

## Degradation of trace concentrations of alachlor by medium frequency ultrasound



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### ABSTRACT

In this novel research study, the degradation of aqueous alachlor by ultrasonic irradiation was investigated. 575 kHz ultrasonic oxidation has obeyed first order kinetic model. The rate constant has increased with the applied power:  $k = 2.00 \times 10^{-2} \text{ min}^{-1}$  (at 45 W),  $k = 2.70 \times 10^{-2} \text{ min}^{-1}$  (at 60 W),  $k = 13.07 \times 10^{-2} \text{ min}^{-1}$  (at 90 W). Alachlor oxidation was achieved, leading to 100% pesticide removal for both 60 and 90 W while 12% mineralization for 60 W and 25% for 90 W. The alachlor removal was terminated in 30 min at 90 W application and the speed of the process did not allow the investigation of the intermediate and/or by-products appearing and disappearing during the pathway. For this reason the reaction mechanism was studied by using the 60 W process. A detailed reaction mechanism was proposed for the degradation of 100 ppb alachlor. The operation was also evaluated by the Microtox toxicity measurement of treated solutions. The fluctuations in the toxicity levels were explained by the simultaneous detection of the pesticide and the intermediate products throughout the process. For the recalcitrant feature of the pesticide, the process required high energy ultrasonic irradiation to achieve non-toxic solutions.

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### 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 affect the human beings and/or the environment, strict regulations have been set by the authorities [9]. Pesticide residues reach the aquatic environment through manufacturing plants, direct surface run-off, leaching, careless disposal of empty containers, equipment washings, etc. In the world, alarming levels of pesticides have been reported to be persistent, toxic, mutagenic, carcinogenic and tumorigenic. Due to their high toxicity, biological treatment of agro-industrial effluents is often perturbed and sometimes blocked [7,16]. Alachlor (Fig. 1) is a widely used herbicide which controls most annual grasses and many broad-leaved weeds. This compound is slightly soluble in water ( $140 \text{ mg L}^{-1}$ ,  $20^\circ \text{C}$ ) and toxic to aquatic organisms: ( $\text{EC}_{50}$  (48 h) to water flea (*Daphnia magna*)  $10 \text{ mg L}^{-1}$ ) [3]. This chloroacetamide type of herbicide has molecular weight of  $269.77 \text{ g mol}^{-1}$  and it is persistent with a half-life of over 70 days in soil and 30 days in water. Because of its bioaccumulative properties in the animal

bodies, its removal from the life-cycles is very important. It is classified as a priority substance (PS) by the European Commission (EC) within the scope of the Water Framework Directive, Directive 2000/60/EC [1]. The concentration of alachlor is usually in ppb levels in natural waters and as for the Turkish Standards for the Drinking Water the maximum accepted levels of total pesticides 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, alachlor was degraded by ultrasonic irradiation (US) which is a technique that has been proposed as one of the techniques for degradation of hazardous organic compounds [15]. Ultrasound results in the formation and collapse of micro scale bubbles and generating local high temperature [13,14]. The bubbles are thought to work as the reaction field and to promote the degradation reaction [8,12]. The hydroxyl radicals generated by water sonolysis may either react in the gas phase or recombine at the cooler gas-liquid interface and/or in the solution bulk to produce hydrogen peroxide and water.

Depending on the type of reaction media and other physical properties, highly volatile compounds are better degraded by low frequency ultrasound, while the non-volatile ones are treated by medium to high frequency ultrasound [5]. The Henry's Law Coefficient ( $3.2 \times 10^{-5}$  to  $1.2 \times 10^{-7} \text{ atm-L mol}^{-1}$ ) and its negligible vapor pressure show that alachlor degradation by medium-high

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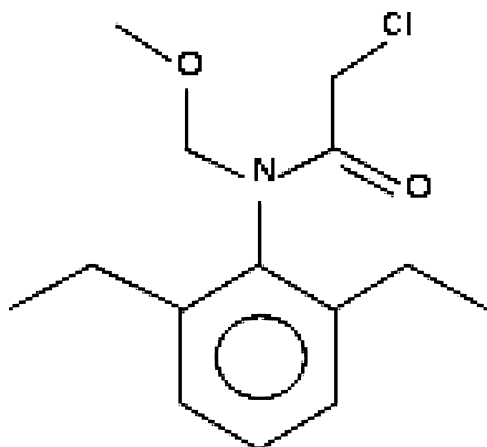


Fig. 1. Structural formula of alachlor ( $C_{14}H_{20}ClNO_2$ , 2-chloro-2',6'-diethyl-N-methoxymethyl acetanilide).

frequency ultrasound is favored. For this reason, three different frequencies (575–861–1141 kHz) were performed on the degradation of alachlor and the effect of applied power was observed.

The degradation kinetics for the advanced oxidation scheme was studied and the newly formed chemical products (intermediates) together with the Microtox toxicity were deeply investigated while the optimum conditions for alachlor removal have been proposed.

In a previous study on alachlor removal, [11], had focused on treatment of highly concentrated alachlor solutions ( $6 \times 10^{-4}$  M), by using 358 kHz ultrasound for 40 min reaction times. The author did not reach any satisfactory results because the only observed change was the cleavage of the chloride ion from the alachlor compound.

The originality of this paper arises from the fact that the decomposition of the alachlor must be carefully investigated because the degradation intermediates might end-up with much toxic compounds and this paper shows the optimum conditions for removal of the alachlor together with removal of toxic compounds and toxicity of the solution.

## 2. Experimental

Alachlor (99.9%) was purchased from Labor Dr. Ehrenstorfer. Working solutions of 100 ppb were prepared by using the ultrapure water obtained from Sartorius 61316 and 611UV ultra

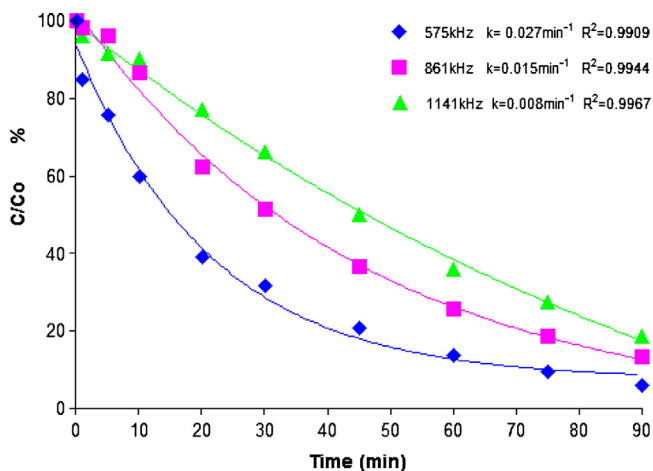


Fig. 2. Effect of ultrasonic frequency on alachlor degradation.

ultrapure water system. This concentration of alachlor represents the possible concentration found in natural water bodies after contamination. The methanol (Merck), acetonitrile (Merck), ammonium formate (Fluka) and acetone (Merck) were all liquid/gas chromatograph grade and were used as received. The SPE (solid phase extraction) columns were Technokrom Finisterre C18 columns.

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 transducer was connected at the bottom of a double jacketed 500 mL cylindrical glass reactor. The cooling was obtained by running water around the reactor jacket to keep the temperature constant at around 25 °C.

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 column was Synergi 4  $\mu$  Fusion-RP 80A, 50  $\times$  2.0 mm  $\times$  4  $\mu$ m and the mobile phase was methanol and ultra-pure water buffered with ammonium formate. The gradient program applied in alachlor measurements was: methanol rises to 95% (in volume) in 4 min, then holds at 95% for 1 min, decrease to 5% in 50 s and stop the run after 10 s hold. In the MS/MS detection system the  $m/z$  value of alachlor was 269 amu and the most intense fragment ions used for identification were 160 and 45 amu.

The intermediate-products formed during the degradation reactions were determined by using GC-MS system (Shimadzu, GCMS-QP2010 Plus) with a TRB-5MS capillary column (length 30 m, ID 0.25 mm, with a 0.25  $\mu$ m thin film coating). The GC temperature program was: initial value 100 °C, initial time 1 min; oven temperature rate 15 °C/min, oven final temperature 260 °C; oven temperature post time 5 min. Injection port temperature was 260 °C and ion source temperature was 250 °C. Before GC-MS analysis, samples were concentrated into the organic solvent phase by solid phase extraction (SPE). SPE method was carried out as follows: 20 mL methanol was used for conditioning the cartridges then washed with 20 mL of distilled water. 200 mL treated effluent sample was introduced into injection port and elution was made by 5 mL of acetonitrile.

The acute toxicity tests were run by using Microtox SDI OMNI500 Analyzer. The osmotic adjustment solution, the dilution solution, the reconstitution solution and the acute reagent were all purchased from Azur Environmental, Delaware USA. The standard protocol obtained from the company was applied, so that the light emission of the test organisms (*v. fischeri*) were measured before and after the exposure of the toxic solutions and compared with the blank.

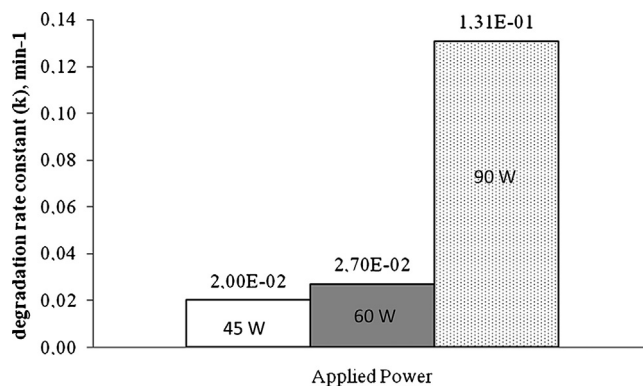


Fig. 3. Effect of ultrasonic power on alachlor degradation (575 kHz).

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