



Photocatalytic degradation of thimerosal in human vaccine's residues and mercury speciation of degradation by-products



Orlando Yepsen^a, David Contreras^a, Paola Santander^a, Jorge Yáñez^{a,*}, Héctor D. Mansilla^{b,*}, Dulasiri Amarasiwardena^c

^a Department of Analytical and Inorganic Chemistry, Faculty of Chemical Sciences, University of Concepción, Edmundo Larenas 129, PO Box 160-C, Concepción, Chile

^b Department of Organic Chemistry, Faculty of Chemical Sciences, University of Concepción, Edmundo Larenas 129, PO Box 160-C, Concepción, Chile

^c School of Natural Science, Hampshire College, Amherst, MA 01002, USA

ARTICLE INFO

Article history:

Received 27 January 2015

Accepted 2 February 2015

Available online 10 February 2015

Keywords:

Thimerosal degradation

Vaccines

Mercury

Heterogeneous photocatalysis

TiO₂

Mercury speciation

Mercury vapor

ABSTRACT

Thimerosal (sodium ethylmercury thiosalicylate) has been intensively used as a stabilizer of pharmaceuticals, mainly in human and veterinary vaccines. Yearly loss of thousands of vaccines occurs due to expiration, loss of cold chain and overstock; therefore safe disposal of expired vaccines containing thimerosal has become high priority. In this work, UVA light assisted TiO₂ heterogeneous photocatalysis has been applied for the first time in order to degrade thimerosal contained in hepatitis B vaccine residues (HibTITER). The photocatalytic process was optimized using the Response Surface Methodology (RSM). Most favorable experimental conditions to achieve the maximum degradation of thimerosal were pH 2 and 0.2 g L⁻¹ TiO₂ under nitrogen bubbling. Under these conditions thimerosal contained in vaccine residues was completely degraded within 20 min by UV-A assisted photocatalysis. The mercury in thimerosal was reduced to elemental mercury and removed from the solution in vapor form. The organic groups of thimerosal were oxidized to thiosalicylic acid, salicylic acid and dithiosalicylic acid, identified as by-products. The degradation pathway of thimerosal by photocatalysis and photolysis is proposed. This photocatalytic procedure is environmentally friendly and it could be considered as promising treatment approach for hazardous organomercurial compounds.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The toxicological effect of mercury and its organic derivatives has been extensively studied in the last decades, revealing a high potential risk to human health and to the environment [1]. Human exposure to mercury occurs mainly through three ways: (a) elemental mercury released from dental amalgams, (b) methylmercury intake by the ingestion of contaminated food, and (c) direct incorporation of thimerosal contained in vaccines [2–7]. Thimerosal, sodium ethylmercury thiosalicylate is an organometallic compound containing divalent mercury covalently linked to ethyl and thiosalicylate groups (Fig. 1). It is used in vaccines to inhibit the growth of fungi and bacteria [2]. In human beings, thimerosal is metabolized to ethylmercury and thiosalicylate. Ethyl mercury has been described as highly toxic that could lead to some neurological disorders [8,9]. A critical relationship between exposure to thimerosal and neurological diseases has been reported early [10–13]. However, this issue is still under debate with a lack of conclusive agreement based on the toxicological and epidemiological evidences [14–21].

On the other hand, the thimerosal residues appear in the environment through the uncontrolled effluent release from the pharmaceuticals, cosmetics, preservatives, personal care products and hospitals or clinical facilities [22]. Additionally thimerosal enters into the environment due to the discharge of expired pharmaceuticals and/or vaccines, which are not properly pretreated before its final disposal [22,23]. In the recent years, degradation of some organometallic pharmaceutical residues such as thimerosal has received considerable attention [23–25]. The conventional treatment methods for the wastewater containing thimerosal are based on phase separation process, for example adsorption using commercial activated carbon [26]. Moreover, biological treatment of effluents containing thimerosal is difficult due to antimicrobial activity of this compound. Accordingly, it is necessary to develop more efficient treatment technologies in order to eliminate safely this organometallic substrate. Advanced oxidation processes (AOPs), in particular heterogeneous photocatalysis, have been successfully used to degrade pharmaceuticals from wastewater [27–30]. In particular, methyl mercury and phenylmercury have been treated with heterogeneous photocatalysis reducing mercury to Hg(0), oxidizing simultaneously the organic groups [31,32]. The semiconductor catalysts such as titanium dioxide nanoparticles (TiO₂) and zinc oxide (ZnO) are the most widely used in photocatalytic studies. They can be photoactivated with light below 390 nm. When the catalyst is irradiated

* Corresponding authors at: Faculty of Chemical Sciences, University of Concepción, Edmundo Larenas 129, Concepción, Chile. Tel.: +56 41 220 4329; fax: +56 41 2245974. E-mail addresses: jyanez@udec.cl (J. Yáñez), hmansill@udec.cl (H.D. Mansilla).

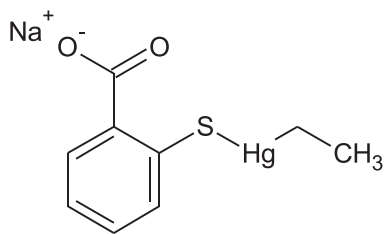
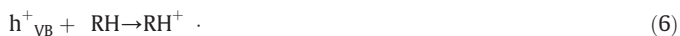


Fig. 1. Chemical structure of thimerosal (sodium ethylmercury thiosalicylate).

with photons having energies greater than its band gap, the electrons from the valence band (vb) migrate to the conduction band (cb), generating the charge carriers, holes (h_{vb}^+) and active electrons (e_{cb}^-), promoting redox reactions (Eq. (1)). The electrons in the conduction band could promote reduction reaction of molecular oxygen producing superoxide anion ($O_2^{\cdot-}$) and subsequently hydroperoxide radical (HO_2^{\cdot}) (Eq. (2)). Furthermore photo-generated electrons can also induce the reduction of some metals such as mercury (Eq. (3)). On the other hand, photogenerated holes can split adsorbed water molecules or reduce hydroxide anions producing hydroxyl radicals (OH^{\cdot}) (Eqs. (4), (5)). Finally, the holes can also provoke the direct oxidation of the organic matter (Eq. (6)) [31–34].



The goal of the present study is to apply photocatalysis to oxidize thimerosal organic groups with the simultaneous reduction of divalent mercury into elemental mercury addressing the recovery and safe

disposal. The feasibility of thimerosal degradation contained in real human vaccines was evaluated.

2. Experimental

2.1. Reagents

Thimerosal ($\geq 97\%$) was obtained from Sigma (USA); TiO_2 P 25 composed of anatase and rutile crystallites (ratio typically 7:3 or 8:2) was purchased from Degussa (now Evonik, Germany). HCl, KOH, formic acid, methanol (LiChrosolv), ortho-phosphoric acid, thiosalicylic acid, mercury nitrate, dithiosalicylic acid, $KBrO_3$, KBr and hydroxylamine hydrochloride were obtained from Merck (p.a., Germany). Nitrogen (99.995% minimum) was purchased from Linde (Chile). Ultrapure water was obtained using an EASY Pure water purification device (Millipore, USA). Standard mercury (II) (1000 mg L^{-1} CertiPUR) was purchased from Merck (Chile)

2.2. Photocatalytic reaction

The photocatalytic degradation of standard solution of thimerosal was tested in the closed reactor shown in Fig. 2. The system consists of a 250 mL cylindrical borosilicate flask transparent to radiation between 300 nm and 400 nm. In a typical reaction, 40 mg L^{-1} standard solution of thimerosal (150 mL) was mixed with known amount of TiO_2 adjusting the pH by adding HCl 0.1 mol L^{-1} or KOH 0.1 mol L^{-1} [31, 32]. The suspension was homogenized using a magnetic stirrer at 300 rpm. The irradiation was carried out with a commercial solarium, Phillips HB 311. The solution was kept in dark during 20 min before irradiation in order to achieve the adsorption equilibrium. The photon source was located at a fixed distance (15 cm) from the reactor. The irradiance, measured at 360 nm (radiometer UVP model UVX radiometer, Jena, Germany) in the border of the reactor was 21.6 W m^{-2} . In order to remove dissolved oxygen, all reactions were carried out under a stream of nitrogen at flow rate of 1000 mL min^{-1} . Formic acid was used as sacrificial reagent.

The procedure for photocatalysis of thimerosal in the vaccine follows the same methodology without standard solution of thimerosal. The thimerosal content in the vaccine was 40 mg L^{-1} as analyzed by HPLC. Before irradiation the sample was diluted by 2 times.

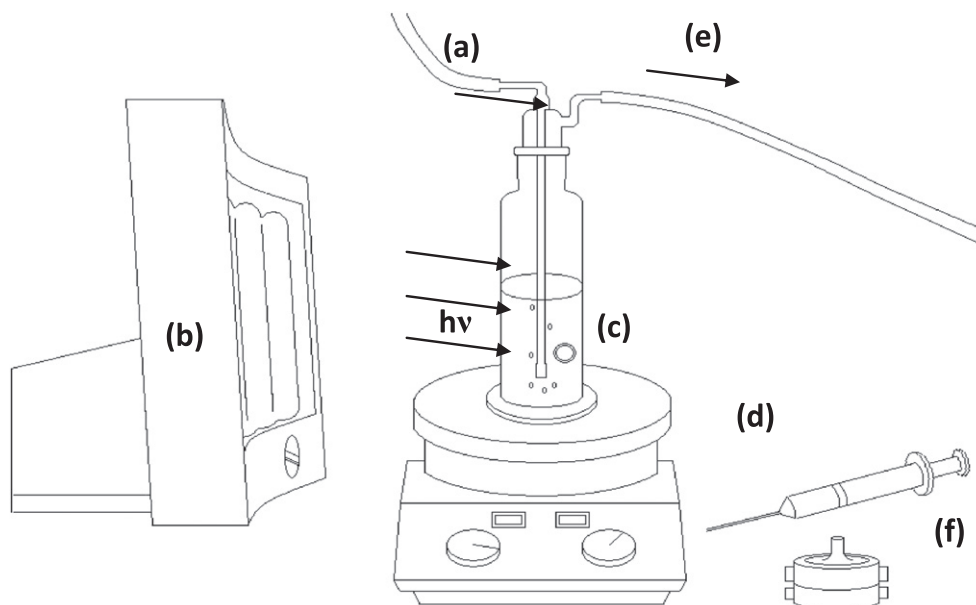


Fig. 2. Photocatalytic reactor. (a) Nitrogen input, (b) solarium, (c) cylindrical borosilicate flask, (d) magnetic stirrer, (e) gas output, and (f) sampling system.

Download English Version:

<https://daneshyari.com/en/article/1227680>

Download Persian Version:

<https://daneshyari.com/article/1227680>

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