OC-11: Degradation of Alachlor by Ultrasound, Ozone and Their Combination

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The degradation of aqueous alachlor by ultrasonic irradiation, ozonation and their combination was investigated. The effects of frequency and power of ultasonic irradiation on the degradation rate were examined. At 100 ppb aqueous solutions, which is in typical range of the pollutant in natural waters, among the three frequencies (575 kHz, 861 kHz and 1141 kHz), 575 kHz has given the best degradation rates, while the higher ultrasonic power has also resulted in higher degradation rates than lower power applications. The coupling of ozone with ultrasound had performed increased degradation and mineralization effects because the resulting degradation rate constants were greater than the rate constants alone. The pseudo first order kinetic model was observed for all types of degradations and the mineralization was determined by the decrease in TOC values. Under the conditions applied, all three systems proved to be effective in inducing alachlor oxidation, leading to 100% removal and 79.5% of mineralization for O_3 and 93.8% removal and 21.24% of mineralization for US after 90 min of treatment. The improvement observed in the combined schemes, mainly due to the effects of US in enhancing the O_3 decomposition, led to 100% alachlor removal in 20 min and 82.3% mineralization in 90 min treatment.

1. Introduction

Today, the increasing production and extensive use of pesticides for agricultural purposes have caused the pollution of soil, ground and surface water. As there is the risk that the residues directly or indirectly effect the human beings and/or the environment, strict regulations have been set by the authorities (Ma et al., 2002). Due to their high toxicity, biological treatment of agro-industrial effluents is often perturbed and sometimes blocked (Lapertot et al., 2007; Torres et al., 2009). The Turkish Standards for the Drinking Water the maximum accepted levels of total pestidices are limited to 0.5 ppb. The degradation procedure and analysis of the compounds at such low levels require high technology systems and extreme attention.

In this study the degradation of alachlor by ultrasonic irradiation (US), ozonation and their combination was investigated. Ultrasonic irradiation has recently been proposed as one of the techniques for degradation of hazardous organic compounds (Suslick et al., 1990). Ozonation is a very well known advanced oxidation technique and studies have shown that it is very effective at rather higher concentrations of pollutants. When ozone is injected into water simultaneously with ultrasonic irradiation, an additional pathway of hydroxyl radical generation arises upon the decomposition of ozone in the gaseous bubbles during implosive collapse. In this study the effect of the ultrasonic frequency on the degradation of alachlor was studied. The results have revealed that among the three frequencies (575, 861 and 1141 kHz) 575 kHz has given the best degradation results.

2. Experimental

A multi-frequency medium-high frequency ultrasonic system (Meinhardt Ultraschalltechnik) composed of a generator, an amplifier and a titanium plate type transducer operating at three different frequencies (575, 861 and 1141 kHz) was used to perform all the reactions. The ozone was generated from air using OPAL OG 400 model ozone generator with a maximum production capacity of 40 mg/h O_3 and the ozonation was performed in the same glass reactor with or without ultrasound combination. Introduction of ultrasound and/or ozone into alachlor solutions were conducted for 90 min. During reactions 1 mL of aliquot samples were collected at regular time periods. To measure the change of concentrations of alachlor in the degradation reactions, HPLC (Shimadzu 3200) which was coupled with MS/MS system (BioApplied Sciex Q-TRAP) was used. The total mineralization of alachlor was determined by TOC measurements during the 90 minute-experiment.

3. Results and Discussion

The presence of trace amounts of certain organic compounds, such as synthetic pesticides has been of great concern, as their negative impacts are highly risky for human health. Changes in alachlor concentration as a function of time for the sonication of 100 ppb aqueous alachlor solutions at 60W and 45 W acoustic power and at 575, 861 and 1141 kHz frequencies have been measured. The alachlor concentration decreased much more rapidly at 575 kHz

than at other frequencies. The kinetic observations obtained from the fitted curve of the data gives a first-order rate constants (k_{obs}) of 0.029 min^{-1} for 575 kHz, 0.023 min^{-1} for 861 kHz and 0.018 min^{-1} for 1141 kHz at 60 W applied power. Fig. 1. shows the degradation rate constant is nearly 1.5 times faster at 575 kHz than at 1141 kHz, revealing the lower the frequency the faster the degradation. The applied power has an enormous effect on the degradation rate, as the energy for degradation is dependent on the power applied.

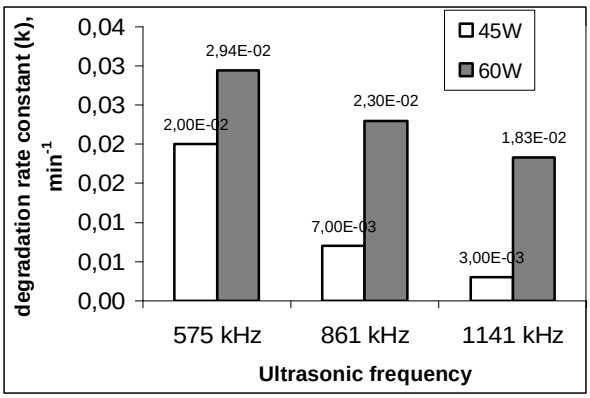

Fig. 1. Effect of ultrasonic frequency and power on alachlor degradation

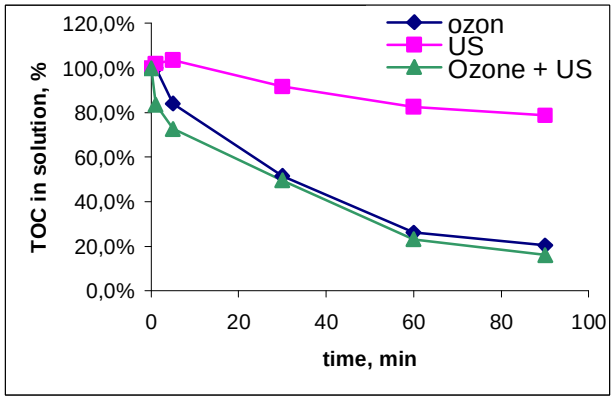

Fig. 2. Decrease in the aqueous TOC, as an indication of mineralization with three process.

The decrease in the organic carbon is a direct indication of complete oxidation of the pesticide. The complete oxidation enables the production of gaseous carbondioxide and water vapour as final products, thus reduction in the initial Total Organic Carbon (TOC). As seen in Fig. 2, TOC was not completely removed under any of the reaction systems. Ozonation and US /ozone combination has revealed a great mineralization percentage, but on the other hand US alone was not effective enough in means of mineralization, leading to the need of further examination on by-products for their toxic characteristics, because we cannot exclude the possibility of generating new compounds , or in other words the by-products.

4.Conclusions:

The most efficient way for applying AOPs is not aiming at the mineralization of organic pollutant but transforming its chemical structure to its more biodegradable forms. In the study, we have observed that despite high dissapearence rate of the pesticide itself, application of ultrasound alone is not sufficient for its mineralization. The study here points out that further investigations must be performed to see the change in the toxicity of the medium comparing the before and after AOP applied conditions.

References

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