Analysis of control parameters in a TiO₂/UV reacting system for wastewater treatment containing benzothiazole and aniline

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Abstract Heterogeneous photocatalysis UV/TiO₂ is considered in this work for the treatment of a highly toxic industrial effluent, as an economical and sustainable alternative to conventional processes. To this end, some favorable conditions and modes of operation have been selected to treat an industrial effluent by means of a pilot plant scale tubular reactor. The aqueous effluent contains aniline and benzothiazole at 22.0 mg/L, two contaminants collected in the list of priority substances. The analysis of the different operating variables was performed considering the kinetics of degradation, approaching pseudo-first order kinetics. It was determined that the most favorable conditions for a degradation higher than 95%, after 15 h of reaction and room temperature, was for aniline at pH=12.0 and catalyst dose of 100.0 mg/L with k_{app}=0.39 1/h. Meanwhile, for benzothiazole was at pH=8.0 and a TiO₂ dose of about 100.0 mg/L with k_{app}=0.18 1/h. Finally, it was found that the arrangement of the catalyst in a support was more advantageous than in suspension. In addition, it is not necessary to apply subsequent separation steps and it reduces catalyst losses, which facilitates its industrial implementation.

Keywords: TiO₂, degradation kinetics, aniline, benzothiazole, photocatalysis

1. Introduction

Industrial wastewater considered here is subject to extensive legislation restrictions because it contains organic compounds that are difficult to remove by conventional secondary treatment. Aniline and benzothiazole are typical effluent residues from industries related to the manufacture of textile dyes, accelerants for vulcanization and petroleum refining. These compounds are responsible for causing ecological damage to the aquatic environment, as they cause alterations in the blood, in addition to being carcinogens. Moreover, they are substances that require long periods of biodegradation. Many chemical plants that dump effluents containing substances like aniline and benzothiazole employ conventional treatments, such as Fenton. However, these practices have serious drawbacks in terms of operating costs (hydrogen peroxide, steam). In this way, heterogeneous photocatalysis with TiO₂ is considered as a non-toxic, photochemical stable alternative and more economic for its implementation in small factories (Sánchez *et al*., 2011).

Heterogeneous photocatalysis with TiO₂ is a process based on the excitation of a catalytic solid, by the absorption of light at a wavelength between 365 and 370 nm, in order to produce hydroxyl and hydroperoxyl radicals, as well as superoxide anion. The organic compounds are attacked and oxidized in the presence of these radicals. The overall catalytic process is similar to that of a conventional process, except of the mode of activation, which is photonic rather than thermal (Dominguez *et al*., 2016). Therefore, the final efficiency of the photocatalytic reaction depends on several factors such as pH, catalyst dose, light intensity.

There are scarce articles in the literature related to the degradation of benzothiazole or aniline. Most of them contribute fundamental and theoretical studies of the evolution along time of some of the operational variables (Sánchez *et al*., 1997; Shahrezaei *et al*., 2012; Wols and Hofman-Caris, 2012). Nevertheless, this work, unlike others, aims at the theoretical and experimental analysis of the decomposition kinetics of those compounds contained in aqueous solutions varying the pH, catalyst dose and arrangement, as a preliminary step to a processes design and optimization.

2. Experimental methodology

2.1. Operational system

The pilot plant had an available capacity of 16 L with an intensity of 72 μW/cm². The experimental system consists of a tubular reactor, a mercury lamp and its corresponding power supply, a 20 L mixing tank and a centrifugal pump. The reactor consisted of a titanium pipe with a volume of 1350 mL, length of 45 cm, diameter 7.5 cm and thickness of 5 mm. Besides, the reactor had TiO₂ deposited therein on a structural substrate as a coating, through which the water stream went through. With regard to the layer arrangement, it was oriented vertically with the entrance orifice of the effluent to be treated on the bottom, two orifices on the top and one on the side. The side one was used to insert the probe containing a compact infrared

temperature meter, together with a pyranometer. The two remaining orifices were used to connect/disconnect the pipe with the water to be treated.

A medium pressure mercury lamp (GPH436T5L/4-Eubizz Water) held into a quartz sheath was connected to a power source (Cnlight) of 21 W. The emission spectrum of the lamp was comprised between 185 and 300 nm. The mixture was homogenized at 1750 rpm using a helical mechanical stirrer (Ika RW 20 Digital). A pump (Pool Pump-72512) moved the effluent at a flow rate of 1.0 m^3/h, from the homogenization tank to the reactor.

The tests were carried out by oxidizing 16.0 L of aqueous solutions of aniline and benzothiazole of 20.0 mg/L. The catalyst was dissolved in demineralized water, using an ultrasonic bath (Selecta Ultrasons) for 10 minutes to avoid conglomerates. The reaction mixture was transferred to the mixing vessel, which was protected from light, until it reaches equilibrium adsorption. The pump and stirrer were turned on by keeping the fluid in recirculation and mixing for 1 hour. The pH of the solution was adjusted using dilute NaOH or HCl. All experiments were carried out at room temperature. The samples were filtered with a 0.45 μm membrane (MF-Millipore) for further analysis.

2.2. Analytical methods

The concentration of aniline and benzothiazole was analyzed by a gas chromatograph (Agilent 6890N) coupled to a mass spectrometer (Agilent 5975). The chromatograph was equipped with a 30 cm non-polar phase capillary column. Because the concentrations were very small, the sample was concentrated by extraction with dichloromethane (0.1% diphenylamine) at pH=11.0. Then, 0.4 μl of sample was injected into a stream of helium (1:50) circulating at a flow rate of 1 mL/min. The pH was measured with a pH meter (Knicks 911).

2.3. Reagents

Ttitanium dioxide catalyst utilized was Aeroxide® P25 from Evonik Industries, with an anatase and rutile weight ratio around 80/20, a particle size of 21 nm and a specific surface of 50 m^2/g. For adjusting the pH of the aqueous mixtures, 50% sodium hydroxide and 33% hydrochloric acid were used.

3. Results and discussion

3.1. Catalyst Arrangement

The effect of the catalyst layout on the efficiency of the treatment has been analyzed. Figure 1 shows the results obtained when carrying out degradation of aniline using two ways. Firstly, TiO$_2$ deposited on a matrix (heterogeneous catalysis) and, secondly, as suspension using two dosages (TiO$_2$=20.0 and 60.0 mg/L). The results obtained show that when the catalyst is suspended at a high concentration (TiO$_2$=60.0 mg/L), degradation outputs almost 100% are obtained during the first 15 hours of the reaction. Meanwhile, working at a suspended catalyst concentration around 20.0 mg/L, the aniline is degraded completely at 45 hours.
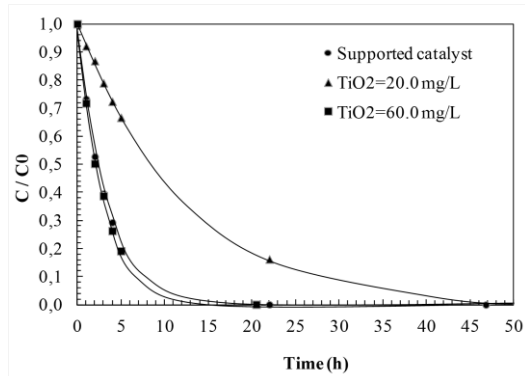

Figure 1. Comparison between two catalytic configurations for the degradation of aniline. Experimental conditions: pH=12.0; UV=72.0 μW/cm^2; P=1.0 atm; T=25.0 ºC.

By employing the suspension catalyst, since it is dispersed in the form of fine particles, catalyst contact is encouraged with the UV light and the contaminating load. However, it is necessary to optimize the catalyst dosage to obtain high yields for lower reaction times.Operating with the deposited catalyst shows a slight whitish darkening of the reaction mixture. This fact makes it difficult for light to penetrate to the active centers of the catalyst. However, in the tests performed, efficiencies similar to those obtained when operating with the catalyst in suspension have been obtained. On the other hand, it must be considered that when conducting with deposited catalyst, the need to employ post-treatment separation steps is reduced, reducing notably the expenses. Then, costs are higher when the reaction is carried out with the suspended catalyst. In addition, deposited catalyst is a safer technique from the environmental point of view, because it reduces the probability of catalyst loss.

3.2. pH effect

The elimination of aniline and benzothiazole is shown in Figure 2, when carrying out the oxidation tests performing at different pH values. The results have been compared, showing that in the case of aniline removal (Fig. 2a) the photocatalytic oxidation rate is favored by operating at alkaline pH values (above pH=12.0). When employing pH values higher than the isoelectric point of the catalyst TiO$_2$ P25 (pH$_{zpc}$=6.5), (Rioja *et al*., 2016), this is negatively charged, which favors the adsorption of the aniline. This phenomenon is due to the fact that aniline presents a protonated amino group in its molecular structure, so that attractive forces are established with the surface of the catalyst, favoring a better performance of the photocatalytic process.As regards the removal of benzothiazole (Fig. 2b), slower oxidation kinetics are obtained than in the case of aniline. The kinetic degradation constants have been estimated (Table 1), proving that they fit first order kinetics. On the other hand, the oxidation of benzothiazole is favored by operating at pH=8.0. The presence of the hydroxyl groups in the benzothiazole molecule causes an increase in the electronic density of its aromatic system, increasing the adsorption capacity of TiO$_2$.
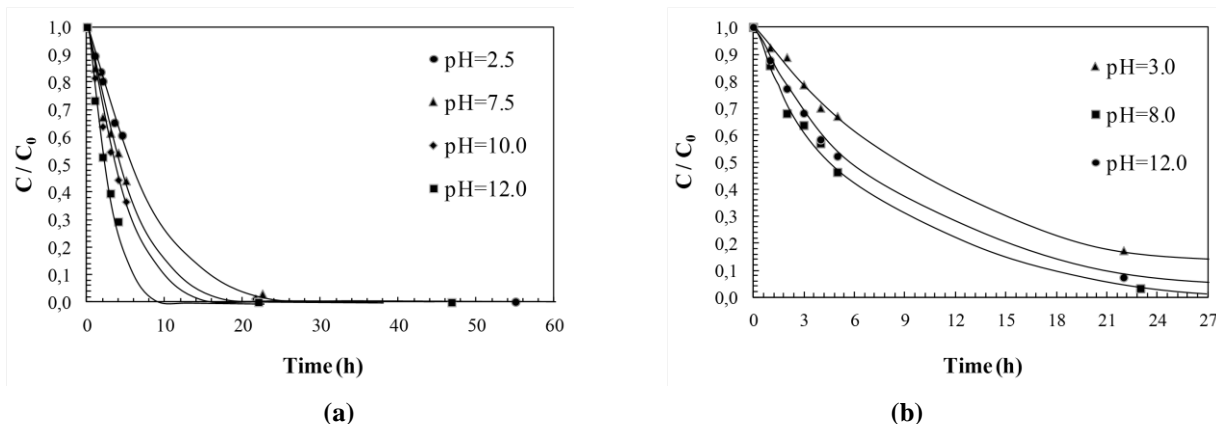
Figure 2. Effect of pH on photocatalytic degradation of aniline (a) and benzothiazole (b) using TiO_2 supported catalyst. Experimental conditions: UV=72.0 μW/cm^2; P=1.0 atm; T=25.0 ºC.

Operating at acidic pH intensifies the condensation reactions that lead to the formation of polyaniline on the lamp (Yang and Bard, 1992). This polymeric compound precipitates, being insoluble in water, whereby it prevents the passage of UV light to the catalyst surface, causing low degradation output.

3.3. Kinetic modeling of the photocatalytic oxidation

The model of Langmuir-Hinshelwood has been applied in order to perform the kinetic modeling of the pollutant degradation considered in this work, Eq. (1), (Shahrezaei et al., 2012; Sánchez et al., 1997).

$$r = -\frac{dC}{dt} = \frac{k \cdot K_{ad} \cdot C}{1 + K_{ad} \cdot C} \qquad (1)$$

The concentrations of benzothiazole and aniline are lower than 1.0×10^{-3} mol/L in this study. Then, the product $K_{ad} \cdot C << 1.0$ and, consequently, Eq. 1 can be fitted to Eq. 2, as proposed by Wols & Hofman-Caris (2012).

$$r = -\frac{dC}{dt} = k \cdot K_{ad} \cdot C \qquad (2)$$

Integrating the mass balance, it results:

$$Ln\left(\frac{C_0}{C}\right) = k \cdot K_{ad} \cdot t \approx k_{app} \cdot t \qquad (3)$$

being,

C: concentration of contaminant at time t (mg/L)

t: reaction time (h)

k_{app}: kinetic constant of pseudo-first order (1/h)

The values of the pseudo-first order kinetic constants for the degradation of the aniline (Fig. 3a) and the benzothiazole (Fig. 3b) were estimated, applying different catalyst concentrations (Table 1). In the case of aniline, it is observed that the oxidation rate increases as higher concentrations of catalyst are dosed, until it reaches a limit value (TiO_2 in suspension=100.0 mg /L), where the highest value of the kinetic constant is reached (k_{app}=0.39 1/h). Utilizing higher concentrations, the rate of degradation slows down, because a screen effect is generated by an excess of particles in suspension, which hinders the passage of UV light to the active centers of the catalyst. In addition, certain deactivation reactions are favored at high catalyst concentrations. When benzothiazole is oxidized, the kinetic degradation constant does not experience significant variations as the catalyst dose changes. The effect of pH (Fig. 4a) and catalyst dose (Fig. 4b) on the pseudo-first order kinetic constants has been analyzed.
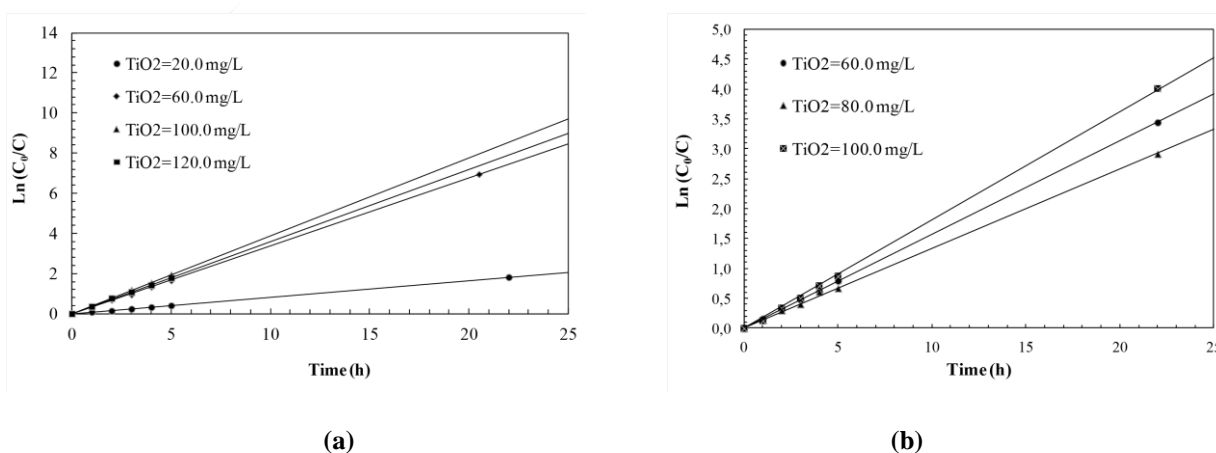

Figure 3. Prediction of the proposed pseudo-first order model for the photocatalytic degradation of the aniline, operating at pH=12.0 (a) and the benzothiazole at pH=8.0 (b), carrying out the treatment with different doses of TiO_2 catalyst. Experimental conditions: UV=72.0 μW/cm^2; P=1.0 atm; T=25.0 ºC.
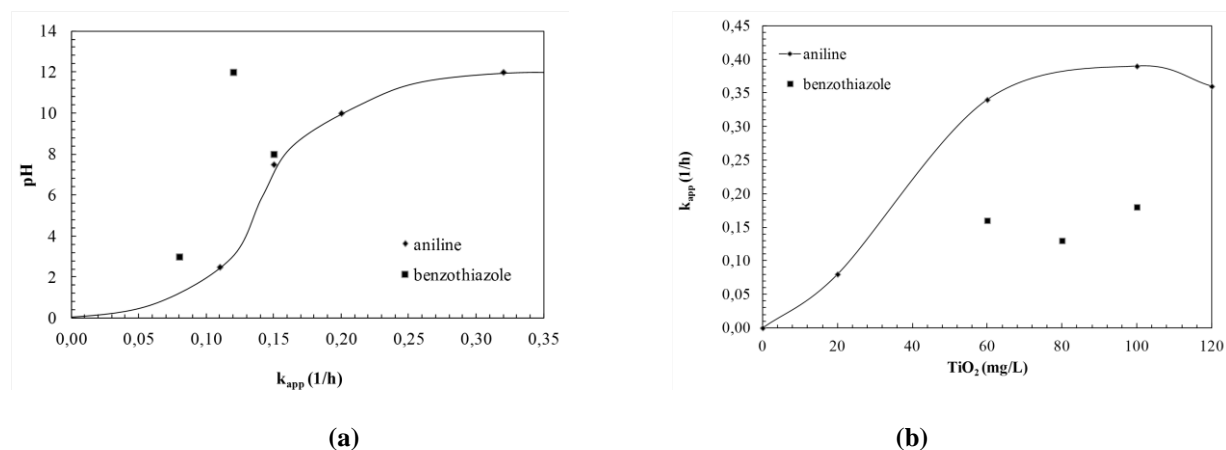
| (a) | (b) |

Figure 4. Effect of the catalyst dosage on the kinetic constants of pseudo-first order estimated for aniline degradation. Experimental conditions: pH=12.0; UV=72.0 μW/cm^2; P=1.0 atm; T=25.0 ℃.

Table 1. Kinetic parameters of the adjustment to the pseudo-first-order model for aniline and benzothiazole. Experimental conditions: UV=72.0 μW/cm^2; P=1.0 atm; T=25.0 ℃.

Benzothiazole

C_0 mg/L	pH	k_{app} 1/h	σ	C_0 mg/L	TiO_2 mg/L	k_{app} 1/h	σ
19.7	3.0	0.080	0.022	25.0	60.0	0.156	0.036
25.3	8.0	0.150	0.040	16.6	80.0	0.133	0.054
27.6	12.0	0.120	0.035	22.0	100.0	0.181	0.039

Aniline

C_0 mg/L	pH	k_{app} 1/h	σ	C_0 mg/L	TiO_2 mg/L	k_{app} 1/h	σ
23.9	2.5	0.112	0.055	22.8	20.0	0.082	0.025
20.8	7.5	0.154	0.064	20.9	60.0	0.338	0.036
22.7	10.0	0.200	0.021	21.0	100.0	0.388	0.014
27.3	12.0	0.327	0.091	17.9	120.0	0.359	0.096

For the case of aniline, an upward trend of the kinetic constant is observed with the pH increase, achieving a maximum value of 1/h at pH=12.0. This effect is mainly due to the fact that, at alkaline pH, the surface of the catalyst is negatively charged. This aspect facilitates the interaction of the aniline with the hydroxyl radicals located on the surface of the catalyst. Moreover, in the elimination of benzothiazole, an increase of the oxidation with a kinetic constant of 0.15 1/h was observed at pH=8.0. This enlargement in the kinetic constant can be explained by the raise in electronic density of the benzothiazole molecule, caused by the presence of the hydroxyl radical.

In the analysis of the catalyst concentration there was an increasing tendency of the kinetic constant in the oxidation, until reaching a maximum with a dose of 100.0 mg/L and a constant of 0.39 1/h. This phenomenon may be due to a screen effect and masking of the surface of the catalytic particles. Meanwhile, in the benzothiazole degradation there was no clear increase in the apparent kinetic constant with the catalyst dose.

4. Conclusions

In this work, the favorable operating conditions have been determined for the elimination of aniline and benzothiazole above 95% in 15 h. The study of the effect of the catalyst arrangement on the efficiency of the treatment presents a similar efficiency of almost 100%, both with the catalyst on a support and in a suspension of 60.0 mg/L. Moreover, taking into account the economic and environmental factors, the use of the catalyst on a support results in more advantages, since it is not necessary to apply subsequent separation steps and it reduces catalyst losses. Considering the effect of pH for the removal of aniline, it is determined that the highest oxidation rate is reached at pH=12, with k_{app}=0.33 1/h. This is because it facilitates the interaction of the aniline with the hydroxyl radicals on the catalyst surface. Operating at a pH=2.5, the condensation reactions leading to the formation of polyaniline are favored, although yielding a low output of k_{app}=0.11 1/h. As for the oxidation of benzothiazole, a higher reaction rate is obtained at k_{app}=0.15 1/h and pH=8.0. This fact can be due to the existence of hydroxyl groups in the benzothiazole molecule, as they cause an increase in its electronic density, augmenting the adsorption capacity of TiO_2. From the study of the catalyst dosage for aniline degradation, it

is determined that growing the TiO_2 concentration leads to enlarge the oxidation rate, up to a dose of 100,0 mg/L and k_{app}=0.39 1/h. Nevertheless, increasing these values results in a lowering the oxidation rate, which is attributed to the screen effect and masking of the catalytic particles surface. On the other hand, in the degradation of benzotizol is not observed an appreciable augmenting of the kinetic constant.

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