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# Application of intensified Fenton oxidation to the treatment of hospital wastewater: kinetics, ecotoxicity and disinfection

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## Abstract

Fenton oxidation has proved to be effective for the treatment of a real hospital wastewater. The intensification of the process *viz.* the improvement on the efficiency of H<sub>2</sub>O<sub>2</sub> consumption, by increasing the temperature, is necessary to operate in a single step and avoid high reaction times and the need of large H<sub>2</sub>O<sub>2</sub> and iron concentrations. This approach would allow taking advantage of the heat energy contained in the laundry stream since the washing process is performed at high temperature to assure disinfection of the hospital textiles. In this work, temperatures within the range of 50-90 °C have been tested, which allowed an effective oxidation of the real wastewater ([COD]<sub>0</sub> = 365 mg L<sup>-1</sup>, [Phenols]<sub>0</sub> = 8.4 mg L<sup>-1</sup>, [total coliforms]<sub>0</sub> = 4.16 x 10<sup>6</sup> MPN/100 mL, 5 toxicity units) with the stoichiometric amount of H<sub>2</sub>O<sub>2</sub> (1000 mg L<sup>-1</sup>) and a relatively low iron concentration (25 mg L<sup>-1</sup> Fe<sup>3+</sup>). Operating at 90 °C, complete disappearance of phenolic compounds and 70% and 50% reduction of COD and TOC were achieved in 1 h reaction time. Time evolution of those global parameters were appropriately fitted to pseudo-first and second order kinetic equations, providing a useful approach for design purposes. [The main by-products were short-chain organic acids \(oxalic and formic\), being the final effluents non-toxic.](#) Disinfection of the hospital wastewater was also achieved at all the operating temperatures tested, as confirmed by the absence of coliforms.

## 1. Introduction

Contamination of water bodies by discharges of different types of wastewaters is a long-standing problem of environmental relevance. During the last three decades, the interest of the scientific community has been focused on the removal of priority pollutants such as pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls, which have been monitored in the aquatic environment according to the legislation [1]. In recent years, increasing attention is being paid to the presence of emerging pollutants (EPs), unregulated compounds which may be candidates for future regulation depending on their potential health and environmental impact as well as their frequency. EPs include personal care products, disinfectants, surfactants, hormones and pharmaceuticals. Due to their high consumption, they have been detected in both surface and ground waters in most developed countries [2, 3]. Among EPs, pharmaceuticals are considered especially relevant due to their negative effects on aquatic living organisms. Some representative examples are fish reproduction changes due to the presence of estrogenic compounds [4, 5] or specific inhibition of photosynthesis in algae caused by  $\beta$ -blockers [5].

Hospitals appear as one of the main sources of EPs water pollution. They consume high amounts of water on a daily basis, ranging from 400 to 1200 L day<sup>-1</sup> bed<sup>-1</sup> [6], which exceed by far the minimal domestic water consumption of 100 L per inhabitant per day [7]. Consequently, large volumes of hospital wastewater are continuously generated. Those streams have a fairly complex composition, including the aforementioned EPs, pathogenic microorganisms, toxic chemicals and radioactive elements. Thus far, hospital effluents have been commonly discharged into the municipal sewer system without preliminary treatment and their pollutants have been found in the inlet and exit streams of wastewater treatment plants (WWTP) as well as in surface water bodies [8-12]. Jelic et al. (2011)[11] followed the evolution of 32 pharmaceuticals in concentrations ranging from low ng L<sup>-1</sup> to a few  $\mu$ g L<sup>-1</sup> upon treatment in a conventional WWTP, showing that 29 of them were present in the exit stream and 21 were accumulated in sewage sludge at concentration up to 100 ng g<sup>-1</sup>. On the other hand, hospital

wastewaters are also considered a major source of pathogenic and antibiotic-resistant microorganisms that are released into the aquatic ecosystems.

For the aforementioned reasons, a number of authors [5-7, 11, 13-15] have claimed that the common practice of co-treatment of hospital and urban wastewaters in WWTPs is not a suitable solution, and intense research efforts must be done in the field of hospital wastewater treatment. Several physico-chemical methods have been recently tested. Gautam et al. (2007)[6] investigated the treatment of hospital wastewater by coagulation with  $\text{FeCl}_3$  and disinfection using calcium hypochlorite, achieving 65% COD removal and microbial reduction around 98.5%. Similarly, Suarez et al. (2009)[16] studied the pre-treatment of hospital wastewater by the combination of coagulation-flocculation and flotation, paying special attention to the removal of pharmaceuticals and personal care products. Musk fragrances were eliminated at 78-83% but pharmaceuticals were quite resistant to that treatment. Maximum removals of 46%, 42% and 23% were achieved for diclofenac, naproxen and ibuprofen, respectively, whereas the other pharmaceuticals present in the raw wastewater such as carbamazepine, diazepam, sulfamethoxazole, roxithromycin, trimethoprim and erythromycin were not affected. On the other hand, although Wilde et al. (2013)[17] reported a high degradation of  $\beta$ -blockers (<90%) by oxidation-coagulation using  $\text{K}_2\text{Fe}_2\text{O}_4$ , COD removal was relatively low (<20%) and no mineralization was achieved, giving rise to a wide diversity of degradation products. Besides the relatively low efficiency of those treatments, their non-destructive character makes necessary a careful disposal of the resulting sludge. Advanced oxidation processes (AOPs) can provide a more environmentally-friendly solution [18], being the Fenton process one of the most cost-effective technologies in this field [19]. So far, it has been successfully applied to the treatment of different industrial wastewaters such as cosmetics [20, 21], pesticides [21], power plant [21], textile [22] or sawmill [23]. Its potential application to EPs has been studied with promising results by several authors [24-26]. In previous contributions, we have proved the degradation of different and highly-persistent EPs such as triclosan [25] and carbamazepine [26] using low concentrations of iron (1-2  $\text{mg L}^{-1}$ ) and  $\text{H}_2\text{O}_2$  (25-60  $\text{mg L}^{-1}$ , corresponding to the theoretical stoichiometric amount). Nevertheless, the application of Fenton oxidation to the treatment of hospital

wastewaters has been scarcely studied in the literature so far. Berto et al. (2009)[27] applied the combined septic tank/Fenton treatment to a hospital effluent with 1138 mg L<sup>-1</sup> of average COD working at ambient temperature but using extremely high iron (5.8 g L<sup>-1</sup>) and H<sub>2</sub>O<sub>2</sub> concentrations (7.2 g L<sup>-1</sup>), much above the stoichiometric amount. The pollutants and multi-resistant bacteria were completely removed, but implying long reaction times and at unfeasible cost given the high reagent consumption and the need of dealing with high sludge volume. In this sense, increasing the temperature in Fenton oxidation could allow the treatment of the hospital wastewater in a single step as it has been proved to lead to a significant improvement of the oxidation rate and the mineralization percentage as well as a more efficient use of H<sub>2</sub>O<sub>2</sub> [28]. The proposed approach would allow taking advantage of the heat energy contained in the laundry stream since the laundering procedures imply the use of high temperature (>70 °C) to assure disinfection of the hospital textiles [29-31], being responsible for 50% of hospitals water consumption [32].

The aim of this work is to analyze the capability of the intensified Fenton process working at temperatures above the ambient for the *in-situ* treatment of a real hospital wastewater. [The evolution of global pollution parameters viz. COD and TOC has been measured along the reactions.](#) The concentration of phenolic compounds has been followed as an indicator of the presence of EPs. The ecotoxicity and total coliforms concentration of the Fenton oxidation effluents have been also determined at the end of the treatment.

## 2. Materials and methods

### 2.1. Fenton experiments

Oxidation runs were performed batch-wise in 100 mL stoppered glass flasks shaken in a constant-temperature bath at an equivalent stirring velocity of 200 rpm. The raw hospital wastewater (70 mL) acidulated at pH=3 (HNO<sub>3</sub> 1 M) was placed in the reactor and heated at the desired temperature. Once the temperature was reached, 2.5 mL of the H<sub>2</sub>O<sub>2</sub> solution (29 g L<sup>-1</sup>) followed by 2.5 mL of the Fe(NO<sub>3</sub>)<sub>3</sub> solution were added. According to previous works [21, 23, 33], the H<sub>2</sub>O<sub>2</sub> doses were tested within the range of 50 to 200% of the theoretical stoichiometric amount relative to COD (2.125 g H<sub>2</sub>O<sub>2</sub> g<sup>-1</sup> COD) and the Fe<sup>3+</sup> concentration was varied in the range of 10 – 50 mg L<sup>-1</sup>. The effect of temperature was investigated within a wide range (50–90 °C) since this variable has demonstrated to affect significantly the efficiency of H<sub>2</sub>O<sub>2</sub> consumption [23, 34, 35] and is also representative of the hospital laundry exit streams [31]. The experiments were performed in triplicate being the standard deviation less than 5% in all cases. Blank tests in absence of H<sub>2</sub>O<sub>2</sub> and Fe<sup>3+</sup> were also carried out at all the temperatures.

### 2.2. Analytical methods

Samples from the reactor were analyzed immediately after taken. Total Organic Carbon (TOC) was measured using a TOC analyzer (Shimadzu, mod. TOC, VSCH) and the H<sub>2</sub>O<sub>2</sub> concentration was determined by colorimetric titration following the titanium sulfate method [36] with a 1603 Shimadzu UV/Vis spectrophotometer. The concentration of phenolic compounds was determined with the Folin-Reagent test at 700 nm using a UV/Vis spectrophotometer. COD measurements were carried out by the closed reflux method with potassium dichromate (APHA, 2012). Short-chain organic acids were quantified by ion chromatography with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A sup 5-250 column (25 cm length, 4 µm internal diameter) was used as stationary

phase and an aqueous solution of  $3.2 \text{ mmol L}^{-1} \text{ Na}_2\text{CO}_3$  and  $1 \text{ mM NaHCO}_3$  as the mobile phase. The presence of dissolved trace metals in the raw wastewater was determined by TXRF.

### 2.3. *Ecotoxicity tests*

The ecotoxicity of the raw wastewater and samples from reaction was determined with the Microtox toxicity test (ISO 11348–3, 1998) with *Vibrio fischeri*. A photomultiplier M500 Microtox Analyzer (Azur Environmental) was used to measure the bioluminescence after 15 min of exposure. The test was conducted at  $15 \text{ }^\circ\text{C}$ , previously adjusting the osmotic pressure to 2% NaCl and the pH within 6–8.  $\text{IC}_{50}$ , defined as the dilution ratio (%) of the sample that yields 50% light emission reduction, was determined. The  $\text{IC}_{50}$  values are inversely proportional to the biological toxicity expressed as toxicity units (TU).

### 2.4. *Quantitative determination of total coliforms*

Total coliforms in the raw wastewater and final Fenton oxidation effluents were determined using the Colilert®-18 system (ISO 9308–2:2012). This method allows quantifying organisms in all types of water without preliminary pH adjustment and/or solid matter filtration. The results are expressed as the most probable number of coliforms (MPN) per 100 mL. The quantification limit for this method is 1 MPN/100 mL.

### 3. Results and discussion

#### 3.1. Wastewater characterization

The raw wastewater for this study comes from a hospital located in Alcorcón, Madrid (Spain). Its representative characteristics are collected in Table 1 (see Table S1 of the Supplementary Material for more details). The pH is in the expected alkaline range commonly found in this kind of wastewater [6, 8, 10, 37]. The values of TOC and COD, total nitrogen, total suspended solids, total coliforms and ecotoxicity are in good agreement with the values reported in the literature for hospital wastewaters [8, 10, 37].

The locally allowable limits for wastewater discharge into the municipal sewer system (Act 10/1993, Community of Madrid) are fixed at 3 mg L<sup>-1</sup>, 1000 mg L<sup>-1</sup>, 1750 mg L<sup>-1</sup> and 25 TU for total phenols, suspended solids, COD and ecotoxicity, respectively. As observed, with the exception of total phenols, the raw wastewater fulfills those regulations. Therefore, hospital wastewater streams are usually discharged into the municipal sewer systems without preliminary treatment. However, it is important to note that total phenols concentration, not usually considered in the literature dealing with hospital wastewaters treatment [18, 27, 38, 39], is almost three times higher than the allowable limit. This parameter can be used as indicative of the presence of emerging pollutants since it can be associated with pharmaceuticals, disinfectants, reagents and drug components, widely used in hospitals (see Table S2 of the Supplementary material for pharmaceuticals present in the hospital wastewater).

As aforementioned, hospital wastewaters represent an important way of dissemination of antibiotic-resistant microorganisms in natural ecosystems. Therefore, although wastewater disinfection is not compulsory according to the current legislation, it should be addressed to avoid undesirable evolution and spread of such resistant organisms in the water ecosystem. It is interesting to mention that the coliform concentration is somewhat lower than that typically present in the municipal sewage system (10<sup>8</sup> MNP/100 mL), which can be related to the presence of disinfectants and antibiotics [8].

### 3.2. Fenton oxidation

Figure 1 shows the evolution of COD, TOC and H<sub>2</sub>O<sub>2</sub> conversion upon Fenton oxidation of the hospital wastewater at different temperatures. The effect of catalyst concentration and H<sub>2</sub>O<sub>2</sub> dose were previously evaluated (see Fig. S1 and Fig. S2 of the Supplementary Material for experimental data). A dose of 25 mg L<sup>-1</sup> and the stoichiometric amount of H<sub>2</sub>O<sub>2</sub> were selected to prevent an uncontrolled generation of radicals and allow an efficient consumption of hydrogen peroxide. As expected, the rate of H<sub>2</sub>O<sub>2</sub> decomposition increases with temperature. Its effect is quite significant within the 40-degrees range tested where complete conversion of H<sub>2</sub>O<sub>2</sub> was achieved upon 1.5 h reaction time at 90 °C while it did not exceed 30% at 50 °C. Consistently with this, the rate of oxidation of the organic matter was significantly higher at increasing temperature. Around 70% COD reduction and 50% TOC mineralization were achieved working at or above 70 °C, whereas scarcely 25% and 40% were reached at 50 °C after the 4 h experiment. To distinguish the contribution from thermal decomposition of H<sub>2</sub>O<sub>2</sub>, blank experiments in the absence of catalyst were conducted under the same operating conditions. It was demonstrated that the catalyst plays a key role in the process since in its absence H<sub>2</sub>O<sub>2</sub> decomposition was below 10% and TOC mineralization was not significant (<10%) at the end of the 4h-experiment (see Fig. S3 of the Supplementary Material for experimental data).

A second-order equation was used to describe the rate of COD and TOC decay, an approach that served to fit well the experimental results. The values of the kinetic constants together with the apparent activation energies are collected in Table 2. The activation energies are comparable to the reported by Guedes et al. (2003)[40] and Bautista et al. (2007)[20] for different industrial wastewaters.

The H<sub>2</sub>O<sub>2</sub> efficiency in terms of mineralization (defined as TOC removal per unit mass of H<sub>2</sub>O<sub>2</sub> decomposed) remained constant around 60 mg TOC g<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> within the temperature range tested. Therefore, although the temperature has a significant effect on the oxidation rate and mineralization percentage it does not affect the efficiency of H<sub>2</sub>O<sub>2</sub> consumption under the operating conditions of this

work. With the aim of increasing its consumption efficiency, the feeding of  $\text{H}_2\text{O}_2$  was distributed along the reaction in three sequential additions (50% + 25% + 25% of total) (see Fig. S4 of the Supplementary Material for details). This strategy allowed improving moderately the  $\text{H}_2\text{O}_2$  efficiency up to 70 mg TOC  $\text{g}^{-1}$   $\text{H}_2\text{O}_2$  operating at 70 °C but implying longer reaction times. In any case, the values of  $\text{H}_2\text{O}_2$  efficiency obtained are similar to the reported for cosmetic wastewaters (59 mg TOC  $\text{g}^{-1}$   $\text{H}_2\text{O}_2$ ) [21] and close to the obtained with security inks aqueous wastes (64 mg TOC  $\text{g}^{-1}$   $\text{H}_2\text{O}_2$ ) but lower than those for sawmill [23] and pesticide [21] wastewaters (83 and 88 mg TOC  $\text{g}^{-1}$   $\text{H}_2\text{O}_2$ , respectively). This result could be related to the presence of relevant amounts of urea in the hospital wastewater (up to 77 mg  $\text{L}^{-1}$ , which represents a TOC of 15 mg  $\text{L}^{-1}$ , Table 1) since this compound has proved to be quite refractory to Fenton oxidation under these operating conditions (see Fig. S5 of the Supplementary Material for experimental data). Nevertheless, it can be expected that urea would be further degraded in the WWTP due to its high biodegradability.

As indicated before, the concentration of phenolic compounds can be used as indicative of the presence of EPs such as pharmaceuticals, disinfectants, reagents and drug components. Therefore, total phenols concentration was followed upon the reaction at different temperatures, being the results collected in Figure 2. As can be seen, phenolic compounds were completely removed in all cases although significant differences were found on the rate of disappearance depending on the temperature. While it took 4 h at 50 °C, only 1 h was required operating at 90 °C. The concentration vs. time values fitted well a pseudo-first-order equation. The resulting kinetic constants and activation energy are also included in Table 2. The complete degradation of phenolic compounds upon the treatment is crucial since those compounds are quite resistant to biodegradation, and thus would pass through WWTP without significant reduction.

In general, short-chain organic acids have been identified as main reaction products from Fenton oxidation [21, 41]. Their evolution in this case is depicted in Figure 3. Formic, oxalic and acetic acids were identified in all cases whereas maleic, malonic or fumaric did not appear. [Due to the formation of](#)

those organic acids, the pH of the reaction mixture was moderately reduced from its initial value ( $\text{pH}_0 = 3.0$ ) to values around 2.5. Both formic ( $6.4 \text{ mg L}^{-1}$ ) and acetic ( $42.5 \text{ mg L}^{-1}$ ) acids were present in the raw wastewater prior the oxidation treatment. Significant amounts of formic acid (up to  $31.4 \text{ mg L}^{-1}$ ) were formed upon oxidation although it was partially degraded at 70 and 90 °C. On the opposite, acetic acid formation was practically negligible, remaining its concentration almost constant throughout the reaction. The concentration of oxalic acid progressively increased during the oxidation experiments. Increasing the operating temperature leads to a higher production rate of this organic acid but its degradation was not observed in any case. These results are consistent with the well-known resistance of oxalic and acetic acids to Fenton oxidation [21, 41]. The amount of carbon in those compounds represented around 50% of the measured TOC when the temperature was at or above 70 °C and only 34% working at 50 °C. Therefore, a significant relative amount of the oxidation products were not identified and thus some additional information is needed to learn on the nature of the compounds contained in the final effluent.

### *3.2.1. Ecotoxicity*

Ecotoxicity analysis of the final oxidation effluents at different temperatures were carried out to get further insights on the reaction products nature. The results obtained are depicted in Figure 4. As observed, the oxidation of the raw wastewater at 50 °C led to an increase on the ecotoxicity, which indicates the formation of oxidation by-products with higher toxicity than the initial compounds. That result is in agreement with the aforementioned low decomposition of  $\text{H}_2\text{O}_2$  (~50%) and consequently, the low degree of mineralization (~25%) achieved under those operating conditions. The increase on the ecotoxicity upon oxidation of different industrial and synthetic wastewaters in mild operating conditions has been also reported in the literature [21, 33, 42, 43]. It has been associated to the formation of partially oxidized species whose ecotoxicity is considerably higher than those of the starting pollutants. Notably, increasing the temperature led to a significant reduction of ecotoxicity, which is also consistent

with the results obtained for COD and TOC degradation. Strikingly, the treated effluents at 70 and 90 °C were above 4 times less toxic than the raw wastewater. It should be highlighted that the abovementioned presence of urea in the final oxidation effluents does not contribute to the ecotoxicity as it has been proved in the literature [44].

### 3.2.2. *Disinfection*

Since coliforms have been in contact with significant concentrations of drugs and antibiotics, they can no longer be regarded as harmless indicators of fecal pollution but as antibiotic-resistant bacteria responsible for dissemination of multiple antibiotic resistance [5, 13, 15]. Therefore, disinfection of hospital wastewater streams is particularly necessary from both environmental and public health concerns. The efficiency of the process tested in that respect can be seen in Figure 5. [Blank experiments \(in the absence of Fe<sup>3+</sup>, and in the absence of both Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub>\) but at the pH 3.0 and temperatures of the Fenton oxidation runs are also included. As can be seen, a high reduction of microbial concentration was achieved by the thermal treatment, which, as expected, was more pronounced at increasing temperature. However, complete inactivation was only achieved in the presence of H<sub>2</sub>O<sub>2</sub> in the reaction medium.](#)

## 4. **Conclusions**

Intensified Fenton oxidation has proved to be effective for the treatment of hospital wastewater. The results show that increasing the temperature above the ambient (70 – 90 °C) allows improving significantly the oxidation rate and mineralization percentage with relatively low iron concentration (25 mg L<sup>-1</sup> Fe<sup>3+</sup>) and H<sub>2</sub>O<sub>2</sub> dose (1000 mg L<sup>-1</sup>). This approach would allow taking advantage of the heat energy contained in the laundry stream since the washing process is performed at high temperature to

assure disinfection of the hospital textiles. Moreover, the exothermic character of the oxidation process and the heat recovery from the treated effluent would also allow saving energy. Under those operating conditions, fairly high COD reduction (70%), significant TOC mineralization (50%) and the complete degradation of hazardous phenolic compounds was achieved, leading to non-toxic effluents at the end of the treatment. Furthermore, this treatment allowed disinfection of the wastewater, as confirmed by the absence of coliforms. This is crucial to avoid further dissemination of resistant bacteria into the environment.

## Tables

**Table 1.** Representative analysis of the raw hospital wastewater.

**Table 2.** Values of the rate constants ( $k_{\text{phenols}}$ :  $\text{min}^{-1}$ ;  $k_{\text{COD}}$ ,  $k_{\text{TOC}}$ :  $\text{L mg}^{-1} \text{min}^{-1}$ ) and activation energies,  $E_a$  ( $\text{kJ mol}^{-1}$ ) ( $[\text{H}_2\text{O}_2]_0 = 1000 \text{ mg L}^{-1}$ ;  $[\text{Fe}^{3+}] = 25 \text{ mg L}^{-1}$ ;  $\text{pH}_0 = 3$ ).

## Figure captions

**Figure 1.** Time-course of COD, TOC and  $\text{H}_2\text{O}_2$  decomposition (conversion) upon Fenton oxidation of the hospital wastewater at different temperatures ( $[\text{H}_2\text{O}_2]_0 = 1000 \text{ mg L}^{-1}$ ;  $[\text{Fe}^{3+}] = 25 \text{ mg L}^{-1}$ ;  $\text{pH}_0 = 3$ ).

**Figure 2.** Evolution of total phenols upon Fenton oxidation of the hospital wastewater at different temperatures ( $[\text{H}_2\text{O}_2]_0 = 1000 \text{ mg L}^{-1}$ ;  $[\text{Fe}^{3+}] = 25 \text{ mg L}^{-1}$ ;  $\text{pH}_0 = 3$ ).

**Figure 3.** Evolution of short-chain organic acids upon Fenton oxidation of the hospital wastewater at different temperatures ( $[\text{H}_2\text{O}_2]_0 = 1000 \text{ mg L}^{-1}$ ;  $[\text{Fe}^{3+}] = 25 \text{ mg L}^{-1}$ ;  $\text{pH}_0 = 3$ ).

**Figure 4.** Ecotoxicity values (TU) of the hospital wastewater and the effluents from Fenton oxidation (4 h) at different temperatures.

**Figure 5.** Hospital wastewater disinfection upon thermal treatment at acidic pH (3.0) and after Fenton oxidation at different temperatures ( $[\text{H}_2\text{O}_2]_0 = 1000 \text{ mg L}^{-1}$ ;  $[\text{Fe}^{3+}] = 25 \text{ mg L}^{-1}$ ;  $\text{pH}_0 = 3$ ).

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Table 1

pH	8.6 (20 °C)
COD (mg L <sup>-1</sup> )	365
TOC (mg L <sup>-1</sup> )	110
Total N (mg L <sup>-1</sup> )	94
NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	75
NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	0.64
Suspended solids (mg L <sup>-1</sup> )	138
Ecotoxicity (TU)	4.8
Total phenols (mg L <sup>-1</sup> )	8.4
Total coliforms (MPN/100 mL)	4.16 x 10 <sup>6</sup>

Table 2

Temperature (°C)	Total phenols		COD		TOC	
	$k_{\text{Phenols}} \times 10^2$	$r^2$	$k_{\text{COD}} \times 10^5$	$r^2$	$k_{\text{TOC}} \times 10^3$	$r^2$
50	1.85	0.967	1.61	0.995	2.4	0.889
75	4.98	0.995	4.74	0.997	8.1	0.953
90	13.1	0.951	12.9	0.978	22.3	0.988
Ea	47.7	0.995	50.7	0.999	54.2	0.985

Figure 1 revised

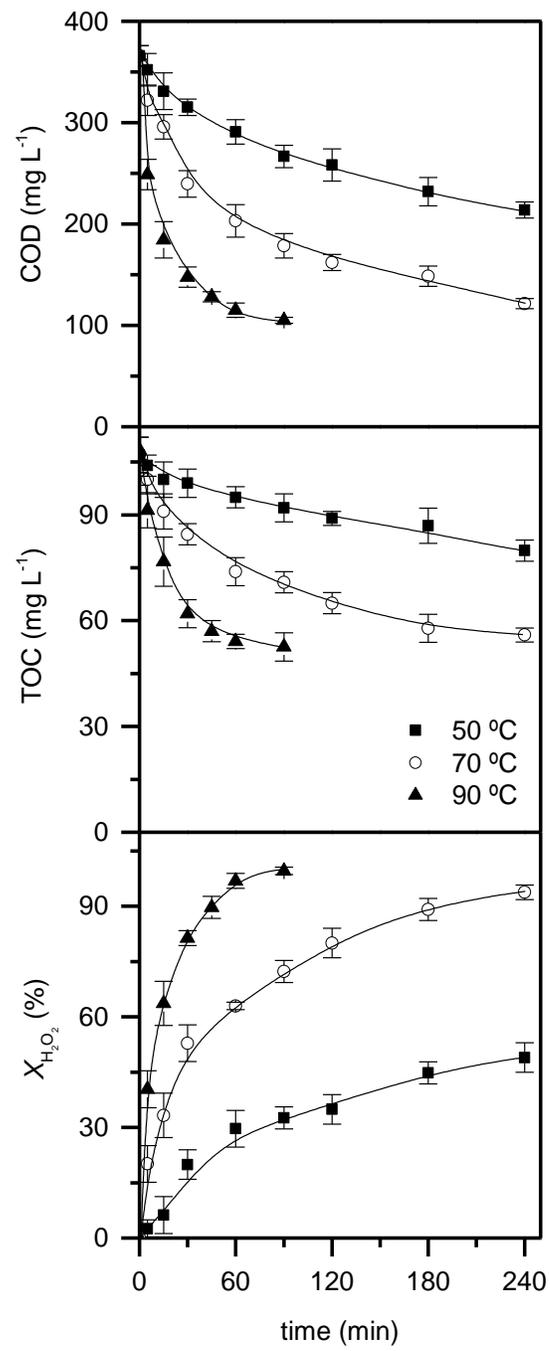


Figure 2 revised

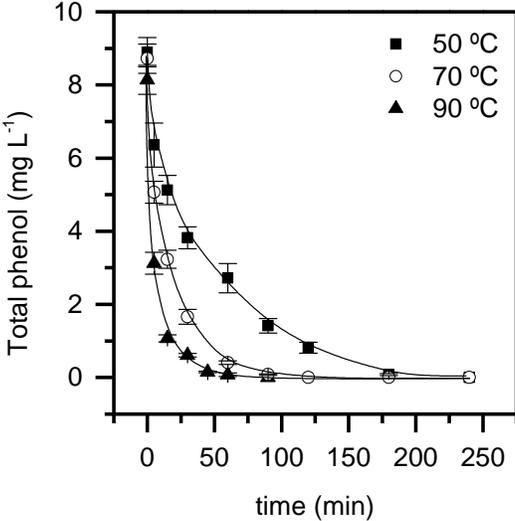


Figure 3 revised

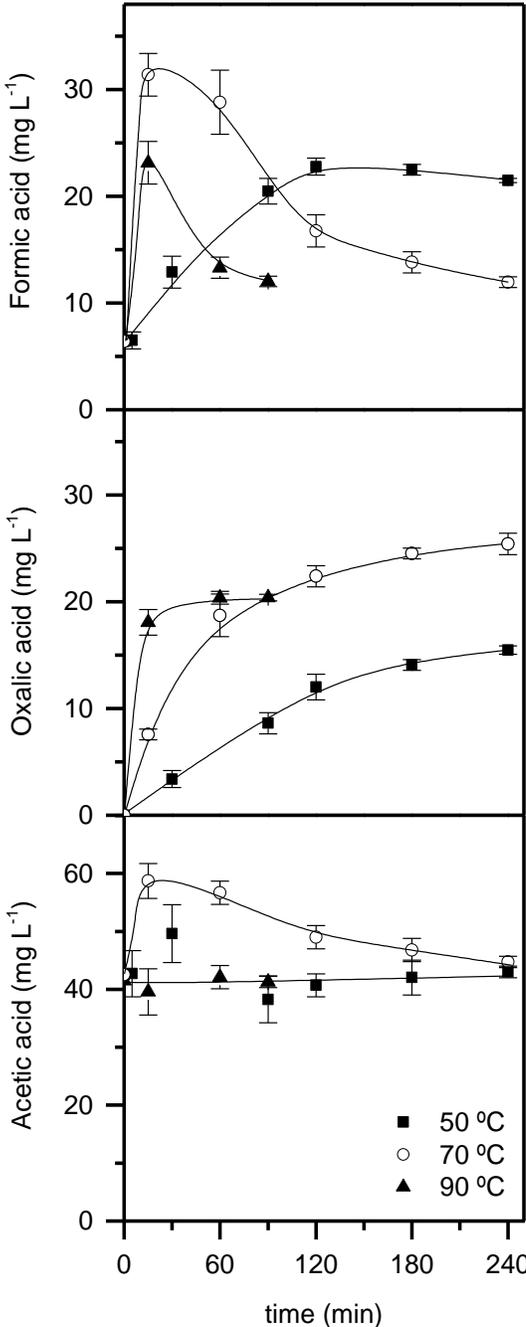


Figure 4 revised

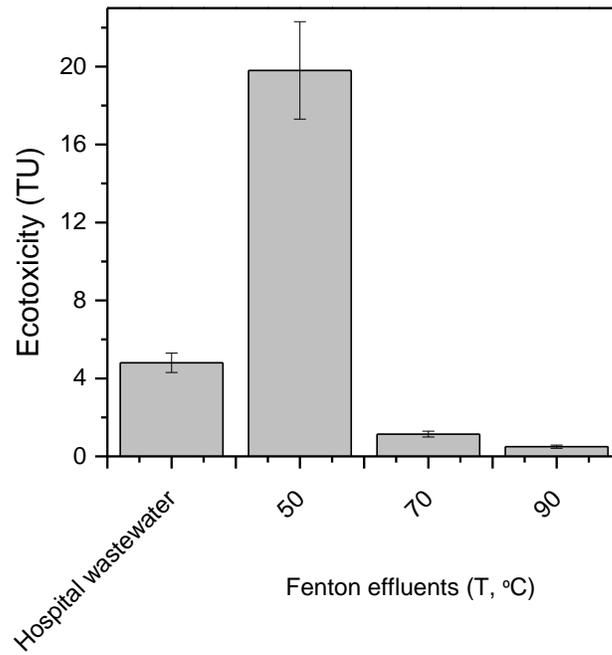


Figure 5 revised

