The effect of the ozonation process on the toxicity and biodegradability of chlorophenol containing wastewater

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INTRODUCTION

The choice to combine one or more wastewater treatment processes depends on the composition of the wastewater, the effluent standards to be met and the most effective treatment with the lowest reasonable cost (Oller et al., 2011). While biological processes are the most widespread technology for the treatment of wastewater, satisfactory results are not always achieved due to the presence of toxic and/or non-biodegradable pollutants (Esplugas et al., 2004). In particular, the chlorophenol contamination is a serious threat because of its widespread occurrence (Czaplicka, 2004). Under aerobic conditions, specific isolated microbial cultures are able to utilize some chlorophenols as sole carbon and energy source (Farrell and Quilty, 1999). Furthermore, co-metabolic biodegradation of phenolic compounds can be successfully enhanced by the presence of a growth substrate such as glucose and phenol (Li and Loh, 2005; Wang et al., 2003). Nevertheless, the biodegradation of chlorophenols is often very difficult, due to the specific conditions or the long reaction time required.
In this context, Advanced Oxidation Processes (AOP) are considered an appropriate tool in the treatment of such wastewater. Although a complete mineralization by AOPs is usually not economically feasible, the combination of both chemical and biological technologies is widely reported to reduce operational costs (Oller et al., 2011). The conversion of refractory compounds into more biodegradable intermediates is induced by partial chemical oxidation, allowing for efficient contaminant destruction by subsequent biological degradation.
Oller et al. (2011) concluded that the extensive research on the use of AOPs as a pretreatment stage needs more studies on individual and global degradation efficiencies in multiple substrate solutions and multiple substrate kinetics for biological mixed cultures. In this context, the ozone degradation of 2,4-dichlorophenol (2,4-DCP) as toxic contaminant is investigated in the presence of readily biodegradable substrates. Given that the elimination of the toxic compound alone does not always indicates the successful treatment, it is desirable to assess the residual toxicity and/or biodegradability of the ozonated solutions. Hence, in this study, biodegradation efficiencies and microbial activity of both non-acclimated and acclimated biomass are assessed by means of respirometry.

MATERIALS AND METHODS

Different synthetic wastewater solutions are prepared to investigate the effect of the nature of the biodegradable fraction. Table 1 lists the composition of the synthetic wastewaters used in this study. The solution containing only 2,4-DCP is used as reference to compare ozone degradation efficiencies. The ozone batch experiments are performed in a lab-scale glass reactor filled with 2.0 L synthetic wastewater. The ozone gas is produced by an ozone generator (WEDECO GSO30) at a flow rate of approximately 6 $gO_3.h^{-1}$. The reaction time is varied between 2, 5 and 10 min. At the start of the experiments, the pH of the synthetic wastewater is adjusted to pH 9. During ozonation the pH is not adjusted.
A simple respirometric procedure is set up to detect effluent toxicity and biodegradability. The apparatus consists of six glass batch reactors (1.0 L) at constant temperature (20 °C). The oxygen concentration is monitored by dissolved oxygen sensors (Visiferm LDO, Hamilton) and controlled between 3 $mgO_2.L^{-1}$ and 5 $mgO_2.L^{-1}$. Activated sludge at an MLSS concentration of 3.00 $g.L^{-1}$ (MLVSS = ±2.04 $g.L^{-1}$) is added to the reactor. At the start of each experiment, the activated sludge is aerated in the absence of substrate to determine the endogenous respiration rate.

Table 1: Overview of the composition of each synthetic wastewater.

Product	Synthetic wastewater 1	Synthetic wastewater 2	Synthetic wastewater 3
2,4-DCP	100 $mg.L^{-1}$	100 $mg.L^{-1}$	100 $mg.L^{-1}$
Sodium Acetate	320 $mg.L^{-1}$	320 $mg.L^{-1}$	-
Glucose	235 $mg.L^{-1}$	-	-
Milk Powder	-	159 $mg.L^{-1}$	-

RESULTS & DISCUSSION

The concentration of 2,4-DCP decreases by increasing the ozone reaction time. For example, when treating Wastewater 3, degradation efficiencies of 54%, 83% and 97% are observed at reaction times of 2 min, 5 min and 10 min, respectively. For Wastewater 1 and 2, slightly lower degradation efficiencies are observed, i.e. 96% and 90% after 10 min ozonation, respectively. Also, the free chloride concentration increases by increasing the ozone reaction time for all types of wastewaters, indicating the dechlorination of 2,4-DCP. Nevertheless, after 10 minutes ozonation COD degradation efficiencies of only 13%, 12% and 54% are observed for Wastewater 1, 2 and 3, respectively.

The results of the respirometric experiments are represented as specific oxygen uptake rate (SOUR, $mgO_2.gMLVSS^{-1}.h^{-1}$) profiles (Figure 1). The SOUR-value represents the consumption rate of oxygen due to biodegradation of substrate. The vertical line in Figure 1 represents the time at which the wastewater solution is added to the biomass. In the case of non-acclimated biomass (Figure 1(A)), the SOUR-values of the original wastewater remain similar to the endogenous SOUR for almost 14.5 h. Moreover, the maximum SOUR is only observed after 22.12 h respiration time, indicating that a lag phase in biological activity occurs. The lag phase is obviously reduced by increasing the ozone reaction time. For example, due to pretreatment of Wastewater 1 the lag phase is reduced from 22.12 h to 0.17 h for 10 min ozone reaction time. Moreover, the maximum SOUR increases by increased ozone reaction time. The latter is also observed with acclimated biomass (Figure 1(B)). The ratio of $SOUR_{max.}$ and $SOUR_{max.,ref.}$ increases from 0.48 to 1.02 for non-acclimated biomass and from 0.62 to 0.93 for acclimated biomass after 10 min ozone reaction time. The COD value after biodegradation using non-acclimated biomass decreases from 92 $mgO_2.L^{-1}$ for the initial wastewater to 85 $mgO_2.L^{-1}$, 50 $mgO_2.L^{-1}$ and 37 $mgO_2.L^{-1}$ due ozone pretreatment for 2, 5 and 10 min, respectively. Similar results are obtained for both acclimated biomass and Wastewater 2.

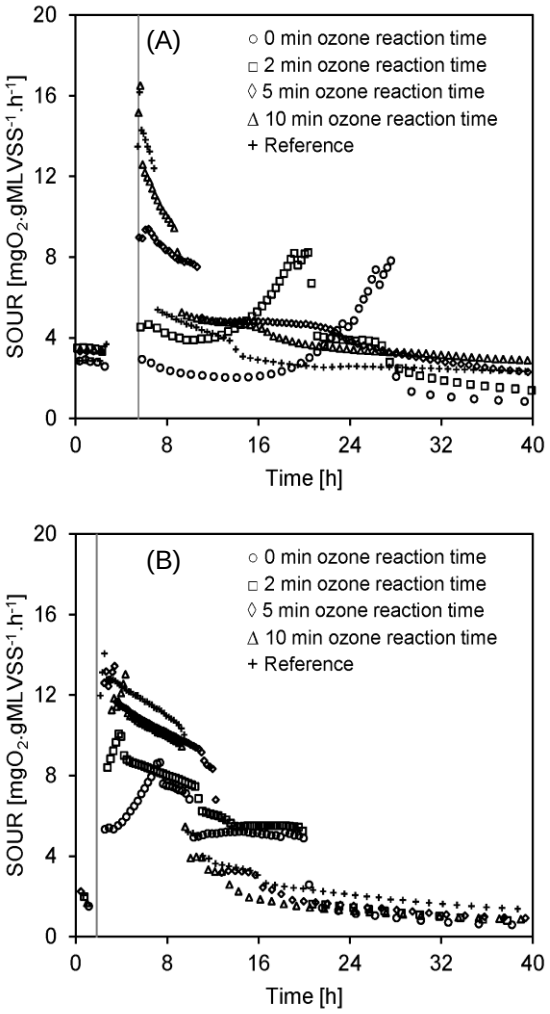

Figure 1: SOUR profiles of ozonated solutions of Wastewater 1, using non-acclimdated (A) and acclimated (B) biomass.

CONCLUSION

Ozone pre-treatment results in a decrease of the concentration of 2,4-DCP and an increase in free chloride concentration. Furthermore, the COD degradation due to the pretreatment is rather limited. Hence, the pollutant is not completely mineralized but instead degraded into dehalogenated intermediates (not identified in this study). The degradation rate of 2,4-DCP decreases when other organic matter is present in the wastewater and the extent of this decrease depends on the nature of the biodegradable matter.

Due to the pretreatment, the toxic effect of 2,4-DCP decreases. The lag phase, which has an important impact on non-acclimated biomass, is significantly reduced and the maximal SOUR increases with increasing ozone reaction time. Furthermore, the amount of refractory COD is decreased by the ozone treatment because of the degradation of the toxic pollutant. Hereby, the biodegradation can be performed in a shorter period of time.

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