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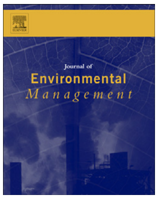

Research article

Photocatalytic degradation of aniline using an autonomous rotating drum reactor with both solar and UV-C artificial radiation

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ABSTRACT

The aim of this work was to evaluate the performance of a novel self-autonomous reactor technology (capable of working with solar irradiation and artificial UV light) for water treatment using aniline as model compound. This new reactor design overcomes the problems of the external mass transfer effect and the accessibility to photons occurring in traditional reaction systems. The UV-light source is located inside the rotating quartz drums (where TiO_2 is immobilized), allowing light to easily reach the water and the TiO_2 surface. Several processes (UV, H_2O_2, Solar, TiO_2, Solar/TiO_2, Solar/TiO_2/H_2O_2 and UV/Solar/H_2O_2/TiO_2) were tested. The synergy between Solar/H_2O_2 and Solar/TiO_2 processes was quantified to be 40.3% using the pseudo-first-order degradation rate.

The apparent photonic efficiency, ζ, was also determined for evaluating light utilization. For the Solar/TiO_2/H_2O_2 process, the efficiency was found to be practically constant (0.638–0.681%) when the film thickness is in the range of 1.67–3.87 μm. However, the efficiency increases up to 2.67% when artificial UV light was used in combination, confirming the efficient design of this installation. Thus, if needed, lamps can be switched on during cloudy days to improve the degradation rate of aniline and its mineralization. Under the optimal conditions selected for the Solar/TiO_2/H_2O_2 process ($[H_2O_2] = 250$ mg/L; pH = 4, $[TiO_2] = 0.65-1.25$ mg/cm^2), 89.6% of aniline is degraded in 120 min. If the lamps are switched on, aniline is completely degraded in 10 min, reaching 85% of mineralization in 120 min. TiO_2 was re-used during 5 reaction cycles without apparent loss in activity (<2%). Quantification of hydroxyl radicals and dissolved oxygen allows a chemical-based explanation of the process. Finally, the UV/Solar/TiO_2/H_2O_2 process was found to have lower operation costs than other systems described in literature (0.67 €/m^3).

1. Introduction

An increasing number of chemicals is being used to meet the social and economic goals of the world community. Many of these chemical substances have shown to be resistant to conventional biological treatments in the urban wastewater treatment plants. As a consequence, these compounds, commonly called "emerging contaminants" (ECs), are accumulating in trace concentrations in water bodies, posing a risk for the natural ecosystems and human health (Aga, 2007). ECs have been analyzed for the last 20 years after the development of analytical methods that were sensitive enough to detect their low concentration levels (López-Roldán et al., 2010; Stuart et al., 2012; Noguera-Oviedo and Aga, 2016).

Among these, aniline (also known as phenilamine) is a liquid organic compound ($C_6H_5NH_2$) used to manufacture a wide variety of products such as polyurethane foam, agricultural chemicals, synthetic paints, antioxidants, stabilizers for the rubber industry, herbicides, varnishes and explosives (Rappoporty, 2007). It is a persistent pollutant commonly produced as a by-product of the petroleum, paper, coal and chemical industries. It is also formed during degradation of water containing antipyrine (Expósito et al., 2017) and thus requires additional treatment prior to disposal. The concentration of aniline varies from 0.6 to 12 μg/L in surface water (Howard, 1989), and from 0.48 to 14 μg/L in shale oil wastewater (Hawtone and Sievers, 1984), reaching a maximum concentration of 6200 μg/L in wastewater from rubber additives factory (Reemtsma and Jekel, 2006). The U.S. Environmental Protection Agency, has established $1{\bullet}10^{-6}$ upper bound lifetime cancer risk (expressed in units of proportion of a population affected per mg of substance/kg body weight-day) in drinking water at concentration

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levels of aromatic amines ranging from 0.2 to 20 ng/L (Jurado et al., 2012).

Advanced oxidation processes have shown to be potential techniques for the removal of ECs and avoiding their introduction in the natural water cycle (Parsons, 2004; Tan et al., 2013; Ribeiro et al., 2015). However, the cost of some of these processes, such as photocatalytic systems, is still too high for use in real wastewater treatment plants. Therefore, to make this technology more competitive, it is necessary to decrease the process cost, for example by using solar energy in autonomous reactors.

Heterogeneous photocatalysis using TiO_2 has been widely used in wastewater treatment with different reactor configurations. Both slurry reactors, where the catalyst is suspended, or other configurations (monoliths, tubular, etc.), where the TiO_2 is supported, have been used (Chong et al., 2010). The disadvantages of TiO_2 are the difficulty in the scale up and the presence of the semiconductor being suspended in water (Domínguez et al., 2015). The latter problem can be solved if TiO_2 is immobilized. There is a wide range of immobilization techniques that enable the easy regeneration of TiO_2 such us Sol-Gel, Previously Made Titania Powder (PMTP), Chemical vapor deposition (CVD) and other deposition techniques including sputtering, thermal treatment and electrophoretic deposition (Doll and Frimmel, 2004; Shan et al., 2010). When the semiconductor is irradiated by light with enough energy to equal or exceed the band gap energy, the electrons are excited and move from the valence band to the conduction band generating electron/hole pairs that can reach the surface of the catalyst to react with the adsorbed molecules. The holes act as oxidants and can react with water to generate hydroxyl radicals or oxidize the organic pollutant adsorbed on the surface (Rodríguez et al., 2010).

However, it is known that the increase of the catalyst film thickness may lead to two important problems: (1) light attenuation due to the absorption by the catalyst and (2) the internal mass transfer become highly significant (Chen et al., 2001; Boiarkina et al., 2011). This is due to the so-called “back-irradiation”: as the coating thickness increases, the charge carriers are produced farther from the liquid-catalyst interface and consequently, they are more vulnerable to recombination (Lin and Valsaraj, 2005). This phenomenon is present in all photoreactors because the light source is located on the external side. To overcome this problem, we have designed and constructed a reactor with rotatory cylinders coated by TiO_2 and lamps located inside the cylinders along the axis. In this way, both the solar light from outside or UV artificial light from inside can reach the water, improving the efficiency.

While other rotating disk photocatalytic reactors have already been reported in the literature for the degradation of organic pollutants in water (Dionysiou et al., 2000, 2002), the location of the lamps in the previous work was quite different, the reactor was smaller and it was not energetically self-sufficient.

The aim of this research was to increase the effectiveness and sustainability of wastewater treatment through the design of a novel self-autonomous reactor technology able to work with solar radiation and artificial UV light if necessary. The addition of H_2O_2 also improves efficiency because H_2O_2 reacts with TiO_2, extending the absorption range by generation of titanium peroxide (TiOH) (Sánchez et al., 2013) which has also studied in this work.

2. Materials and methods

2.1. Materials

Aniline (99%) and 30% hydrogen peroxide (H_2O_2) were purchased from Sigma-Aldrich and Fisher Scientific respectively and were used as received. Sodium persulfate ($Na_2S_2O_8$, 98%) was obtained from Panreac. The pH of the solution was adjusted with H_2SO_4 and NaOH. Deionized water used for preparing the solutions was obtained from a purifying machine (ELGA PURELAB).

The photocatalyst employed was technical grade TiO_2 P-25 Degussa (anatase/rutile = 3.6/1 wt, surface area $56\ m^2\ g^{-1}$, impurities including Al_2O_3, SiO_2, Fe_2O_3 and HCl lower than 0.81%). TiO_2 usually shows two predominant structures: anatase and rutile. While both of these exhibit photocatalytic activity, anatase is the more active phase (Bui et al., 2011), since it can generate more oxidative species than rutile with a lower recombination rate of holes and electrons. Fig. S1 (supplementary material) shows the X-Ray diffraction (XRD) patterns of TiO_2. The crystalline structure is formed by anatase ($2\theta = 25.2°$) and rutile ($2\theta = 27.4°$) with an 87:13 proportion.

Typical SEM image of TiO_2 is exemplified in Fig. S2 (supplementary material). The morphology of TiO_2 consists of aggregated clusters formed by agglomeration of TiO_2 nanoparticles of different sizes.

2.2. Experimental setup and procedure

A rotating drum reactor coated by TiO_2 was used for

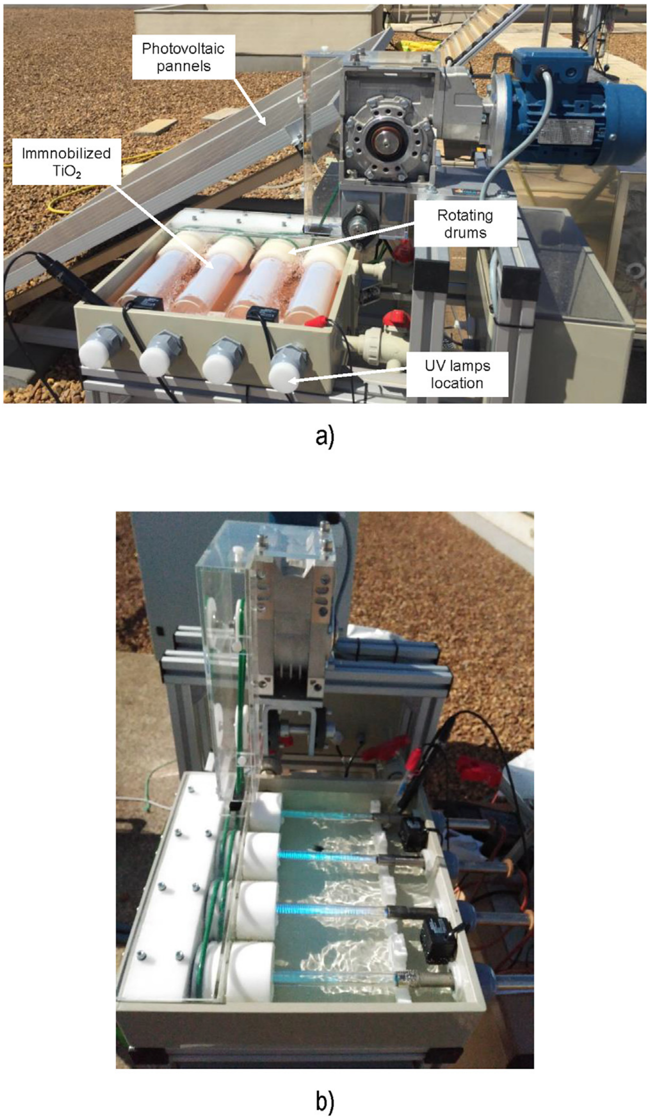

Fig. 1. Experimental setup based on rotary drum reactor. a) Basic configuration with immobilized TiO_2 on drums; b) Detail of lamps switched on.