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10 **ANTIPYRINE REMOVAL BY TiO₂ PHOTOCATALYSIS BASED**
11 **ON SPINNING DISC REACTOR TECHNOLOGY**
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ABSTRACT

The photo-degradation of the emerging contaminant antipyrine (AP) was studied and optimized in a novel photocatalytic spinning disc reactor (SDR). A heterogeneous process (UV/H₂O₂/TiO₂) was used. TiO₂ was immobilized on the surface of a glass disc using a sol-gel method. A factorial design of experiments followed by a Neural Networks fitting allowed the optimal conditions to be determined for treating 50 mg/L of AP. Under these conditions (pH= 4; [H₂O₂]₀= 1500 mg/L; disc speed= 500 rpm; flowrate = 25 mL/s), AP was completely degraded in 120 minutes and regeneration of the disc allowed 10 cycles with no loss in efficiency. The value of the apparent volumetric rate constant was found to be $6.9 \cdot 10^{-4} \text{ s}^{-1}$ with no apparent mass transfer limitation.

Based on the main intermediates identified, a mechanism is proposed for antipyrine photodegradation: Firstly, cleavage of the N-N bond of penta-heterocycle leads to the formation of two aromatic acids and N-phenylpropanamide. An attack to the C-N bond in the latter compound produces benzenamine. Finally, the phenyl ring of the aromatic intermediates are opened and molecular organic acids are formed.

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Keywords: AOPs; emerging contaminant; neural networks; pathway; pharmaceuticals; UV radiation

1. INTRODUCTION

Emerging contaminants (EC) have received significant attention in the recent years since they are new chemicals whose effects are unknown on environment and human health (Durán et al., 2013). Therefore, EC are shown as potential pollutants which must be removed. Antipyrine (AP), which is included in this group, is a common analgesic and anti-inflammatory drug used ubiquitously by the pharmaceutical industry. AP is a complex molecule which is not able to be removed by the traditional techniques used in wastewater treatment, hence it can be accumulated in the natural water cycle (Verlicchi et al., 2012). At present, low concentrations of antipyrine have been measured in previous works at up to the $\mu\text{g/L}$ level in municipal sewage effluents, ground water and drinking water (Cai et al., 2013).

Advanced Oxidation Processes (AOPs) have been shown to be a potential technique that is able to remove refractory molecules. These processes are based on the production of highly reactive radicals (Liu et al., 2016). The radicals have a short life, reacting quickly and can mineralize the organic pollutants. One of the most interesting AOPs consists of the use of semiconductors as photocatalysts. The semiconductor TiO_2 has been extensively studied because of its high photo-reactivity, stability to corrosion/dissolution, low price, ready availability and ability to generate electron-hole pairs when illuminated by UV which initiate both radical generation and direct oxidation of organic pollutant species, enabling mineralization to be achieved (Naeem and Ouyang, 2013; Domínguez et al., 2015). In addition, it is not toxic, it is biologically and chemically inert and it can be regenerated several times without significant loss of activity. However, comparing TiO_2 results between different scales and configurations is difficult, complicating its

applicability (Rao and Chu, 2009; Domínguez et al., 2015). This is in the main due to the almost universal application of TiO_2 as a powder suspension, which when applied in different reactor systems and at different scales produces a difficult to predict change in photo-reactivity due to complex to model effects such as light scattering, shadowing, mass transfer limitations in multiphase flow systems (such as is the norm in gas-liquid-solid or liquid-solid photocatalytic systems). Recovery of the suspended catalyst can also complicate and increase the cost of the overall process, which may be a further barrier to implementation and comparison between different configurations. Consequently, using immobilised/supported TiO_2 is a simple way to overcome most, if not all, of these problems, in particular enabling simpler scale-up since there is no solid phase creating multiphase flow, shadowing and avoiding the need for photocatalyst separation (Boiarkina et al., 2011). Sol-gel coating is an established method for the synthesis of thin and porous layers of TiO_2 and as such is used in this work (Miranda-García et al., 2014).

The use and properties of H_2O_2 as an oxidant is thoroughly known. It can be easily activated by UV light generating hydroxyl radicals. Furthermore, H_2O_2 is cheap, easily stored and it is soluble in water, with negligible mass transfer limitations (Li et al., 2015). There are several studies which have shown the improvement of TiO_2 effectiveness in the presence of H_2O_2 because it can react with TiO_2 giving rise to the formation of Ti-OOH complexes (Li et al., 2001; Domínguez-Sanchez et al., 2013). This complex has a coloured surface which enhances the photocatalyst effect (Li et al., 2001).

Despite all of the extensive work on photocatalysis and processes based on TiO_2 they still suffer from particularly slow kinetics and low mass transfer. It is therefore necessary to find new ways able to improve the efficiency. Intensification processes can

reduce costs, increase the intrinsic safety and minimize the environmental impact, as well as enhance the efficiency (Ling et al., 2004). The Spinning Disc Reactor (SDR) is an intensification process based on the creation of a thin film. The reactor consists of a spinning disc, where the feed fluid is fed to the centre top surface of the disc. In the photocatalytic SDR, the surface of the disc is coated with the photocatalyst. The feed fluid is spread out over the surface of the disc because of the centrifugal acceleration, generating a thin film of 20-200 μm (Boothoo et al., 2000). The thin film improves the mass and heat transfer, especially in solid-liquid systems, and the penetration of UV light to the surface of the disc, which can be an advantage over other types of photoreactor systems when using coloured and/or UV light absorbing solutions, since this facilitates higher light penetration to the photocatalyst per volume of feed on the catalyst, increasing the volumetric efficiency of the reaction. Moreover, shorter retention times are needed since the efficiency is increased. Boiarkina et al. (2011) verified that the effect of the flow and the speed of the disc were important in this kind of reactor because these two parameters have a significant influence on the flow regime and therefore in the mass and heat transfer to and from the photocatalyst surface.

The behaviour of the photocatalytic SDR for pollutant removal has been studied for methylene blue (Ling et al., 2004; Boiarkina et al., 2011; Boiarkina et al., 2013) as a common reference pollutant and dehydroabietic acid (Boiarkina et al., 2013), a pollutant from the paper industry.

Therefore, the aim of this paper is to study the applicability of a TiO_2 photo-degradation process to efficiently degrade a synthetic effluent containing antipyrine in a novel spinning disc reactor (SDR). We are the first to comprehensively map out the effect of the important operating parameters of the photocatalytic spinning disc reactor, by applying statistical experimental design. As this has not been done for SDRs in general,

this paper is the first comprehensive assessment of the operating space for this important class of process intensification reactor. To this end, a factorial design of experiments which is a proven technique successfully used in removal of pollutants with AOPs (Monteagudo et al., 2008) was used changing four variables. Later, experimental results of antipyrine degradation were fitted with neural networks (NNs) since they have shown to be robust and applicable in almost all situations (Khatae and Kasiri, 2010). In addition, by analysis of reaction products by high performance liquid chromatography (HPLC) and liquid chromatography-mass spectroscopy (LC-MS), this paper proposes a new and comprehensive photocatalytic degradation pathway for antipyrine.

2. EXPERIMENTAL

2.1. Materials

Antipyrine (99%) was obtained from Acros. 30% hydrogen peroxide (H_2O_2) and methanol (99.8%) were purchased from Fisher Scientific and VWR-Chemical respectively and were used as received. The pH of the solution was adjusted with H_2SO_4 and NaOH.

Acetic acid (99.7%, Sigma Aldrich), acetylacetone (99%, Sigma Aldrich) and isopropanol (99.5%, Sigma Aldrich) were used for sol-gel preparation. Deionized water used for preparing solutions was obtained from a purifying machine (ELGA PURELAB). Glass discs (200mm in diameter, 3mm thick) were supplied by Roman Glass (Bath, UK).

2.2. Experimental set-up and procedure

The experimental setup is shown in Figure 1. The experiments were carried out in recirculating batch mode. For the UV/ H_2O_2 /TiO₂ process, the solution to be treated (750 mL) is initially kept in a 1L reservoir under constant magnetic stirring. After pH fitting,

the solution is fed with a peristaltic pump (MasterFlex Easy-load II) into a tightly sealed glass flask, which avoided the flow pulsations generated in the pumping process. Then the solution is fed into the spinning disc reactor. Both the reservoir and the flask were covered with aluminum foil in order to avoid the light incidence in case some TiO₂ particles were detached from the disc. The solution is cooled with tap water with a Liebig cooler. The liquid containing AP goes into through the center of the disc where it falls down on the disc spreading out the solution. During this process, the solution is irradiated by a low pressure mercury UV lamp inside a quartz tube (20 W, monochromatic, $\lambda=254$ nm, Steriflow, supplied by Davey Water Products NZ, part nr. GPH369N/S). The lamp is situated at the focus of a parabolic mirror in order to leverage the maximum possible radiation. The liquid is collected by a funnel beneath the disc and is returned to the reservoir by gravity.

The speed and flow were set for every experiment according to the experiment design as explained below. The lamp was switched on and the H₂O₂ was added after 20 minutes in the dark to allow pollutant adsorption by the TiO₂. Sodium sulfite anhydrous, Na₂SO₃ was used for quenching immediately after sampling. pH was kept constant (± 0.1) during the experiments. In exceptional cases, addition of drops of sulfuric acid or sodium hydroxide were needed.

Figure 1

2.3. Analytical methods

The removal of antipyrine was evaluated immediately after sampling using a Gilson 231 XL high performance liquid chromatography (HPLC) system with UV detection under an isocratic mode and an Eclipse XDB-C18 column (5 μ m, 4.6 \times 250 mm). 60:40 (v/v)

methanol/(water with 0.1% acetic acid) mixture at acidic pH was used as the mobile phase (detection wavelength, $\lambda = 252$ nm; flow rate of 0.6 ml min^{-1}).

Total organic carbon concentration was determined using a TOC analyzer (Shimadzu TOC-5000A). H_2O_2 concentration was measured by titration with an aqueous solution of potassium permanganate (0.025 mol/L).

Intermediate by-products were identified by mass spectrometry (MS) using a TOF-MS micrOTOF-Q II (Bruker Daltonics Inc., Billerica, MA, USA) with electrospray ionization source and negative and positive-ion polarity equipped with a 2.5 mL or $500 \mu\text{L}$ Hamilton gastight syringe (Hamilton, Reno, NV, USA) to deliver the samples. MS measurements were taken over the range $50 < m/z < 600$.

The X-ray diffraction spectrum obtained with a p-XRD-BRUKER D8-Advance (Cu radiation) shows characteristic anatase peaks. No rutile peaks are present.

2.4. Sol gel method for TiO_2 preparation

TiO_2 was supported onto the surface of the glass discs using a sol-gel process according to the method used by Boiarkina et al. (2013). The glass discs were extracted from the sol at 1 mm/s , allowed to air dry for 5 min in the fume-hood and then transferred to an oven at 100°C for 30 min . This process was repeated once more before the discs were transferred to a furnace (Gallenkamp Muffle Furnace Size 3 with a Vertex VT4826 controller) for calcination at 500°C for 1 hour to obtain the photocatalytically active anatase crystal structure. The furnace was ramped up at a rate of 2°C/min to minimize cracking. Once the discs had cooled, the process was repeated once more to obtain a total of four TiO_2 layers, two of which were calcined.

2.5. Factorial design and neural network strategy

A Central-Composite Experimental Design was applied to investigate the effects of four variables (initial concentration of hydrogen peroxide, speed of the disc, flowrate and pH) on the selected Response Function (degradation of antipyrine). It consisted of three series of experiments for $k=4$ variables (Table 1) including:

- i) a factorial design with 2^k trials with all possible combinations of codified values $+1$ and -1), experiments 1 to 16 in Table 1
- ii) selection of the axial distance of the star points (codified values $\alpha = 2^{k/4} = \pm 2$) consisting of 2^k experiments 17 to 24 in Table 1, and
- iii) replicates of the central point (four experiments, 25-28).

The complete experimental design and additional experiments, including variable ranges and the values of the obtained response functions, are also shown in Supplementary Material (Table 1). Disc speed and flow rate were changed into the allowed limits of the experimental set-up. pH was varied from 4 to 8 (above and below the the zero point charge for TiO_2 , which is between 5.6 and 6.4). Lower pHs were not tested, since the mirrored chrome UV-lamp protection in the reactor could be damaged.

Supplementary material, Table 1

The experimental results (removal of AP in each test) were fitted using a neural network applied with two neurons, previously used in literature (Monteagudo et al., 2008). It uses a simple exponential activation function and a solution strategy based on a back-propagation algorithm (Morgan and Scofield, 1991). Parameters were fitted using the Solver tool in a custom spreadsheet in Microsoft Excel using a nonlinear fitting method. As a final point, a measure of the saliency of the input variables was made to analyze the relevance of each variable with respect to the others (expressed as percentages) based on the connection weights of the neural networks (Nath et al., 1997). Fitting with a

polynomial model derived from the factorial design was also tested, but error estimation was higher, so it was discarded.

3. RESULTS AND DISCUSSION

3.1. Synergic effect

Firstly, some control and initial experiments were carried out to analyze the viability of this novel reactor technology for AP photocatalytic degradation. These experiments were run under the following conditions: speed = 300 rpm; flowrate = 25 mL/s; TiO₂ = 0.4 g; [H₂O₂] = 1000 mg/L. The results obtained are shown in Figure 2.

Figure 2

It can be seen that TiO₂ alone does not degrade AP at all. Molecular degradation with H₂O₂ reaches up to about 12.6 % of AP degradation, whereas UV photo-degradation produces up to 76.4 % of AP removal in 120 minutes. UV/H₂O₂ and UV/H₂O₂/TiO₂ processes reach 93% and 95.9% respectively, although the overall process is faster at the beginning. The increase in the kinetic constant is 6% if we consider the whole operating time. In addition, a low synergic effect can be seen among these processes during the first 40 minutes of reaction. For this reason, this system was selected for the experimental design.

The synergism between the individual processes and the overall UV/H₂O₂/TiO₂ system was quantified using the first order rate constants for AP removal according to equation (1) (Joseph et al., 2011):

$$Synergy (\%) = \frac{k_{UV/H_2O_2/TiO_2} - (k_{UV/H_2O_2} + k_{UV/TiO_2})}{k_{UV/H_2O_2/TiO_2}} = \frac{0.0403 - (0.0223 + 0.0163)}{0.0403} = 4.21 \quad (1)$$

The detailed mechanism of this process has been widely discussed in the literature for different pollutants (Galindo et al., 2001; Daneshvar et al., 2004). The high oxidative

potential of the hole (h_{VB}^+) photogenerated in the catalyst allows the direct oxidation of the organic molecule (AP) to reactive intermediates. Hydroxyl radicals, $HO\bullet$, are produced from H_2O_2 photodecomposition, but can also be formed either by the oxidation of water or by the reaction of the hole with OH^- . The photogenerated electrons in the conduction band (e_{CB}^-) on the catalyst surface can reduce molecular oxygen, adsorbed on the TiO_2 surface or dissolved in water, to superoxide anion or reduce the pollutant molecule. $\bullet OH$ radicals together with other oxidant species such as peroxide radicals are thus responsible for the heterogeneous TiO_2 photodecomposition of AP.

3.2. Effect of variables

A complete set of experiments were made based on the previously described factorial design to analyze the effect of four parameters (speed of the disc, flowrate, pH and initial concentration of hydrogen peroxide). The initial antipyrine concentration was 50 mg/L. However, after analyzing the results, two additional experiments increasing the concentration of H_2O_2 were made in order to obtain the optimal conditions. The complete series of tests is shown in Table 1 together with AP removal after 120 minutes.

The experimental results obtained for AP degradation were fitted with NNs, resulting in an average error of less than 4% (Supplementary material, Figure S1). The equation and fitting parameters are shown Supplementary material (Table 2). N_1 and N_2 are general factors related to the first and the second neurons, respectively. W_{11} to W_{14} are the contribution parameters to the first neuron and represent the influence of each of the variables in the process (initial concentration of H_2O_2 , disc speed, flow and pH); W_{21} to W_{24} are the contributions to the second neuron corresponding to the same variables.

Supplementary material (Table 2, Figure S1)

The results of saliency analysis on the input variables for each neural network (%) are shown in Supplementary material (Figure S2). From these results, it was possible to

deduce the effect of each parameter on the antipyrine removal. Thus, it was confirmed that the removal was mainly influenced by the initial concentration of hydrogen peroxide (69.5%).

Supplementary material (Figure S2)

A simulation of the influence of each parameter from NNs equation is shown in Figure 3. A decrease in pH slightly improves AP degradation (Figure 3a). The differences in photoactivity of various substrates at different pHs are mainly attributable to the different equilibrium species present in solution. It is not easy to correlate the photoreactivity with the properties of molecules, but an attempt can be made by considering their pK_a values. The zero point charge for TiO_2 is at pHs between 5.6 and 6.4 (Monteagudo et al., 2008). Hence, at more acidic pH values, the TiO_2 surface is positively charged. The slight increase in degradation efficiency in our case can be explained by considering that only one main species for AP is likely to exist at the different pHs tested (from 4 to 8), owing to the AP pK_a being 1.4 (Molinari et al., 2006). Considering that a low pH could damage the mirrored chrome UV-lamp protection in the reactor, pH=4 was consequently selected as the optimal value.

Figure 3

The optimal initial concentration of H_2O_2 was found to be around 1500 mg/L (Figure 3a). The excess of H_2O_2 reacts with the $HO\cdot$ radicals to produce $HO_2\cdot$ radicals, which are less reactive, decreasing AP degradation according to the well-known scavenger effect:



Additionally unproductive reactions may also occur:



Finally, it is also evident from Figure 3b that the disc speed and the flowrate favor a mass transfer rate producing a higher AP degradation. For disc speed, an additional effect is the increased mass transfer of oxygen into the system through the air-water interface on the liquid film surface of the spinning disc. This dissolved oxygen has the potential to be an additional oxidant source, potentially enhancing degradation rate. The maximum allowed values of these parameters were consequently selected as optimal conditions (speed = 500 rpm; flowrate = 25 mL/s).

Previous works with SDR treating methylene blue (Boiarkina et al., 2011) concluded that mass transport limitations were affecting the reaction rate, since they did not find any correlation between the photonic efficiency with the film height. The authors recommended to increase mixing and turbulence on the disc in future works in order to eliminate the mass transfer perpetrated reaction rate drop.

In order to determine if mass transfer limitation is occurring in our system, the film height distribution across the surface has been calculated using the Nusselt model that assumes laminar flow across the surface of the disc according to Eq (5) (Burns et al., 2003).

$$h = \left(\frac{3Qv}{2\pi r^2 \omega^2} \right)^{1/3} = Ar^{-2/3} \quad (5)$$

Where h is the liquid film thickness at radius r , Q is the volumetric flow rate, v is the kinematic viscosity, ω is the rotational speed and A is a parameter combining all the constants.

This model can be used as an approximation for Ekman numbers higher than 2 (Burns et al., 2011) or 1.62 (Caprariis et al., 2012). However it can not be used accurately for the inertial flow conditions characterized by low Ekman numbers, which is defined in equation (6) as:

$$E = \left(\frac{\nu}{h^2 \omega} \right) \quad (6)$$

In this work, the Ekman number range was between 0.1 and 6.9, being higher than 2 for $r/R > 0.33$. This means that there will be some error in thin film estimation near the center of the disk. In spite of this limitation, average results for thin film height for all the tests are shown in Table 1. Figure 4 shows the film height distribution for optimal conditions.

Figure 4

On the other hand, assuming a pseudo-first order reaction $R_i = -kC$, with k being a pseudo-constant including the contribution of both the kinetic constant and the concentration of hydrogen peroxide (which would be in great excess) and considering that the SDR behaves like a plug flow reactor (Boiarkina et al., 2011), leads to the following expression for the change in concentration with respect to radius:

$$C = C_0 \exp \left(\frac{Q}{V} \left[\exp \left(-\frac{3\pi A k}{2Q} \left(R^{4/3} - R_0^{4/3} \right) \right) - 1 \right] t \right) \quad (7)$$

where R is the outer radius of the disc and R_0 is the inlet nozzle radius. A plot of $\ln (C/C_0)$ versus time should yield a straight line relationship for a pseudo-first order reaction (see figure S3 in supplementary material).

Figure S3

Although the model is just an approximation, there is no apparent decrease in the order of magnitude of reaction rate (the apparent volumetric rate constant ranges from $2.05 \cdot 10^{-4}$ to $4.82 \cdot 10^{-4} \text{ s}^{-1}$ as summarized in Table 1) with film height (111-222 μm). Additionally, the irradiance profile is relatively uniform due to the parabolic mirror with the UV lamp in its focus. There is no dependence of the photonic efficiency on the film height, since the irradiance profile varies from 12 to 23 W/m^2 , in the same order of

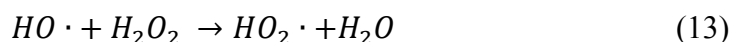
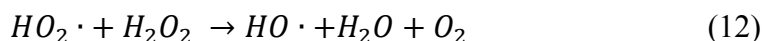
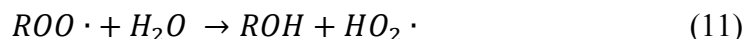
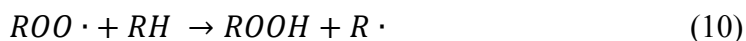
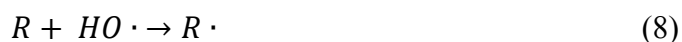
magnitude (Boiarkina et al, 2011). Consequently, it is reasonable to believe that no mass transfer limitations are occurring.

3.3. Optimal conditions selected

The degradation of AP and the evolution of the concentration of H₂O₂ under optimal conditions are shown in Figure 5a. Under these conditions (pH= 4; [H₂O₂]₀= 1500 mg/L; Speed= 500 rpm; Flow= 25 mL/s; [AP]₀= 50 mg/L), AP was completely degraded after 120 minutes. H₂O₂ still remained in solution, so that degradation of intermediate products could be achieved. However, as shown in Figure 5b, mineralization is very slow, reaching only 35% in 4 hours.

Figure 5

New experiments were conducted increasing temperature up to 45 and 60 °C under optimal conditions to try to improve reaction kinetics (Figure 6). However, no positive effect was obtained since dissolved oxygen (DO) is lower when increasing temperature, and accordingly a lower concentration of radicals are formed according to the main reactions involved when H₂O₂ and O₂ are present in solution (Miralles-Cuevas et al., 2014):



Furthermore, H₂O₂ is decomposed by unproductive reactions at high temperatures.

Figure 6

In order to confirm that hydroxyl radical is the main active species responsible for the degradation of antipyrine in this system, comparison experiments of scavenger-loaded conditions with 200 mM methanol (an hydroxyl radical scavenger, $k = 9.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) were undertaken (Matta et al., 2011). It can be seen that methanol slows the antipyrine degradation rate (Figure S4). Total inhibition is not achieved due to UV radiation and in a lower extent to molecular degradation with H_2O_2 (see Figure 1).

Figure S4

3.4. Intermediates and proposed pathway

Intermediates/by-products were identified using a mass spectrophotometer (Figure 7). Although it is a qualitative analysis, the main intermediates could be identified and were observed in the system to be benzenamine, anthranilic acid and butanedioic acid. Their concentration increased until 1 hour of reaction, and decreased slowly later, indicating that they are very difficult to mineralize using the UV/ H_2O_2 /TiO₂ system in the SDR. Other intermediates found in minor concentration were fumaric acid, 4-oxo-pentanoic acid, 1,4 benzenedicarboxylic acid and N-phenyl propinamide.

Figure 7

The toxicity of some intermediates, especially benzenamide (which is the main constituent) is higher than antipyrine (Miao et al., 2015), so its mineralization is extremely important.

The knowledge on the degradation products of AP during UV-based AOPs is highly limited (Tana et al., 2013). According to literature, degradation of AP with different AOPs may proceed with different intermediates. Tana et al. (2013) also identified N-phenylpropinamide and benzenamine in the UV/ H_2O_2 treatment process, while only N-

phenylpropinamide was detected in the UV/persulfate system. They proposed a degradation pathway based on the attack of C-C bond in the pentacyclic ring by HO• leading to the formation of N-phenylpropinamide. Subsequently, hydroxyl radicals continued to attack the C-N bond in branch to produce benzenamine.

In contrast, in the UV/persulfate system, sulfate radicals seemed not to decompose N-phenylpropinamide into benzenamine, so that degradation would progress in a different pathway.

In our case, the high concentration of benzenamide and low concentration of N-phenylpropinamide found seems to indicate that the UV/H₂O₂/TiO₂ process degradation mechanism is similar to that occurring in the UV/H₂O₂ system.

The main intermediates found in this research also included small concentrations of aliphatic acids (1,4-benzenedicarboxylic acid, 4-oxo-pentanoic acid and 2-butenedioic acid) which agrees with previous findings found for AP degradation in a UV/H₂O₂/Fe/US system (Durán et al., 2013). Thus, an adapted mechanism can be proposed for AP photodegradation in Figure 8 for the UV/H₂O₂/TiO₂ process. The cleavage of the N-N bond of penta-heterocycle leads to the formation of two aromatic acids and N-phenylpropanamide. An attack to the C-N bond in the latter would produce benzenamine. Finally, the phenyl ring of all of them is opened and small molecular organic acids are formed. In a later stage, these acids may decompose into CO₂.

Figure 8

Given the above mechanism and the previous results, this work shows that the photocatalytic SDR is an effective and robust wastewater treatment technology for the degradation of antipyrine producing degradation products (such as molecular organic

acids) that could be further mineralised by conventional biological wastewater treatment systems.

3.5. Catalyst operation mode and regeneration

The applicability of the SDR with coated TiO₂ was confirmed, since up to 10 disc regeneration cycles were performed without loss in efficiency (Figure 9), confirming that the SDR is an interesting alternative to traditional reactor configurations, avoiding TiO₂ filtration. Thermal regeneration was performed by calcination each time after the experiment at 500 °C for 2 hours.

Figure 9

4. CONCLUSIONS

- The photo-degradation process of AP was studied in a novel spinning disc reactor (SDR) under a heterogeneous process (UV-H₂O₂/TiO₂). The synergism between the individual processes and the overall UV/H₂O₂/TiO₂ system was quantified to be 47%.
- A factorial design of experiments followed by a Neural Networks fitting allowed to obtain the optimal conditions: pH= 4; [H₂O₂]₀= 1500 mg/L; disc speed= 500 rpm; flowrate = 25 mL/s. Under these conditions, 50 mg/L of AP were completely degraded in 120 minutes. The process can be made after disc regeneration up to 10 cycles with no loss in efficiency. This is the first comprehensive mapping out the effect of the important operating parameters of the photocatalytic spinning disc reactor, by applying statistical experimental design. As this has not been done for SDRs in general, this is therefore the first comprehensive assessment of the operating space for this important class of process intensification reactor.

- There is no apparent decrease in the order of magnitude of reaction rate (the apparent volumetric rate constant ranges from $2.05 \cdot 10^{-4}$ to $4.82 \cdot 10^{-4} \text{ s}^{-1}$) with film height (111-222 μm) as estimated with the approximate Nusselt model. There is no dependence of the photonic efficiency on the film height either, so it is reasonable to believe that no mass transfer limitations are occurring.

- After intermediates identification, a simple mechanism can be proposed for AP photodegradation during the UV/H₂O₂/TiO₂ process. Anthranilic acid, 1,4-benzenedicarboxylic acid and benzenamide would be the main reaction intermediates. The phenyl ring of all of them would be later opened to form small molecular organic acids (2-butenedioic acid, butenedioic acid and 4-oxopentanoic acid).

- Given the above mechanism and optimized reaction conditions determined, this work shows that the photocatalytic SDR is an effective and robust wastewater treatment technology for the degradation of antipyrine producing degradation products (such as molecular organic acids) that could be further mineralised by conventional biological wastewater treatment systems.

5. ACKNOWLEDGEMENTS

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482

483 **NOMENCLATURE**

484 ν kinematic viscosity ($\text{m}^2 \text{s}^{-1}$)

485 ω rotational speed of spinning disc (rad s^{-1})

486 Q volumetric flow rate ($\text{m}^3 \text{s}^{-1}$)

487 h height of the liquid film at radius r (m)

488 R_i reaction rate (mol/L s)

489 C concentration of substrate (mol/L)

490 C_0 initial concentration of substrate (mol/L)

491 V reactor volume (m^3)

492 k_{app} pseudo-first or second order reaction rate constant based on reactor volume (s^{-1})

493 A Nusselt film height equation constant ($\text{m}^{5/3}$)

494 R outer disc radius (m)

495 R_0 inlet nozzle radius (m)

496 t time (s)

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FIGURE CAPTIONS

Figure 1. Experimental installation. a) schematic diagram, b) reactor, c) detail of the scanning disc.

Figure 2. Antipyrine removal (%) under different systems. $[AP]_0 = 35$ mg/L; $[H_2O_2]_0 = 1000$ mg/L; Speed = 300 rpm; Flow = 15 mL/s.

Figure 3. Effect of variables in antipyrine degradation for the UV/ H_2O_2 /TiO₂ process. Simulation from neural networks at the central point. a) $[H_2O_2]_0$ vs pH (Flow = 15 mL/s, Speed = 300 rpm), b) Speed vs Flow ($[H_2O_2]_0 = 1000$ mg/L; pH = 6).

Figure 4. Distribution of film thickness on the disc according to Eq (5) under optimal conditions.

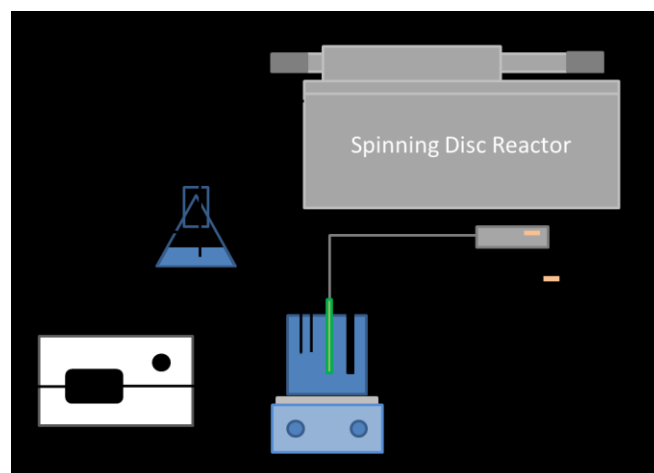
Figure 5. Results under optimal conditions (pH = 4; $[H_2O_2]_0 = 1500$ mg/L; Speed = 500 rpm; Flow = 25 mL/s; $[AP]_0 = 50$ mg/L) a) $[AP]$ and $[H_2O_2]$; b) TOC concentration.

Figure 6. Influence of a) temperature and b) dissolved O₂ concentration under optimal conditions (pH = 4; $[H_2O_2]_0 = 1500$ mg/L; Speed = 500 rpm; Flow = 25 mL/s; $[AP]_0 = 50$ mg/L).

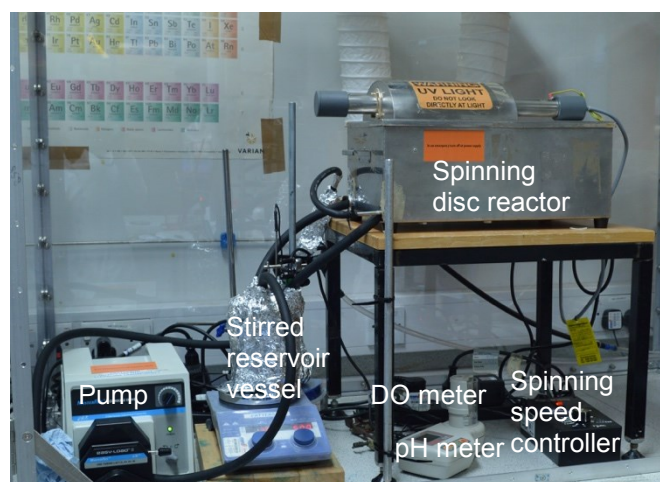
Figure 7. Intermediates evolution obtained by MS (Conditions: pH = 4; $[H_2O_2]_0 = 1500$ mg/L; Speed = 500 rpm; Flow = 25 mL/s; $[AP]_0 = 50$ mg/L).

Figure 8. Antipyrine degradation pathway induced by UV/ H_2O_2 /TiO₂ (adapted from [28])

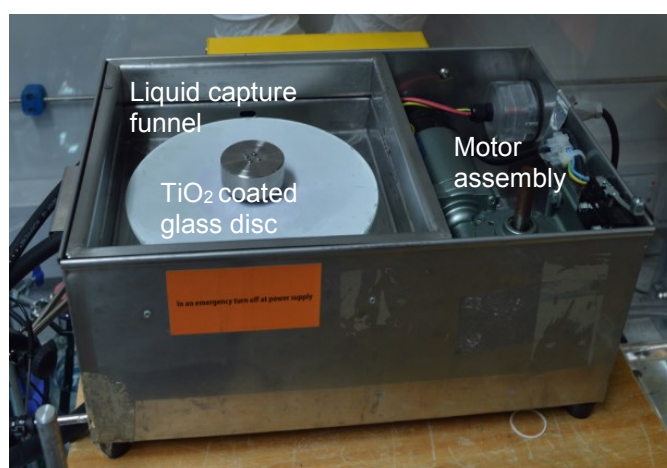
Figure 9. Catalysis behavior after regeneration under optimal conditions (pH = 4; $[H_2O_2]_0 = 1500$ mg/L; Speed = 500 rpm; Flow = 25 mL/s; $[AP]_0 = 50$ mg/L)



a)



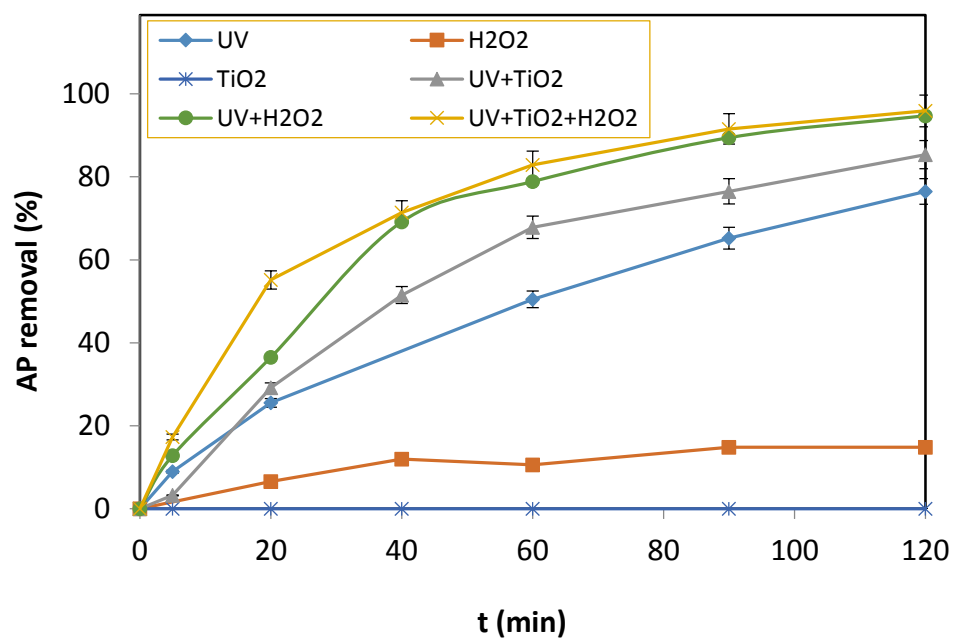
b)



c)

FIGURE 1

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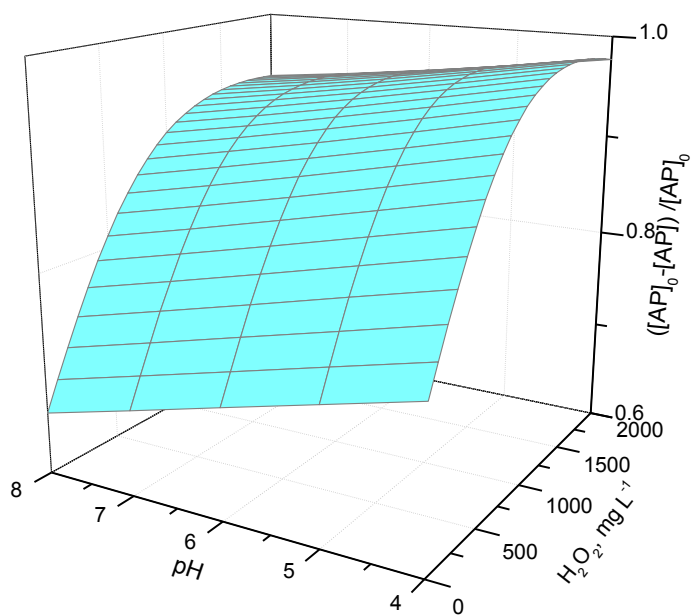
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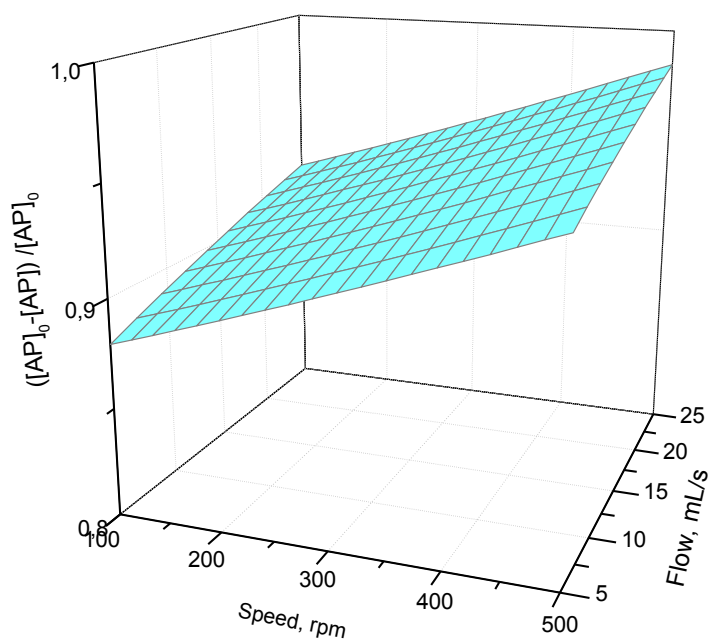
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FIGURE 2

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a)



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FIGURE

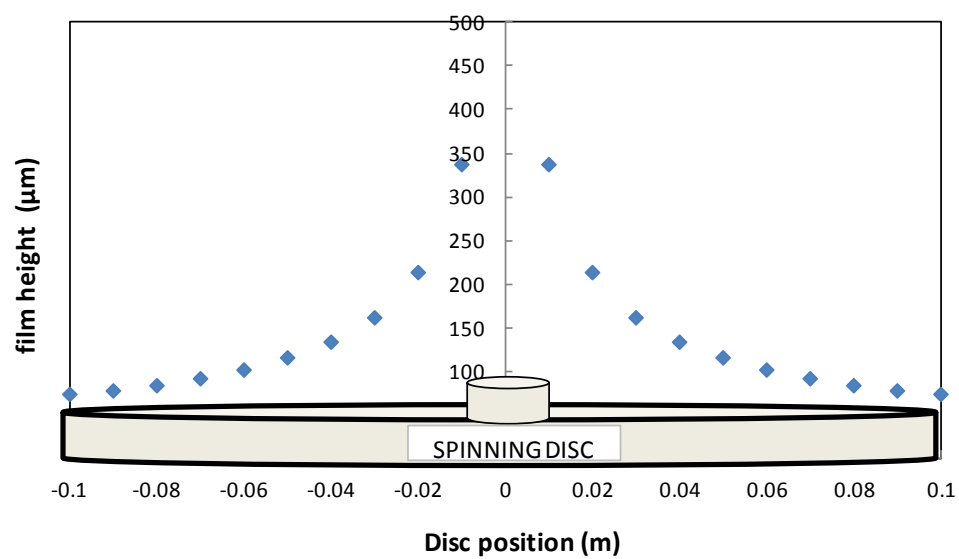
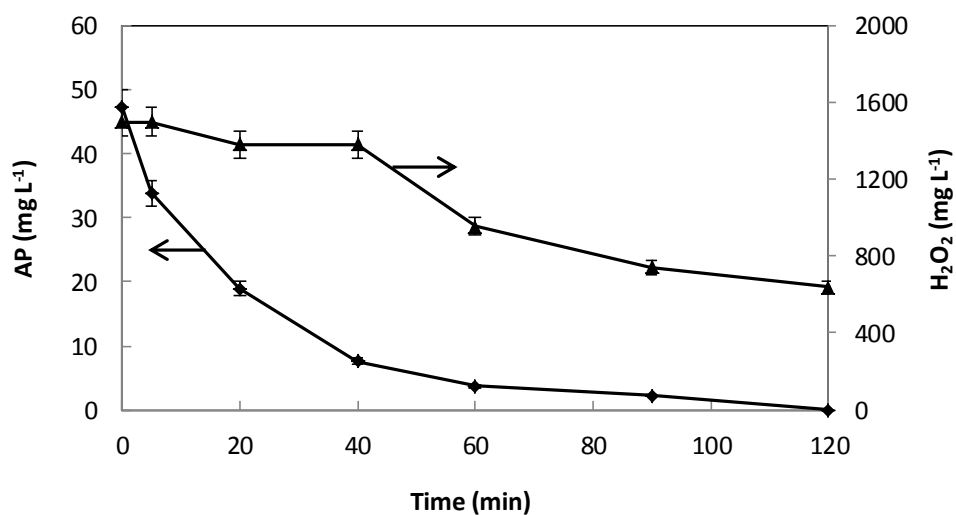
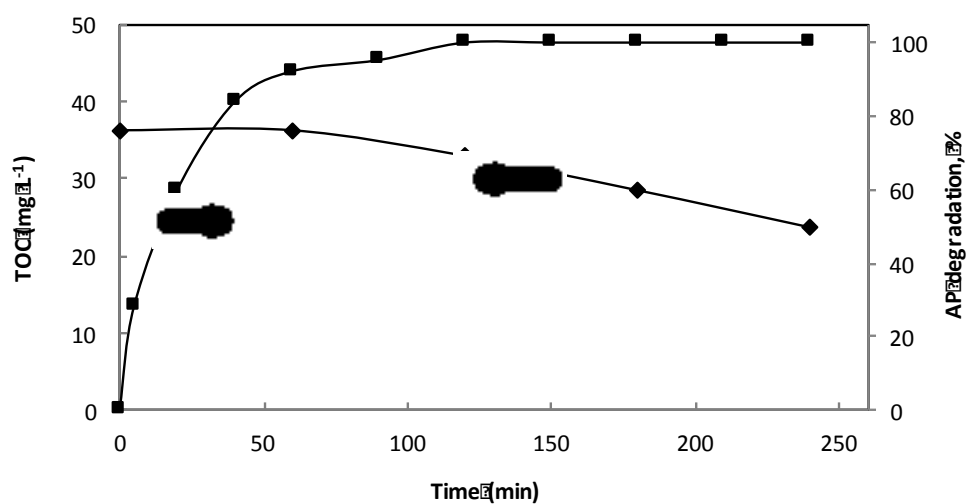


FIGURE 4

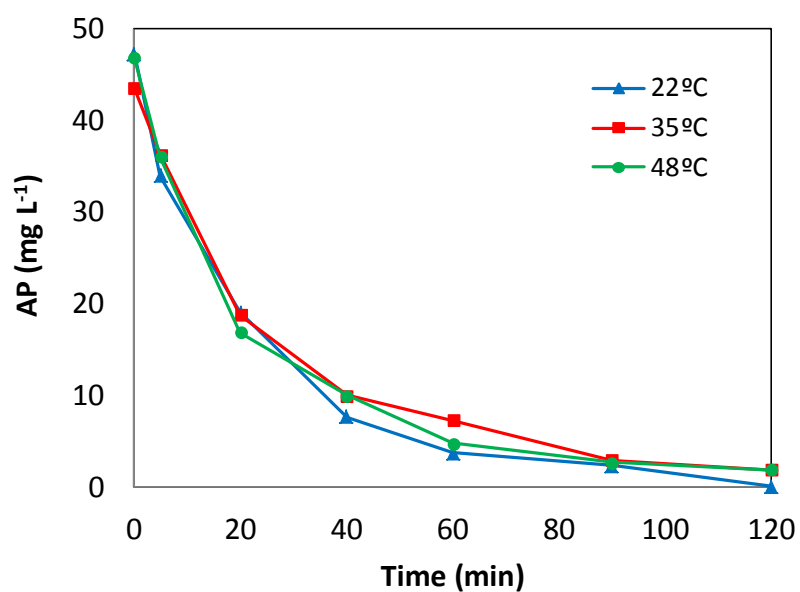


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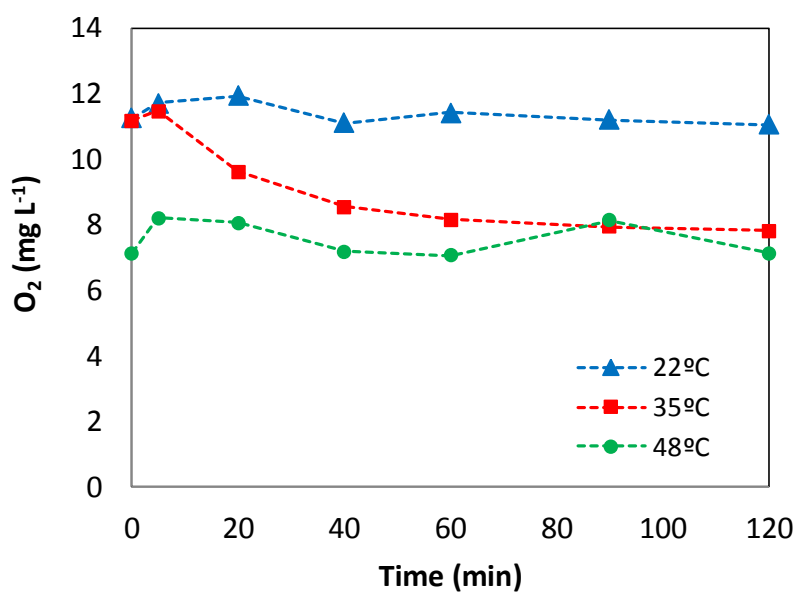


b)

FIGURE 5



a)



b)

FIGURE 6

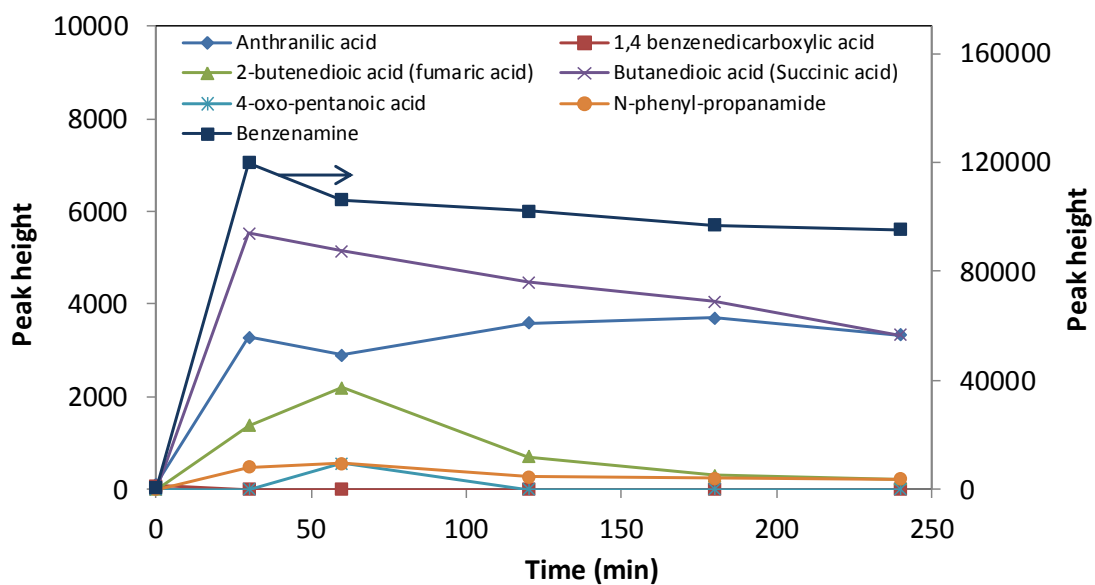


FIGURE 7

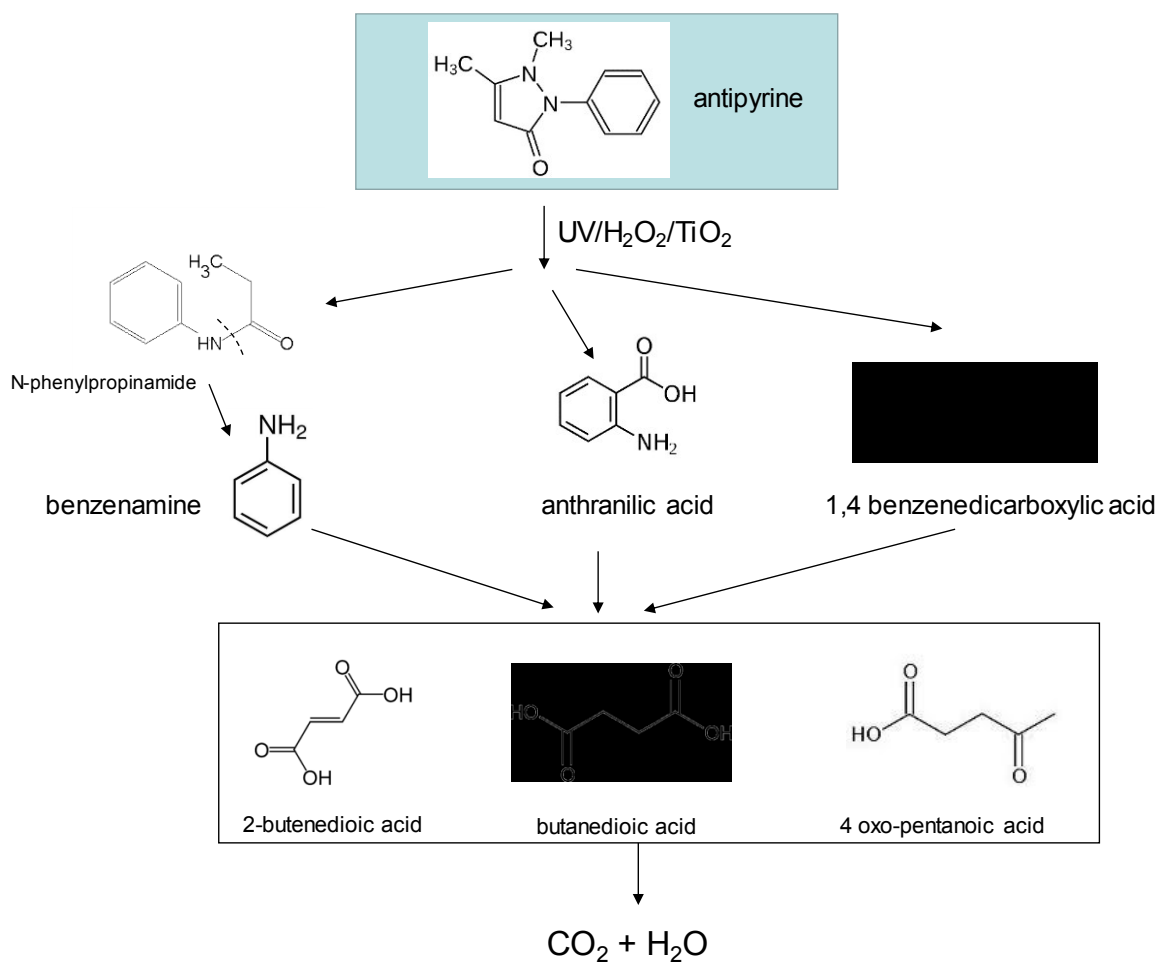


FIGURE 8

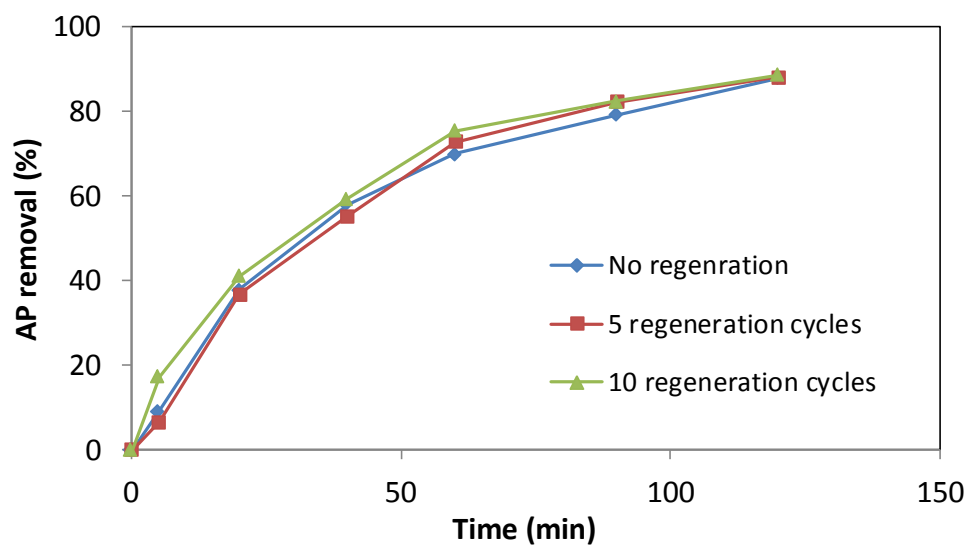


FIGURE 9

SUPPLEMENTARY MATERIAL

Table 1. Experimental design, film thickness and apparent volumetric rate constant for the degradation of antipyrine in SDR.

Process: UV/H₂O₂/TiO₂

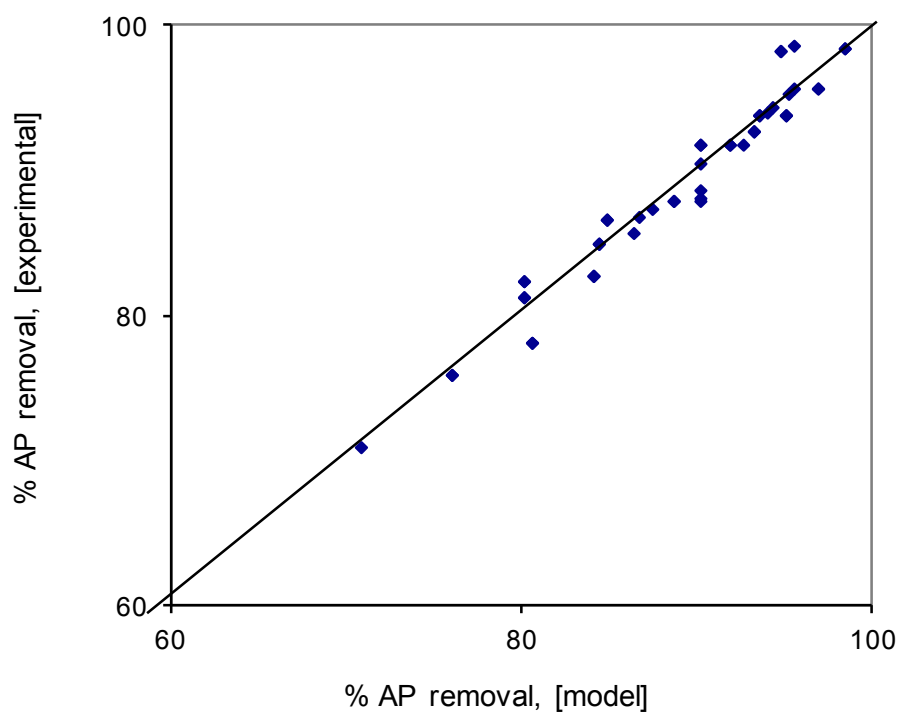
Factorial Design					Response Function after 120 minutes		
Experiment	H ₂ O ₂ (mg/L)	Speed (rpm)	Flow (mL/s)	pH	([AP] ₀ - [AP])/[AP] ₀	k *10 ⁴ (s ⁻¹)	h (μm)
1	1125	400	20	7	0,981	4.848	138.1
2	375	400	20	7	0,827	3.322	
3	1125	400	20	5	0,984	5.180	
4	375	400	20	5	0,879	2.930	
5	1125	400	10	7	0,926	3.607	111.0
6	375	400	10	7	0,812	2.523	
7	1125	400	10	5	0,956	4.384	
8	375	400	10	5	0,865	2.694	
9	1125	200	20	7	0,918	3.352	222.0
10	375	200	20	7	0,824	2.323	
11	1125	200	20	5	0,938	3.838	
12	375	200	20	5	0,849	2.657	
13	1125	200	10	7	0,918	3.362	176.2
14	375	200	10	7	0,759	2.055	
15	1125	200	10	5	0,937	3.670	
16	375	200	10	5	0,780	2.118	
17	1500	300	15	6	0,985	4.297	153.9
18	0	300	15	6	0,709	1.689	
19	750	300	15	8	0,856	3.320	
20	750	300	15	4	0,943	3.938	
21	750	300	25	6	0,917	3.503	182.5
22	750	300	5	6	0,872	3.007	106.7
23	750	500	15	6	0,940	3.770	109.4
24	750	100	15	6	0,868	2.850	320.3
25	750	300	15	6	0,904	3.460	153.9
26	750	300	15	6	0,879	2.888	
27	750	300	15	6	0,880	3.027	
28	750	300	15	6	0,886	2.887	
Additional Experiments (for determination of optimum conditions)							
29	1750	300	15	6	0,956	4.372	153.9
30	2000	300	15	6	0,951	4.389	

**Table 2. Equation and parameters for the NN fitting.
(Process: UV/H₂O₂/TiO₂)**

$$\frac{[AP]_0 - [AP]}{[AP]_0} = N_1 \cdot \left(1 + \frac{1}{e^{(W_{11} \cdot [H_2O_2]_0 + W_{12} \cdot Speed + W_{13} \cdot Flow + W_{14} \cdot pH)}}\right) + N_2 \cdot \left(1 + \frac{1}{e^{(W_{21} \cdot [H_2O_2]_0 + W_{22} \cdot Speed + W_{23} \cdot Flow + W_{24} \cdot pH)}}\right)$$

Neurons and Weight Factors	Parameters	Values of neurons and factors
N₁	Neuron	0.88
W ₁₁	[H ₂ O ₂] ₀	3.81
W ₁₂	Speed	0.11
W ₁₃	Flow	0.43
W ₁₄	pH	-0.1
N₂	Neuron	0.44
W ₂₁	[H ₂ O ₂] ₀	-1.44
W ₂₂	Speed	0.59
W ₂₃	Flow	0.01
W ₂₄	pH	-0.66

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872 Figure S1. Neural network fitting for the UV/H₂O₂/TiO₂ system

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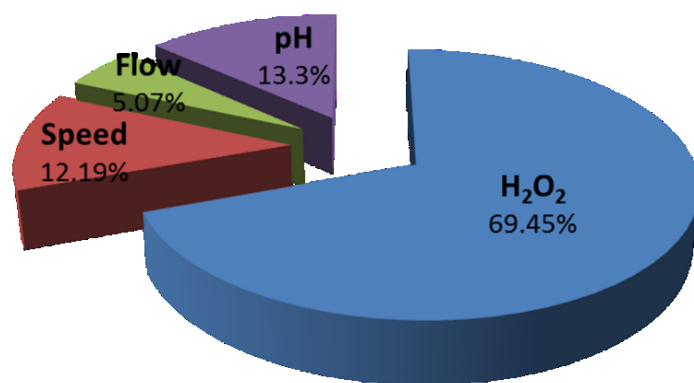
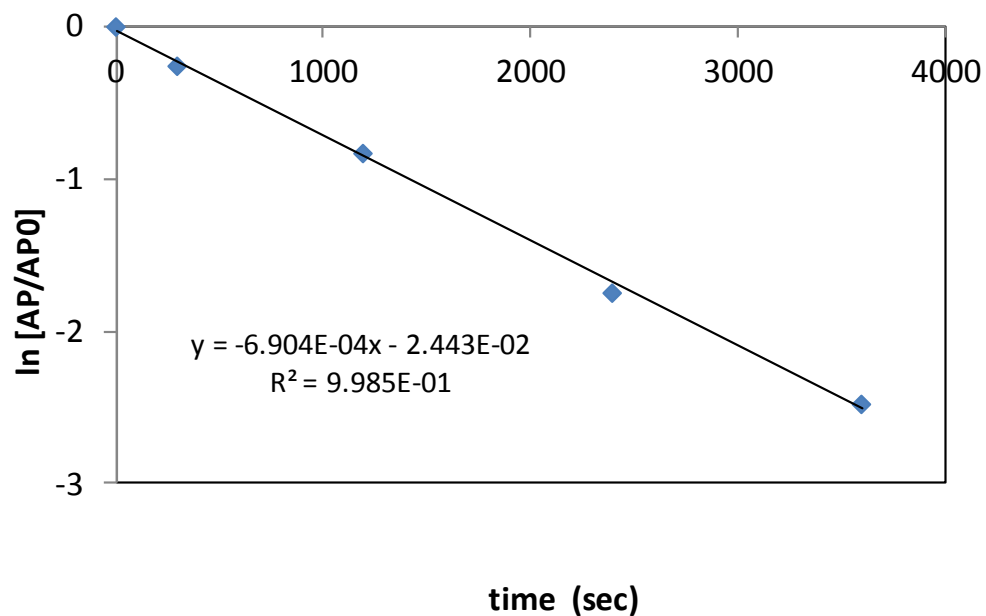


Figure S2. Saliency Analysis for the UV/H₂O₂/TiO₂ system (%).

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908 Figure S3. Example of fitting of the reaction order for the UV/H₂O₂/TiO₂ system

909 Conditions: pH= 4; [H₂O₂]₀= 1500 mg/L; Speed= 500 rpm; Flow= 25 mL/s; [AP]₀= 50

910 mg/L.

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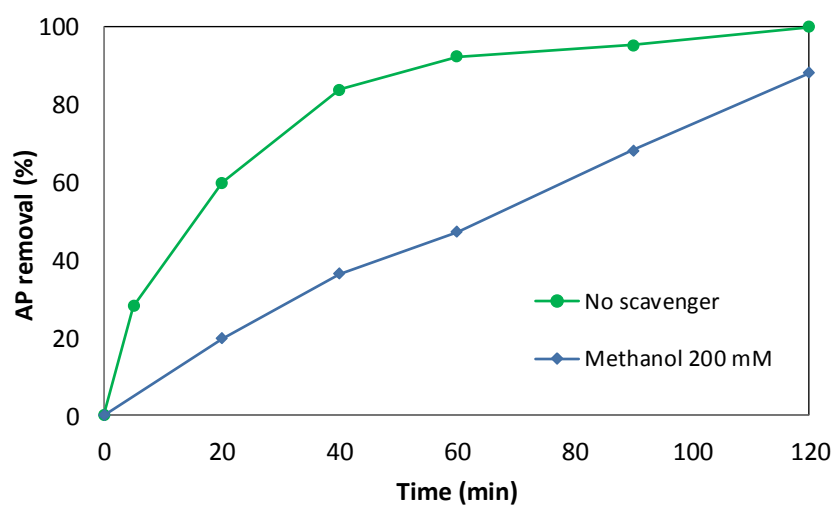


Figure S4. Scavenger effect (effect of methanol addition to the UV/H₂O₂/TiO₂ system).

Conditions: pH= 4; [H₂O₂]₀= 1500 mg/L; Speed= 500 rpm; Flow= 25 mL/s; [AP]₀= 50 mg/L.