



Detoxification of waters contaminated with phenol, formaldehyde and phenol–formaldehyde mixtures using a combination of biological treatments and advanced oxidation techniques



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ABSTRACT

The detoxification process of waters contaminated with phenol, formaldehyde and phenol–formaldehyde mixtures was studied using advanced oxidation treatments (heterogeneous photocatalysis and Fenton), biological techniques (aerated biological and wetland reactors) and combinations of the two. It is shown that photocatalysis was efficient in the detoxification of concentrations below 50 mg L^{-1} of those compounds. Sample toxicity increased at higher concentrations due to the generated intermediates. Phenol–formaldehyde mixtures were impossible to detoxify by heterogeneous photocatalysis at any of the studied concentrations. Treatments using the Fenton reaction were able to degrade concentrations above 1000 mg L^{-1} , though the use of a reagent such as peroxide makes it a costly technique. The efficiency of the biological aerated filter (BAF) mainly depended on initial concentration and toxicity, with removal rates of 3.08 and $0.26 \text{ g L}^{-1} \text{ d}^{-1}$ obtained for phenol and formaldehyde, respectively. Taking into account the results obtained for the treatment of complex phenol–formaldehyde mixtures, the best combination of techniques for the treatment of concentrations found in the industrial wastewater studied in this paper was the Fenton + BAF technique which was able to detoxify phenol–formaldehyde concentrations (1:1) of 1000 mg L^{-1} .

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1. Introduction

In recent decades industrial development has become associated with an increasing use of natural available resources. Almost 59% of the water used in developed countries is for industrial purposes and these same countries are responsible for 80% of the world's industrial waste waters. As for the developing countries, 70% of factory-generated effluent is discharged without receiving any sort of treatment, with consequent contamination of the available water resources [1]. There is then a clear need for treatment systems suitable for such contaminated effluents.

One of the main difficulties concerning the treatment of toxic effluents is their variable chemical nature and concentration [2]. Because of the high levels of toxicity and the short- and long-term biological effects legislation is commonly required to govern the discharge of such waste materials. Conventional treatments of

household waste waters are insufficient for these types of effluents which can often create problems for the waste water treatment plant due to the presence of persistent and toxic organic compounds [3]. Treatments specifically designed for those types of industrial effluents tend to be complicated and expensive.

One of the procedures developed over the last decade for the treatment of various organic compounds involves the use of biological aerated filter (BAF) reactors. They basically comprise a submerged bed of particles colonized by different strains of bacteria with a continuous supply of air. They are noted for their high efficiency, small size and low cost [4–6]. This type of reactor has begun to be used for the treatment of various waste materials including tri-nitrophenols [7], trinitrotoluene [8], *n*-alkanes [9], etc.

The other biological treatment considered in this study involves the use of artificial wetlands. The processes involved resemble those found in conventional treatment of waste waters in combination with natural processes such as photosynthesis, assimilation by plants, etc. The main difference is that in conventional treatments the processes take place in different reactors at speeds accelerated by an additional input of energy, whereas in the artificial wetlands

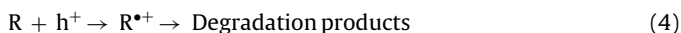
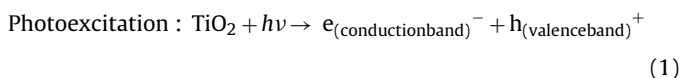
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all the processes occur in a single-system reactor at natural speed. The main advantage of biological systems is their low cost and maintenance requirements [10,11].

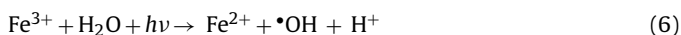
In Nature, biodegradation is the main route of treatment of many xenobiotics though other abiotic processes such as hydrolysis or photolysis can play an important role. The fundamental problem is that many of the compounds present in industrial wastewater are not biodegradable and/or toxic [12].

For the removal of the most resistant compounds one option is the use of the so-called advanced oxidation techniques (AOTs), which are based on the generation of strongly oxidising radicals able to remove or transform these substances into more biodegradable compounds. These techniques include heterogeneous photocatalysis with TiO₂ and homogeneous photocatalysis such as Fenton or photo-Fenton. On occasions, AOTs will give rise to reaction intermediates which are in fact more toxic than the initial compound. This is the case with phenol, whose principal intermediates are hydroquinone and catechol which are much more toxic than phenol itself [13,14].

Heterogeneous photocatalysis is based on the incidence of UV light on a photocatalyst, generally a broad-band semiconductor like titanium dioxide (1). If the radiation has energy equal to or greater than the E_g then an electron is promoted from the valence band to the conduction band, generating an electron–hole pair. This electron–hole pair has to diffuse out to the surface of the photocatalyst before it can intervene in oxidation and reduction reactions that can generate •OH radicals ((2)–(3)) capable of oxidising the pollutants. The pollutants can also be oxidized directly through the photogenerated holes which diffuse out to the photocatalyst surface (4) [15,16]:



The Fenton reaction (5) consists of a catalytic reaction between the Fe²⁺ and H₂O₂ to generate •OH radicals. Light can accelerate the process regenerating the Fe⁺² from the Fe⁺³ formed in the reaction (6). This is known as the photo-Fenton process [17,18].



While many studies in recent years have suggested combining biologically-based techniques and AOTs for optimization of the treatment of a waste material, not only in terms of the removal of the compound but also its complete detoxification, few studies

have in fact been made on such combinations. Those that have been carried out have not taken into account the effect of the presence of various pollutants with different degrees of biodegradability, nor have they considered the case of high concentration levels of one pollutant inhibiting the biodegradation of another [12]. Likewise, studies rarely contemplate the costs involved to show that a particular combination can be considered both innovative and competitive for industrial application [12].

The present paper is based on a study of the removal and detoxification of some of the compounds commonly found in industrial waste waters, namely phenol, formaldehyde and phenol–formaldehyde mixtures (see Table 1), using a combination of biological and photocatalytic treatments which are innovative and economically competitive in comparison with commonly used industrial effluent treatment techniques.

2. Methodology

Phenol (99%) and formaldehyde (35–40%, w/v) were purchased from Aldrich and Panreac respectively. All reagents were of analytical grade.

The photocatalyst used was Evonik P25 TiO₂ (anatase–rutile: 80–20, particle size of 30 nm and BET surface area of 50 m² g^{−1}). After addition of the photocatalyst (1 g L^{−1}), final pH value was adjusted at the beginning of the reactions to 4.5–5 with sulfuric acid or sodium hydroxide.

For Fenton reactions, high purity FeSO₄·7H₂O (Panreac) and 35% (w/v) H₂O₂ from Scharlau were used. All experiments were performed without aeration and at pH 3. When necessary, initial pH was adjusted with H₂SO₄ (95–97% Scharlau). At the end of the experiment, catalase from *Micrococcus lysodeikticus* (243,075 U/mL; Fluka) was used to remove the peroxide remaining from the Fenton processes and avoid its interference in the toxicity measurements.

The heterogeneous photocatalytic and Fenton reactors were 250 mL Pyrex cylinders. Aqueous solutions were prepared with Milli-Q water.

The 60 W UV source was a Solarium Philips HB175 UV set of lamps, comprising 4 × 15 W Philips CLEO fluorescent tubes (emission spectrum from 300 to 400 nm, maximum at 365 nm), which gave an irradiation level of 8.9 mW cm^{−2} (Graseby 5370 photometer) at a distance of 10 cm.

Total organic carbon (TOC) measurements were made using a Shimadzu 5000-A analyser. Formaldehyde analysis was performed by the chromotropic acid method [19] which gave a detection limit of 3 mg L^{−1}.

Remaining phenolic compounds concentrations at different reaction times were HPLC measured with a Supelco Discovery C18

Table 1
Main characteristics of the compounds used in this study.

Compound	Industrial process	Untreated effluent concentration [mg L ^{−1}]	Toxicity [EC ₅₀ , mg L ^{−1}]	Maximum legal discharge concentration
Phenol	Metallurgy	800–8000 [23]	13.1 ^a –510 ^b [27]	<0.5 μg L ^{−1} [28]
	Refinery	35–1000 [23]		
Formaldehyde	Coal industry	1500–2000 [23]	5.8 ^c –34.1 ^d [27]	1 mg L ^{−1} [29]
	Adhesives	220–4000 [24]		
Resins (Mixtures)	Resins	500–1300 [25,26]	–	–
	Resins	Phenol: 600–2000 [26] Formaldehyde: 500–1300 [26]		

^a Fish (48 h).

^b Mixed bacterial culture (120 h).

^c Crustacea (48 h).

^d Mixed bacterial culture (120 h).

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