



Photocatalytic-assisted ozone degradation of metolachlor aqueous solution



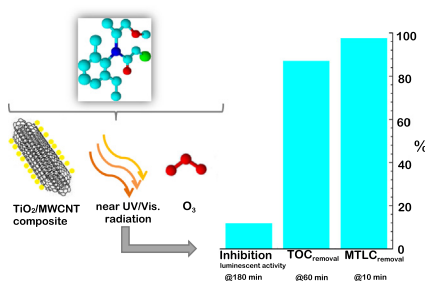
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HIGHLIGHTS

- O₃ assisted photocatalytic degradation of metolachlor was investigated.
- O₃ by itself is enough to achieve total removal.
- High mineralization was only easily attained with O₃, light and tested samples.
- The combined method led a pronounced decrease in the toxicity of the solutions.
- Prepared catalysts presented remarkable performance during metolachlor degradation.

GRAPHICAL ABSTRACT



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ABSTRACT

Photocatalytic-assisted ozone degradation of metolachlor (MTC) aqueous solutions was investigated using neat TiO₂ (prepared by sol-gel method) and TiO₂/carbon composite (prepared from commercial available metal oxide and carbon phase) as catalysts. In terms of MTC degradation, O₃ on its own is enough to achieve 100% removal, but the introduction of light increased the rate of removal. On the other hand, the combination of O₃ with light and the tested catalysts is mandatory to reach high mineralization in short reaction times. After 60 min of reaction, the TOC removal was 87% and 75% in the presence of the prepared composite and TiO₂, respectively. The concentration of two short chain carboxylic acids, oxalic and oxamic acids, was followed during MTC degradation. The amount of these acids decreased when O₃ and light were combined.

In general, nitrogen ions, such as nitrate and ammonium, were detected in the studied processes. All treatments released ammonium and light based processes also produced nitrate. Microtox[®] analysis showed that the combined process in the presence of the prepared catalysts led to a remarkable reduction in the toxicity of the treated solution, decreasing the inhibition of luminescent activity of *Vibrio Fisheri* from 74% to 12%.

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1. Introduction

The pollution caused by pesticides has significantly increased due to their extensive use in agriculture. Their residues are known

to be persistent in surface water and ground water supplies posing a major problem in many countries [1]. Pesticides are highly noxious, sometimes non-biodegradable and very mobile throughout the environment [2]. Chloroacetamides are the most widely used herbicides and their operation mode consists in inhibiting the early development of susceptible weeds by preventing biosynthesis of very long fatty acid chains, thus affecting cell integrity [3–5].

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Among the most commonly used chloroacetamides are acetochlor, alachlor and metolachlor (MTLC) [3,6] and they have been detected in surface water and ground water from 0.1 to 10 µg/L [7–10]. MTLC is listed in the Drinking Water Contaminant Candidate List of the US Environmental Protection Agency [11]. MTLC and its metabolites are alleged or confirmed carcinogens.

Many conventional water treatment processes, such as coagulation and chlorination, have been found to be ineffective to remove alachlor and MTLC [12]. Therefore, successfully elimination of pesticides in aqueous environment requires application of unconventional processes [1,2].

Sunlight is an efficient degradation pathway of MTLC in soil, with the drawback of leaving behind some of its hazardous metabolites. It is estimated that about 50% of applied MTLC degrades in eight days on sunlit soil [13]. The degree of photodegradation diminishes rapidly with the deepening of soil incorporation. In water, it undergoes mesolytic degradation to give primarily 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholine [14].

The photocatalytic degradation of MTLC using pure TiO₂ and Ag modified TiO₂ was investigated by Sakkas et al. [15]. Working with low to moderate amounts of TiO₂, they concluded that in the early degradation steps the toxicity of the solution increases due to the formation of more toxic by-products.

In the presence of organic matter the photodegradability of MTLC is hindered, while in the presence of nitrate the opposite is observed, because the production of HO· radicals is increased [16].

Simulated drinking water samples containing a mixture of chloroacetamide herbicides and chloroacetamide derivatives were subjected to different treatments by Hladik et al. [12]. Coagulation provided little removal of the parent and derivative compounds, but chlorination was able to remove completely the by-products. However, ozonation proved to be even more efficient than chlorination [12].

According to Munoz et al., homogeneous Fenton-like oxidation (H₂O₂/Fe³⁺) of monochlorophenols is strongly dependent of the operating conditions [17]. The stoichiometric amount of H₂O₂ and Fe³⁺ is the key to achieve suitable results.

The use of organic matter from compost to promote the photocatalytic degradation of two herbicides and a fungicide by solar light was studied by Coelho et al. [18]. Following their findings the main conclusion was that hydroxyl radicals are the principal species involved in the reactions, mainly due to their high reactivity.

On the other hand, Avetta et al. [19] proposed a different mechanism suggesting the participation of singlet oxygen species in the photodegradation of monochlorophenols in the presence of soluble bio-based substances (SBO). For different organic substrates the toxicity assays showed a progressive, up to a complete, detoxification of the system, mediated by the singlet oxygen species with no significant contribution of the present SBO.

Even though a direct comparison of the efficiency of TiO₂ and ZnO may not be precise due to differences in their surface properties, Fennoll et al. verified that ZnO was more efficient during photocatalytic degradation of a mixture of triazina and chloroacetanilide herbicides [20].

Other studies reported the ozonation of MTLC, individually or in a mixture of emerging pollutants, in semi-batch and continuous operation [21,22]. In terms of toxicity, the by-products released with O₃ alone are more toxic than the parent compound, but the addition of the carbon material reduces this impact. Multi-walled carbon nanotubes and carbon nanofibers grown on a honeycomb cordierite were used as catalysts.

A study on the toxicity of photoproducts formed during UV-treatments of three chloroacetamide herbicides showed that 90% of the original pesticide was converted in compounds with more or equal toxicity than the parent compound [3].

In summary, this study focuses on using photocatalytic-assisted ozone process for MTLC degradation. To the best of our knowledge, the present work describes the MTLC degradation using photocatalytic ozonation by the first time. For that purpose two catalysts were prepared, one composite made of commercial TiO₂ and multi-walled carbon nanotubes and another consisting in TiO₂ synthesized by the sol-gel procedure. Experiments without catalysts and with only ozone and radiation were also performed in order to better understand the results. The performance of the prepared materials was compared with the commercial TiO₂ (P25).

2. Experimental

2.1. Reagents and materials

MTLC (C₁₅H₂₂ClNO₂, PESTANAL Analytical Standard), nitric acid (HNO₃, ≥65%), oxalic acid (C₂H₂O₄, ≥99%), oxamic acid (C₂H₃O₃N, ≥98%), *tert*-butanol ((CH₃)₃OH, ≥99.5%), titanium (IV) isopropoxide (Ti[OCH(CH₃)₂]₄, 97%), 2-ethyl-6-methylaniline (C₂H₅C₆H₃(CH₃)NH₂, ≥99.5%) and 2,6-pyridine dicarboxylic acid (C₇H₅NO₄, 99%) were purchased from Sigma-Aldrich. Sodium carbonate (Na₂CO₃, ≥99%) was obtained from Fluka. Acetonitrile (C₂H₃N, HPLC gradient grade) and sulfuric acid (H₂SO₄, 95–98%) was supplied by Fisher Scientific. Methanol (CH₃OH, MS grade) was acquired from VWR International. Ultrapure water was supplied by a Milli-Q water system. Commercial TiO₂, sample P25, was supplied by Evonik Degussa Corporation. The commercial multi-walled carbon nanotubes, MWCNT, were supplied by Nanocyl (ref. 3100).

2.2. Kinetic experiments

Photocatalytic ozonation of MTLC was performed in a glass immersion photochemical reactor according to the experimental conditions described in [23]. The initial concentration of MTLC was 20 ppm and the reactor was loaded with 0.5 g L⁻¹ of catalyst. The reaction system was the same for all tested processes; however, in the case of photolytic reactions the ozone was replaced by oxygen and for ozonation experiments the radiation source was turned off.

In the experiments carried out with *tert*-butanol, the radical scavenger is presented in excess with a concentration 10 times higher than the initial concentration of the parent compound (C_{*tert*-butanol} = 0.7 mmol L⁻¹).

For this study, different catalysts were tested in the kinetic reactions. Recent researches of our group have confirmed that composites based on TiO₂ and carbon nanotubes present high catalytic activity in the photocatalytic oxidative degradation of several pollutants [23–27]. The sol-gel method has been widely applied to prepare TiO₂ photocatalysts to be used in the development of prototypes at laboratorial scale [28–30]. Composite of 90:10 (w/w) P25 and MWCNT was synthesized by the hydration-dehydration technique, sample P25₉₀MWCNT₁₀ [25,27]. In the composite preparation, a selected amount of MWCNT was dispersed in water under ultrasonication. P25 was added to the suspension 30 min later and the mixture was heated up to 80 °C and magnetically stirred until the water was completely evaporated. The resulting composite was dried at 110 °C overnight. TiO₂ sample was obtained by the sol-gel technique [30]. The preparation consisted in the slowly addition of Ti[OCH(CH₃)₂]₄ to ethanol. After 30 min under continuous stirring, nitric acid was added. The solution was loosely covered and kept stirring until the homogeneous gel formed. After grinding the xerogel, a fine powder was obtained and afterwards it was calcined at 400 °C in a nitrogen flow for 2 h.

The textural characterization of the materials was obtained from the N₂ equilibrium adsorption/desorption isotherms,

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