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The use of $W_{10}O_{32}^{4-}$ coupled with UV light to reduce the concentration of triclosan and hexavalent chromium in aqueous solutions

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ABSTRACT

The decatungstate of sodium $Na_4W_{10}O_{32}$ (DTA) was synthesized according to the bibliography and characterized by the UV-visible spectra. It was used for the total degradation of the biocide "Triclosan" (TCS) and the reduction of the hexavalent chromium (Cr^{6+}) into trivalent chromium (Cr^{3+}) in aqueous solutions using ultraviolet radiation. This was achieved through a photocatalytic cycle. The effect of oxygen has been deeply investigated. It appeared essential for decatungstate regeneration since its absence induced the inhibition of Triclosan disappearance and completely stopped the photocatalytic cycle.

Keywords: Photocatalyst; Decatungstate of sodium; Hexavalent chromium; Triclosan

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INTRODUCTION

The increase of the industrials activities has become a serious problem that leads to an increasing contamination of air, water and soil. In order to avoid this problem, important scientific works have been devoted to find new methods to eliminate such pollution.

Various methods have been used for the degradation of organic pollutants [1], among them Advanced Oxidation Process (AOPs) that are considered to have a big potential, that have been widely developed. These techniques are very appealing alternatives for the degradation of organic pollutants since they mainly permit complete mineralization of organic pollutants. It is based on the production of very reactive and nonselective entities (more particularly the hydroxyl radical $OH^{\cdot}$) having a higher oxidizing capacity than traditional oxidants (O_2, Cl_2, ClO_2, H_2O_2, O_3…) [2-4].

The development of new photocatalysts is attracting more and more interest. Among them polyoxometalates [5] (POMs) demonstrate an interesting redox chemistry acting as electron as well as hydrogen relays. Numerous authors have confirmed that the decatungstate (DTA) ions, such as $W_{10}O_{32}^{4-}$, are efficient photocatalysts in homogeneous solutions. [6-10]. The DTA reactivity under light excitation comes from the formation of an oxidative specie in the excited state $W_{10}O_{32}^{4-*}$, which allows the degradation of organic pollutants by Hydrogen atom abstraction or/and by electron transfer processes. The DTA reduced species (namely $W_{10}O_{34}^{5-}$) lead to the regeneration of $W_{10}O_{32}^{4-}$ in the presence of oxygen. Thus, the obtained catalytic cycle permits the continuous oxidation of organic molecules and to their total elimination and in some cases to their minerlization. [11-12]. The application of this photocatalyst in the field of water decontamination was largely explored by Papaconstantinou and co-workers. [13-14].

The present paper is dedicated to the results of oxidation of Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) and reduction of hexavalent chromium transformation induced by homogenous photocatalysis using decatungstate of sodium.

Triclosan (TCS) is an antibacterial product used in personal and health product care. Due to this application, TCS has been largely detected in wastewaters [15-17]. This compound presents low toxicity and it is partially removed during usual wastewater treatments [18]. However, attention has been drawn to this compound due to its chemical structural resemblance with very toxic and persistent contaminants such as dioxins, and the odds of its transfer to these harmful compounds. Therefore, the environmental fate of triclosan is a subject of special and important concern [19-21]. Moreover, The hexavalent chromium (Cr^{6+}) is highly toxic and a well-known human carcinogen, mutagen, and due to its solubility, it is highly mobile in aquatic systems. It is used in various industrial processes, such as textile, dyeing, eventually making its way into soils and waters through industrial spills or waste depositions, so reactions that reduce Cr^{6+} have received great attention because they diminish or eliminate the threat to aquatic life and to human health owing to hexavalent chromium contamination.

MATERIALS AND METHODS

Triclosan (5-chloro-2-(2, 4-dichlorophenoxy) phenol) was obtained from Dr. Ehrenstofer GmbH (Germany) and used as received. Decatungstate of sodium is not a commercial product. It was synthesized from $Na_2WO_4.2H_2O$ according to the published procedure [22] and characterized by the UV-visible spectra by dissolving the powder in water. Potassium dichromate was obtained from sigma Aldrich (99%) and used without further treatment as Cr^{6+} source.

Two irradiations devices were used: the device used for the polychromatic irradiation is a reflective enclosure equipped with six circular fluorescent tubes type Philip 15 W with a maximum emission at 365 nm. The solution was placed in a central position in a quartz tube and was cooled by a ventilator. The monochromatic irradiation was conducted with a Xenon lamp (1600 W) equipped with a Schoffel monochromator.

The deaeration and the oxygenation of the solutions were accomplished respectively by bubbling N_2 and O_2 for 30 min at room temperature prior to irradiation and the deaeration was kept all along the irradiation period.

The degradation of the triclosan (TCS) was followed by high performance liquid chromatography (HPLC) using a Hewlett Packard liquid chromatography system (1050) equipped with photodiode array detector and an automatic injector. The experiments were performed by a UV detection at either 250 nm or 280 nm and by using a reverse phase Nucleodur column (C18 150x4.6mm, 5µm). The flow rate was 1 $mL.min^{-1}$ and the injected volume was 50 µL. The elution was accomplished with water, formic acid (0, 05%) and methanol (80/20, v/v).

The disappearance of hexavalent chromium was monitored by using a Thermo scientific ion chromatography. The experiments were performed by a UV-visible detector at 520 nm and by using a CS5A column and a CG5A pre-column. The flow rate was 0.5 mL min^{-1} and the injected volume was 0.25 $mL.min^{-1}$.

UV-visible spectra were recorded on a carry 300 double beam spectrophotometer.

RESULTS AND DISCUSSION

3.1. Ultraviolet absorption Spectrum

The UV absorption spectrum of DTA at a concentration $2.0x10^{-4}$ mol L^{-1} in aqueous solution is given in Fig.1. It exhibits a characteristic band with a maximum of absorption at 324 nm.

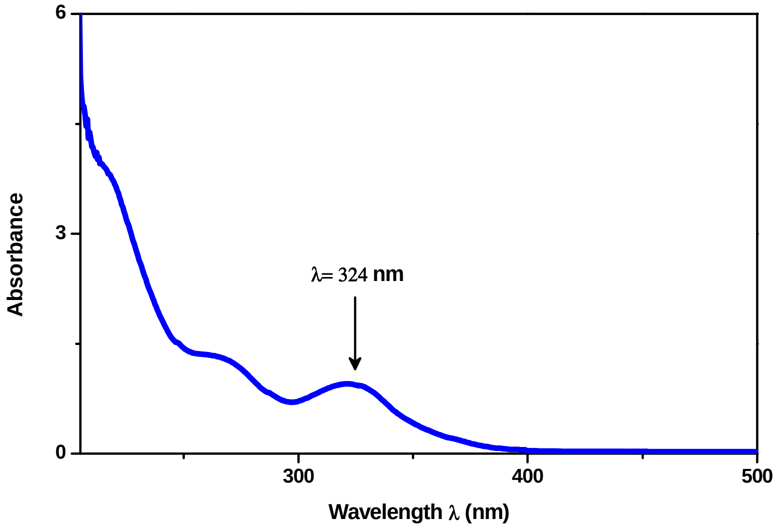

Figure 1: UV- visible absorption spectrum of decatungstate sodium in water

The UV absorption of triclosan (3.5x10^{-5} mol L^{-1}) presents a band with a maximum at 280 nm and a shoulder at 232nm (Fig. 2).

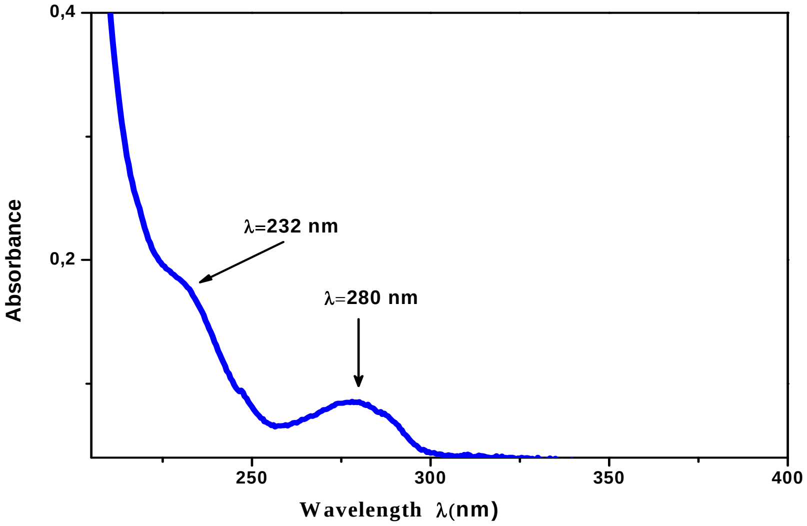

Figure 2: UV- visible absorption of Triclosan in water

3.2. Effect of oxygen on Triclosan degradation and Chromium reduction

The oxygen plays an important role in photocatalytic process, to understand its role in the decatungstate system two solutions one of triclosan and the other with chromium were irradiated with three different oxygen concentrations, namely aerated, oxygenated and deoxygenated.

3.2.1. Triclosan

The degradation of Triclosan (3,5x10^{-5} mol L^{-1}) was studied in the presence of DTA (2.0x10^{-4} mol L^{-1}) under irradiation at 365 nm in different oxygen concentrations (Fig.3.).

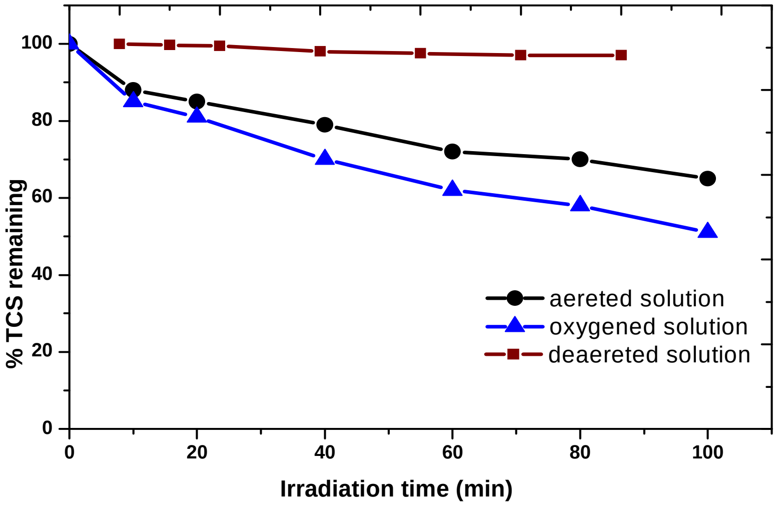

Figure 3: Influence of oxygen concentration on the photodegradation of TCS (3, 5 x 10-5 mol L^{-1}) upon irradiation in the presence of DTA (2x10^{-4} mol L^{-1})

As shown in Fig.3. Triclosan degradation was inhibited in deaereted condition while in oxygened conditions the rate of degradation increased. In the absence of oxygen the degradation inhibition could be explained by the limited re-oxidation of the reduce catalyst. This reaction occurs by the accumulation of the reduced species $W_{10}O_{32}{}^{5-}$ in the solution leading to the catalytic cycle interruption and thus, justifies the observation of the blue coloration during the irradiation (Fig.4.)

About the degradation in oxygen statured condition, the augmentation of the concentration of oxygen leads to the increase of the reoxidation of $W_{10}O_{32}{}^{5-}$ and the anion superoxyde is produced improving the degradation photocatalytic.

These results confirm the role major of oxygen in the re-oxidation of $W_{10}O_{32}{}^{5-}$ and its involvement in the photocatalytic reaction.

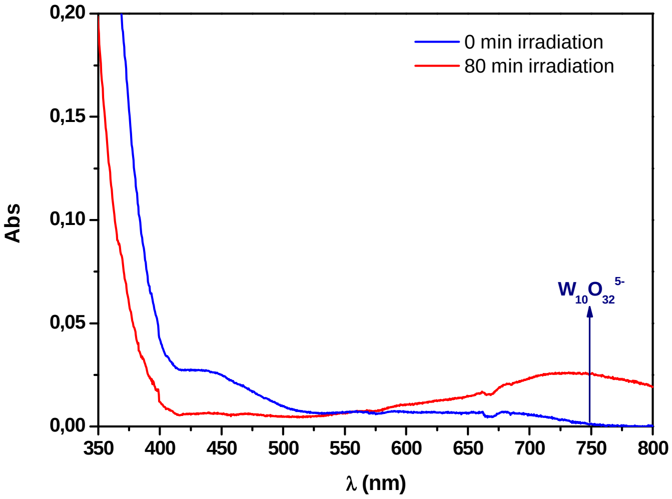

Figure 4: Absorption spectrum of decatungstate anion and its reduced form obtained by irradiation at 365nm decatungstate ion (2.010^{-4} mol L^{-1}) in oxygen free solution

3.2.2. Hexavalent chromium

The reduction of hexavalent chromium (1.0 x 10^{-4} mol L^{-1}) was studied in the presence of DTA (2.0x10^{-4} mol L^{-1}) under a monochromatic (320 nm) and polychromatic beam (365 nm) in three different conditions: aerated, oxygenated and deoxygenated (Fig.5).

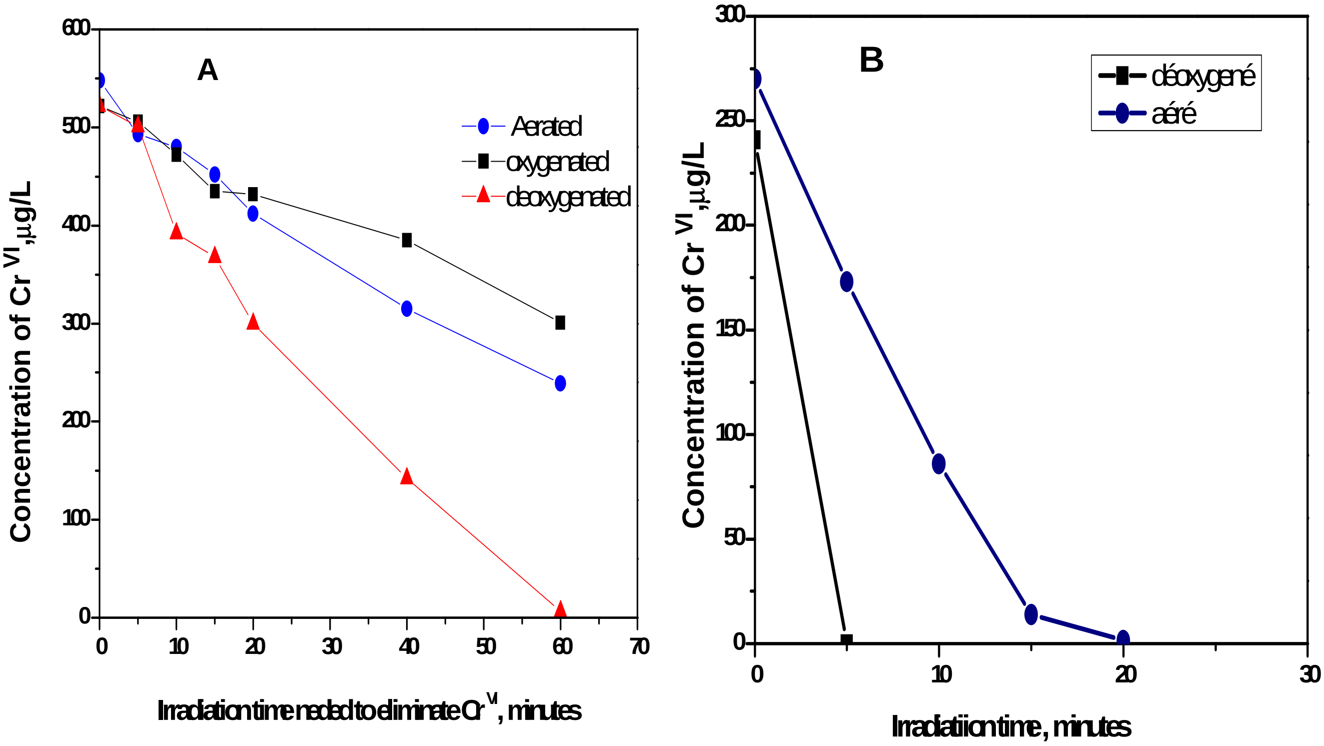

Figure 5: Influence of oxygen on the reduction of Cr^{6+} (1.0 x 10-4 mol L-1) in the presence of DTA (2.0x10^{-4} mol L^{-1}). A: monochromatic beam; B: Polychromatic beam

The results listed in Fig.5 shows that after 60 min of irradiation Cr^{6+} present in the deoxygenated solution disappeared, whereas in aerated and oxygenated solutions the degradation reached 50% and 33% respectively. However when irradiated with polychromatic beam Cr^{6+} disappeared after 5 minutes in deoxygenated solution and 20 min in aerated condition.

In the absence of oxygen, the reduction of Cr^{6+} could be explained by the limited re-oxidation of the reduced catalyst, and the electrons are captured by Cr^{6+} which will be reduced to Cr^{3+}.

In the presence of oxygen, chromium is competing with oxygen which explains the fact that the reduction of Cr^{6+} took time comparing to the deoxygenated solution.

The rate of the reduction of Cr^{6+} by DTA also depends on the intensity of the light source as showed in fig.5 (B), the irradiation by a polychromatic beam (365 nm) leads to an efficient degradation of Cr^{6+}.

3.3. Influence of Triclosan on hexavalent chromium reduction.

The reduction of Cr^{6+} (1.0 x 10^{-4} mol L^{-1}) in the presence of DTA (2.0 x10^{-4} mol L^{-1}) under polychromatic beam (365nm) was studied by adding triclosan (3,5 x 10^{-5} mol L^{-1}) to the solution in two different conditions: aerated and oxygenated.

The influence of Triclosan addition on reduction the Cr^{6+} is shown in figure 6. Cr^{6+} reduction is reached after 60 minutes of irradiation in oxygened solution, however in aerated solution only 40% of Cr^{6+} was reduced after 100 minutes of irradiation.

The reduction of Cr^{6+} depends on the degradation of triclosan; this could be explained by the photocatalytic process of DTA, in oxygened condition, the increase of the concentration of oxygen leads to the improvement of Triclosan degradation and oxidation of $W_{10}O_{32}{}^{4+}$ to $W_{10}O_{32}{}^{5+}$ which leads to the an efficient reduction of $Cr^{6+.}$

In aerated solution the reduction of Cr^{6+} was delayed until the triclosan was degraded for the oxidation of $W_{10}O_{32}^{4+}$.

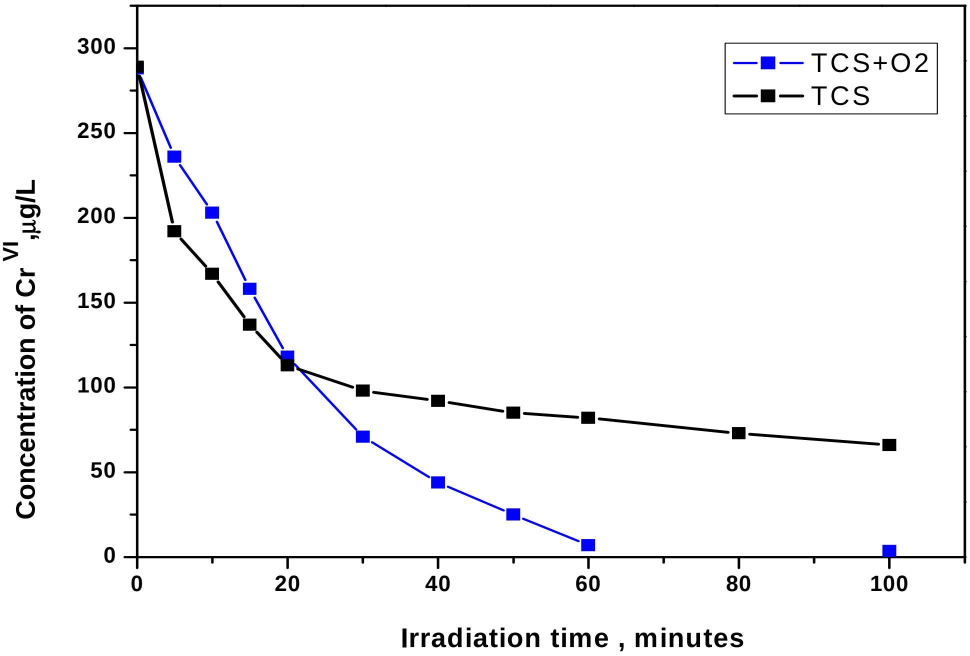

Figure 6: Influence of Triclosan on the reduction of Cr^{6+} (1.0×10^{-4} mol L^{-1}) in the presence of DTA (2.0×10^{-4} mol L^{-1}) upon polychromatic beam

CONCLUSION

During the present study, we established that the decatungstate of sodium was efficient in the reduction of hexavalent chromium and the degradation of Triclosan in aqueous homogeneous conditions under UV irradiation. The reduction of Cr^{6+} was delayed in the presence of triclosan, which was explained by the photocatalytic process of DTA.

The entire process revealed to be oxygen dependent because of restricted $W_{10}O_{32}^{5+}$ re-oxidation step. The intensity of the light source has an important effect on the rate of the reduction of Cr^{6+} as was proven in the study.

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