

Degradation of 4-Chlorophenol by Gamma Radiation of ^{137}Cs and X-rays

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Abstract. This paper presents results of radiolytic degradation of 4-chlorophenol in the presence of TiO_2 , Al_2O_3 , y SiO_2 , using different radiation sources than ^{60}Co , which is so common in this type of experiment. The radiation sources used were X-rays with energy of 100 keV and radiation from ^{137}Cs (662 keV). After irradiation with a dose of 50 cGy X-ray and TiO_2 obtained a degradation of about 5%, no degradation was obtained with ^{137}Cs source and other oxides. This may be due to the fact that X-rays have a linear energy transfer (LET) greater value, and in the case of TiO_2 present a crystalline structure, whereas the other two oxides are amorphous. Both characteristics result in better formation of a reactive species that allows the degradation of the compound.

Keywords: Radiocatalysis, Photocatalysis, Radiation Induced Catalysis, 4-Chlorophenol.

Resumen. Se presentan los resultados de la degradación de 4-clorofenol por catálisis inducida por radiación ionizante, en el experimento se utilizaron TiO_2 , Al_2O_3 , y SiO_2 como catalizadores y radiación gamma de ^{137}Cs (662 keV) además de rayos X con energía de 100 keV. Después de la irradiación con una dosis de 50 cGy de rayos X en combinación con TiO_2 se obtuvo una degradación de alrededor del 5%, sin embargo no se registró degradación empleando los otros óxidos y la radiación gamma de ^{137}Cs , esto puede ser atribuido a que los rayos X presentan mayores niveles de transferencia lineal de energía mayores que la radiación gamma. Por otro lado, de los tres óxidos empleados, el TiO_2 presenta una estructura cristalina, mientras que los otros son amorfos, estas dos características originan una mejor formación de especies reactivas que hacen posible la degradación del compuesto.

Palabras clave: Radiocatálisis, fotocatalisis, catálisis inducida por radiación, 4-clorofenol.

Introduction

Photocatalysis, an effective method that uses visible and UV radiation and semiconductors, such as TiO_2 , to treat wastes present in the environment, consists of an advanced oxidation process related to the use of $\bullet\text{OH}$ radical as the main oxidant. Another process, radiocatalysis, is conceptually similar to photocatalysis, in which radicals generated by radiation gamma of ^{60}Co in the presence of oxides such as TiO_2 , Al_2O_3 , and SiO_2 , allow electronic transferences and generation of reactive species that result in oxidation-reduction of organic compounds. Both are used in the treatment of such organic compounds as dichloromethane, chloroform, phenols, and pesticides [1].

Recent work on radiolysis in heterogeneous systems has been done by Henderson [2], Zacheis et al. [3], Dimitrijevic [4], Milosavljevic and Thomas [5], and Gonzalez and Jiménez [6], all of which propose that radiocatalysis is an extension of photocatalytic processes that occur with visible and UV light. In these, the energy is absorbed by the catalyst (semiconductor) as titanium dioxide, causing the formation of a pair of electron-holes (e^-/h^+) [7] and the posterior formation of radicals as the $\bullet\text{OH}$. Other authors, such as Follut and Leither [8-9], have concluded that the presence of TiO_2 , Al_2O_3 during irradiation causes only adsorption effects.

The oxides used in photocatalysis, such as TiO_2 , require 3.2 eV to produce a pair of charged carriers while Al_2O_3 or SiO_2 need more than twice that amount of energy [4] to be excited. Thus it is possible that sources such as ^{137}Cs , which have energy of 0.662 MeV, and X-rays with energy of 100

keV, could be used to promote radiocatalysis (Fig. 1).

The use of X-rays in combination with oxides, such as TiO_2 , Al_2O_3 and SiO_2 , has not been reported; therefore, this paper aims to demonstrate the feasibility of using radiation sources other than the gamma radiation of the ^{60}Co commonly used in radiocatalysis, and no experiments were performed with another dose.

Results and discussion

In the gamma and X-ray irradiation for which aluminum and silicium oxides were used as catalysts, no 4-CP degradation was obtained by radiolysis and radiocatalysis; only in using

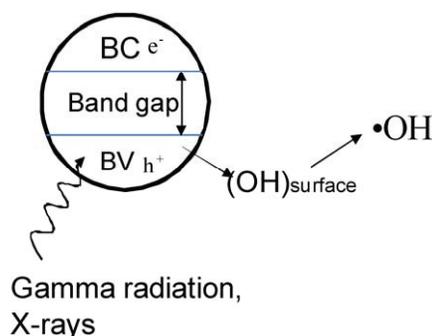


Fig. 1. Excitation of catalyst using gamma radiation and X-rays, this interaction cause the formation a pair of electron-hole and posterior formation of $\bullet\text{OH}$ radicals.

titanium dioxide and X-rays was 4-CP degradation observed. No evidence of adsorption of 4-CP in the TiO₂ was obtained. The results are presented in Table 1.

The results presented in Table 1 indicate that the dose of 50 cGy of X-rays is not enough to degrade 4-CP by radiolysis; nevertheless, degradation was observed when TiO₂ was used. As the absence of radiolysis was observed in the experiment, the degradation obtained was due only to the interaction of the radiation-oxide.

In previous experiments [6], degradation of 4-CP with ⁶⁰Co was observed and was necessary up to 1 kGy to degrade 92% of a solution of 25 mg/L; therefore, a dose of 1 Gy is not enough to degrade 9.65 mg/L. That is, in the present experiments, all degradation of 4-CP was a consequence of the catalysis induced by radiation; however, this effect was observed only with TiO₂ and X-rays.

The gamma radiation with ¹³⁷Cs and X-rays had similar interactions with the matter. A Compton scattering predominates in both, since the photoelectric effect occurs between 1 keV and 30 keV, and the pair production does not occur at energies less than 1.02 MeV [10].

On the other hand, the radicals and molecular products generated by X-rays (100 keV) and the gamma radiation of ¹³⁷Cs (662 keV) are different. Yamaguchi [11] calculated the yields of species in water irradiated by monoenergetic photons with energies of 50 eV-2 MeV. Yields of •OH are 2.909 for 100 keV and 3.129 for 662 keV energies, corresponding to X-rays and gamma radiation of ¹³⁷Cs, respectively, in terms of G (G = number of molecules of products formed or molecules changed per 100 eV energy absorbed). Stafford *et al.* (1994) conducted studies of the degradation of 4-chlorophenol with gamma rays and UV radiation, and proposed that degradation of 4-CP is originated mainly by •OH radicals.

As can be seen, for radiation of the ¹³⁷Cs (662 keV), the generation of •OH, H₂O₂, and H₂ is greater than with X-rays; however, the dose used in the present work was not sufficient to induce the radiolytic degradation.

To explain the degradation of 4-CP occurring with X-rays and TiO₂, we can consider Linear Energy Transfer (LET). The LET is a measure of the rate of energy deposition and is defined as the linear rate of loss of energy by an ionizing particle traversing a material medium—that is, the amount of energy deposited by ionizing radiation. The LET to ⁶⁰Co in water is 0.22 keV/μm⁻¹; to ¹³⁷Cs, 1 keV/μm⁻¹; and around 4.7 keV/μm⁻¹ for X-rays with 100 keV. The suspensions irradiated in these experiments have a density similar to that of water [10].

The LET value is greater for X-rays; therefore, energy deposition is bigger for X-rays than for ¹³⁷Cs gamma rays.

Table 1. Degradation of 4-CP by radiolysis and radiocatalysis with X-rays irradiation using TiO₂ initial concentration = 9.65 mg/L of 4-CP at dose of 50 cGy.

	Final Concentration of 4-CP (mg/L)
Radiolysis	9.65 ± 0.1
Radiocatalysis	9.21 ± 0.1

This fact explains that degradation was obtained only with X-rays. On the other hand, of the three oxides used, the degradation was achieved only with TiO₂. This is due to the crystallinity of the catalyst (SiO₂ and Al₂O₃ are amorphous) Rabe *et al.* [12] observed, that generate pairs of electron-hole augments with the grade of crystallinity of the oxide.

Because of these two factors, the 4-CP degradation was observed only with X-rays and the simultaneous use of TiO₂.

Conclusions

Low doses of gamma radiation of ¹³⁷Cs and X-rays are not sufficient to degrade 4-CP by radiolysis, even with the addition of Al₂O₃ and SiO₂. In past experiments with ⁶⁰Co, the necessary doses were on the order of kGy, while the doses used in the present work are on the order of Gy.

Furthermore, TiO₂ is the only oxide of the three employed that has a crystalline structure. This feature seems to cause a more efficient energy migration from inside the material to the surface so that the energy promotes a better electron hole pair production and consequently the best generation of the reactive species. In addition, the X-rays deposited greater quantities of energy, compared with ¹³⁷Cs gamma radiation, which makes possible the degradation of 4-CP using X-rays (100 keV) and TiO₂.

Experimental

Chemicals

The following chemicals were used as received: TiO₂, SiO₂, and Al₂O₃ (Degussa Co.); 4-chlorophenol (4-CP), amine-4-antipirine, and Na-K-tartrate (Aldrich); ammonium chloride, potassium ferrocyanide (Baker), and ammonium hydroxide; NaOH and HNO₃ (Merck).

Gamma irradiation and degradation measurement

Twenty milliliters of 4-CP aqueous solution (9.65 mg/L) and 20 mg of oxide were mixed to obtain dispersions of 1.0 g oxide/L of solution. The dispersions obtained were bubbled with O₂ for 2 min at a flow of 120 cm³/min and sealed. Sealed vials were gamma irradiated with 1 Gy in a Gammatron ¹³⁷Cs irradiator with a dose rate of 165 cGy/h. For the irradiation with x-rays, a W X-ray tube (Philips MCN321) with a focal spot of 8.7 cm was used, and the vial was placed 100 cm from the source to provide a dose of 50 cGy. The X-ray beam was filtrated with a filter of Cu of 1.9 mm and operated at a high voltage of 200 kV and a current of 10 mA to generate a beam of 100 keV.

After irradiation, samples were filtered using 0.4 μm Millipore membranes. The 4-CP degradation data were recorded with an UV-Vis Shimadzu 265-FW, and color development was carried out using the amino-4-antipirine method.

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