Bisphenol-S Mineralization by photo-Fenton catalyzed by Cu_2O/Al_2O_3

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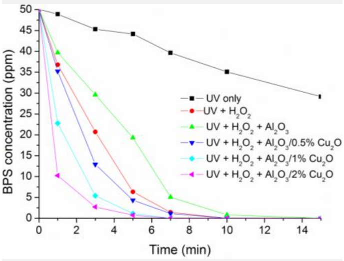
***E. De la Cruz**[1], O. Olea-Mejía[1], R. Romero[1], D. Amado-Piña,[1] S. Brewer[2], K. Donkor[2], R. Natividad[1]. (1) Centro Conjunto de Investigación en Química Sustentable (CCIQS) UAEM-UNAM, Universidad Autónoma del Estado de México, Carr. Toluca-Atlacomulco km 14.5, 50200 Toluca, MEX, Mexico, egdelacruza001@alumni.uaemex.mx. (2) Department of Chemistry, Thompson Rivers University, Kamloops, BC, Canada.*



Two catalysts were prepared, synthezised and characterized: Cu_2O nanoparticles inmovilized on foam monolith and on Al_2O_3 powder. In both cases, the NPs were synthesized by liquid laser ablation. The size, shape and crystalline structure of the NPs were determined by TEM and the presence of copper on the surface of the Al_2O_3 was verified by SEM and EDS. The activity of the catalysts was tested in the degradation of Bisphenol S (BPS) by a photo-Fenton like process. The results were compared to those obtained with the catalyst in powder. The addition of catalyst improved the BPS removal rate by two-fold as well as BPS mineralization compared to the tests where only UV radiation with H_2O_2 was applied. The results are attributed to the fact that the Cu_2O nanoparticles favor the generation of the radical •OH, responsible for the complete degradation and mineralization of BPS.

Introduction

Bisphenol S (BPS) is an emerging contaminant that acts as an endocrine disruptor by interfering with these systems in humans and animals, causing defects and transformations [1]. It has the capacity to alter the secretion, transport, combination and action of hormones, causing effects on the reproductive and endocrine systems of organisms. The continuous release of this molecule allows animal and plant species to be exposed to this contaminant for a long time and continuously. BPS is detected in water, food, plastics, sediments, thermal papers such as purchase receipts and in human urine. It is known that in approximately 80% of the planet's population traces of BPS can be identified in the urine [2].

Different methods have been proposed to eliminate these contaminants from water, including microbial degradation, adsorption and advanced oxidation processes (AOP) [3]. Within AOP, photo-Fenton process outstands due to its efficiency and possibility of achieving mineralization of the contaminant.

This work aimed to,

i) Establish the efficiency of Cu_2O/Al_2O_3 as catalyst of the photo-Fenton process to remove and mineralize BPS, without modifying pH.
ii) Inmovilize Cu_2O nanoparticles on alumina foam monoliths.
iii) Asses the plausibility of catalyzing the photo-Fenton process with Cu_2O/Al_2O_3 inmovilized onto a foam monolith.

Material and Methods

Cu_2O Nanoparticles were synthesized by Liquid Laser Ablation (LAL) with a Continuum Surelite laser system at a wavelength of 1064 nm, a pulse of 6 ns and a frequency of 10Hz. A Cu target (2.5 cm in diameter and 99% purity) was immersed in 5 mL of deionized water. The size, shape and crystal structure of the nanoparticles were determined using a JOEL JEM-2100 microscope at 200 keV. The presence of Cu_2O on the alumina surface was determined by scanning electron microcopy (SEM) and energy dispersive X-ray spectroscopy (EDS) with a JOEL JSM-6510LV.

For the Cu nanoparticles deposition, the alumina powder was treated with a 1M NaOH solution with stirring for one hour and dried. Finally, the Al_2O_3 was added to the solution containing the Cu nanoparticles and evaporated at 80 °C, thus obtaining Cu_2O/Al_2O_3. The amount of Cu was determined by weight difference. The weight percentages of Cu in the alumina were 0.5%, 1% and 2% by weight with respect to the mass of the alumina.

The resulting catalyst was characterized by Scanning Electron Microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS) system to confirm that Cu has been deposited on the alumina surface.

The catalyst (200 mg/L) was tested in a photo-Fenton reaction in a batch reactor (50 mL) for the degradation of BPS (50 mg/L) with a monochromatic UV lamp (254 nm) at the center of the reactor; the catalyst was dispersed homogeneously by stirring. The reaction was carried out at 26°C with initial pH at 6.7, the pH was not adjusted and the temperature was controlled by a cooling jacket. H_2O_2 was added at 10 times the stoichiometric amount related to BPS mineralization.

During the reaction, at intervals of 10 min, 20 min and 30 min, total organic carbon was determined for the determination of mineralization using a TOC-VCSH analyzer, at a combustion catalytic oxidation temperature of 680°C.

Results and Discussion

For the TEM characterization of copper(I) oxide (Cu_2O) nanoparticles obtained by LAL, it was found that they have an irregular spherical shape and an average size of 11 nm. The crystalline phase of the nanoparticles was determined by electron diffraction. According to the JPCDS card 01-075-1531 for Cu_2O, the observed rings correspond to planes 110, 111, 200 and 211. Although the ablation was carried out with pure Cu, during the process Cu_2O was obtained, which indicates that in the ablation process the nanoparticles generated were oxidized (**Figure 1**).

To identify Cu_2O on the surface of the alumina, EDS mapping was carried out, observing a homogeneous dispersion of the Cu signal, which is a desired characteristic in a catalyst.

In the degradation of BPS, it was observed that when only UV radiation was used, up to 40% degradation is obtained after 15 min; when H_2O_2 is added, the degradation is complete in less than 10 min. This is due to the fact that H_2O_2 generates •OH radicals with UV radiation according to equation (**1**). By adding only Al_2O_3 to the system, a marginal increase in the time required for BPS degradation is observed. For the case of 0.5%, 1% and 2% Cu_2O/Al_2O_3, the time for complete degradation of BPS was less than 10 min, 7 min and 5 min, respectively (**Figure 2**); which can be attributed to the ability of Cu^{+1} to generate •OH radicals (**2**) that finally degrade and mineralize the contaminant molecule. The highest mineralization percentage (94%) was achieved with the system 2% Cu_2O/Al_2O_3 and the photo-Fenton like process.

In the case of the catalyst, it is observed that it does not require an acidic pH like the typical Fe fenton reagent and that it can be reused after recovery.

$$H_2O_2 + h\nu \rightarrow 2\ \bullet OH \quad (\mathbf{1})$$

$$Cu^{+1} + H_2O_2 \rightarrow Cu^{2+} + \bullet OH + {}^{-}OH \quad (\mathbf{2})$$

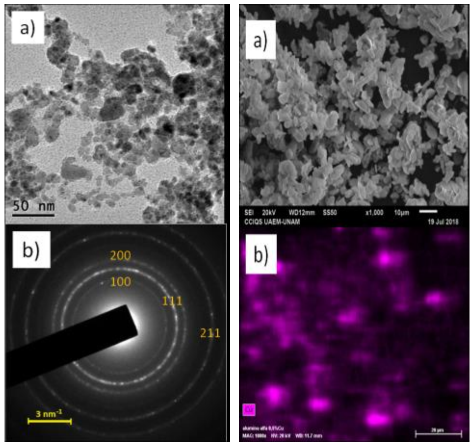


Figure 1. Letf. TEM (a) and electron diffraction (b) imagen of Cu_2O nanoparticles. Right. EDS Cu mapping of 2% Cu_2O/Al_2O_3 catalys.

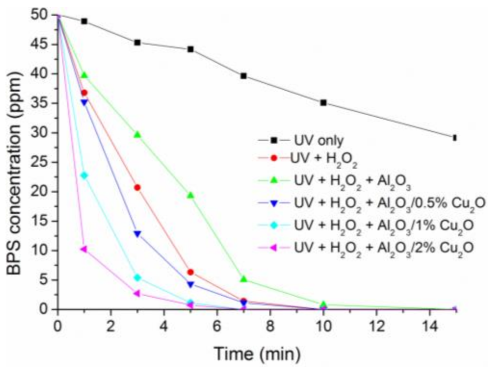


Figure 2. BPS degradation for the different reaction systems.

Conclusions

A structured and powdered catalyst were prepared with copper(I) oxide (Cu_2O) nanoparticles obtained by laser ablation on alumina (Al_2O_3) in different proportions of copper. It was shown that the distribution of the nanoparticles was uniform. The use oft he catalyst Cu_2O/Al_2O_3 improves by two-fold the BPS removal rate and its mineralization degree was the higuest achieved (94%); thus demonstrating the photocatalytic character of the prepared material. The removal rate was also found to be Cu content dependant.

The alumina used was in powder form, so the recovery of the catalyst requires a centrifuging, filtering and drying process for reuse. Preparing the catalyst in a foam-type structure makes it possible to make the degradation of this type of contaminants more efficient; since it eliminates the catalyst recovery processes, which would finally make it possible to scale the degradation process with efficiencies similar to those found so far.

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