Assessment of the ozonation and Fenton process as a pretreatment of a subsequent biological treatment based on respirometric measurements

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Abstract

During the last decades, the industrial sector has been confronted with important challenges concerning the water treatment. Stricter norms and a rising fresh water cost make a more profound effluent purification, possibly coupled with water reuse, more and more necessarily. In this paper, the potential contribution of the integration of chemical oxidation with biological treatment in realising these challenges, has been examined. In this study, the Fenton process and the ozonation process are evaluated based on both conventional analytical measurements and respirometry. During the past decades, respirometry has increasingly been employed to obtain biokinetic characteristics, and it is considered one of the most important information sources in activated sludge process modelling. From the investigated AOPs, the Fenton process leads to the best results based on both degradation of organic pollutants and enhancement of biodegradability. An overall COD degradation by the combined treatment between 69% and 86% can be achieved.

Key-words: Ozone, Fenton, Respirometry, Biodegradability

Introduction

Selection of the best treatment option for remediation of a specific industrial wastewater is a highly complex task. In a given situation, the choice of one or more processes to be combined depends on the quality standards to be met and the most effective treatment with the lowest reasonable cost (Oller et al., 2010). In general, conventional biological processes are preferred for the treatment of industrial wastewaters. Indeed, activated sludge processes currently represent the most widespread technologyfor the secondary treatment of municipal wastewater and constitutes “the heart” of many wastewater treatment plants (Lessard and Beck, 1991). However, due to the fact that many of the organic substances present in industrial wastewaters are toxic or biorecalcitrant, biological treatment does not achieve satisfactory results.

In this context, the majority of complex organic chemicals present in water effluents can be oxidised by Advanced Oxidation Processes (AOPs), characterised by the formation of highly reactive hydroxyl radicals. Therefore, AOPs are considered a promising water treatment technology for the removal of those organic pollutants not treatable by conventional techniques (Oller et al., 2010). Although chemical oxidation for complete mineralisation is usually expensive, the coupling of chemical oxidation and biological treatment can be a suitable solution for the removal of complex organic compounds present in industrial wastewaters. The main idea is to apply an AOP to a toxic and/or non-biodegradable effluent during a limited time, optimising chemicals and energy consumption, and generating an intermediate sample that is fully biodegradable, thus opening the possibility of a subsequent biological treatment for the complete removal of organic matter (Farré et al., 2006). Experimental research has been performed by Cokgor et al. (2004), Lafi et al. (2009) and Sarria et al. (2002). Exhaustive reviews on this topic have been published by Mandal et al. (2010), Scott and Ollis (1995) and Tabrizi and Mehrvar (2004). It should be emphasised that the success of this approach cannot be guaranteed beforehand and depends strongly on the wastewater characteristics.

From the various advanced oxidation processes that have been adopted for the wastewater treatment, a distinction can be made based on the oxidant that has been used. In this study, an ozone-based and a hydrogen peroxide-based oxidation process are compared. More specifically, the Fenton process and the ozonation process are investigated for the degradation of the organic substances. Additionally, the enhancement of the biodegradability, based on BOD and respirometric measurements, has been monitored.

The Fenton reagent is an example of a homogeneous, catalytically driven •OH radical production process (Rigg et al., 1954). This reagent is a solution of H_2O_2 and Fe^{2+} ions, which act as a catalyst for the production of hydroxyl radicals. In this process, the Fe^{2+} are oxidised to Fe^{3+} ions. The Fenton reagent is very effective for various wastewaters, however, the final sludge is contaminated with Fe^{2+}/Fe^{3+} ions. This leads to high regeneration or sludge treatment costs and therefore the applicability of the Fenton reagents for industrial wastewater streams is seriously limited.

A frequently used oxidant is O_3, as it furthermore features a short half-life time. O_3 oxidises the target molecules either directly or through the formation of highly reactive hydroxyl radicals •OH. The latter mechanism corresponds to an AOP. The dominating oxidation mechanism depends on the pH of the solution and the target molecules. These •OH radicals would be able to oxidize almost all organic compounds to carbon dioxide and water, except for some of the simplest organic compounds, such as acetic, maleic and oxalic acids, acetone or simple chloride derivatives as chloroform (Bigda, 1995). The latter components are of a very interesting kind because they are typical oxidation products of larger molecules after fragmentation and they take part in energetic cycles of most living organisms. The long-chain compounds are split into partial oxidation products, often more biodegradable (Lopez et al., 1998 and Tzitzi et al., 1994).

Respirometry is the measurement and interpretation of the biological oxygen consumption rate under well-defined experimental conditions. Because oxygen consumption is directly associated with both biomass growth and substrate removal, respirometry is a useful technique for modelling and operating the activated sludge process. In the early years, application of the technique was focused mainly on measurement of the biochemical oxygen demand (BOD) of (waste) water. At that time, respirometry was seen as an instrument-based alternative to the original BOD test. Later, starting in the 1960s, respirometry was developed further and the technique began to generate much interest in process control. During the past decades, respirometry has increasingly been employed to obtain biokinetic characteristics, and it is considered one of the most important information sources in activated sludge process modelling. (Spanjers et al., 1998)

Material and methods

The homogeneous Fenton process

$FeSO_4.H_2O$ and H_2O_2 (30%, 1.11 kg/l) were used as Fenton reagents. Experiments were conducted at room temperature in a batchwise reactor of 1,00 l capacity, placed on a flocculator. A volume of 0.5 l of the wastewater was treated. In all the experiments, pH was adjusted to 3,0 and a reaction time of 30 minutes was obtained. The examined dosages of hydrogen peroxide (0,1 - 0,2 - 0,3 - 0,4 - 1,0 g H_2O_2/g COD) are based on literature data (Pera-Titus et al., 2004). The dosages of iron catalyst are dependent of the dosed amount of hydrogen peroxide. In the literature, ratios $[Fe^{2+}]/[H_2O_2]$ between 2/1 and 1/25 can be found. The used ratios in this research are 1/4 - 1/2 -1/1 - 2/1. The experimental set-up of the Fenton process is given in *Table 1*.

Table 1: Experimental set-up of the Fenton process

Oxidant Hydrogen peroxide: H_2O_2 (27%)	**Reaction time** 20 minutes
Catalyst Iron(II)ions: $FeSO_4.7H_2O$	**Reactor volume** 1000 ml (glass)
Reaction conditions Roomtemperature (20 °C) & pH 3	**Dosage oxidant** 0,1 - 0,2 - 0,3 - 0,4 - 1,0 g H_2O_2/g COD
Reaction volume 500 ml	**Dosage Catalyst** Ratio $[Fe^{2+}]/[H_2O_2]$: 1/4 - 1/2 - 1/1 - 2/1

The Ozonation process

The ozone experiments are performed in a lab-scale reactor, given in ***Figure 1***. The reactor operates batschwise and has a total internal volume of 10l. The construction material for the reactor vessel is stainless steel. The ozone generator of Pacific Ozone delivers a constant ozone flow rate of 16 g/h. The ozone-air flow is injected into the water by a venture build in a recirculation circuit. The experiments are performed at constant pH. The pH will be varied between pH 3 (direct) and pH 9 (indirect) through which the effect of the reaction type can be observed. More specific, ozone dosages of 0,05 - 0,10 - 0,15 - 0,20 g O_3/g COD are examined. Because of the high amount of organic substances present in the wastewater, only such low ozone dosages are considered. Higher dosages results in very long reaction times through which the application is not economical interesting. The experimental set-up of the ozonation process is given in .

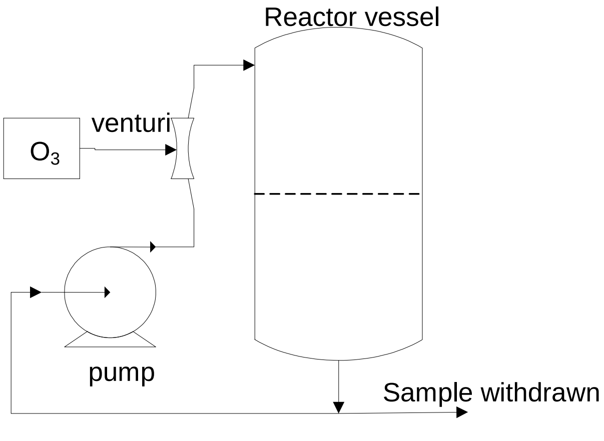

Figure 1: Schematic diagram of the labscale reactor

Table 2: Experimental set-up of the ozonation process

Oxidant Ozone: 0,05 - 0,10 - 0,15 - 0,20 g O_3/g COD	**Reaction volume** 10 liter
Reaction conditions Roomtemperature (20 °C) pH: 3 & 9	**Reaction time** 45 – 90 – 135 - 180 minutes
	Reactor Stainless steel

Analytical methods

The COD determinations based on the oxidation of the pollutants with potassium dichromate in acidic environment were carried out by using 0-1500 mg/l range vials. Samples of 2 ml were required for those analyses. A Nanocolor® COD reactor and a Nanocolor® 500 D colorimeter from Machery-Nagel were used during the analysis. The vials were heated for 2 hours on 150 °C.

The BOD determinations were carried out by a manometric measurement. The samples and a certain amount of micro-organisms were mixed into a closed recipient. The consumed amount of oxygen by the micro-organisms was measured for 5 days. The used instrument is the BODTrak, produced by HACH (1995-1998).

The TOC determinations were carried out by the on-line TOC analyser (TOC-4110) from Shimadzu. This high performance analyser uses the established 680 °C catalyst-aided combustion and the non-dispersive infrared detection method.

The biodegradation rates are determined by respirometry. The samples are mixed with activated sludge and the oxygen consumption in the water is measured for at least three hours. From these measurements, the total oxygen demand can be calculated. This value indicates the amount of biodegradable fraction of the COD in the sample. After the biodegradation, the COD value of the effluent is also measured.

Results and discussion

Characterisation of the wastewater

The fysico-chemical characteristics of the considered wastewater are mentioned in ***Table 3***. Based on the high COD and TOC value, it can be concluded that the wastewater is confronted with a very high amount of organic pollutants. Further, the biodegradability of the wastewater is rather limited. Hence, a ratio BOD/COD of 0,21 can be observed.

Table 3: Fysico-chemical characteristics of the considered wastewater

Parameter	Unit	Value
Chemical Oxygen Demand (COD)	[mg O_2/l]	25.000
Biological Oxygen Demand (BOD)	[mg O_2/l]	5.160
Ratio BOD/COD	[-]	0,21
Total Organic Carbon	[mg C/l]	5.500
pH	[-]	7,5

The Fenton process

Based on the results shown in ***Figure 2***, several links can be observed. The TOC and COD degradation are strong dependent of the applied dosage of both oxidant and catalyst. Higher dosages result in higher degradation yields. Nevertheless, yields concerning COD degradation fluctuate between 13% and 30%. Because of the high initial COD value of 25.000 mg O_2/l, these low yields were expected. Previous research has shown that maximum COD degradation of the Fenton process can be achieved in case of initial COD values below 5.000 mg O_2/l.

On the other hand, higher yields concerning TOC degradation are observed, namely between 16% and 74%. Hence, it can be assumed that the oxidised organic pollutants are properly mineralised to smaller carbon chain molecules which can be more biodegradable. The best results are obtained with the hydrogen peroxide dosage of 1 g H_2O_2/g COD and the ratio $[Fe^{2+}]/[H_2O_2]$ of 2/1. At these dosages, a COD and TOC value of respectively 17.400 mg O_2/l and 1.440 mg C/l can be achieved, which corresponds with degradation yields of respectively 30% and 74%.

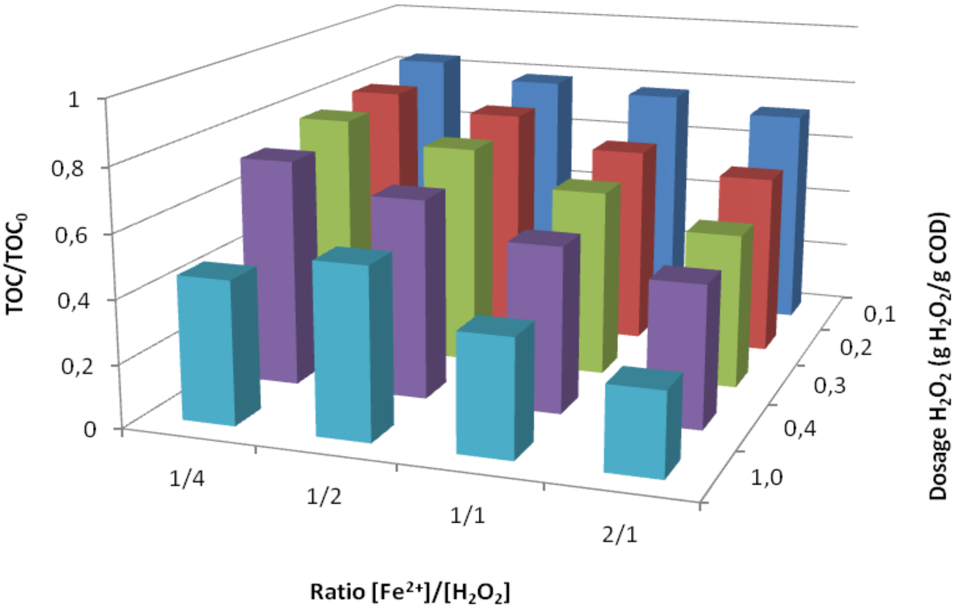

Figure 2: TOC degradation versus oxidant and catalyst dosage

Based on the BOD values, a degradation yields between 12% and 54% are observed. In the first place, the degradation of the BOD value indicates that the amount of biodegradable organic pollutants is decreased. Compared with the COD and TOC degradation, the biodegradability of the treated wastewater still can be the same or even enhanced. Therefore, the measurements based on respirometry are necessary. ***Figure 3*** hows the oxygen consumption during the respiration tests. Because oxygen consumption is directly associated with both biomass growth and substrate removal, it can be concluded that the amount of substrate, i.c. biodegradable organic pollutants, is increased by the Fenton treatment. However, in this case the enhancement of the biodegradability of the wastewater is rather limited. An overall COD degradation by the combined treatment between 69% and 86% can be achieved.

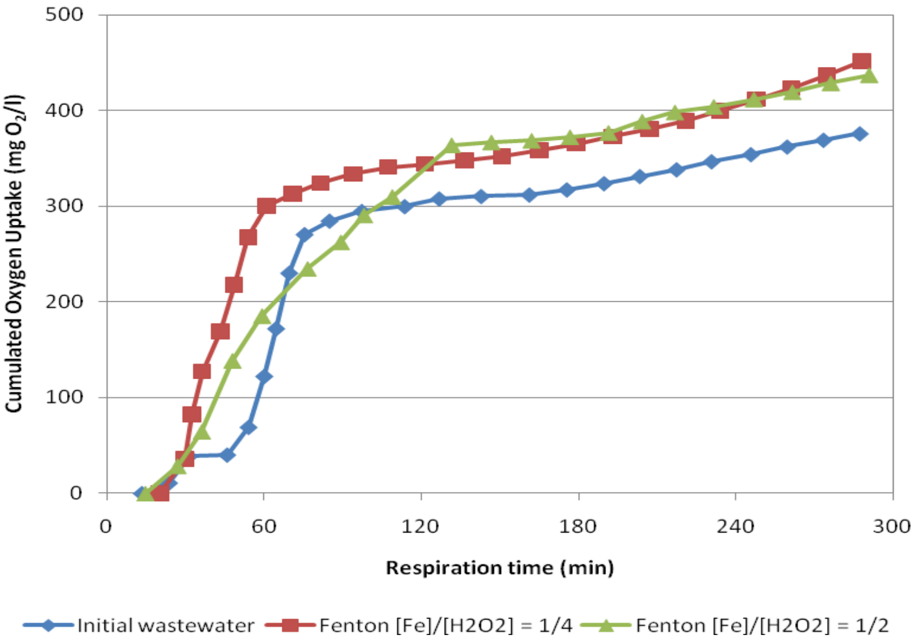

Figure 3: Respirometric measurements of the Fenton treated effluent ($[H_2O_2]$ = 0,1 g H_2O_2/g COD)

The ozonation process

Figure 4 shows the results of the ozone treatment. Based on the results of the COD measurements, degradation yields between 17% and 30% are observed, regardless the pH of the wastewater. The ozonation process can achieve maximum degradation yields when the initial COD value of the wastewater is below 2.000 mg O_2/l. Hence, the low degradation yields, comparable with those of the Fenton oxidation process, were expected.

Similar to the Fenton process is the link between the degradation of the COD and TOC value and the applied ozone dosage. A higher dosage results in a higher degradation yield. Because of the low applied ozone dosages, this effect is rather limited.

The effect of the reaction type on the COD and TOC degradation was also examined. Based on the COD results, the ozone reaction at low pH will achieve better degradation yields. At an ozone dosage of 0,20 g O_3/g COD, the COD value decreases from 25.000 mg O_2/l to 17.600 mg O_2/l. On the other hand, the effect of the direct ozone reaction on the TOC degradation is hardly visible. The degradation yield fluctuate between 1% and 5%. The indirect ozone reaction achieves degradation yields between 12 and 16%. Therefore can be assumed that, in this case, OH radicals (indirect ozone reaction) are more reactive with the organic pollutants than the ozone molecules (direct ozone reaction).

After consideration of the respirometric measurements can be concluded that the ozone process will enhance the biodegradability of the wastewater. Compared with the Fenton process, the enhancement is rather limited. An overall COD degradation by the combined treatment between 59% and 66% can be achieved.

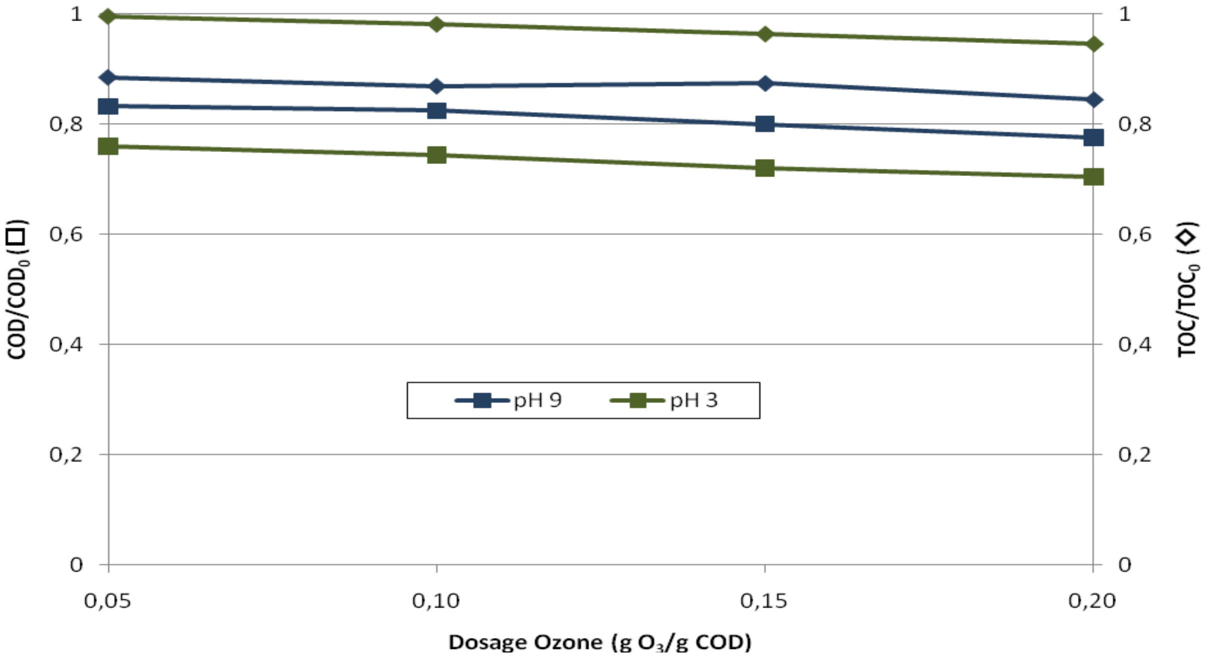

Figure 4: COD and TOC degradation versus oxidant dosage

Conclusions

The possible synergy upon combining AOPs and biological degradation is evaluated for an industrial wastewater. The evaluation was based on conventional analytical methods, such as COD, TOC and BOD measurements, and respirometry. The biological oxygen consumption rate was measurement during a certain period. Experiments are performed with the dosage of ozone and hydrogen peroxide as oxidant. The combination of hydrogen peroxide and iron catalyst will result in the Fenton oxidation. From the investigated AOPs, the Fenton process leads to the best results based on both degradation of organic pollutants and enhancement of biodegradability.

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