

Use of TiO₂ as Catalyst in Degradation Induced with Gamma Radiation of Methylene Blue

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Summary: Heterogeneous radiocatalysis is a catalytic process promoted by the direct adsorption of high radiant energy capable of activating a semiconductor such as TiO₂, which generates free radicals very reactive at the surface that allow oxidation-reduction reactions with adsorbed species, breaking some molecular bonds and reducing or oxidizing them less complex species. We irradiated methylene blue with ⁶⁰Co gamma rays and added of TiO₂ during irradiation with different doses of gamma radiation, measuring the remaining methylene blue concentration by spectrophotometry UV. The degradation of the organic compound was enhanced when doses increased and with the addition of semiconductors of up to 1g of catalyst per liter of suspension.

Keywords: degradation, radiocatalysis, radiolysis, methylene blue.

Introduction

During water irradiation, radicals of species involved in the degradation of pollutants in aqueous systems are produced. These products are ^eOH, ^eH, H₂, H₂O₂, H₃O⁺, e⁻_h. They are used in gamma radiolysis [1] or heavy (helium) ions [2], where the proposed mechanism, methylene blue, in aqueous solutions is attacked in several positions. Radiocatalysis is a process that involves the effect of gamma radiation over a catalyst and the formation of molecular products used for degradation of organics in water solutions [3], where the presence of a semiconductor increases the degraded amount compared to gamma radiolysis.

Radiation-induced degradation of dyes is widely studied [4], because it is relatively easy to measure color change during the course of an experiment. There are many works that show photodegradation of dyes with the use of titanium dioxide supported on activated carbon [5], or TiO₂ nanotube arrays [6]. Dyes are commonly used as model pollutants, partly because their concentration can be easily monitored using a spectrometer. However, as dyes also absorb light, especially in the visible range, the influence of this photoabsorption by dyes should be excluded for evaluation of the real photocatalytic activity of photocatalyst [7]. However, methylene blue radiocatalysis is not reported.

The effect of TiO₂ in aqueous solutions of methylene blue with gamma irradiation is reported in this communication. Radiolysis and radiocatalysis have been performed to observe the difference in the

methods and the effect of the presence of the TiO₂.

Results and Discussion

Fig. 1 shows the results obtained in the process of degradation of methylene blue at a concentration of 150 ppm, as a function of doses, taking the doses rate as 27.92 kGy/h. When the sample was not irradiated, the methylene blue initial concentration did not vary after seventy-two hours, but when samples were gamma irradiated, radiolytic degradation was observed in fig 1(b). During gamma radiolysis of methylene blue in aqueous solutions [1], it has been demonstrated that methylene blue can be decolorized and degraded by gamma radiolysis. The extent of dye destruction depends mainly on its concentration and radiation dose. Oxygen has little effect on the dye removal. The radiation chemical yield (G-value) depends on the absorption bands of the dye, the concentration, and the radiation dose. Three [•]OH radicals produced from water radiolysis lead to the removal of one dye molecule.

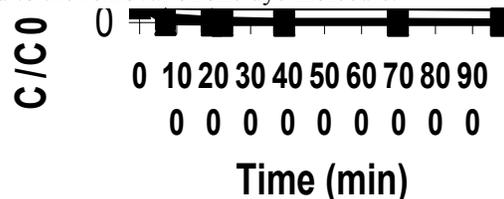


Fig. 1: Methylene blue degradation, amount remaining from a) with oxide and without gamma radiation, b) radiolysis and c) radiocatalysis at an initial concentration C₀ 150 ppm.

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Until a small shift at 664 nm peak was observed in irradiated solutions, measurements in absorbance between samples were compared to determine methylene blue degradation. Adsorption of methylene blue in TiO₂ was higher in irradiated samples than in non-irradiated samples (Table 1), and then those previous adsorption values were considered in each experiment, calculating relation C/C₀. For non-irradiated samples, adsorption was ~5% and for irradiated samples was ~50%.

Table 1: Adsorption of methylene blue in TiO₂ in function of gamma irradiation dose.

TiO ₂ irradiated (kGy)	Methylene blue in solution after contact with catalysts (mg/L)
0	1.90±0.06
500	1.53±0.05
1000	1.46±0.05
1500	1.75±0.06

This change in adsorption properties was attributed to the phenomenon called Radiation-Induced Surface Activation [8], where the surface hydrophilicity of a sample is caused by chemisorptions of the hydroxyl group on the surface. This phenomenon could affect two steps in the degradation reaction: photoactivity and adsorption of organics. First, if $\{>Ti^{IV}\cdot OH^+\}$ and $\{>Ti^{III}OH\}$ represent the surface-trapped valence band electron and surface-trapped conduction band electrons, respectively, then the surface-bound $\cdot OH$ radical represented by $\{>Ti^{IV}\cdot OH^+\}$ is chemically equivalent to the surface-trapped hole, allowing the use of the former and latter terms interchangeably. The trapped hole and a surface-bound $\cdot OH$ radical are indistinguishable species. Second, only the molecules that are in direct contact with the catalyst surface undergo photocatalytic degradation [9]. Meanwhile, the results in this work show that both effects— increase of doses and catalyst addition— promote methylene blue photodegradation. Also, methylene blue degradation is improved using titanium dioxide irradiated compared with experiments using non irradiated titanium dioxide. So, it is possible to modify the surfaces of materials with available gamma irradiation in industrial facilities.

Although intermediates were not analyzed, we expect that according to the degradation pathway of methylene blue in water provided by Houas *et al.* [10-13], $\cdot OH$ radical makes the main contribution to degradation of methylene blue and its intermediates, where the first steps use six hydroxyl radicals, and produce an alcohol, then an aldehyde which is spontaneously oxidized into acid, and decarboxylates into CO₂ by photo-Kolbe reaction.

Conclusion

Methylene blue that has contact with a semiconductor (TiO₂) shows an increase in the removal of the compounds in aqueous solutions. We found increasing the dose of radiation increases the degradation of the compound in the solution. Radiocatalysis method removes more polluting compounds in aqueous solution.

Experimental

The degradation of methylene blue was effected with gamma radiation using the optimized parameters obtained from previous work [3]. Gamma irradiation doses ranged from 2.5, 7, 8, 14, 25 and 35 kGy with gamma radiation of ⁶⁰Co in the facility Transelektro irradiator at Instituto Nacional de Investigaciones Nucleares, Mexico, at a dose rate of 27.92 kGy/h, using absolute dosimetric techniques. These doses correspond to 69.8, 195.4, 223.4, 390.9, 698, 977.2 min. Personnel monitoring equipment is used by individuals entering restricted areas. The specified annual dose to the whole body of adults is 0.05 sievert (5 rems). It is necessary to monitor all gamma irradiators with a film badge, thermoluminescent dosimeter, or other device when facility is used.

Methylene blue aerated aqueous solutions were prepared a concentration of 150 ppm; samples of 10 mL were taken in clean and dry glass vials. For control, three replicate series of samples remained without irradiation; other series of samples were gamma irradiated, and finally, to another samples, 10 mg of TiO₂ (commercial Degussa P25, 80 -20%, anatase-rutile) were added without any special preparation, in order to have a relation of 1g of catalyst/L of methylene blue solution.

Then the samples were hermetically sealed, wrapped in individual and labeled bags with the name of the compound, concentration of solution, dose of irradiation and date of preparation.

For each irradiation, three samples were used in order to observe reproducibility. After irradiation, samples were filtered with Millipore filters of 0.45µm for later analysis of remainder methylene blue, with a UV-Vis Shimadzu model F-2350 spectrophotometer at 664 nm.

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