DISINFECTION OF MUNICIPAL WASTEWATER BY TiO2 PHOTOCATALYSIS WITH UV-A, VISIBLE AND SOLAR IRRADIATION AND BDD ELECTROLYSIS

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ABSTRACT
The efficiency of TiO2 photocatalysis induced by ultraviolet and visible irradiation and salt-free electrolysis over boron-doped diamond electrodes to inactivate total (TC) and fecal (FC) coliforms in secondary treated municipal wastewater was evaluated. Photocatalytic experiments were conducted with two types of titania (Degussa P25 and sulfur-doped catalyst) at loadings in the range 0.1-0.5 g l-1 and three types of irradiation, i.e. artificial UV-A, artificial visible and solar. Electrolysis was conducted in a flow-through cell at anodic current densities of 14.3 and 28.6 mA cm-2 without the addition of auxiliary chemicals. Inactivation followed a first-order kinetic expression with regard to bacteria population and the rate was dependent of the experimental conditions in question. In general, electrochemical disinfection was up to about two orders of magnitude faster than photocatalysis; for instance, TC population decreased to less than 5% of the initial population after 9 and 4 min at 14.3 mA cm-2 and 28.6 mA cm-2 respectively. Similar efficiencies with TiO2 photocatalysis would require at least 30 min of contact time. Interestingly, energy consumption for the electrochemical process was computed to about 0.5 kWh per m3 of treated effluent, well below the respective value for photocatalysis.

KEYWORDS: heterogeneous photocatalysis, electrochemical oxidation, disinfection, boron-doped diamond, wastewater.

1. INTRODUCTION
The disinfection agents commonly used both at drinking water and wastewater treatment plants are chlorine and its related compounds, such as sodium and calcium hypochlorite and chlorine dioxide, with chlorine being by far the most widely used disinfectant. However, in the early 1970s, it was found that chlorine reacts with the natural organic matter present in water and wastewater to produce various undesirable chlorinated disinfection by-products (DBPs) (Crittenden et al., 2005). Of the wide variety of chlorinated DBPs formed, trihalomethanes and haloacetic acids are of primary concern since many of them have been found to be carcinogenic and/or mutagenic. In addition, chlorination of water has been associated with taste and odor problems caused not only by chlorine itself but also from odorous disinfection by-products (Freuze et al., 2005). Moreover, wastewater disinfection by chlorine requires subsequent de-chlorination of the treated effluent to minimize the potential toxic effects of low level chlorine residuals on aquatic organisms as well as to prevent the formation of DBPs in the receiving water bodies (Crittenden et al., 2005).

Because of the concerns over the formation of DBPs, ongoing research focuses on the development of alternative disinfection methods. In recent years, advanced oxidation processes (AOPs) have been successfully employed for the degradation of a wide range of organic micro-pollutants, as well as for the disinfection of water and wastewaters (Behnajady
et al., 2008a; Dincer et al., 2008; Parsons, 2004). AOPs can be broadly defined as aqueous phase oxidation methods based primarily on the intermediacy of hydroxyl radicals HO• in the mechanism leading to the destruction of the target pollutants to mineral end products such as CO2, H2O and inorganic ions. Important AOPs include ozonation, electrochemical oxidation, UV irradiation alone or in combination with H2O2 and TiO2 photocatalysis amongst others.

In particular, heterogeneous photocatalysis based on semiconducting materials such as TiO2, ZnO and CdS and UV or visible light has received enormous attention for environmental remediation, i.e. water and wastewater clean-up, air pollution abatement and disinfection (Behnajady et al., 2008b).

On the other hand, electrochemical oxidation has been widely investigated for wastewater treatment over electrodes made of several different materials such as graphite, Pt, TiO2, SnO2, IrO2, RuO2, PbO2 and several Ti-based alloys (Chen, 2004). In recent years, a new type of electrode material, namely boron-doped diamond (BDD) has received growing attention for pollutants oxidation since it exhibits significant chemical and electrochemical stability, good conductivity as well as it achieves increased rates of effluent mineralization with very high current efficiencies (Martinez-Huitie and Ferrero, 2006). The high over-potential for oxygen evolution and the low adsorption density of hydroxyl radicals onto the BDD surface, allow favorable conditions for effective oxidation: a very high concentration of hydroxyl radicals can be reached in a thin liquid film near the electrode surface where the organic compounds are mineralized.

The aim of the present work was to study the application of TiO2 photocatalysis under different light sources and electrochemical oxidation over BDD electrodes for the disinfection of secondary treated municipal wastewater. Various experimental conditions were tested and the populations of total and fecal coliforms were monitored versus time in order to assess the disinfection efficiency.

2. MATERIALS AND METHODS

2.1. Wastewater samples

The effluent was taken from the outlet of the activated sludge process at the municipal wastewater treatment plant of Chania, W, Crete, Greece. The samples were transferred to the laboratory immediately after collection and subjected to advanced treatment. The effluent had 30-40 mg l⁻¹ total solids, 4.7-7.2 mg l⁻¹ total organic carbon, neutral pH, 2.2 10⁴-5 10⁵ CFUs/100ml total coliforms (TC) and 10⁴-1.3 10⁵ CFUs/100ml fecal coliforms (FC).

2.2. Photocatalytic experiments

Setup for runs with UV-A irradiation

UV-A irradiation was provided by a 9 W lamp (Radium Ralutec, 9W/78, 350-400 nm). Photocatalytic experiments were conducted in an immersion well, batch type, laboratory scale thermostated photoreactor, purchased from Ace Glass (Vineland, NJ, USA) which is described in detail elsewhere (Kritikos et al., 2007).

Setup for runs with artificial visible irradiation

Visible irradiation was provided by nine fluorescent lamps (Osram, 58W/765). The lamps were placed parallel to each other in a rectangular frame which was positioned 30 cm above the reaction vessel.

Setup for runs with solar irradiation

Solar irradiation experiments were conducted at the University campus (35° 53’ latitude, 24° 08’ longitude) in the afternoon hours of October and November. The sun radiation intensity was between 134 and 650 W m⁻².
Procedures

A 400 ml sample was slurried with the appropriate amount of titania (0.1-0.5 g l⁻¹) and magnetically stirred for 60 min in the dark to reach equilibrium. Irradiation was then provided to initiate disinfection under continuous stirring and aeration. Two photocatalysts were tested, namely: (i) Aeroxide P25 supplied by Degussa AG (75:25 anatase:rutile, 21 nm particle size, 50 m² g⁻¹ surface area) and (ii) titania doped with sulfur (S/TiO₂) supplied by Toho Titanium Ltd (Japan). All experiments were run in triplicate and mean values are quoted as results.

2.3. Electrolytic experiments

Experiments were conducted in a unit consisting of a DiaCell® (type 100) single-compartment electrooxidation cell manufactured by Adamant Technologies (Switzerland) and the corresponding power supply, a 20 l plastic tank equipped with a stainless steel spiral coil for cooling, a 50 µm filter, a peristaltic pump, and a flow meter. Both electrodes are made of a thin film of boron-doped diamond (BDD) supported on silicon. The electrodes are circular and their surface area was 70 cm² and the distance between them 10 mm. Ten liters of effluent were batch loaded in the tank and continuously recirculated in the cell through the peristaltic pump operating at a flowrate of 0.01 m³ min⁻¹. Disinfection experiments were conducted without the addition of any supporting electrolyte at current intensities of 1 and 2A (these correspond to current densities of 14.3 and 28.6 mA cm⁻²) and voltage of 27.5 and 48V respectively. All experiments were run in triplicate and mean values are quoted as results.

2.4. Analytical methods

At specific time intervals aliquots of the treated samples were withdrawn and analyzed for TC and FC populations employing the serial dilution-membrane filter technique. A hundred milliliters of diluted or undiluted samples were filtered with 0.45 µm pore diameter filters (Whatman) and placed over the surface of the appropriate nutrient medium (m-Endo TC Broth, Millipore and M-FC with rosolic acid FC broth, Millipore) in 45 mm Petri dishes. After incubation at 35°C for TC and 45°C for FC for 24 h, the numbers of colonies were counted and the results were expressed in terms of colony forming units of the microorganisms per 100 mL of water sample (CFUs/100ml).

3. RESULTS AND DISCUSSION

3.1. Effect of titania on bacteria cultivability in the dark

In preliminary experiments, the effluent was slurried with P25 or S/TiO₂ particles at 0.1 and 0.25 g l⁻¹ concentrations and stirred for 60 min in the dark. As seen in Figure 1, the cultivable bacteria population decreased in all cases and this was more pronounced at increased catalyst concentrations. In general, the population decreased substantially during the first 20-30 min of contact beyond which it remained relatively stable.

These results imply that bacteria interacted with the catalyst surface and this interaction resulted in partial degradation of cell membrane integrity and consequently loss of cultivability. However, this does not necessarily imply that titania was toxic to bacteria as, in such case, complete destruction would have occurred. In a recent study (Paleologou et al., 2007), a similar effect was observed concerning E. coli loss of viability during its contact with P25 particles in the dark; nonetheless, other studies report that titania has no detrimental effect on the viability of E. coli (Paleologou et al., 2007) or, indeed, other species (Daneshvar et al., 2007).

3.2. Photocatalytic disinfection with ultraviolet irradiation

Figure 2 shows changes in TC and FC populations during UV-A irradiation in the presence of P25 particles at three catalyst loadings. Comparing Figures 1 and 2, the beneficial role of UV-A/TiO₂ photocatalysis in disinfection is evident.

It is generally accepted that hydroxyl radicals HO⁻ are the main oxidative species responsible for the bactericidal action of TiO₂ photocatalysis. However, there is also some evidence that
other reactive oxygen species generated photocatalytically, such as superoxide radicals $\text{O}_2^{-}$, perhydroxyl radicals $\text{HO}_2^{\cdot}$ and hydrogen peroxide $\text{H}_2\text{O}_2$ also contribute to the photocatalytic inactivation (Cho et al., 2004). Cell membrane is the crucial site of attack for effective inactivation regardless the oxidative species involved in the process. It has been proposed that the cell wall is initially damaged, followed by a progressive damage of the cytoplasmic membrane and intracellular components, thus eventually leading to loss of essential cell functions (Sunada et al., 2003).

![Figure 1. Effect of titania particles on TC and FC populations in the dark](image1)

![Figure 2. Photocatalytic destruction of (a) TC and (b) FC under UV-A irradiation with P25 particles at 0.1, 0.25 and 0.5 g l$^{-1}$](image2)

Increasing titania loading from 0.1 to 0.5 g l$^{-1}$ improved TC destruction which was over 96% after 30 min of irradiation; interestingly though, the opposite behavior was observed for FC destruction which decreased with increasing loading in the same range. A feasible explanation would involve the effect of sample turbidity in conjunction with the relative ratio of catalyst active sites to bacterial population. As turbidity increases with catalyst loading, particle clusters are formed and the light is blocked from reaching the catalyst surface, thus reducing efficiency. However, as TC population is about 4-5 times greater than FC population, the former has still proportionately greater chance than the latter for inactivation.

Bacterial inactivation usually follows a first order kinetic expression:

\[
\frac{N_t}{N_0} = e^{-kt} \iff \ln \frac{N_t}{N_0} = -kt \quad (1)
\]

where $N_t$ and $N_0$ are the populations at time $t$ and zero, respectively and $k$ is the inactivation rate constant. Table 1 summarizes $k$ values computed from the data of Figure 2 alongside the respective coefficients of linear regression.
3.3. Photocatalytic disinfection with visible light

Figure 3 shows changes in TC and FC populations during artificial visible irradiation in the presence of P25 or S/TiO₂ particles at two catalyst loadings, while Table 1 also shows the respective rate constants. At the conditions in question, inactivation induced by the P25/UV-A system was far more effective than the P25/Vis one. For instance, the average (over the common catalyst loadings employed, i.e. 0.1 and 0.25 g l⁻¹) inactivation constant for either population was 0.05-0.07 min⁻¹ under ultraviolet irradiation and 0.01-0.02 min⁻¹ under visible irradiation. This was expectedly so as titania with a band gap energy of 3.2 eV is activated at wavelengths below 385 nm. In this view, it was decided to test the S/TiO₂ catalyst as doping titania with non-metallic elements such as carbon, nitrogen and sulfur is capable of extending its absorbance wavelength range in the visible region (Thomson and Yates, 2006).

Interestingly, S/TiO₂ was nearly equally effective to P25 with the average inactivation constant being 0.01 min⁻¹ for either population.

In a final photocatalytic experiment, solar irradiation was employed with 0.1 g l⁻¹ S/TiO₂ and the results are shown in Table 1. Inactivation was remarkably faster than the respective runs with artificial visible irradiation and almost equally effective to the runs with P25/UV-A. Although direct comparison of the three photocatalytic processes is not fair given that different experimental setups (e.g. configuration and intensity of light source) were employed, these results imply that the use of renewable energy may form the grounds for a cost-effective disinfection technique.

![Figure 3. Photocatalytic destruction of (a) TC and (b) FC under artificial visible irradiation with P25 or S/TiO₂ particles at 0.1 and 0.25 g l⁻¹](image)
3.4. Electrolytic disinfection over BDD electrodes

In a preliminary control experiment, 10 l of effluent were recirculated in the electrooxidation unit for 60 min. It was found that TC population remained practically unchanged after 60 min, thus showing that the bacteria did not suffer cell damage due to mechanical stress.

Figure 4 shows changes in TC population during BDD electrolysis as a function of applied current. Over 96% inactivation was recorded after 9 min at 1A, while 99.9% destruction occurred after 6 min at 2A. From eqn (1), the respective inactivation constants are computed equal to 0.36 (0.999) and 0.99 (0.967) min⁻¹ at 1 and 2A (numbers in brackets show linear fitting coefficients). These values are an order of magnitude greater than those reported in the literature (Polcaro et al., 2007) for the inactivation of *E. coli* and enterococci over BDD electrodes with similar current densities, thus showing the increased disinfection efficiency of the treatment unit employed in the present study.

![Figure 4. Electrolytic destruction of TC at 1 and 2A applied current](image)

The strong bactericidal action observed at the BDD anode can be attributed to surface and bulk processes: at the electrode/solution interface high concentration of hydroxyl radicals, as well as local acid pH values can lead to cell death, whereas in the bulk of the solution the disinfection can be attributed to electrogenerated oxidizing species. Moreover, it has been found that electric fields are themselves harmful to the cells of the microorganisms due to the irreversible permeabilization of cell membrane. It should be emphasized that electrooxidation using traditional anodes (such as Pt and RuO₂) exhibits high disinfection efficiencies only when the solution contains chloride ions. Under electrolytic conditions, chloride ions lead to the formation of active chlorine species such as chlorine and hypochlorite, thus explaining the disinfection efficiency of the traditional anodes. However, in the present experiments, no chloride ions were added at the wastewater prior to the electrooxidation experiments.

3.5. Cost comparison between photocatalytic and electrolytic disinfection

Comparing BDD electrolysis and TiO₂ photocatalysis, the former is at least 1-2 orders of magnitude faster than the latter in terms of inactivation rates. More importantly though, one has to compare the energy consumption required to achieve a common disinfection level with either process. For e.g. ≥95% TC destruction, BDD electrolysis would take 4 and 9 min at 2 and 1A respectively and this corresponds to 0.65 and 0.4 Kw m⁻³ of treated effluent. The respective value for the UV-A/TiO₂ system (30 min with 0.5 g l⁻¹ P25 catalyst) is 11.3 kW m⁻³.
4. CONCLUSIONS

The conclusions drawn from the present study can be summarized as follows:

- AOPs like heterogeneous photocatalysis and electrolysis can potentially be employed for wastewater disinfection whose efficiency is dictated by the specific operating conditions in question.
- The efficiency of TiO$_2$ photocatalysis appears to depend on the source of irradiation as well as the photocatalyst loading, while electrolyte-free electrochemical disinfection over BDD electrodes depends on the applied current.
- Disinfection by BDD electrolysis is up to about two orders of magnitude faster than photocatalysis.
- Energy consumption for the electrolytic treatment is far lower than that for photocatalysis. However, the latter may become an economically attractive option considering the use of sunlight instead of artificial irradiation to drive the process.

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REFERENCES


