Biodegradability assessment of Advanced Oxidation Processes by means of respirometric measurements

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Abstract
Advance Oxidation Processes are considered a promising technology in degrading hazardous organic compounds into readily biodegradable intermediates. In this context, a proper measurement tool to determine the enhancement of the biodegradability of the wastewater is necessary. In this study, the opportunities of respirometric measurements to determine the possible enhancement of biodegradability of toxic wastewaters due to ozone treatment was investigated. Phenol was chosen to represent organic toxic wastewaters.
Firstly, the inhibitory effect of phenol on the respirometric oxygen consumption of unacclimated biomass has been determined. Further, a solution with a phenol concentration of 250 mg/l has been treated with ozone at pH 3 and pH 9. Based on the performed COD, TOC, BOD, phenol concentration and respirometric measurements, it can be observed that in this case the ozone treatment at pH 9 a lower ozone dosage was necessary to enhance the biodegradability of the phenol solution. Furthermore, the SOUR graphs shows a significant difference between the ozone treatments and the ozone dosages. Hence, respirometric measurements can be used to determine the enhancement of the biodegradability due to ozone oxidation.
Further investigation on this topic is necessary to determine the effect of acclimated biomass on the respirometric measurements.

Keywords
Advanced Oxidation Processes; Biodegradability assessment; Dissolved Oxygen; Respirometric measurements

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., 2011). In general, conventional biological processes are preferred for the treatment of industrial wastewaters. Indeed, activated sludge processes currently represent the most widespread technology for the secondary treatment of municipal wastewater and constitutes “the heart” of many wastewater treatment plants (Lessard and Beck, 1993). 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 order to resolve this drawback, Advanced Oxidation Processes (AOPs), characterised by the formation of highly reactive hydroxyl radicals, are capable to degrade or mineralise the majority of complex organic chemicals present in water effluents. However, the operational costs of these processes are relatively high compared to those of biological treatment. Nevertheless, AOPs are considered a promising technology for the removal of hazardous organic compounds. Certainly when the chemical oxidation is combined with a biological treatment. 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 a 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). Hence, the AOP can be seen as a pre-treatment system of the biodegradation, which degrade the complex organic chemicals and use less oxidant compared to complete

mineralisation. This concept of integrated chemical and biological treatment is well illustrated by Mantzavinos and Psillakis (2004). The so-called partial chemical oxidation will therefore reduce operational costs. Several experimental studies (Sarria et al., 2002; Cokgor et al., 2004; Lafi et al., 2009) demonstrated the synergetic effects of a combined chemical and (aerobic) biological oxidation. Exhaustive reviews on this topic has been published by Scott and Ollis (1995), Mantzavinos and Psillakis (2004), Tabrizi and Mehrvar (2004) and Mandal et al. (2010). It should be emphasised that the success of this approach cannot be guaranteed beforehand and depends strongly on the wastewater characteristics.

Mantzavinos and Psillakis (2004) summarized the research into chemical oxidation pre-treatment and concluded that several different pr-treatments have been employed and of these, ozonation (alone or in conjunction with another oxidant) appears to be the most popular pre-treatment. Ozone features a short half-life time and oxidises the target molecules either directly or through the formation of highly reactive hydroxyl radicals. The latter mechanism corresponds to an AOP. The dominating oxidation mechanism depends on the pH of the solution and the target molecules. These hydroxyl 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 (Tzitzi et al., 1994; Lopez et al., 1998). Hence, ozonation has been applied in this study.

Regarding the biological step, the effect of chemical pre-treatment on the properties of the effluent is usually assessed by means of biodegradability tests, toxicity tests, integrated studies where the partially treated effluent is fed to biological post-treatment or a combination (Mantzavinos and Psillakis, 2004). The most significant biodegradation systems are based on bacteria or fungi. Therefore, respirometry, characterised by the determination of the biological oxygen consumption rate under well defined experimental conditions, is an optimal tool to measure the correct activity and viability of micro-organisms present in aerobic activated sludge (Oller et al., 2011). The oxygen consumption during the respirometric experiments is directly associated with both biomass growth and substrate removal. Hence, this measurement technique has increasingly been employed to obtain biokinetic characteristics and it is considered one of the most important information source in activated sludge process modelling (Spanjers et al., 1998).

The objective of the present work was to study the opportunities of respirometric measurements to determine the possible enhancement of biodegradability of toxic wastewaters due to advanced oxidation treatment. Therefore, phenol was chosen to represent organic toxic wastewaters. Phenol is an important industrial product for synthesis of drugs, weed killers, and synthetic resins. It can be found in several types of industrial wastewater, depending on the industry branch (such as pulp mills, paint and dyes manufactories, textiles industry, etc.) (Turhan and Uzman, 2008). Because of the environmental risk, the presence of phenolic pollutants in natural waters should be avoided.

MATERIAL AND METHODS

Chemicals

Reagent phenol (Acros Organics, 99%, extra pure) was used as received. Different phenol solutions (125 mg/l, 250 mg/l and 500 mg/l) are prepared by dissolving into tap water. Only the solution of 250 mg/l phenol was treated with ozonation.

The activated sludge is originating from a domestic wastewater treatment in Mechelen, Belgium. The sludge has been taken in the retour circuit from the clarifier to the aeration tank through which the sludge has been concentrated. The Total Suspended Solids (TSS) varies between 4,5 g/l and 7,5 g/l, of which 70% are Volatile Suspended Solids (VSS).

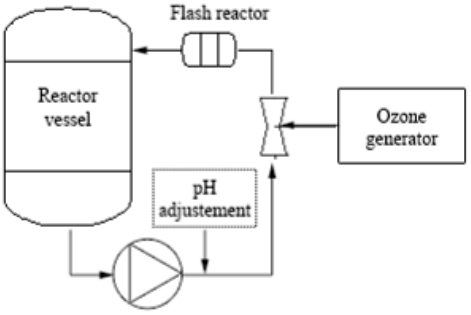

Figure 1. Schematic overview of the ozone reactor.

Ozonation

The ozone experiments were performed in a pilot-scale reactor, schematically showed in figure 1. The reactor operates batchwise and has a total internal volume of 70 liters. The construction material for the reactor vessel is stainless steel. The ozone generator of ITT Wedeco delivers a constant ozone flow rate of 32 g/h. The ozone-air flow is injected into the water by a venturi build in a recirculation circuit. To achieve a better solubility of the ozone into the water, a flash unit is placed after the venture. During the experiments, the Etatron D.S. HD PH pump was used to ensure a constant pH. At certain moments during the ozone experiments, samples are withdrawn from the reactor vessel.

Respirometric measurement

The respirometer is based on the measurement of the concentration of Dissolved Oxygen (DO) in the liquid phase. Consider a system consisting of a static liquid phase, containing biomass and wastewater, and a gas phase both being ideally mixed. The DO mass balance over the liquid phase is $dS_0/dt = -r_0$. According to Farkas (1969), Takamatsu et al. (1982) and Randall et al. (1991), the contribution of surface aeration is negligible and the danger of oxygen shortage in the system can be solved by repeatedly aeration for a short period of time. In the unaerated periods, the oxygen concentration in the system will decrease because of the biodegradation of organic compounds and the endogenous aeration of the activated sludge. From the measured DO concentrations during the unaerated periods, the Oxygen Uptake Rate (OUR) can be calculated based on Least Squares Fitting, a mathematical procedure for finding the best-fitting curve to a given set of points by minimizing the sum of the squares of the offsets of the points from the curve (Kennedy and Keeping, 1962). The overall quality of the fit is then parameterized in terms of a quantity known as the correlation coefficient.

A schematic overview of the respirometer is showed by figure 2. Sample, in this case the phenol solutions, and activated sludge are collected in the sample vessel and sludge vessel, respectively. In these vessels, the sample and sludge can be pretreated (e.g. aeration, pH-adjustment) if necessary. Firstly, the activated sludge is pumped into the respirometric reactor in order to measure the endogeneous oxygen consumption of the micro-organisms. Next, the sample is added to the activated sludge in the reactor through which the respiration measurement can be started. The pumps used to fill and clear the vessels and the reactor are peristaltic OEM pumps of Verderflex. For the pH adjustement, the Etatron DS ROME HDS PH pump is used. The aeration pumps are from the type Tornado 7500 from Olympia Garden. The level in the both vessels and the reactor are controlled by Ceraphant T PTC31 sensors of Endress Hauser. The concentration of dissolved oxygen and suspended solids are measured with respectively the Oxi::lyser and Soli::lyser, both optical probes, of S::can. The measurements are obtained by the con::lyte terminal and further, sent to the control unit. During the respiration experiments, the oxygen concentration is regulated between 4 mg O_2/l and 7 mg O_2/l and 1 litre phenol solution is added to 5 litres of activated sludge. Finally, the total amount of sludge (MLSS) is taken into account to determine the Specific Oxygen Uptake Rate (SOUR).

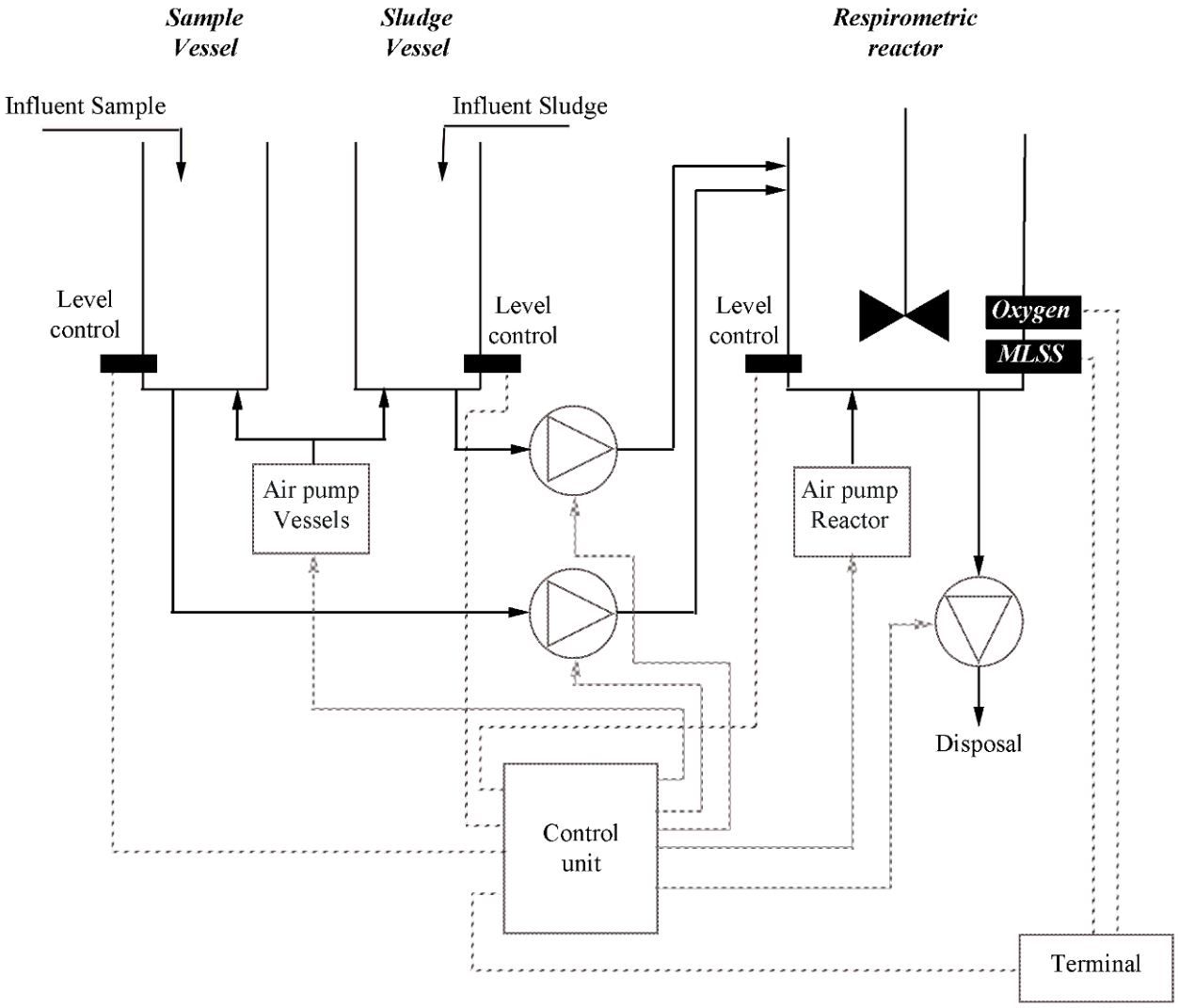

Figure 2. Schematic overview of the respirometer.

Analytical determinations

The COD measurements, based on the oxidation of the pollutants with potassium dichromate in acidic environment, were carried out by using 100-1500 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 (http://www.macherey-nagel.com/) were used during the analysis. The vials were heated for 2 hours on 150 °C.

The BOD measurements 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 measurements 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 duration time of the analysis cycle corresponds with 4 minutes.

The phenol measurements were carried out by the Nanocolor® Phenolic-Index 5 of Machery-Nagel. This tube test has a measurement range from 0,2 mg/l to 5.0 mg/l, through which dilutions of the phenol solutions are necessary. This measurement is used as an indicative approximation of the phenol concentration in the different solutions. Samples of 4 ml were required for those analyses. A Nanocolor® 500 D colorimeter from Machery-Nagel was used during the analysis. The vials were incubated for 5 minutes at room temperature.

RESULTS AND DISCUSSION

Respirometric measurements of initial phenol solutions

Initially, respirometric experiments were performed to evaluate the effect of the phenol concentration on the SOUR of activated sludge. The results of the respirometric measurements of three phenol solutions are showed by figure 3. In the first period of time, the SOUR values are rather low or even negative. This phenomena can be explained by the inhibitory effect of phenol on the respirometric oxygen consumption of unacclimated biomass. The inhibition of phenol biodegradation has been already been reported by several authors (Kumar et al., 2005; Contreras et al., 2008) and it was associated with the hydrophobic perturbation of the microorganisms' membrane (Leonard and Linfley, 1999).

Further, the SOUR values shows an exponential increase in function of the time, until a maximum value has been reached. The maximum SOUR value has been reached at approximately 2 hours, 4 hours and 10 hours of respiration time for respectively the 125 mg/l, 250 mg/l and 500 mg/l phenol solution. Hence, the period of time before reaching the maximum value is depending of the phenol concentration. The exponential curve can be interpreted by two explanations. The first possible interpretation is that a certain amount of the active biomass is deceased. Due to this, the SOUR can become negative. From the moment that the phenol become available for biodegradation, the SOUR increases. The second possibility is that the working of the biomass has been decelerated, through which also lower SOUR values can be observed. Further investigation is necessary confirm to these assumptions.

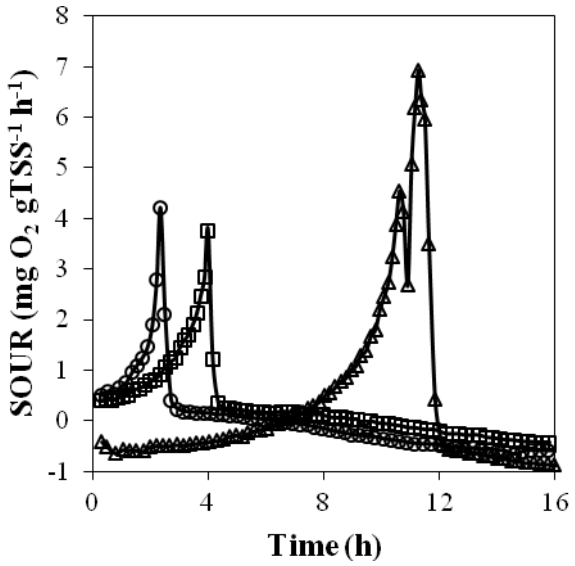

Figure 3. Effect of the phenol concentration on the SOUR of activated sludge (phenol solutions: 125 mg/l[○]; 250 mg/l[□]; 500 mg/l[△]).

Respirometric measurements of ozonated phenol solutions

To investigate the opportunities of respirometric measurements for the determination of the biodegradability, the solution with a phenol concentration of 250 mg/l has been treated with ozone at two different pH values, i.e. pH 3 and pH 9. At different treatment times (0, 20, 40 and 60 minutes), samples has been taken to be analysed. These treatment times corresponds with the following ozone dosages: 0; 0,20; 0,40; 0,60 g O_3/g COD_0, respectively.

Santos et al. (2002) has shown that the degradation of phenol involving hydroxyl radicals proceeds via aromatic hydroxylation followed by further hydroxylation/oxidation to yield generally CO2 and H2O. The main intermediates detected were hydroquinone, catechol and benzoquinone which further break down to form CO2 and short chain fatty acids, such as maleic, formic, oxalic and acetic acids. These results have been confirmed by Bremmer et al. (2006) and Turhan and Uzman (2008).

The results of the COD, BOD, TOC and phenol measurements are shown in table 1. As expected, the COD values as well as the phenol concentrations decrease during the ozone treatment while the BOD values slightly increases. These combined effects results in an enhancement of the BOD/COD ratio. Hence, it can be expected that the inhibitory effect of the phenol will decline and that the amount of readily biodegradable COD will increase. This COD fraction will be oxidised at the start of the respirometric measurement.

The respiration measurements of the different untreated and treated phenol solutions are shown in figure 4. The results show that due the ozone treatment, at both investigated pH values, the peak of the SOUR values occur faster than in the case of the initial phenol solution. Moreover, due to a higher ozone dosage higher SOUR values can be noticed at the beginning of each respiration experiment and the peak due to the phenol compound decreases. At pH 3 and pH 9, the phenol peak cannot be noticed at an ozone dosage of 0,60 g O_3/g COD_0 and 0,40 g O_3/g COD_0, respectively. In this case, the formed intermediates are totally readily biodegradable. Therefore, the ozone treatment, at both investigated pH values, is capable to convert the phenol in more biodegradable intermediates.

When both pH values are compared with each other, it can be seen that the conversion of slowly biodegradable COD into readily biodegradable COD occur faster at pH 9, and this because of several reasons:

- The reaction rate constants at pH 3 and pH 9 are equal to 8.10^{-4} s^{-1} and $1{,}6.10^{-3}$ s^{-1}, respectively. Hence, at pH 9 the phenol concentration degrades faster compared to pH 3.
- At the ozone dosage of 0,20 g O_3/g COD_0, the measured BOD value at pH 9 is 70 mg O_2/l higher compared to pH 3. Therefore, the formation of BOD occurs faster at pH 9.
- At pH 9, the phenol peak cannot be observed at a lower ozone dosage compared to pH 3.

Table 1. The results of the COD, BOD, TOC and phenol measurements during the ozone respiration at different pH values.

Time (min)	Ozone treatment at pH 3				Ozone treatment at pH 9			
	COD (mg O_2/L)	BOD (mg O_2/l)	TOC (mg C/l)	Phenol (mg/l)	COD (mg O_2/L)	BOD (mg O_2/l)	TOC (mg C/l)	Phenol (mg/l)
0	665	6	190	250	672	6	191	250
20	559	16	175	130	539	86	178	80
40	459	45	165	30	433	78	163	10
60	353	76	151	19	358	78	149	1

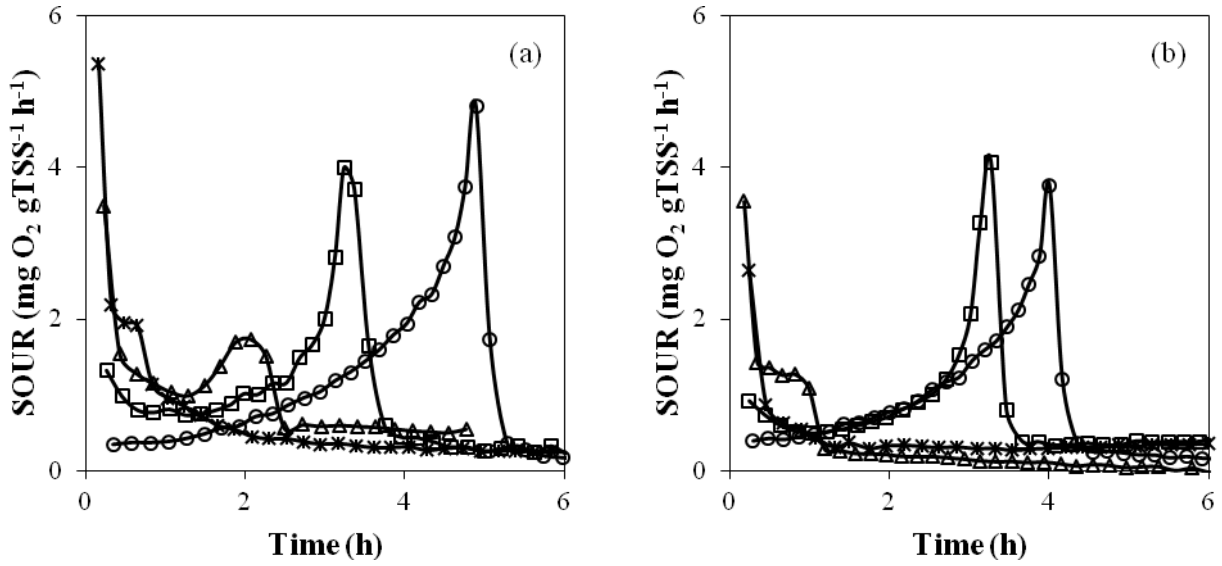

Figure 4. The effect of the ozone treatment on the respiration measurement of phenol solutions at pH 3 (a) and pH 9 (b) (Ozone dosages: 0 g O_3/g COD_0 [○]; 0,20 g O_3/g COD_0 [□]; 0,40 g O_3/g COD_0 [△]; 0,60 [*] g O_3/g COD_0).

CONCLUSIONS

In this paper, respirometric measurements were performed to investigate their opportunities to determine the possible enhancement of biodegradability of toxic wastewaters due to advanced oxidation treatment. Therefore, phenol was chosen to represent organic toxic wastewaters and ozone treatment was selected as oxidation technique. The respirometer is based on the measurement of the concentration of Dissolved Oxygen in the liquid phase and the danger of oxygen shortage in the system was solved by repeatedly aeration for a short period of time. From the measured DO concentrations during the unaerated periods, the Specific Oxygen Uptake Rate was calculated based on Least Squares Fitting.

Firstly, respiration measurements were performed on three solutions with different phenol concentration. The inhibitory effect of phenol on the oxygen consumption of unacclimated biomass has been determined. Also, an exponential increase of the SOUR values in function of the respiration time has been observed. The period of during before reaching the maximum SOUR value is depending of the phenol concentration.

Further, the solution with a phenol concentration of 250 mg/l has been treated with ozone at two different pH values, i.e. pH 3 and pH 9. Due to the ozone treatment, a decrease of the COD value and the phenol concentration has been observed. The BOD value, however, was increased. The SOUR graphs shows a significant difference between the ozone treatments and the ozone dosages. Hence, respirometric measurements can be used to determine the enhancement of the biodegradability due to ozone oxidation.

In this study, unacclimated biomass was used to perform the respirometric measurements. So, further investigation on this topic is necessary to determine the effect of acclimated biomass on the respirometeric measurements.

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