Photochemical degradation of alachlor in water

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Summary

This study investigates the photochemical degradation of alachlor, a chloroacetanilide herbicide. All experiments were conducted in ultra-pure deionized water (ASTM Type I quality) using direct ultraviolet (UV) photolysis and the UV/H_2O_2 advanced oxidation process. The direct UV photolysis and UV/H_2O_2 experiments were conducted in a commercial photochemical reactor with a quartz reaction vessel equipped with a 253.7 nm UV low pressure mercury lamp (Philips TUV 16 W). The experimental results demonstrate that UV photolysis was very effective for alachlor degradation (up to 97% removal using a high UV fluence of 4200 mJ/cm^2). The UV/H_2O_2 process promoted alachlor degradation compared to UV photolysis alone, with a high degree of decomposition (97%) achieved at a significantly lower UV fluence of 600 mJ/cm^2 when combined with 1 mg H_2O_2/L. The application of UV photolysis alone with a UV fluence of 600 mJ/cm^2 gave a negligible 4% alachlor degradation. The photo degradation of alachlor, in both direct UV photolysis and the UV/H_2O_2 process, followed pseudo first-order kinetics. The degradation rate constant was about 6 times higher for the UV/H_2O_2 process than for UV photolysis alone.

Keywords: degradation, alachlor, direct UV photolysis, UV/H_2O_2 process

Introduction

The contamination of the environment by a large number of organic micropollutants, including acetanilide herbicides, poses a significant risk to the quality of surface and groundwater. Thus, alachlor was chosen for this investigation as it is one of the most heavily used chlorinated acetanilide herbicides, which are an important group of pollutants of the environment, and which are classified as group B2 carcinogens by the US Environmental Protection Agency due to their strong carcinogenic effects on animals (Zhu et al., 2006; Qiang et al., 2010). Alachlor is known as a highly toxic endocrine disrupting chemical (Ryu et al., 2003). Due to the increasing use of this type of herbicide, the US EPA set a maximum contaminant level (MCL) of 2.0 μg/ L for drinking water (US EPA, 2001; Bagal and Gogate, 2013; Wang et al., 2016).

Alachlor cannot be removed from water by conventional treatments such as coagulation/flocculation, adsorption and membrane separation, due to its toxicity and biorefractory nature. Consequently, advanced oxidation processes (AOPs) have been suggested for the treatment of micropollutants such as alachlor. Most advanced oxidation processes involve the generation of very reactive hydroxyl radical ($^{\bullet}OH$), which has a very high oxidation potential. Studies have shown that natural organic matter, carbonate species and other organic and inorganic compounds present in water can significantly affect the removal rates of organic pollutants during AOPs. These species in the water matrix show scavenging effects by reacting with hydroxyl radicals, which further affects the determination of the optimal dose of H_2O_2 (Wols and Hofman-Caris, 2012; Autin et al., 2013; Ribeiro et al., 2015). Various authors have reported the fast and effective degradation of alachlor under different oxidation treatments, including O_3, O_3/H_2O_2, UV/H_2O_2, TiO_2/UV, Fenton and photo-Fenton (Ryu et al., 2003; Wong and Chu, 2003; Kim et al., 2005; Katsumata et al., 2006; Li et al., 2007; Bagal and Gogate, 2013; Wang et al., 2016). This work aims to investigate the photochemical degradation efficiency of alachlor in ultra-pure deionized water using direct UV photolysis and UV/H_2O_2 process, through the evaluation of key factors affecting treatment efficacy and kinetics.

Materials and methods

Chemicals and reagents

Alachlor standard (Pestanal®) was obtained from Sigma-Aldrich and internal standard pentachlornitrobenzene (PCNB, 5000 mg/mL in methanol) from Supelco. Solvents methanol and hexane were obtained from J.T. Baker and were organic residue analysis grade; 30% w/w reagent grade H_2O_2 was purchased from POCH S.A. Laboratory

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ultrapure deionised water was produced by LABCONCO, WaterPro Ro/Ps Station. All other chemicals were analytical grade and were used without further purification.

Photochemical experiments

The photochemical degradation of alachlor was carried out in a commercial reactor with a quartz vessel equipped with a low pressure mercury lamp (Philips TUV 16 W), emitting monochromatic radiation at 253.7 nm. Further details on the design of the photochemical reactor are presented elsewhere (Molnar et al., 2015). Degradation was performed using 700 mL of ultrapure deionised water spiked with an aqueous solution of alachlor to achieve an initial concentration of about 100 μg/L. Prior to each treatment, the lamp had been warmed up for 20 minutes. The sample was held in a reservoir above the reactor, connected via tap by a teflon tube. Once the lamp had warmed up, hydrogen peroxide was added to the sample at concentrations of 1 mg H_2O_2/L. The water samples were then introduced into the reactor from above, and were drained out of a separate tap at the bottom of the reactor at the end of the treatment. For the direct UV photolysis, a UV fluence from 600 to 4200 mJ/cm^2 was applied. Additionally, 1 mg H_2O_2/L was applied for the UV/H_2O_2 process with a UV fluence in the range 100-600 mJ/cm^2.

Analysis

Alachlor concentrations in water were measured by gas chromatograph with a mass spectrometer (Agilent Technologies 7890B/5977A GC/MS system with an HP-5ms capillary column (30 m x 0.25 mm, 0.25 μm), constant flow of 1.0 mL/min). The initial oven temperature was 70 °C, which was held for 0 min. It was increased to 280 °C at 15 °C/min, held for 0 min. The injector temperature was 230 °C and the detector temperature was 150 °C. Splitless injection mode was applied. The method detection limit for alachlor was 10 ng/L.

Results and discussion

Alachlor degradation by direct UV photolysis

In the first stage of the experiment, the influence of direct UV photolysis (UV fluence 600-4200 mJ/cm^2) on the degradation of alachlor in ultra-pure deionized water without the addition of hydrogen peroxide was investigated (Fig. 1). In these treatment conditions, the obtained results showed direct UV photolysis achieved alachlor removals from 4 to 97%. The degree of removal increased with the increasing UV fluence, with a maximum 97% removal achieved at 4200 mJ/cm^2.

The direct photolysis of alachlor depends on the quantum yield (Φ_{254}) and molar absorption coefficient (ε_{254}), which represent two fundamental parameters that govern the direct photolysis rate (Kwona et al., 2015). The high efficiency of alachlor degradation by direct UV photolysis can be explained by its relatively high molar absorption coefficient at 253.7 nm. Spectra of alachlor show two peaks, which correspond to π-π* bands (Feigenbrugel et al., 2005). Bagal and Gogate (2013) reported at 93% removal of alachlor using UV photolysis in a synthetic matrix spiked with alachlor, with a reaction time of 15 min.

Alachlor degradation by UV/H_2O_2 process

It is well known that the concentration of hydrogen peroxide is one of the most important parameters influencing the final extent of degradation by UV/H_2O_2 process. During the UV/H_2O_2 experiments, the UV fluence was varied in the range 100-600 mJ/cm^2 with initial H_2O_2 concentrations of 1 mg/L. Nearly complete degradation of alachlor (97%) by the UV/H_2O_2 process was observed at 600 mJ/cm^2 (Fig. 2). During the UV/H_2O_2 treatment, very high percentages of alachlor degradation (from 25 up to 97%) were again achieved, but with much lower UV fluences: 97% degradation was achieved with 7 times less UV fluence in the UV/H_2O_2 process than by UV photolysis alone. During UV/H_2O_2 treatment, $^{\bullet}OH$ radicals the major mechanism for the degradation of alachlor, achieved a higher degradation rate than by applying UV photolysis alone. It is known that H_2O_2 is readily converted to $^{\bullet}OH$ under UV irradiation (λ=254 nm). Thus, the decrease in the concentration of alachlor in the presence of H_2O_2 was due to the favoured oxidation by $^{\bullet}OH$ radicals.

Due to the very high level of the oxidative degradation of alachlor achieved at the initial H_2O_2 concentration of 1 mg/L, additional investigations with UV radiation in combination with larger doses of hydrogen peroxide were not deemed necessary. Theoretically, if hydrogen peroxide is added in excess, it may react with the hydroxyl radicals, acting as a "scavenger" and thus reducing treatment efficacy (Sultan and Cho, 2016).

Kinetic degradation of alachlor

The degradation of alachlor followed the pseudo first order kinetic model and could be expressed as Eq (Sharpless and Linden, 2003; Shu et al., 2013):

$$\frac{-d[P]}{dt} = k_d[P] \qquad (1)$$

where k_d (min^{-1}) is the time-based pseudo first-order rate constant for direct UV photolysis, while $[P_0]$ and $[P]$ are the initial and final concentrations of pollutants in water. If $\ln([P_0]/[P])$ is plotted versus the UV dose (mJ/cm^2), the corresponding direct UV photolysis fluence-based rate constant k'_d is obtained (Bolton and Stefan, 2002).

Degradation during UV/H_2O_2 involves both direct UV photolysis and oxidation by UV/H_2O_2 (Sharpless et al., 2003; Shu et al., 2013):

$$\frac{-d[P]}{dt} = (k_d + k_i)[P] = k_t[P] \qquad (2)$$

where k_i is the pseudo first-order rate constant for oxidation by UV/H_2O_2 and is a function of the second-order reaction rate constant for $^{\bullet}OH$ radical attack and the steady-state concentration of $^{\bullet}OH$ radicals. k_t can be determined from the slope of a plot of $\ln([P_0]/[P])$ vs. reaction time. K'_t can be obtained from a plot of $\ln([P_0]/[P])$ versus the UV dose (mJ/cm^2).

For both processes, direct UV photolysis and radical reaction, the degradation of alachlor fits well ($R^2 > 0.98$) with the first-order rate equation described above. When these two processes are compared, it is revealed that the alachlor degradation rate was significantly enhanced by the UV/H_2O_2 process. $k't$ was 6 times higher (6.10×10^{-3} cm^2/mJ) compared to the k'_d (0.950×10^{-3} cm^2/mJ) (Fig. 3). It can be concluded that the addition of hydrogen peroxide leads to a significant increase of the alachlor degradation rate, due to the generation of strongly oxidizing hydroxyl radicals by hydrogen peroxide photolysis.

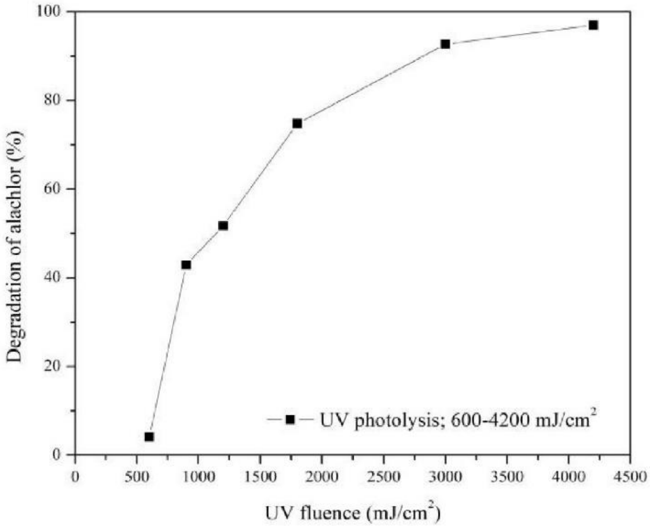

Fig. 1. Degradation of alachlor by direct UV photolysis

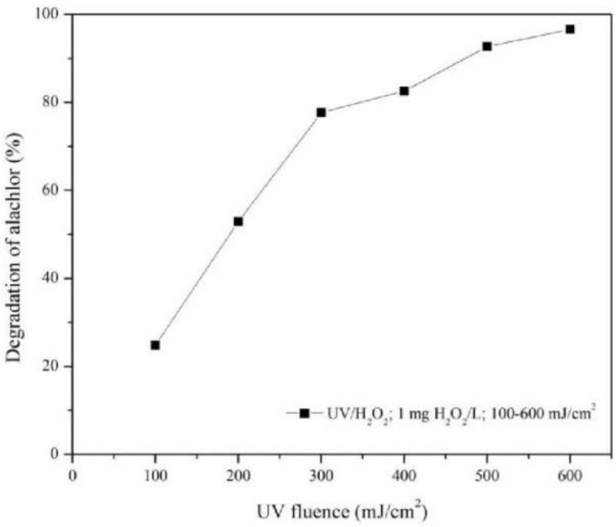

Fig. 2. Degradation of alachlor by UV/H_2O_2 process

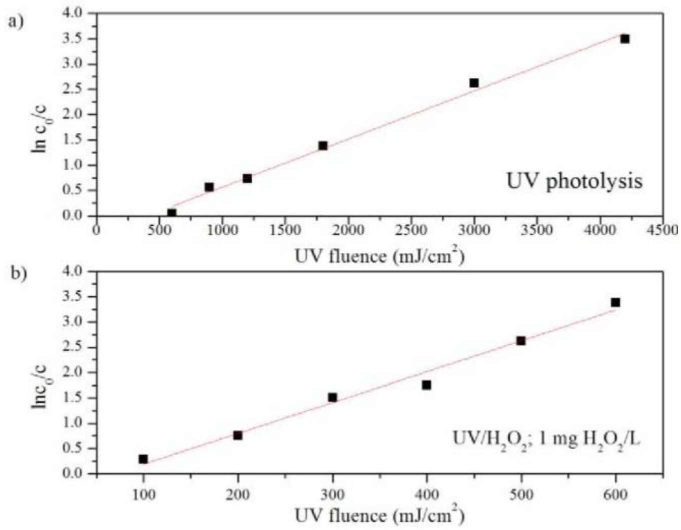

Fig. 3. Kinetic study of alachlor by a) direct UV photolysis; b) UV/H_2O_2 process

Conclusions

The degradation of alachlor by the UV/H_2O_2 process was shown to depend on the UV fluence and the initial concentration of hydrogen peroxide. A high degree of alachlor degradation (>97%) was achieved, either using UV photolysis alone with a high UV fluence or by the UV/H_2O_2 process with 1 mg H_2O_2/L and a 7 times lower UV fluence. Pseudo-first-order rate constants were about 6 times higher for the UV/H_2O_2 process than for the UV photolysis alone as a consequence of the accelerated generation of highly reactive and unselective hydroxyl radicals during the advanced oxidation process. Further research should be focused on investigating the influence of the water matrix on alachlor degradation in order to simulate conditions during real water treatment.

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