



Insights into the removal of terbuthylazine from aqueous solution by several treatment methods



Pedro M. Álvarez*, Diego H. Quiñones, Isidro Terrones, Ana Rey, Fernando J. Beltrán

Departamento de Ingeniería Química y Química Física, Instituto Universitario de Investigación del Agua, Cambio Climático y Sostenibilidad (IACYS), Universidad de Extremadura, Av. de Elvas s/n, 06071 Badajoz, Spain

ARTICLE INFO

Article history:

Received 29 December 2015

Received in revised form

9 April 2016

Accepted 13 April 2016

Available online 16 April 2016

Keywords:

Adsorption

Activated carbon

Carbon nanotubes

Solar photo-ozonation

Terbuthylazine

Titania

ABSTRACT

This paper reports the removal of the s-triazine herbicide terbuthylazine (TBA) from aqueous solution by various treatment methods including adsorption onto activated carbon (AC) and multiwalled carbon nanotubes (MWCNT), UV₂₅₄ photolysis, UV₂₅₄/H₂O₂, single ozonation, O₃/H₂O₂, catalytic ozonation (AC, MWCNT and TiO₂ as catalysts) and some solar driven processes such as TiO₂ photocatalytic oxidation and photo-ozonation. TBA was adsorbed onto AC and MWCNT following a pseudo-second order kinetics and Freundlich isotherm. Rapid small scale column tests showed that TBA could be removed from solution by adsorption onto AC better than atrazine. The UV₂₅₄/H₂O₂ treatment resulted in excellent removal of TBA primarily due to the oxidation capability of hydroxyl radicals ($k_{\text{HO}^\bullet} = 3.3 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$) generated from H₂O₂ photolysis. As the H₂O₂ initial concentration was increased from 5 to 50 mg L⁻¹ the HO[•] exposure per UV fluence ($R_{\text{HO}^\bullet, \text{UV}}$) increased, making the process more efficient. Single ozonation also allowed complete removal of the herbicide though the process was slow ($k_{\text{O}_3} = 15.4 \text{ M}^{-1} \text{ s}^{-1}$ at pH > 4). The ozonation process could be greatly accelerated by the enhanced generation of HO[•] through O₃/H₂O₂ and O₃/AC processes, which also led to more efficient processes in terms of ozone utilization. Commercial TiO₂ (TiO₂-P25) and lab prepared anatase TiO₂ (TiO₂-cat) nanoparticles catalyzed the removal of TBA by solar photocatalysis. In contrast, a lab prepared MWCNT-TiO₂ composite was not useful as catalyst in solar photo-oxidation processes because of the HO[•] scavenging nature of the MWCNT used as support. A mechanism for TBA degradation by O₃ and HO[•] has been suggested after TBA degradation intermediates identification.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

S-triazine herbicides (e.g., atrazine, simazine, or terbuthylazine) are widely used pesticides for the control of broadleaf and grassy weeds in corn, sugarcane, grape and other crops. Significant amounts of these compounds reach the groundwater due to the high quantity used, relatively long persistence in soil and tendency to move with water (i.e., percolation). While atrazine is recognized as the most detected pesticide in surface water by the US Environmental Protection Agency, the European Union (EU) banned its use in 2004 because of persistent surface and groundwater contamination. Since then, the less soluble terbuthylazine (TBA) has been used as the main substitute of atrazine in some EU countries including Spain, Italy and Portugal. As a result, TBA is

nowadays one of the most frequently detected pesticides in groundwater and surface waters of these countries, sometimes exceeding the Environmental Quality Standards imposed by EU regulations (Bottoni et al., 2013; Köck-Schulmeyer et al., 2014; Silva et al., 2015). In contrast to atrazine and simazine, TBA is not yet considered a priority pollutant in the field of water policy by the EU. However, it is a pesticide of emerging concern because of its persistence in natural waters (Navarro et al., 2004) and toxicity towards aquatic organisms (López-Roldán et al., 2013; Palma et al., 2014). Moreover, the treatment methods usually applied in the process of drinking water production do not lead to its complete removal. For instance, Ormad et al. (2008) found that the chlorine treatment usually applied in drinking water treatment plants (WTP) removed barely 30% of TBA (initial concentration 0.5 µg L⁻¹) and brought about the formation of carcinogen trihalomethanes while a coagulation treatment using aluminium sulphate as coagulant (10–40 mg L⁻¹ as Al) led to only 20% removal. These authors also showed that ozonation and adsorption onto activated carbon

* Corresponding author.

E-mail address: pmalvare@unex.es (P.M. Álvarez).

(AC) were more efficient methods leading to 45% and 60% TBA removals, respectively. Moreover, a sequential process comprising ozonation, AC adsorption and coagulation steps allowed a higher 90% TBA removal.

Studies on methods to remove TBA from water are much scarcer in the literature than those devoted to other s-triazines and most of them have been carried out using TBA in a mixture of pesticides (Ormad et al., 2010; Dražević et al., 2011; Pinto et al., 2012; Fenoll et al., 2012; Gardi et al., 2015; Pereira et al., 2015). Therefore, the study of methods to degrade TBA in water deserves more research. In this sense, advanced oxidation processes (AOPs), such as ozone and UV-based methods, as well as adsorption onto carbonaceous materials such as AC or carbon nanotubes (CNT) can be highlighted among those found most effective to remove other s-triazine herbicides, such as atrazine and simazine, for which extensive research has been carried out (e.g., Beltrán et al., 1996, 1998; Ma and Graham, 2000; Rivas et al., 2001; Chen et al., 2009; Jain et al., 2009; Guzmán-Pérez et al., 2011; Brooks et al., 2012; Luo et al., 2015; Oulton et al., 2015). Recently, some solar-driven catalytic AOPs have also been revealed promising for the enhanced mineralization of atrazine (Jiménez et al., 2011; Li et al., 2012; Pineda-Arellano et al., 2013; Andersen et al., 2013).

This study investigates a number of treatment methods to remove TBA from aqueous solution, including adsorption onto AC and multi-walled CNT (MWCNT), UV photolysis, UV/H₂O₂, single ozonation, O₃/H₂O₂, catalytic ozonation (AC, MWCNT and TiO₂ as catalysts) and some solar driven processes such as photo-ozonation, TiO₂-photocatalytic oxidation and TiO₂-photocatalytic ozonation. This work seeks to gain a better scientific understanding of these methods to remove TBA.

2. Material and methods

2.1. Herbicides, adsorbents and catalysts

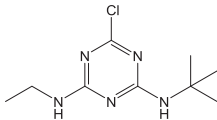
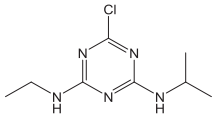
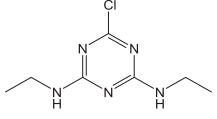
Terbutylazine and atrazine were purchased from Sigma-Aldrich (Spain) and used without further purification. Table 1

shows some selected physical, chemical and toxicological properties of TBA and, for the sake of comparison, other two s-triazines. Granular activated carbon (DARCO[®], 12–20 mesh, Sigma-Aldrich, Spain) and MWCNTs (purity >95% carbon, OD × L = 6–9 nm × 5 μm, Sigma-Aldrich, Spain) were used as adsorbents. Commercial titanium dioxide (AEROXIDE[®] TiO₂ P25, Evonik, Germany) and other two lab-synthesized TiO₂-based materials (hereafter TiO₂-cat and MWCNT-TiO₂) were used as photocatalysts. To obtain TiO₂-cat particles, typically, 4.3 mL of titanium (IV) butoxide 97% (Sigma-Aldrich, Spain) were mixed with 1.4 mL of isopropanol >99% (Sigma-Aldrich, Spain). This mixture was added dropwise into 34 mL of Milli-Q ultrapure water, which had previously been acidified with HNO₃ 65% (Panreac, Spain) to reach pH 2.0. The suspension was stirred under reflux at 75 °C for 24 h. After that, the sample was transferred to a rotary evaporator operating at 80 °C under vacuum (40 mm Hg) to remove the excess of solvent in order to obtaining a TiO₂ sol, which was repeatedly washed with Milli-Q ultrapure water and dried at 100 °C overnight. A MWCNT-TiO₂ composite was also synthesized. To do this, the TiO₂ sol obtained as described above was dispersed with 0.2 g of MWCNT under sonication at 37 kHz for 1 h (Elmasonic S60/H model, Elma GmbH&Co, Germany) and then dried under vacuum (40 mm Hg) at 80 °C. Finally, the residue was washed with Milli-Q ultrapure water several times and dried at 100 °C overnight. According to the amount of reagents used, the percentage of TiO₂ in the MWCNT-TiO₂ composite was expected to be about 70–80 wt%, composition that had been proven useful for photocatalytic purposes in a previous work where TiO₂-AC composites were synthesized (Quiñones et al., 2014).

2.2. Characterization of adsorbents and catalysts

BET surface area and pore structure of solid samples were determined from their nitrogen adsorption–desorption isotherms obtained at –196 °C using an Autosorb 1 apparatus (Quantachrome Instruments, USA). Prior to analysis the samples were outgassed at 250 °C for 12 h under high vacuum (<10^{–4} Pa). From the nitrogen

Table 1
Some physical, chemical and toxicological properties of TBA and other s-triazine herbicides.^a

Herbicide	Molecular structure	MW g mol ^{–1}	Log K _{OW} ^b	Sol. ^c mg L ^{–1}	pK _a ^d	GUS leaching potential index ^e	EC ₅₀ ^f mg L ^{–1}	Aqueous photolysis DT ₅₀ ^g days
TBA		229.71	3.4	6.6	1.9	3.07	21.2	Stable
Atrazine		215.68	2.7	35.0	1.7	3.30	85	2.6
Simazine		201.66	2.3	5.0	1.6	2.0	1.1	1.9

^a Data taken from the Pesticide Properties Database developed by the Agriculture & Environment Research Unit (AERU) at the University of Hertfordshire (<http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>).

^b K_{OW} = Octanol-water partition coefficient at pH 7 and 20 °C.

^c Sol. = Solubility in water at 20 °C.

^d Dissociation constant (pK_a) at 25 °C.

^e GUS (groundwater ubiquity score) leaching potential index is a measure of the tendency a pesticide has to leach. GUS > 2.8, likely to leach; 1.8 < GUS < 2.8, intermediate leachability; GUS < 1.8, unlikely to leach.

^f Acute 48-h EC₅₀ (*Daphnia magna*).

^g Half-life (DT₅₀) = time for pesticide concentration to decrease 50%.

Download English Version:

<https://daneshyari.com/en/article/4481000>

Download Persian Version:

<https://daneshyari.com/article/4481000>

[Daneshyari.com](https://daneshyari.com)