible, and the balance in the infrared. A traceable UV light meter with range of 5 μW/cm<sup>2</sup>–19.99 mW/cm<sup>2</sup> (VWR, Suwanee, GA) was used to measure the UV light intensity transmitted (λ = 320–390 nm). This is the range at which 16% of the lamp power is radiated. The intensity of the incident radiation entering the inner wall of the annulus ( $I_{(\eta,R),z^*}$ ) is also reported following the method described in [27].

**Table 5**  
First order kinetics analysis for UV/TiO<sub>2</sub> experiments.

Parameter	Leachate Type	C <sub>0</sub> (mg/L)	TiO <sub>2</sub> (g/L)	UV Intensity (μW/cm <sup>2</sup> )	I <sub>(t,R)</sub> z* (μW/cm <sup>2</sup> )	Quantum Yield (mol/J)	Time (min)	Removal (%)	k (h <sup>-1</sup> )	r <sup>2</sup>	Theta <sup>†</sup> (h)
COD	Simulated individual	1060	1.0	1960	1755	0.072	240	95%	0.79	0.97	5.8
COD	Simulated individual	1060	4.0	1960	1755	0.128	240	99%	1.41	0.94	3.3
COD	Simulated individual	1060	3.7	2480	1755	0.092	240	99%	1.01	0.89	4.6
COD	Simulated mixture	6160	28.4	2360	1755	0.002	240	11%	0.02	0.83	190
COD	Real leachate (Broward County)	5340	35.5	1400	1755	0.012	360	55%	0.13	0.92	37
COD	Real leachate (Broward County)	140	4.0	1960	1755	0.044	240	86%	0.49	0.99	9.5
COD	Real leachate (Polk County)	330	4.0	1960	1755	0.028	240	71%	0.31	0.97	15
BOD <sub>5</sub>	Simulated individual	490	4.0	nr	1755	0.008	240	41%	0.09	0.99	52
BOD <sub>5</sub>	Real leachate (Broward County)	514	35.5	2600	1755	0.005	360	34%	0.06	0.75	73
Ammonia	Simulated individual	1425	4.0	nr	1755	0.016	240	51%	0.18	0.99	26
Ammonia	Simulated mixture	2300	10.7	2360	1755	0.005	240	23%	0.06	0.94	81
Ammonia	Real leachate (Broward County)	2150	35.5	2240	1755	0.018	360	71%	0.20	0.96	23
Lead	Real leachate (Broward County)	Not detected	4.0	2240	1755	n/a	240	n/a	n/a	n/a	n/a
Color	Real leachate (Broward County)	>500 PCU	35.5	1400	1755	0.053	360	>90%	0.58	0.99	8

\* The value of theta is the estimated time required to achieve 99% removal.

For each experiment, 8 reactors were tested at various distances from the UV source to gauge the treatment efficiency resulting from different levels of UV light intensity (two at  $49 \pm 11 \mu\text{W}/\text{cm}^2$ , two at  $19 \pm 4 \mu\text{W}/\text{cm}^2$ , two at  $8 \pm 2 \mu\text{W}/\text{cm}^2$ , one IMA dark control, and one UV control at  $19 \pm 11 \mu\text{W}/\text{cm}^2$ ). For all experiments, the leachate samples were placed in quartz reactors and the dark control samples were placed in identical borosilicate glass test tube reactors. To eliminate any light reaching the dark control sample, a shield was placed between the reactor and the UV source. The iron reactant was prepared as described in [11,27]. The IMA reactors were operated in a recirculating batch mode, whereby constituents were continuously passed through the iron reaction zone by means of an air lift pump.

#### 2.4. TiO<sub>2</sub> bench reactor

The bench scale pilot reactor for TiO<sub>2</sub> experiments were carried out in a annular photocatalytic reactor system consisting of a photochemical safety cabinet, axially mounted 450 W medium pressure mercury vapor lamp and power supply, quartz immersion well, plug flow water cooling system for the lamp, and humidified aeration system, as described in [26]. The TiO<sub>2</sub> reaction chamber was a 375 mL photoreactor vessel with magnetic stirring, which was operated in a batch mode. Leachate constituents were completely mixed using a magnetic stirrer and aeration tubes, and only one reactor vessel was tested at a time. Experiments were conducted with commercially available titanium dioxide (Degussa P25, Evonik Industries, Essen, Germany) or particles synthesized in the laboratory by adding 5 mL of titanium isopropoxide (97%, supplied by Aldrich Chemical) and 25 mL of Ethanol (99%, supplied by Aldrich Chemical). A second solution of 0.5 mL deionized water, 0.5 mL 0.1 M HCl (supplied by VWR) and 25 mL of ethanol (supplied by VWR) was combined in an ice bath for 15 min to be used as the hydrolysis catalyst. The gel preparation process started when the first solution was added dropwise to the second solution under vigorous stirring. The mixture was removed from the ice bath, stirred for 1 h, and the ethanol was allowed to evaporate overnight. The prepared precipitates were dried for 1 h at 105 °C and finally annealed at 450 °C for 2 h. The resulting material was washed with ethanol once and with deionized water twice, with centrifugation (3000 rpm, 20 min) in between.

#### 2.5. Experimental conditions

For both processes, solution pH and temperature were monitored with a pH meter and digital recording thermometer. The effect of UV intensity (from 0 to 2600 μW/cm<sup>2</sup>) was tested by varying the distance from the source and varying the lamp power. Reaction times varied from 0 to 24 h. Aeration was varied from 0 to 5 Lpm, and the mass of catalyst/reactant was varied to optimize the amount needed to obtain the desired removal. For the PIMA experiments, the amount of iron reactant varied from 4 to 20 g/L, and for the UV/TiO<sub>2</sub> experiments, the amount of photocatalyst varied from 2.5 to 36 g/L.

#### 2.6. Water quality analysis

Samples were analyzed for the following constituents using Standard Methods [28]:

- Chemical Oxygen Demand, COD (SM5220D) using potassium hydrogen phthalate (KHP) crystals as the model contaminant (KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub>).
- 5-day Biochemical Oxygen Demand, BOD<sub>5</sub> (SM5210B) analyzed using seed obtained from the City of Boca Raton Wastewater Treatment Facility in Boca Raton, FL.
- Lead (SM3120B inductively coupled plasma method).
- Ammonia (EPA Method# 350.1 [SM4500-NH<sub>3</sub>G] and 350.2).
- Color (SM2120B using a Hach Model CO-1 color comparator (2234-00; lot number: A7984). For each sample, 5.0 mL was placed into the 15 mL sample viewing tube. Samples were diluted with deionized water, and values were reported in APHA platinum cobalt units.

For both PIMA and TiO<sub>2</sub> photocatalytic experiments, the initial contaminant concentration was measured prior to starting the reactor. At different time steps after the reaction started, sub-samples were collected and prepared for analysis, as described above. For PIMA test, sub-samples were collected using 1000 μL pipettors and filtered using 0.45 μm glass microfiber syringe-less filters to remove any particles of iron that would interfere with spectroscopic analysis. For larger sample volumes, filtration was accomplished using a vacuum filtration apparatus with 0.45 μm glass microfiber filters and 250 mL plastic filter holders. As with the



prior work, no effects due to post-filtration were noted [11,12]. For TiO<sub>2</sub> photocatalysis samples, the volume collected at each sampling time was 5.0 mL using a 5 mL pipettor. The sub-sample was then centrifuged in a 14 mL centrifuge tube at 4000 rpm for 25 min and decanted for analysis. The recovered TiO<sub>2</sub> particles were washed three times in deionized water and dried overnight at 70–105 °C in a drying oven, prior to reuse.

The results were analyzed in terms of a simple first-order kinetic model, including the effects of photon absorption by modeling the radiation field under heterogeneous (photocatalysis) conditions and by determining the spatial distribution of the volumetric rate of photon absorption (VRPA) in the reactor and the quantum yield using the method described in [29,30].

### 3. Results and discussion

#### 3.1. Simulated leachate tests with PIMA

Simulated leachate was spiked with each individual target compounds (COD, BOD, ammonia and lead), and then with a mixture of all of these consistent to see how removal changed with competing constituents. The first PIMA experiments were conducted on COD (COD<sub>0</sub> = 1050 mg/L and iron reactant = 16 g/L). The results are presented in Fig. 1. After only 4 h of treatment, the PIMA samples were at or below the sewer discharge target limit of 800 mg/L, and after 24 h, the maximum removal was recorded at 55%. Similar removal efficiencies (45–60%) were achieved for starting COD concentrations of 3300 mg/L and 10,900 mg/L. The observed removal was highest when the UV intensity was greatest (49 μW/cm<sup>2</sup>), although at 8–19 μW/cm<sup>2</sup> the removal was only slightly less (Fig. 1). The results were analyzed in terms of a first-order kinetic model (Table 4). The value of theta is the estimated time required to achieve 99% removal, calculated from the first order rate equation ( $\theta = -\ln(0.01)/k$ ).

For BOD<sub>5</sub>, the maximum removal efficiency was recorded at 55% after 16 h of treatment (see Table 4). It should be noted that advanced oxidation processes generally increase BOD as a consequence of converting recalcitrant COD to more biodegradable forms (increased BOD/COD ratio) [31–35]. Because these tests were conducted in simulated leachates, we could rule out pH effects (which was precisely controlled and monitored), and the lack of competing oxidizing constituents could have decreased the catalyst efficiency.

For ammonia, experiments were performed using initial concentrations of 110, 540, and 930 mg/L as NH<sub>3</sub>-N, but essentially no removal was recorded. It was hypothesized that the reactor design and conditions were not allowing the ammonia to escape

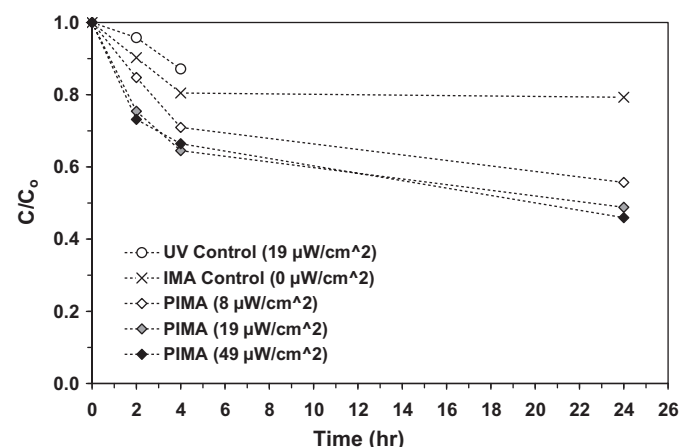


Fig. 1. PIMA scoping test results with COD<sub>0</sub> = 1050 mg/L.

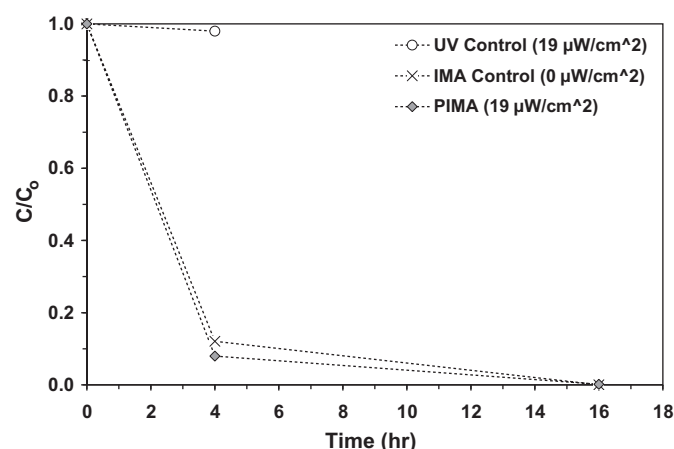


Fig. 2. PIMA scoping test results with Pb<sub>0</sub> = 0.3 mg/L.

the reaction zone, artificially limiting removal. Therefore, another set of experiments was conducted using a starting concentration of 540 mg/L as NH<sub>3</sub>-N with: (1) pH adjustment to 10 with lime addition, (2) pH adjustment with the reactor cap removed, and (3) pH adjustment with a modified reactor cap designed to facilitate ventilation of the ammonia gas. After 150 min, the results confirm the findings of [22] that ammonia removal is pH-dependent and a function of the reactor design. By including pH adjustment and maximizing the ability of the ammonia to escape the reactor with a modified cap design, the process removal efficiency improved from 2% to 29% in just 150 min of reaction.

Lead was used as a surrogate for metals as the PIMA process has previously been demonstrated to remove metals efficiently [11,12]. For simulated leachate, all lead-spiked samples had starting concentrations between 0.03 and 0.35 mg/L. After 16 h of PIMA treatment, all samples were at or below the method detection limit of 0.088 μg/L. Most of the removal was found to occur in the first few hours of treatment (Fig. 2); it should be noted that for low initial starting concentrations, the lead removal percentage was lower due to the starting concentration being so close to the method detection limit. The results suggest that the lead is either co-precipitated out of solution or plated out on the surface of the iron reactant.

The next set of experiments involved simulated leachates that contained mixtures of all target contaminants. These experiments were conducted at 16 h of treatment. Results are reported in Table 4. Removal efficiencies achieved for ammonia and lead in the simulated mixtures were similar to the individual scoping tests, but the COD removal was slightly lower than the individual tests. The presence of competing constituents (i.e. ammonia, lead, etc.) in the mixture likely explains the lower COD removal efficiency. More contact time may be necessary to counteract this mass transport limitation or differential constituent affinity for the reactant. This observation may have implications on real leachate tests, particularly if constituents compete for reaction sites with less reactive species. No experiments were conducted beyond 24 h of contact due to excessive heat generated from the UV lamp, despite the cooling process.

#### 3.2. Real leachate tests with PIMA

Simulated leachates do not contain hardness, microorganisms, foam, color, odor, and natural organic materials (NOM), so actual leachate samples were tested for removal of COD, BOD<sub>5</sub>, ammonia, and lead in the presence of the other constituents found in natural leachate. The results of testing for COD removal efficiency

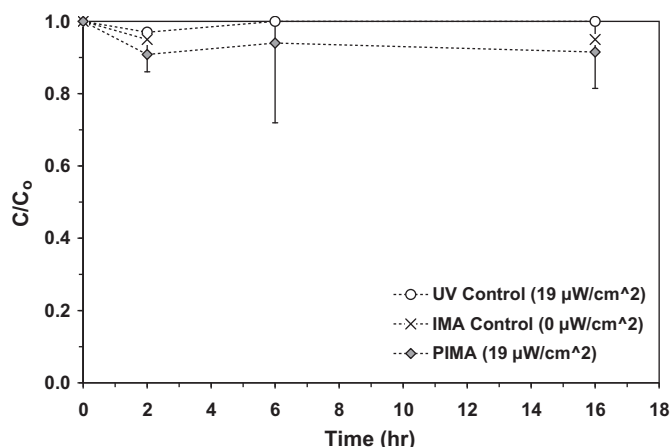


Fig. 3. PIMA test results on real leachate with  $COD_0 = 2950$  mg/L.

are shown in Fig. 3. The highest removal of COD was observed to be 10%, while for  $BOD_5$ , the highest removal was 20%. These values are lower than the 40–60% removal values recorded for the simulated leachates under similar conditions. Two possible explanations for the lower removal efficiency are the color (>500 NTU) and turbidity (>45 NTU) of the real leachate, Turbidity lowers the UV penetration into the bulk solution. Pre-filtration would be expected to increase the removal efficiency of processes involving UV by reducing the scatter caused by turbidity particulates on the effective radiation intensity. However, after filtration with a  $0.45 \mu\text{m}$  filter, no change in process removal efficiency was noted.

The real leachate samples were characterized by a very dark brown color, even after filtration, suggesting that the organic color may be responsible for this loss in treatment efficiency. After 4 h of treatment, the PIMA process was able to reduce the raw leachate color from greater than 500 PCU to 10–60 PCU (Table 4). These results suggest that the organic color may have been converted to non-chromophoric organic intermediates, without completely mineralizing them. In that case, they would still contribute to the COD concentration, which would lead to the reduced degradation noted.

From the results of the simulated leachate experiments, lead was expected to have the highest removal efficiency. However the average initial concentration of lead in the raw leachate was very low (<0.003 mg/L), and none of the simulated leachate experiments were performed at such low initial levels. The best removal achieved during real leachate tests with lead after 16 h of treatment was 93%, which comports with the results from prior work indicating that low levels of lead are not removed preferentially as they appear to be with larger concentrations. This mechanism needs further investigation.

To gain a better understanding of the lead removal mechanism, the amount of iron reactant was varied to observe the effect on lead removal. Lowering the amount of iron from 2.0 g (16.4 g/L) to 1.0 g (8.2 g/L) actually reduced the removal efficiency from 66% to 46%, but lowering it further to 0.5 g (4.1 g/L) showed the best removal efficiency (93%), suggesting that the amount of iron reactant can be optimized to improve performance. This effect is also seen with respect to ammonia (Table 4). The PIMA process performed slightly better in the real leachate compared to the simulated leachate because less iron reactant was used and the UV intensity was higher for the real leachate test. None of the experiments with real leachate used pH adjustment or reactor modifications to maximize ammonia removal.

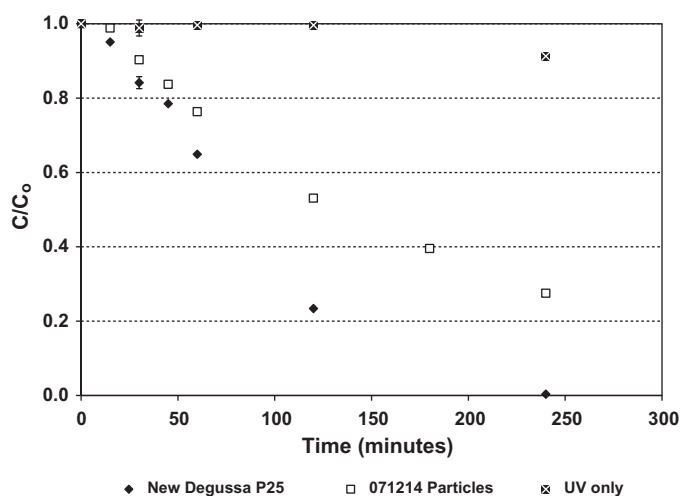


Fig. 4. Photocatalytic scoping tests for COD removal ( $COD_0 = 1060$  mg/L) using commercially available and laboratory synthesized  $TiO_2$  particles at  $1960 \mu\text{W}/\text{cm}^2$ .

### 3.3. Tests with $TiO_2$ photocatalysis on simulated leachate

For comparison, data was gathered in parallel using  $TiO_2$  photocatalysis. The results shown in Fig. 4 indicate that the  $TiO_2$  particles are capable of reducing the COD concentration in simulated leachates from a starting concentration of 1060 mg/L to below the permissible sewer discharge limit for the City of Boca Raton (800 mg/L) in approximately 45–60 min under the experimental conditions tested. After 4 h of treatment with UV/ $TiO_2$ , 94–99% of the original COD content was removed by the process. This agrees with [22,36] who also reported COD removal by  $TiO_2$  photocatalysis is possible in landfill leachates (refer to Table 1). Using first order kinetics, the commercially available Degussa P25 ( $k = 1.41 \text{ h}^{-1}$ ;  $r^2 = 0.938$ ) performed slightly better than the laboratory synthesized  $TiO_2$  particles ( $k = 0.332 \text{ h}^{-1}$ ;  $r^2 = 0.997$ ). This may be due to the less uniform particle size of the laboratory synthesized particles.

To evaluate the benefits of recycling the  $TiO_2$  particles, the photocatalysts were recovered and reused multiple times. Fig. 5 shows the results for Degussa P25 particles, which indicate that very little difference is observed after being reused three times. The first order decay coefficients for COD removal decreased only slightly from  $k = -1.41 \text{ h}^{-1}$ ;  $r^2 = 0.938$  to  $k = -0.740 \text{ h}^{-1}$ ;  $r^2 = 0.953$

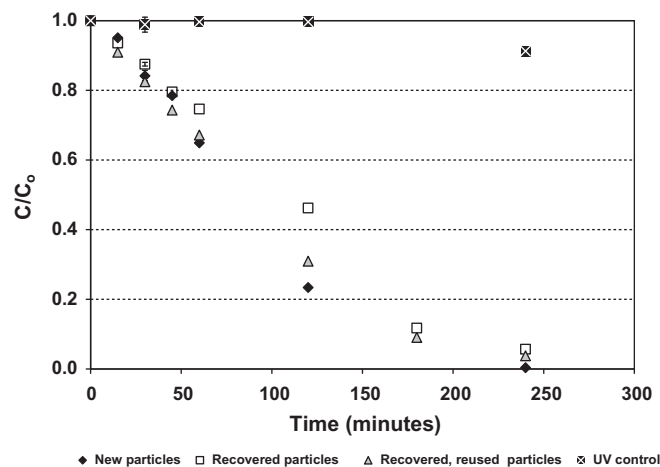


Fig. 5. Photocatalytic scoping tests for cod removal ( $COD_0 = 1060$  mg/L) using new and used photocatalyst particles at  $1960 \mu\text{W}/\text{cm}^2$ .

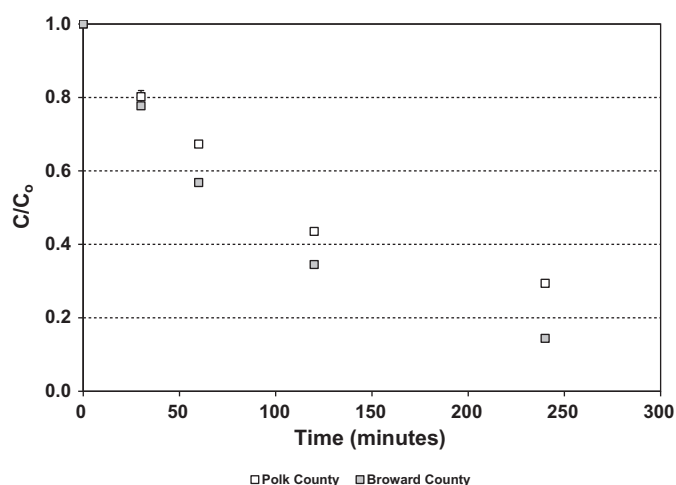


Fig. 6. COD removal efficiency of photocatalysis using Broward County and Polk County leachate at 1400–1960  $\mu\text{W}/\text{cm}^2$ .

and  $k = -0.850 \text{ h}^{-1}$ ;  $r^2 = 0.978$ , after two uses and three uses, respectively. The UV control process showed essentially no removal during the same period.

To investigate the BOD removal under similar conditions, a starting concentration of 490 mg/L was simulated using a mixture of glucose and glutamic acid. After 4 h of treatment, 41% removal was achieved using 4.0 g/L of  $\text{TiO}_2$  particles. For the BOD experiments, only three sample times were collected (0, 1, and 4 h), and the first order kinetics are  $k = -0.089 \text{ h}^{-1}$ ;  $r^2 = 0.99$ .

Scoping tests for ammonia removal showed positive results (Table 5). The simulated leachate using an initial concentration of 1425 mg/L as  $\text{NH}_3\text{-N}$  achieved 51% removal in 4 h with a photocatalyst dose of 4 g/L ( $k = -0.175 \text{ h}^{-1}$ ;  $r^2 = 0.994$ ). The removal was reduced to 23% when the simulated leachate included the other constituents including COD, BOD, and lead in similar concentrations to those measured in the real leachate samples from Broward County. This is further evidence that constituents are likely competing for photoactive sites or that one of the other constituents exhibits a preferential affinity for the photocatalyst. These results require further investigation. No experiments were conducted with lead or color, but these parameters were evaluated using real leachate samples.

#### 3.4. Real leachate tests with $\text{TiO}_2$ photocatalysis

The first experiments conducted with real leachate used samples collected from the Broward County Central Disposal Landfill and from the Polk County Landfill. Even though the starting COD concentrations for the first several experiments varied from 140 to 330 mg/L, which was considered low for leachate (<400 mg/L), the photocatalytic process performed similarly with leachates from both landfills, as shown in Fig. 6. Removal exceeded 70% after 4 h of contact time. The Broward County leachate had a higher first order rate constant  $k = -0.49 \text{ h}^{-1}$ ;  $r^2 = 0.996$  compared to the Polk County leachate ( $k = -0.31 \text{ h}^{-1}$ ;  $r^2 = 0.968$ ), which had a higher starting concentration ( $\text{COD}_0 = 330 \text{ mg/L}$ ). As with the PIMA process, the effect of pre-filtration was also evaluated, and results are presented in Fig. 7 for the Polk County leachate. No differences were observed between filtered and unfiltered samples; however, it is important to note that the real leachate matrix was of very low strength ( $\text{COD}_0 = 140 - 330 \text{ mg/L}$ ) in this experiment. The possible reduction of COD associated with adsorption onto the photocatalyst particle surface was investigated by loss on ignition tests, which showed essentially the same mass before and after heating in a muffle furnace at 550 °C.

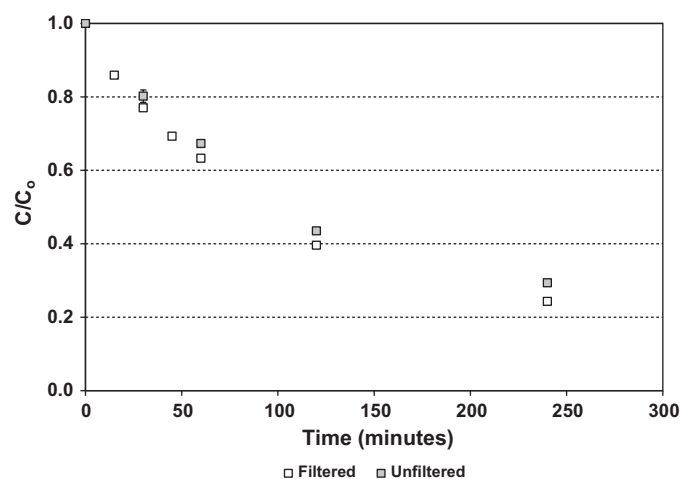


Fig. 7. Effect of filtration on the cod removal efficiency of photocatalysis of Polk County leachate at 1960  $\mu\text{W}/\text{cm}^2$ .

BOD testing with real leachate from Broward County revealed 34% removal in 6 h. These results match closely with the expected removal from the simulated leachate BOD experiments (Table 5). Ammonia testing revealed similar removal compared to the simulated leachate mixtures, in which the first order decay constants were essentially the same. These similar results were found when varying the  $\text{TiO}_2$  concentration based on the COD loading (g  $\text{TiO}_2$  per g COD basis) rather than volumetric loading (g  $\text{TiO}_2$  per L). The lead results were inconclusive because the initial concentration in the real leachate was below detection. Color was removed by at least 90%, but the results for the initial color were difficult to interpret due to the large dilution ratio and the presence of very fine  $\text{TiO}_2$  particulates, even after pre-filtration.

#### 4. Conclusion

The objective of this research is to evaluate the process removal efficiency of PIMA and photocatalysis with  $\text{TiO}_2$  on typical landfill leachate constituents of COD,  $\text{BOD}_5$ , color, ammonia, and lead at the concentrations commonly found in landfill leachate. Both processes show encouraging results in treatment of leachate. The PIMA process showed promising performance for removal of organics, achieving 50% COD removal in 24 h and 40%  $\text{BOD}_5$  removal in 16 h. Removal of ammonia was found to require pH adjustment. Using lead as a surrogate for other heavy metals, greater than 92% lead removal was observed in 4 h with 3-log lead removal in 16 h, which corroborates with previous efficacy studies with other heavy metals such as Hg, Ni, Cd, and oxyanions of As, Cr, and V [11,12]. Removal capacities compare favorably to other well-developed advanced oxidation processes. When PIMA was applied to real leachates, the process was found to remove lead and color effectively (>90%), while removing COD and  $\text{BOD}_5$  less effectively (<50%) in 16–24 h of contact time. It was also found that the PIMA process may be capable of removing ammonia with pH adjustment into the alkaline range (pH > 10). It still remains to be seen if PIMA can be shown to be a catalytic process, but at the conditions tested in this study, the predicted contact times (10–200 h) are at least one order of magnitude higher than those measured using  $\text{TiO}_2$  photocatalysis (3–37 h).

$\text{TiO}_2$  photocatalysis was more rapid than the PIMA process. For  $\text{TiO}_2$  photocatalysis with simulated and real leachates, COD removal was measured on the order of minutes instead of hours compared to the PIMA process, and 100% mineralization of COD to carbon dioxide and water was observed with simulated leachates. The photocatalytic particles could be recovered effectively

(80–86%), and no loss in removal efficiency was observed after 4+ uses. It was also determined that pre-filtration may not be necessary, particularly for low strength leachates, although, it may be desired if the initial color inhibits UV penetration. In tests with real leachate, the TiO<sub>2</sub> process achieved up to 86% conversion of refractory COD by changing the BOD<sub>5</sub>/COD ratio from 0.09 to 0.14, which is considered partially biodegradable [37,38]. Other notable results include up to 71% removal of ammonia without pH adjustment and up to 90% color removal with detention times between 4 and 6 h, in field samples. From these bench scale results, both PIMA and photocatalytic oxidation technologies show promise as effective leachate management strategies.

At this stage, there remain issues of scale to investigate. As a result, a pilot scale system will be tested at one of the landfill facilities to determine whether the technology is cost effective, which is difficult to predict from the bench scale experiments. The impact of variations in flow, water quality and detention time need to be projected based on the results of the next phase of research. For example, based on the literature, the expectation was for much higher concentrations of constituents in the leachate. The landfill sites varied, which impacted process efficiency. The next phase will evaluate the impact of this variability of the technologies.

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## References

- [1] M. Åkesson, P. Nilsson, Seasonal changes of leachate production and quality from test cells, *Journal of Environmental Engineering* 123 (9) (1997) 892–900.
- [2] B. Calli, B. Mertoglu, B. Inanc, Landfill leachate management in Istanbul: applications and alternatives, *Chemosphere* 59 (6) (2005) 819–829.
- [3] H.L. Hickman, *American Alchemy – The History of Solid Waste Management in the United States*, Forester Press, Santa Barbara, 2003.
- [4] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and longterm composition of MSW landfill leachate: a review, *Critical Reviews in Environmental Science and Technology* 32 (4) (2002) 297–336.
- [5] I.S. Oweis, R.P. Kehra, *Geotechnology of Waste Management*, 2nd Ed., PWS Publishing Company, Boston, 1998.
- [6] D.R. Reinhart, T. Townsend, *Landfill Bioreactor Design & Operation*, Lewis Publishers, Boca Raton, FL, 1998.
- [7] R.A. Statom, G.D. Thyne, J.E. McCray, Temporal changes in leachate chemistry of a municipal solid waste landfill cell in Florida, USA, *Environmental Geology* 45 (2004) 982–991.
- [8] G. Tchobanoglous, F. Kreith, *Handbook of solid waste management*, 2nd Ed., McGraw-Hill Handbooks, New York, 2002.
- [9] M.L. Ward, G. Bitton, T.G. Townsend, M. Booth, Determining toxicity of leachates from Florida municipal solid waste landfills using a battery of tests approach, *Environmental Toxicology* 17 (3) (2002) 258–266.
- [10] D.E. Meeroff, R. Teegavarapu, Interactive Decision Support Tool for Leachate Management, Final Report for the William W. Bill Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL, Report # 0832028 (2010).
- [11] D.E. Meeroff, J.D. Englehardt, L.A. Echegoyen, C.A. Woolever, T. Shibata, Development of an energy-assisted iron-mediated aeration process for in situ groundwater applications, *Journal of Environment Engineering* 132 (7) (2006) 747–757.
- [12] J.D. Englehardt, D.E. Meeroff, L.A. Echegoyen, F. Raymo, T. Shibata, Oxidation of aqueous EDTA and associated organics and coprecipitation of inorganics by ambient iron-mediated aeration, *Environmental Science and Technology* 41 (1) (2007) 270–276.
- [13] C.Y. Kwan, W. Chu, Photodegradation of 2,4-dichlorophenoxyacetic acid in various iron-mediated oxidation systems, *Water Research* 37 (2003) 4405–4412.
- [14] H.B. Lockhart, R.V. Blakely, Aerobic photodegradation of Fe(III)-(ethylenedinitrilo)tetraacetate (ferric EDTA), *Environmental Science and Technology* 9 (1975) 1035–1038.
- [15] R. Frank, H. Rau, Photochemical transformation in aqueous solution and possible environmental fate of ethylenediaminetetraacetic acid (EDTA), *Ecotoxicology and Environment Safety* 19 (1990) 55–63.
- [16] F.G. Kari, S. Hilger, S. Canonica, Determination of the reaction quantum yield for the photochemical degradation of Fe(III)-EDTA: implications for the environmental fate of EDTA in surface waters, *Environmental Science and Technology* 29 (4) (1995) 1008–1017.
- [17] S. Metsärinne, T. Tuhkanen, R. Aksela, Photodegradation of ethylenediamine tetraacetic acid (EDTA) and ethylenediamine disuccinic acid (EDDS) within natural UV radiation range, *Chemosphere* 45 (6–7) (2001) 949–955.
- [18] B. Nowack, L. Sigg, Dissolution of Fe(III) (hydro)oxides by metal-EDTA complexes, *Geochimica et Cosmochimica Acta* 61 (5) (1997) 951–963.
- [19] D.C. Schmelling, K.A. Gray, P.V. Kamat, Role of reduction in the photocatalytic degradation of TNT, *Environmental Science and Technology* 30 (8) (1996) 2547–2555.
- [20] M.S. Vohra, A.P. Davis, TiO<sub>2</sub>-assisted photocatalysis of lead-EDTA, *Water Research* 34 (3) (2000) 952–964.
- [21] A.P. Davis, D.L. Green, Photocatalytic oxidation of cadmium-EDTA with titanium dioxide, *Environmental Science and Technology* 33 (4) (1999) 609–617.
- [22] S.P. Cho, S.C. Hong, S.I. Hong, Photocatalytic degradation of the landfill leachate containing refractory matters and nitrogen compounds, *Applied Catalysis B: Environmental* 39 (2002) 125–133.
- [23] A. Hilmi, J.H. Luong, A.L. Nguyen, Utilization of TiO<sub>2</sub> deposited on glass plates for removal of metals from aqueous wastes, *Chemosphere* 38 (4) (1999) 865–874.
- [24] R. Stanforth, R. Ham, M. Anderson, R. Stegmann, Development of a synthetic municipal landfill leachate, *Journal Water Pollution Control Federation* 51 (7) (1979) 1965–1975.
- [25] R.K. Rowe, J. VanGulck, S.C. Millward, Biologically induced clogging of a granular medium permeated with synthetic leachate, *Journal of Environmental Engineering and Sciences* 1 (2002) 135–156.
- [26] D.E. Meeroff, F. Gasnier, C.T. Tsai, Investigation of Energized Options for Leachate Management: Year Two Tests of Advanced Oxidation Processes for Treatment of Landfill Leachate, Final Report Year 2 for the William W. Bill Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL, Report # 0632018 (2008). [http://floridacenter.org/publications/Meeroff\\_Year2Investigation\\_of\\_Energized\\_Options.pdf](http://floridacenter.org/publications/Meeroff_Year2Investigation_of_Energized_Options.pdf).
- [27] F. Gasnier, Photochemical Iron-Mediated Aeration Treatment of Landfill Leachate. A Masters Thesis. Florida Atlantic University, Boca Raton, FL (2007).
- [28] APHA, AWWA, and WEF, Standard Methods for the Examination of Water and Wastewater, 21st Edition, American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC, 2005.
- [29] G. Li Puma, J.L. Khor, A. Brucato, Modeling of an annular photocatalytic reactor for water purification: oxidation of pesticides, *Environmental Science and Technology* 38 (13) (2004) 3737–3745.
- [30] G. Li Puma, V. Puddu, H.K. Tsang, A. Gora, B. Toepfer, Photocatalytic oxidation of multicomponent mixtures of estrogens (estrone (E1), 17β-estradiol (E2), 17α-ethynylestradiol (EE2) and estriol (E3)) under UVA and UVC radiation: photon absorption, quantum yields and rate constants independent of photon absorption, *Applied Catalysis B: Environmental* 99 (2010) 388–397.
- [31] J.S. Kim, H.Y. Kim, C.H. Won, J.G. Kim, Treatment of leachate produced in stabilized landfills by coagulation and Fenton oxidation process, *Journal of the Chinese Institute of Chemical Engineers* 32 (5) (2001) 425–429.
- [32] I.W.C. Lau, P. Wang, S.S.T. Chiu, H.H.P. Fang, Photoassisted Fenton oxidation of refractory organics in UASB-pretreated leachate, *Journal of Environmental Sciences* 14 (3) (2002) 388–392.
- [33] Metcalf, Eddy, in: G. Tchobanoglous, F.L. Burton, H.D. Stensel (Eds.), *Wastewater engineering, treatment and reuse*, 4th Ed., McGraw-Hill Companies, New York, 2003.
- [34] H. Suty, C. De Traversay, M. Cost, Applications of advanced oxidation processes: present and future, *Water Science and Technology* 49 (4) (2004) 227–233.
- [35] J.L. de Morais, P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, *Journal of Hazardous Materials* 123 (1–3) (2005) 181–186.
- [36] R. Poblete, E. Otal, L.F. Vilches, J. Vale, C. Fernández-Pereira, Photocatalytic degradation of humic acids and landfill leachate using a solid industrial by-product containing TiO<sub>2</sub> and Fe, *Applied Catalysis B: Environmental* 102 (1–2) (2010) 172–179.
- [37] J. García Montano, N. Ruiz, I. Muñoz, X. Domenech, J.A. García Hortal, F. Torrades, J. Peral, Environmental assessment of different photo-Fenton approaches for commercial reactive dye removal, *Journal of Hazardous Materials* 138 (2) (2006) 218–235.
- [38] E. Chamorro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, *Water Research* 35 (2001) 1047–1051.
- [39] M. Sanchez, M.J. Rivero, I. Ortiz, Photocatalytic oxidation of grey water over titanium dioxide suspensions, *Desalination* 262 (2010) 141–146.
- [40] R.P.S. Suri, J.C. Crittenden, D.W. Hand, Removal and destruction of organic compounds in water using adsorption, steam regeneration, and photocatalytic oxidation processes, *Journal of Environmental Engineering* 125 (1999) 897–905.
- [41] X. Huang, M. Leal, Q. Li, Degradation of natural organic matter by TiO<sub>2</sub> photocatalytic oxidation and its effect on fouling of low-pressure membranes, *Water Research* 42 (2008) 1142–1150.
- [42] J. Araña, J.A. Herrera Melián, J.M. Doña Rodríguez, O. González Díaz, A. Viera, J. Pérez Peña, P.M. Marrero Sosa, V. Espino Jiménez, TiO<sub>2</sub>-photocatalysis as a tertiary treatment of naturally treated wastewater, *Catalysis Today* 7 (2002) 279–289.



- [43] I.-H. Cho, K.-D. Zoh, Photocatalytic degradation of azo dye (reactive red 120) in TiO<sub>2</sub>/UV system: optimization and modeling using a response surface methodology (RSM) based on the central composite design, *Dyes and Pigments* 75 (3) (2007) 533–543.
- [44] J. Chen, W.H. Rulkens, H. Bruning, Photochemical elimination of phenols and COD in industrial wastewaters, *Water Science and Technology* 35 (4) (1997) 231–238.
- [45] Y. Nakamura, F. Kobayashi, M. Daidai, A. Kurosumi, Purification of seawater contaminated with undegradable aromatic ring compounds using ozonolysis followed by titanium dioxide treatment, *Marine Pollution Bulletin* 57 (2008) 53–58.
- [46] H. El Hajjouji, F. Barje, E. Pinellie, J.R. Bailly, C. Richard, P. Winterton, J.C. Revel, M. Hafidi, Photochemical UV/TiO<sub>2</sub> treatment of olive mill wastewater (OMW), *Bioresource Technology* 99 (15) (2008) 7264–7269.
- [47] P.A. Pekakis, N.P. Xekoukoulotakis, D. Mantzavinos, Treatment of textile dyehouse wastewater by TiO<sub>2</sub> photocatalysis, *Water Research* 40 (2006) 1276–1286.
- [48] M. Bekbolet, F. Cecen, G. Ozkosemen, Photocatalytic oxidation and subsequent adsorption characteristics of humic acids, *Water Science and Technology* 34 (9) (1996) 65–72.