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# Study of the paracetamol degradation pathway that generates color and turbidity in oxidized wastewaters by photo-Fenton technology

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ABSTRACT

This study aims determining the effect that certain kind of water contaminants have on the changes of turbidity during their oxidation. Phenol is considered by its frequent presence in industrial discharges; meanwhile paracetamol is representative of emerging pollutants of pharmaceutical origin. Quite different results are observed in the turbidity changes during the oxidation of both pollutants that evolve following the kinetics of a reaction intermediate. The analysis of paracetamol and phenol degradation pathways reveals that operating conditions are important in the formation of intermediates that cause turbidity. The maximum turbidity levels are achieved operating at the ratios 12 mol $HO^{\bullet}$ per 100 mg contaminant. However the turbidity generated during the paracetamol oxidation only reaches a third of the intensity achieved with phenol.

During the paracetamol degradation, the intermediates causing turbidity are similar to the ones found during the phenol decomposition. These species are generated during the initial minutes of oxidation and possess structures of large size and molecular weight. At the máximum turbidity point, muconic acid and hydroquinone are identified and found to coexist with other compounds such as pyrogallol and resorcinol. Therefore, the path involving metasubstitution would be the main originator of turbidity. It is noteworthy the rapid formation of muconic acid that coexists with resorcinol-like species. These compounds enable the establishment of hydrogen bond interactions that yield supramolecular structures.



## 1. Introduction

This paper focuses on the study of turbidity changes that are produced when waters containing organic contaminants are treated with Advanced Oxidation Processes (AOPs) technologies. The treatment used was the Fenton reagent enhanced by UV radiation. This technology was selected due to ease of operation and efficiency [1]. Moreover, only one kind of treatment was applied because the degradation byproducts generating turbidity with different AOPs were alike, regardless of the techniques employed. Main current research on oxidation of industrial effluents by Fenton technologies focuses on the wastewater treatment from the petrochemical, paper, chemical and pharmaceutical (emerging contaminants) sectors [2].

The ultimate objective in this work is to analyze the origin of the turbidity of the treated water and the factors that affect it. The interest in studying this parameter lies in the determination of treated waters quality, since it is restricted by the environmental legislation in the EU Water Framework Directive (Directive 2000/60/EC). In this way, the characteristics of the reactions that contribute to the turbidity formation and the quality of the water thus treated are identified and discussed.

Two representative contaminants of common industrial and urban effluents were chosen for the oxidation study. Hence, the turbidity induced by the oxidation treatment of phenolic compounds was duly investigated. Additionally, the oxidation of a well known emerging contaminant of pharmaceutical origin, acetaminophen (paracetamol in Europe) was also characterized. These two compounds were selected based on their characteristic concentration levels and the effects they may bear on natural systems.

Phenolic contaminants in water may significantly impact on aquatic echosystems thus affecting rural communities and urban areas [3]. Usually, concentration, temperature, structure, pH of the compound and media determine the degree to which these

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compounds affect living organisms [4,5]. The operating conditions performed by many authors in studies on phenol oxidation have been applied to other matrices, in order to compare their effectiveness. The considered variables in this work were the catalyst and oxidant dosages, because they determine the reaction rate and the extent of oxidation.

Emerging contaminants and their characterization and study are presently raising high interest because of their increasing consumption. Several pharmaceutical products such as analgesics or antibiotics can be recognized in this group of substances since they have been increasingly detected in wastewaters and even potable water. These drugs generate metabolites in the body that are excreted together with their residual active ingredients. As a result, they often reach the wastewater treatment plants [6,7]. Even in low concentrations, these substances can be cause of concern, as they accumulate in the receiving environment [8]. These emerging contaminants are not fully degradated in wastewater treatment plants, so that they end up being dumped into the rivers [9].

To degrade this kind of contaminants, the viability of AOPs are currently applied. In general, these technologies use the following control parameters: decontamination performance achieved dosage of oxidant and catalyst employed, initial charge of contaminant in the water, pH and temperature [10]. Studies reported in the literature show that some organoleptic parameters can be regarded as indicators of water quality [11]. Thus, this paper considers the turbidity and determines its suitability as an efficiency indicator of water treatment. Turbidity analysis can usually be fast, cheap and simple. However, its practical application depends on a number of operating parameters such as nature of contaminating substances, acidity of the medium, temperature, and concentration of dissolved species. Then, it is essential to keep these conditions constant to obtain reliable measurements.

The ultimate objective is to elucidate the origin of the turbidity of the treated water and its control factors. In this way, the characteristics of the reactions contributing to turbidity are discussed, as well as if organic matter affects to it [12,13]. In this way, the work aims to refocus the understanding of AOPs to clarify the relationship between turbidity and oxidation intermediates [14] as well as to study the effect of the substituted groups and their position on the benzene ring.

## 2. Materials and methods

### 2.1. Reaction system

The experimental assays of this work were carried out with respectively aqueous samples of phenol ($C_6H_6O$ Panreac, 99%) and commercial paracetamol ($C_8H_9NO_2$ Efferalgan, sorbitol excipient) of 100.0 mg/L prepared in the laboratory. In this way, 500.0 mL samples were poured into a simple immersion-type photochemical reactor, 600 mL working volume with the inserted cooling sheath [12,13]. The irradiation is effected by means of a medium pressure UV lamp (Heraeus TQ-150, 95% transmission between 300 and 570 nm, 150 W, 87.4 V, 167.3W, 2.20A), operated by utilizing a vertically arranged immersion tube as well as a separate cooling sheath, immersed into the reaction mixture.

Next, the catalyst dose of Fe (II) established in each set of experiments was added to the reactor in each set of experiments, being the rank Fe = 0-50.0 mg/L ($FeSO_4$ $2H_2O$ Panreac, 80%). The reaction mixture was homogenized by a magnetic stirrer at 500 rpm. Finally, hydrogen peroxide was added to the reactant mixture in the interval $H_2O_2$ = 0-15.0 mM ($H_2O_2$ 30%, Foret). Therafter, the reaction started. Acidity was adjusted to pH = 3.0 by pouring NaOH and HCl 0.2 M (Probus, 99.9%) with an automatic burette (Dosimat 665-Metrohm) and temperature was stabilized around 25.0 °C using a cryo-thermostat bath of 1150 W (Selecta Frigiterm-10), and pumping refrigeration water through the cooled reactor sheath, where the UV lamp is inserted.

### 2.2. Analysis methods

The concentration of organic species was analyzed by High Performance Liquid Chromatography, attached to a spectrophotometer UV/Vis (Agilent Technologies 1200 Series). Common concentrations of emerging pollutants in urban wastewaters are around micrograms per liter. However, this work deals with 100.0 mg/L solutions, due to limitations in the detection range of the chromatography equipment.

Analysis was performed injecting manually 20 μL samples, dragged by a carrier current flow of 1.0 mL/min, consisting of a mixture of methanol and distilled water MeOH/$H_2O$:20/80, through a column $C_{18}$, XBridge Phenyl 5 μm 4.6 × 250 mm (Bridge Waters), with detection limit (LOD) 0.1 mg/L. The concentrations of organic species were analyzed at 280 nm: phenol (Panreac, 99%), hydroquinone (Panreac, 99%), catechol (Baker Organic Chemical, 99%), resorcinol (Panreac, 99%) and phloroglucinol (Acros Organics, 99%); ZZ-muconic acid (Acros Organics, 98%) and EE-muconic acid (Acros Organics, 97%) at 242 nm; *p*-benzoquinone (Alfa Aesar, 98%), hydroxyhydroquinone (Aldrich, 99%) and pyrogallol (Sigma, 98%); paracetamol (Efferalgan, sorbitol excipients) at 254 nm and 2,5-dihydroxy-1,4-benzoquinone (Acros Organics, 98%) at 210 nm. The solution turbidity was measured with a nephelometric turbidimeter (2100Qis Hach).

## 3. Results and discussion

### 3.1. Effect of operating pH on turbidity

Several pollutant solutions were oxidized, all containing $C_o$ = 100.0 mg/L, at different pH in the pH = 2.0-5.0 range. Essays were performed dosing with $H_2O_2$ = 14.8 mM and Fe = 20.0 mg/L catalyst, and keeping temperature constant at T = 25.0 °C. Fig. 1 displays turbidity at different pH of phenol and paracetamol aqueous samples after oxidation, when the maximum turbidity is generated ($NTU_{max}$), as well as the turbidity that remains at steady state ($NTU_{oo}$).

Results in Fig. 1 reveal that there are differences in water turbidity that depend on the type of solution contaminant. Thus, paracetamol shows no major effect of pH on turbidity. However, when the contaminant is phenol, a trend is evidenced that shows a

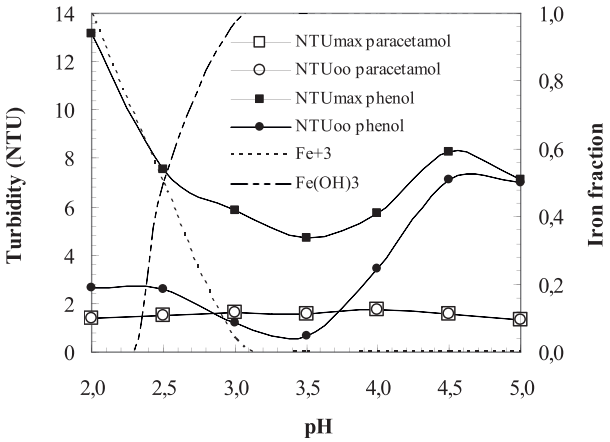


**Fig. 1.** pH effect on the wastewater turbidity during the oxidation of several contaminants in a photo-Fenton system. Experimental conditions: $Ph_o$ = 100.0 mg/L; $Pa_o$ = 100.0 mg/L; Fe = 20.0 mg/L; $H_2O_2$ = 14.8 mM; T = 25.0 °C.