

## TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> as radiocatalyst ceramics.

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**A simple experiment of gamma irradiated radiolytic versus radiocatalytic 4-chlorophenol degradation is presented. Samples of 4-chlorophenol solutions were put in contact with TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> ceramics and gamma irradiated. It was found that addition of these materials improve the degradation in a way similar to photocatalysis.**

**Key words:** Radiocatalysis, TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, 4-chlorophenol.

### Introduction

Advanced oxidation processes are widely studied for the treatment of toxic compounds; photocatalysis and radiolysis have been used in the treatment of persistent organic compounds. Heterogeneous photocatalysis is an advanced oxidation processes that uses an oxide excited by UV or visible radiation, and the radiolysis uses gamma radiation or electrons to generate OH radicals in the water [1, 2].

Some organic compounds have been degraded by radiocatalysis: hexachlorobenzene [3], phenol [4], 4-nitrophenol [5] and 4-chlorophenol [2]. The principle of radiation-induced catalysis is similar to photocatalysis in which excitation of the oxide particles results in charge separation. These charge carriers in the conduction and valence bands, recombine or migrate to the particle surfaces where they participate in the interfacial oxidation or reduction of adsorbed species [3].

In photocatalysis, ultraviolet or visible radiation is used, for this reason, semiconductors with a band-gap less than 3.7 eV are used (ZrO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>); however, in radiocatalysis relatives large band-gap materials such as insulators (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) can be used.

The initial ranges of the photocatalytic reaction are directly proportional to the mass of the semiconductor; but, above a certain value of mass, the reaction rates become independent of the quantity of the semiconductor. These limits correspond to the maximum amount of oxide in which all the particles are illuminated; for the highest quantities of oxide, a screening effect of the excess of particles occurs. In radiocatalysis, this effect is not observed; the gamma radiation has a larger penetration than UV or visible radiation, which makes the use of the highest

amount of sample possible [2]. Because of this, it is possible to increase the degradation by increasing the mass of the oxide in the reaction.

In this study the degradation of 4-chlorophenol by radiocatalysis and the effect of low doses of gamma radiation on SiO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> are presented.

### Experimental

Chemicals were used as received; TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> from Degussa Co.; 4-chlorophenol, amine-4-antipirine, Na-K-tartrate from Aldrich; ammonium chloride, potassium ferrocyanide and ammonium hydroxide from Baker.

Samples of the oxides were put into vials, which were sealed and irradiated with a dose of 50 kGy in a JS 6500 irradiator gamma of <sup>60</sup>Co at a dose rate of 3.33 kGy/h.

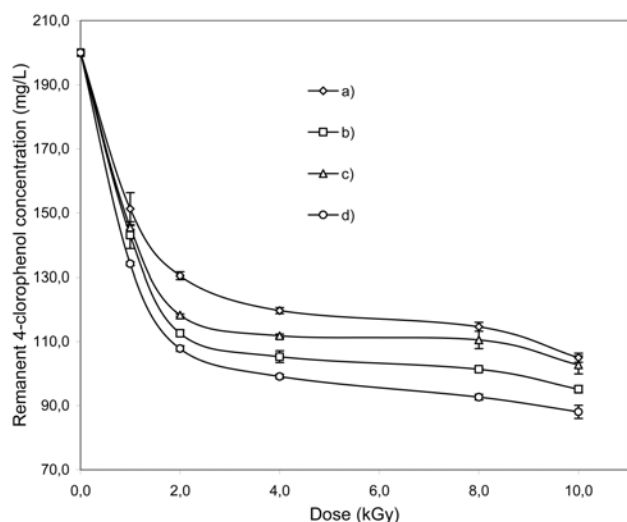
Twenty milliliters of 4-chlorophenol solution (200 mg/l) and 20 mg of oxide were mixed to obtain dispersions of 1.0 g oxide/l of solution. The dispersions obtained were bubbled with O<sub>2</sub> for 2 minute at a flow of 120 cm<sup>3</sup>·minute<sup>-1</sup> and sealed in glass vials. Samples of solutions and a suspension of 4-chlorophenol were gamma irradiated with doses of 1, 2, 4, 8 and 10 kGy in a JS 6500 gamma irradiator of <sup>60</sup>Co. After irradiation, solids were separated by filtration using 0.45 mm Millipore membranes. In the solutions obtained, the 4-chlorophenol degradation data were recorded on a UV-vis Shimadzu 265-FW, and color development was carried out using the amino-4-antipirine method.

### Results and discussion

Fig. 1 presents the results of irradiation of 4-chlorophenol, where an enhancement of degradation is observed with respects to a solution without oxide. From the oxides used, the aluminum oxide produces best degradation, due to a higher capacity of oxidation/reduction.

If the mechanism of radiocatalysis is assumed to be similar to photocatalysis, where the gamma radiation excites

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**Fig. 1.** 4-chlorophenol degradation by a) radiolysis, and radiocatalysis using b) SiO<sub>2</sub>, c) TiO<sub>2</sub> and d) Al<sub>2</sub>O<sub>3</sub>.

the oxides to produce electron-holes at the surface; in this case, the band gaps of the three oxides used, are capable of producing  $\cdot\text{OH}$  radicals (oxidation potential =  $E = 0.8\text{ V}$ ) and oxidizing 4-chlorophenol directly ( $E = 1.9\text{ V}$ ) [6]. So, the additional degradation could be explained by this mechanism.

On the other hand, the kinetic behavior is different compared with photocatalysis. It was not possible to adjust results to a Langmuir Hinshelwood model, which is the most common one used in photocatalysis. Neither models used in radiolysis were useful. It is necessary to acquire

more experimental data to develop a model that takes in to account both phenomena, radiocatalysis and radiolysis.

## Conclusions

Doses of 50 kGy have no effect on the cristallinity and specific surface area of oxides such as TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>; the observed stability is useful in the use of these materials in radiocatalysis. On the other hand, the addition of ceramic oxides during gamma irradiation enhances 4-chlorophenol degradation.

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