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Antibacterial inactivation of spiramycin after titanium dioxide photocatalytic treatment

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ABSTRACT

The photocatalytic degradation of an antibiotic (spiramycin) has been studied using immobilized titanium dioxide (TiO_2) as a photocatalyst in a laboratory reactor under ultraviolet illumination (365 nm). The degradation of the antibiotic was monitored by ultraviolet spectrophotometry and high-pressure liquid chromatography and confirmed by an antibacterial activity evaluation. Two types of TiO_2 (P25 and PC500) immobilized on glass plates were compared. For TiO_2 PC500 immobilization on glass and paper was also studied. A slightly better degradation was obtained with TiO_2 P25 for which the degradation kinetics were investigated. The Langmuir–Hinshelwood kinetic model is satisfactorily obeyed at initial time and in the course of the reaction. Adsorption and apparent rate constants were determined. These results show a complete degradation of spiramycin, which was confirmed by the inhibition of the antibacterial activity of *Staphylococcus xylosus*, when exposed to spiramycin solutions treated with photocatalyst for a short time. In addition, the codegradation of spiramycin and tylosin was investigated and showed that tylosin had a higher affinity to the catalyst TiO_2 P25 than spiramycin. The complete degradation of spiramycin confirms the feasibility of such a photocatalytic treatment process for spiramycin elimination from contaminated water.

Mots clefs:
activité antibactérienne
immobilisation de TiO_2
macrolide
POA
spiramycine

RÉSUMÉ

La dégradation photocatalytique d'un antibiotique (spiramycine) a été étudiée en utilisant comme photocatalyseur du dioxyde de titane immobilisé dans un réacteur de laboratoire sous illumination UV (365 nm). La dégradation de l'antibiotique a été suivie par spectrophotométrie UV–visible et HPLC et a été confirmée par une évaluation de l'activité antibactérienne. Deux types de TiO_2 (P25 et PC500) immobilisés sur des plaques de verre ont été comparés. Pour le TiO_2 PC500 l'immobilisation sur du verre et du papier a aussi été étudiée. La dégradation a été un peu meilleure pour le TiO_2 P25, pour lequel la cinétique a été étudiée. Le modèle de Langmuir–Hinshelwood est suivi de façon satisfaisante à la fois

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au début et au cours de l'expérience. Les constantes d'adsorption et de vitesse apparentes ont été déterminées. Ces résultats montrent la dégradation complète de la spiramycine et a été confirmée par l'inhibition de son action sur la croissance de *S. xylosus*. De plus la co-dégradation de la spiramycine et de la tylosine a été étudiée et a montré une plus grande affinité de la tylosine pour le TiO_2 P25, par rapport à la spiramycine. La dégradation complète de la spiramycine confirme la faisabilité d'un traitement photocatalytique pour l'élimination de cet antibiotique d'eaux contaminées.

1. Introduction

Since the 1900s, the modern world is experiencing a period of great expansion particularly in agriculture and industry. The discharge of nontreated or badly treated industrial and urban effluents into rivers, aquifers, and lakes [1] coupled with the intensification of agriculture creates a multicontaminant pollution of the aquatic environment. Because of the emergence of new analytical methods, micropollutants (at concentrations lower than a few micrograms per liter) are detected in the different aquatic compartments [2,3]. The range of these micropollutants is very large: metals, pharmaceuticals, detergents, fire retardants, and so forth. Several kinds of drugs, such as antibiotics, synthetic hormones, analgesics, and so forth, have been identified in surface water, groundwater, sewage water, and drinking water [4]. Some of them are not significantly adsorbed in the subsoil and may leach into groundwater [5]. In addition, they have a direct effect on the environment by disrupting the ecosystem equilibrium [6]. Finally, environmental bacteria exposed to residual antibiotics could modify their genetic information, developing higher antibiotic resistance and resulting in multiresistant bacterial strains [4]. Antibiotics from the macrolide family, such as spiramycin and tylosin, have been extensively used in human and veterinary medicine to treat and prevent bacterial infections [7].

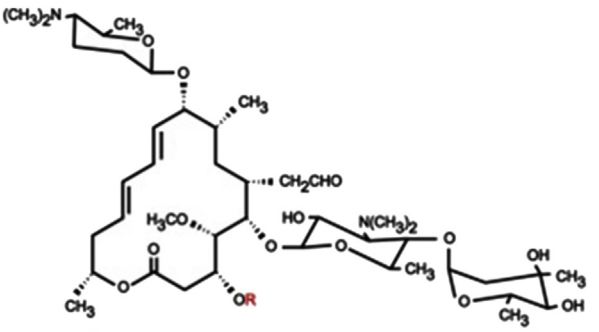
The high cost of physicochemical treatment processes and the limitation of biological treatment led scientists to develop other methods to offer attractive alternatives such as advanced oxidation processes (AOPs) to cope with these micropollutants, which are largely recalcitrant to biological degradation. Chemical treatment by AOPs results in a nonselective oxidation of most organic compounds up to complete mineralization into CO_2 and other inorganic compounds. AOPs such as ultraviolet (UV)–peroxide combinations, ozonation, or photo-Fenton processes have demonstrated their effectiveness in the oxidation of nonbiodegradable organic compounds. Another AOP, photocatalysis, has gradually become an alternative technology to clean up the water. It has been investigated on some antibiotics [8,9]. The photocatalyst is mainly a semiconductor (oxide or sulfide). The most commonly used semiconductor is titanium dioxide (TiO_2), because of its performance, stability, low cost, and resistance to corrosive conditions. Its gap energy is 3.2 eV. This energy can be supplied by the exposure of this material to a UV irradiation around 365 nm. The benefits of TiO_2 are the use of a stable, nontoxic, and inexpensive photocatalyst, which can be activated by natural and artificial light sources.

The aim of this work is to study the degradation of spiramycin by photocatalysis to assess the parameters governing the antibiotic degradation kinetics and the efficiency of the photocatalyst deposit. The influence of experimental conditions, such as flow rate, and the presence of another macrolide (tylosin) in the treated solution were also investigated. To confirm the complete transformation of spiramycin, the antibacterial activity was investigated, with the treated solutions inoculated with *Staphylococcus xylosus* strain.

2. Materials and methods

2.1. Antibiotics

Spiramycin (Fig. 1) active ingredient offered by SAIPH Laboratories, Tunisia (Arab Society of Pharmaceutical Industries) was used without any further purification. Spiramycin is a mixture of three types (Spiramycin I up to 85%, Spiramycin II, and Spiramycin III), depending on the group borne by the carbon 3 of the cycle [10]. Tylosin tartrate (Fig. 2) was purchased from Sigma–Aldrich (Saint-Quentin-Fallavier, France) and used without further purification.



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Spiramycin I	–H
Spiramycin II	–CO–CH_3 (acetyl)
Spiramycin III	–CO–CH_2–CH_3 (propionyl)

Fig. 1. Spiramycin.