

Research Article

Effect of the Mg/Al Ratio on Activated Sol-Gel Hydrotalcites for Photocatalytic Degradation of 2,4,6-Trichlorophenol

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Currently, interest has grown in finding effective solutions for the treatment of water pollution by toxic compounds. Some of the latter that have acquired importance are phenols and chlorophenols, due to their employment in the manufacture of pesticides, insecticides, cords of wood, paper industry, among others. The problem is rooted in that these compounds are very persistent in the environment because they are partially biodegradable and cannot be photodegraded directly by sunlight. Chlorophenols are extremely toxic, especially 2,4,6-trichlorophenol, which is potentially carcinogenic. In this work, Mg/Al-mixed oxide catalysts were obtained from the thermal treatment of hydrotalcite-type materials, synthesized by sol-gel method with different Mg/Al ratios. Hydrotalcites and Mg/Al-mixed oxides were physicochemically characterized by X-ray diffraction, thermal analysis (DTA and TGA), and N₂ physisorption. The results were obtained on having proven the photocatalytic degradation of 2,4,6-trichlorophenol as a pollutant model by water. The catalysts obtained present the hydrotalcite phase with thermal evolution until achieving Mg/Al-mixed oxides at 500°C. The catalysts are of mesoporous materials and exhibiting large surface areas. The catalysts demonstrated good photocatalytic activity with good efficiency, reaching degradation percentages with Mg/Al=1, 2, 4, 5, and 7 ratios of 94.2, 92.5, 86.2, 84.2, and 63.9%, respectively, until achieving mineralization.

1. Introduction

In recent years, there has been a growing need to find effective solutions to environmental problems. Many of the investigations in this regard are focused on the treatment of water to reduce or eliminate its contamination by toxic compounds. There are several hazardous wastes that damage the ecosystems' quality of life, such as chlorophenols. Exposure

to high concentrations or amounts of chlorophenols can cause damage to the liver, the immune system, the reproductive system, and the nervous system. Within the group of chlorophenols, 2,4,6-trichlorophenol is classified by the US Environmental Protection Agency (EPA) within the B2 group due to its being a possible carcinogen. Chlorophenols are introduced into the environment through the discharge of industrial or agricultural effluents that contaminate aque-

ous bodies. Chlorophenols are derived from the uncontrolled use of pesticides, fungicides, and herbicides, as well as processes of degreasing metals, wood processing, and paper bleaching with chlorine, and may even be generated in the potabilization of water as a result of the chlorination of phenols formed by products of the hypochlorite reaction with phenolic acids, with 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol as the most frequent occurrences in water designated for human consumption [1, 2].

There are different technologies for the elimination of these compounds, among which are adsorption with activated carbon, which possesses the disadvantage of requiring a posttreatment to remove toxic compounds from the adsorbent material. Another widely used process is aerobic or anaerobic biological treatment utilizing specific organisms capable of eliminating or bioaccumulating these compounds; however, these processes have the disadvantage of requiring long residence times and exhibiting low biodegradability. Another treatment alternative is degradation by chemical oxidation, which has been shown to be highly effective despite the disadvantage of producing unstable molecules and its high production and operating costs [3–5]. Recently, research in the field of oxidation processes has focused on the degradation of recalcitrant compounds, with photocatalytic degradation, one of the most promising methods, by means of allowing complete mineralization to be achieved through the use of semiconductor solid catalysts, generally of single- or mixed-oxide types [6, 7].

One of the compounds employed as precursors of oxides are hydrotalcites, which have been shown to be an option for obtaining photocatalytically active materials. Hydrotalcites are clay-like compounds whose structure consists of a laminar arrangement and a structural formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/n}^{n-}] \cdot mH_2O$, where M(II) and M(III) are the metal cations of the sheets and A^{n-} is the interlaminar anions. There are different methods to synthesize hydrotalcites, with the sol-gel process as one of the most effective methods to improve the physicochemical properties of the synthesized solids [8]. This work shows the results obtained by using hydrotalcites synthesized by the sol-gel method with different Mg/Al ratios calcined at 500°C as catalysts in the ultraviolet- (UV-) assisted photocatalytic degradation of 2,4,6-trichlorophenol in aqueous phase.

2. Experimental

2.1. Hydrotalcite Synthesis. Hydrotalcites with different molar Mg/Al ratios were obtained by the sol-gel method. A small amount of hydrochloric acid (J. T. Baker) and the stoichiometric amount of magnesium ethoxide (J. T. Baker) and aluminum acetylacetonate (Aldrich) are dissolved in anhydrous ethanol (J. T. Baker) to obtain the different molar ratios. The solutions were refluxed at 70°C under constant stirring until the formation of the gels. The gels were washed and dried at 100°C. The hydrotalcites obtained were identified as HT-1, HT-2, HT-4, HT-5, and HT-7, corresponding to the Mg/Al ratio = 1, 2, 4, 5, and 7, respectively. Later, the hydrotalcites were calcined at 500°C and were identified as

HT-1 500°C, HT-2 500°C, HT-4 500°C, HT-5 500°C, and HT-7 500°C.

2.2. Structural Characterization of the Catalysts. Hydrotalcites dried at 100°C and calcined at 500°C were physicochemically characterized. Thermal analyses were carried out on TA Instruments Thermo-Analyzer at a heating rate of 10°C/min in an air atmosphere at a rate of 100 mL/min and using α -alumina as the reference standard. The diffractograms were obtained in an INEL Equinox Powder Diffractometer coupled to a copper anode and utilizing monochromatic $CuK\alpha$ radiation, whose wavelength (λ) is 1.5418 Å. Nitrogen adsorption-desorption isotherms were determined using ASAP 2010 Automated Micromeritics Equipment with a pretreatment at 150°C and vacuum up to 0.5 mmHg; BET theory was employed to determine the specific area. The bandwidth energy (E_g) of the samples was calculated from the UV absorption spectra of diffuse reflectance, taking into account that $E_g = (1239b/ - \alpha)$, where α and b are coefficients that were linearized in the appropriate region of the spectrum [9].

2.3. Photodegradation of 2,4,6-Trichlorophenol. Photodegradation was carried out in a Batch Reactor at room temperature with continuous magnetic stirring, an air flow of 2 mL/s, and 200 mg of catalyst. It was irradiated with UV-lamp-Pen-Ray (UVP) radiation of 254 nm and emission of 2.5 mW/cm² placed in a quartz tube, immersed in 200 mL of a solution containing 100 ppm of 2,4,6-trichlorophenol (Aldrich). The temperature was stabilized at 25°C with recirculation of water connected to the outer jacket of the reactor. The general reaction procedure was as follows: the 2,4,6-trichlorophenol catalyst solution was stirred in the dark (UV-off light) for 1 h, and a sample was taken to verify the adsorption of the molecule; this was subsequently irradiated with UV light and the progress of the reaction was continued until the disappearance of 2,4,6-trichlorophenol as a function of time employing a UV-vis Cary 100 Spectrophotometer monitoring the characteristic wavelength for 2,4,6-trichlorophenol ($\lambda = 310.5$ nm). Additionally, 2,4,6-trichlorophenol photodegradation was carried out in the absence of photocatalyst (photolysis). The amount of total organic carbon present in the irradiated solution was determined with a Shimadzu 5000 TOC.

3. Results and Discussions

3.1. Analysis of the Crystal Structure. Figure 1 illustrates the diffraction patterns of the materials at three different times: Figure 1(a), before calcination; Figure 1(b), calcined at 500°C, and Figure 1(c), after being used in the photodegradation.

For the case of the materials synthesized before calcination (Figure 1(a)) it can be observed that all materials, independently of the Mg/Al ratio, exhibited the crystalline structure of the hydrotalcite upon the characteristic signals (003), (006), (009), (015), (018), (110), and (113) (JCPDS card 22 0700). As can be noted, there is a slight offset to the left of the peaks as the Mg/Al ratio increases; less as the amount of aluminum decreases, which is associated with a

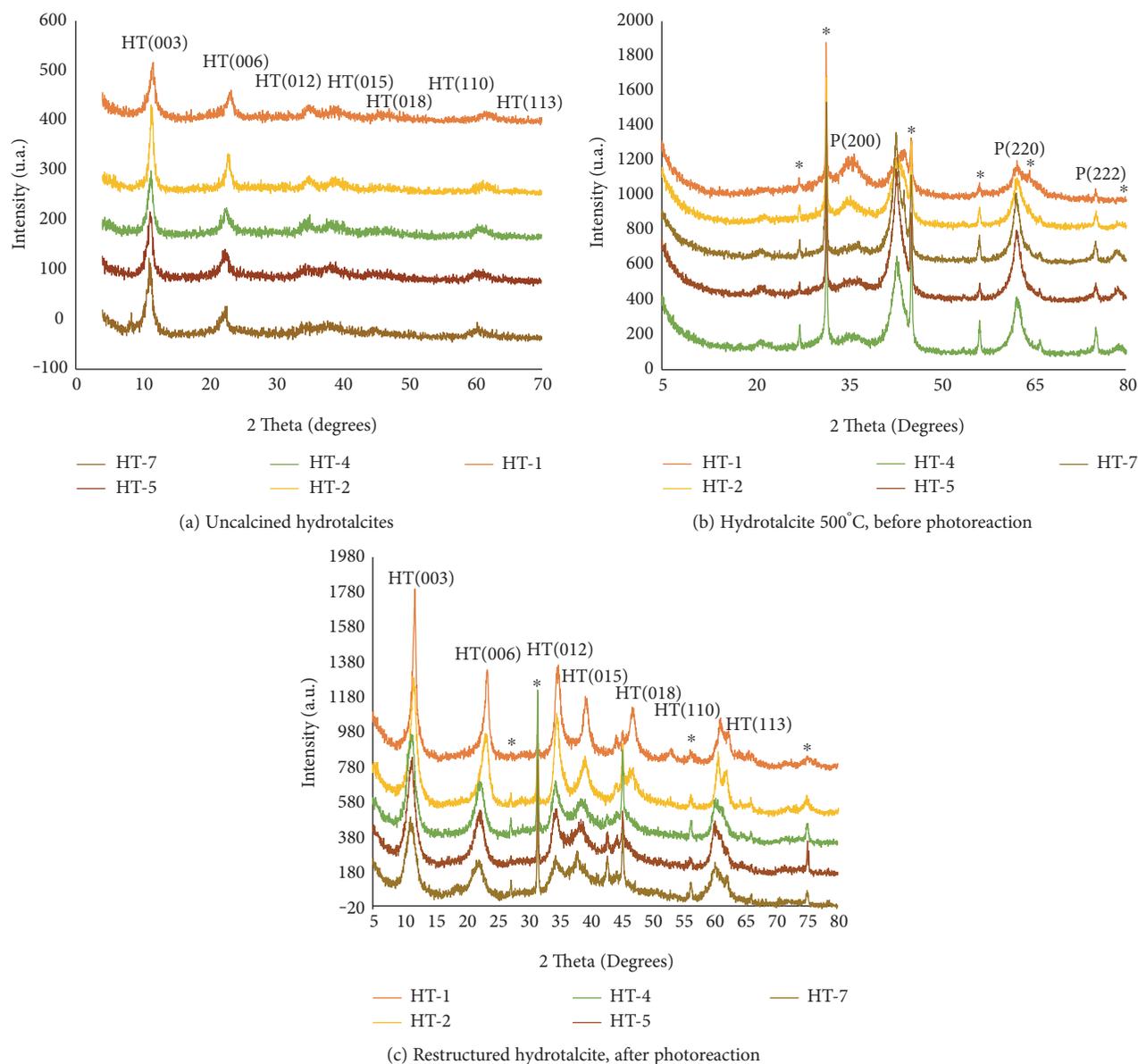


FIGURE 1: X-ray diffraction of Mg/Al mixed oxides after and before 2,4,6-trichlorophenol. HT: hydrotalcite; P: periclase; *polyoxycations of aluminum in solid state.

lower positive interlaminal charge, and thus a lower amount of anions housed in the interlaminal space.

In Figure 1(b), it can be observed that, as the Mg/Al ratio increases, crystallinity increases, which is associated with the increase in peak intensity. For all cases, hydrotalcite structure evolved thermally to a crystalline phase of periclase-type magnesium oxide (MgO) (JCPDS 4-0829), which is accompanied by a small crystalline phase of solid-state aluminum polyoxycation [10], which segregated due to the sol-gel hydrotalcite synthesis method and heat treatment at 500°C during a prolonged time for activation and catalytic application on photodegradation.

Figure 1(c) depicts the X-ray diffraction patterns of the materials after being used in photodegradation, which show all of the characteristic signals of the crystalline structure of

the hydrotalcite and additionally demonstrate the persistence of the crystalline phase of solid-state aluminum polyoxycations and the remaining brucite-type phase, which is present in solids of a high Mg/Al ratio (JCPDS card 7-239) [11, 12]. Accordingly, it can be noted that hydrotalcites are restructured by remaining in the aqueous medium during the photocatalytic degradation of 2,4,6-trichlorophenol, thanks to the memory effect, the latter a characteristic property consisting of hydrotalcites, which have evolved thermally to simple and mixed oxides that can recover the original hydrotalcite structure upon contact with the aqueous solution [13].

3.2. *Thermal Decomposition Profile.* The thermal decomposition profiles of the synthesized hydrotalcites are presented

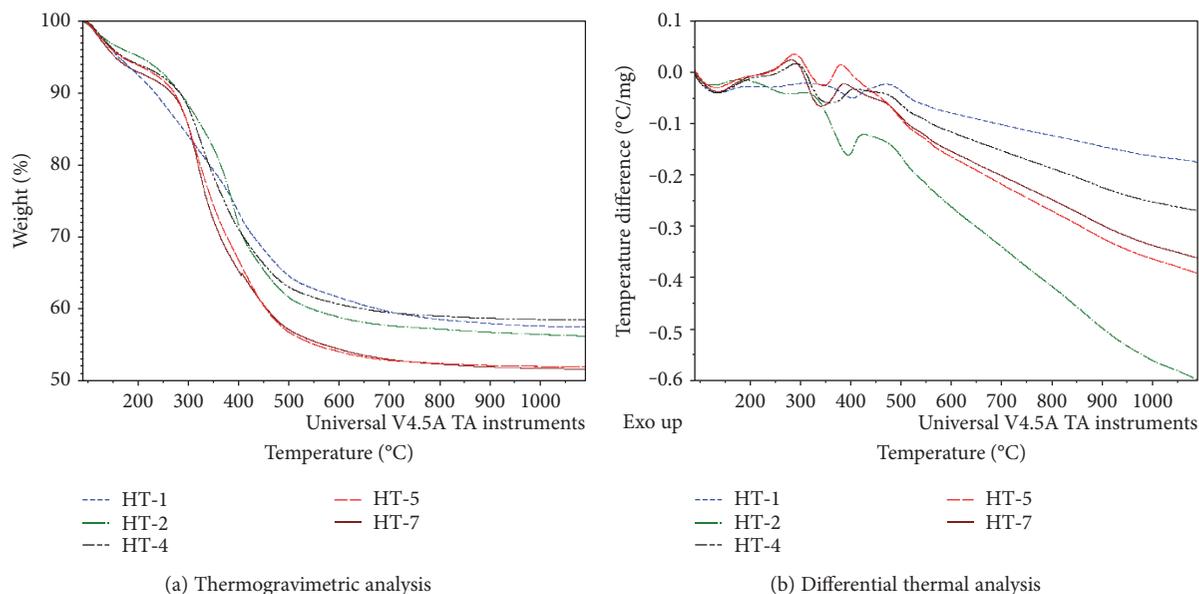
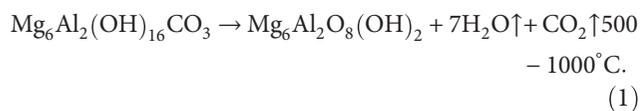
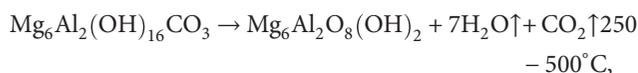
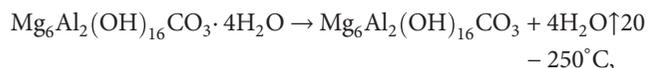


FIGURE 2: Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of Mg/Al hydrotalcites.

in Figure 2. As can be observed, the five hydrotalcites possess a very similar thermogravimetric profile, although with more marked inflections as the Mg/Al ratio increases, due to the fact that the evolution of the phases is favored by there being a greater amount of magnesium. The first loss is between 4 and 8% at 100°C, which is attributed to the desorption of water and the solvent sorbed in the material. The second loss of weight is a loss ranging from 30 to 40% centered between 350 and 400°C, which is attributed to the decomposition of bound hydroxyl groups and the removal of interlaminal carbonate ions. The solids show thermal stability of up to 500°C, with a total mass loss of 40–48% depending on the ratio, where, finally, the laminar structure collapses to segregate the spinel phase of the Mg/Al-mixed oxide and the periclase (MgO). One of the advantages of the sol-gel method is that it allows the obtaining of thermally stable solids in comparison with those synthesized by the coprecipitation method, favoring memory-effect reconstruction and photocatalytic activity [8].

The thermal reactions of hydrotalcites associated with endothermic and exothermic reactions shown in the differential thermal analysis can be represented in the following manner:



With the study of the thermal behavior of the hydrotalcites obtained, the optimal heat-treatment temperature was

found, corresponding to 500°C, in order to ensure that the solid is in the catalytically active phase for the photodegradation process in the form of metal oxides.

3.3. Textural Properties. Adsorption-desorption isotherms of N_2 of hydrotalcites calcined at 500°C for the photoreaction are shown in Figure 3. As can be observed, in all cases, the isotherms are type IV with cycles of type H2 hysteresis, associated with capillary condensation produced in the mesopores of materials in the form of sheets or plates, wherein the pores are characterized by having large pores with a small aperture.

Table 1 presents the values of the specific areas, determined by the BET method, of the hydrotalcites calcined at 500°C and the average pore size calculated by the BJH method. As can be observed, the specific surface area decreases as the Mg/Al ratio increases, with the HT-1 catalyst having a specific area of 341.08 m^2/g and with HT-7 the lowest value of 175.29 m^2/g , which are highly specific areas in comparison with similar materials synthesized by the coprecipitation method [14]. This decrease in porosity is associated with the lower amount of aluminum in the sheets, which results in a lower accumulation of carbonates and molecules in the interlayer; thus, at the moment of calcination, lower porosity is generated in the solid. This behavior is similar in relation to pore size, which decreases as the Mg/Al ratio increases. In the case of the HT-1 and the HT-2 catalyst at 500°C, the specific area is higher, which is attributed to the decrease in the crystallinity of the periclase and the increase in the amorphous structure of the spinel. In HT-4 and HT-5, catalysts at 500°C, their specific areas undergo a small decrease associated with faster thermal evolution than HT-1 and HT-2 catalysts. For hydrotalcite HT-7 at 500°C, the value of the specific area underwent a very significant decrease associated with greater collapse of the precursor's laminar

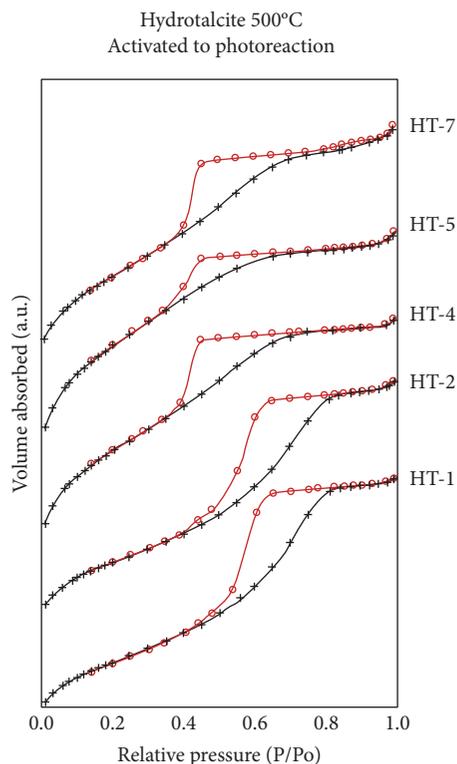


FIGURE 3: N_2 adsorption-desorption isotherms of calcined hydrotalcites before photodegradation.

TABLE 1: Textural properties of hydrotalcites and calcined hydrotalcites.

Solid	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore ratio (nm)
HT-1 500°C	341	0.82	9.6
HT-2 500°C	299	0.67	9.0
HT-4 500°C	271	0.44	6.5
HT-5 500°C	231	0.35	6.1
HT-7 500°C	175	0.31	7.0

structure. Having high specific areas favors access to catalytically active sites by increasing the catalytic capacity of the materials.

3.4. UV-Vis Diffuse Reflectance Spectroscopy. Figure 4 depicts the ultraviolet-visible (UV-vis) spectrum, where band gap energy (E_g) values are observed for catalysts activated at 500°C prior to photodegradation with a maximal absorption wavelength at $\lambda = 230$ nm. Hydrotalcites activated at 500°C have an E_g value ranging from 3.32 to 4.85 eV, in the following order: 3.32 eV HT-2 500°C < 3.38 eV HT-1 500°C < 3.40 eV HT-7 500°C < 4.67 eV HT-5 500°C < 4.85 eV HT-4 500°C. In this case, the HT-2 catalyst is that which presents an E_g value closer to the values of the positive control for TiO_2 photocatalytic degradation, ranging from 3.0 to 3.2 [15].

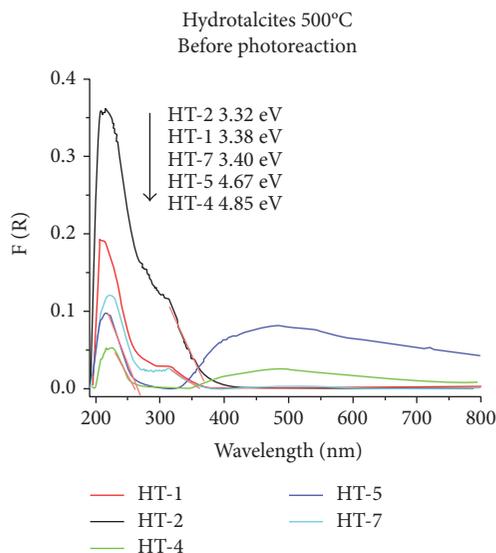


FIGURE 4: UV-vis diffuse reflectance spectra of Mg/Al calcined hydrotalcites at 500°C with different Mg/Al molar ratio.

3.5. Photocatalytic Degradation of 2,4,6-Trichlorophenol. The results obtained from the photolysis test of 2,4,6-trichlorophenol (100 ppm) show that the 2,4,6-trichlorophenol molecule is not destroyed by photolysis in the presence of a UV electromagnetic radiation source (254 nm) without catalyst, since $\pi \rightarrow \pi^*$ transitions are preserved and the intensity of the adsorption band in the wavelength range between 200 and 220 nm was incremented. Only a hypsochromic shift of 310 nm to 284 nm, of the compound 2,4,6-TCP, and also with a small decrease to 210 nm. In order to quantify and monitor the concentration of the molecule, the presence of these two bands at their respective wavelengths was considered and the calibration curve of 2,4,6-trichlorophenol was prepared.

In Figure 5, UV-vis spectra are illustrated during the photocatalytic reaction for degradation of 2,4,6-trichlorophenol. The reaction system was followed for 180 min for each of the activated hydrotalcites at 500°C, as well as for TiO_2 as positive control.

For all materials, no changes were observed in the molecule's adsorption spectra during the first hour of adsorption (absence of light), indicating that the molecule was not adsorbed by the catalyst. In these spectra, the absorption drop in the wavelength at $\lambda = 310.5$ nm is observed from the ignition of the irradiation source, which is characteristic for the molecule of 2,4,6-trichlorophenol, this indicating degradation of the corresponding contaminant, including the aromatic part.

The most active catalyst was HT-1500°C, as the degradation was carried out in a more rapid manner during the first 90 min. The remaining catalysts performed the degradation process in a slightly slower and gradual manner, requiring up to 180 min to achieve further degradation. In the case of the positive control using TiO_2 as a photocatalyst, it can be seen that it is less active as it shows a

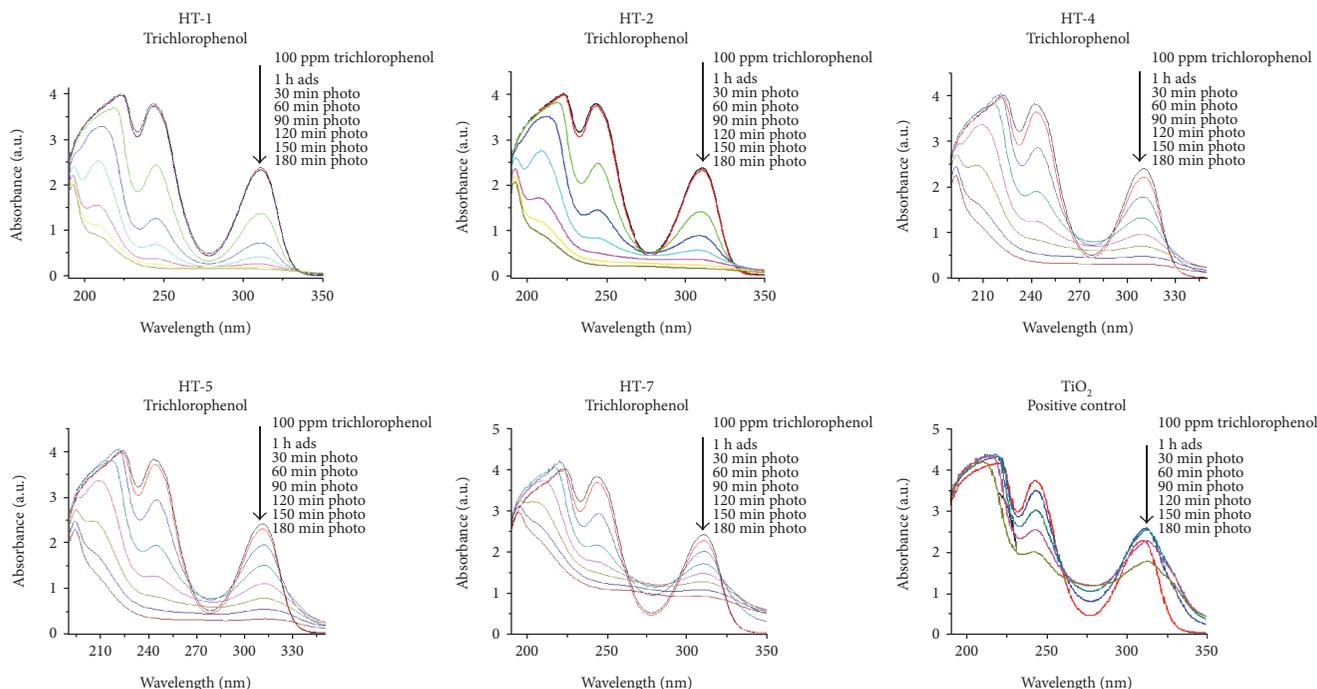


FIGURE 5: UV-vis spectra of photocatalytic degradation of 2,4,6-trichlorophenol by mixed oxide catalysts at 500°C and Degussa p25 TiO₂.

lower degradability at the same irradiation times compared to the hydrotalcites of different Mg/Al ratios tested.

Hydrotalcites, despite not being considered a semiconductor material, precontain a photocatalytic capacity when reconstructed by the memory effect after being thermally activated. Their photocatalytic activity is explained by the presence of electron-hole pairs generated when the hydrotalcites are irradiated with a UV light source ($\lambda = 254$ nm), which possess energy equal to or greater than the band energy of hydrotalcites, generating electron-hole pairs where the electron is displaced toward the electronic deflections of Al³⁺, generating a conduction band, and a gap in the valence band where the hydroxyl groups are oxidized. The gaps generated by light can interact with the hydrotalcite oxides, in addition to reacting with surface H₂O molecules; in both cases, oxydryl (OH·) radicals can be formed. On the other hand, the electrodes that are delocalized toward the electrodefficient charge of Al³⁺ react with dissolved O₂ to form superoxide radicals (O₂⁻). Both the oxydryl radicals and the superoxides act as photocatalytic oxidant species for the degradation of 2,4,6-trichlorophenol [16, 17].

In the case of the hydrotalcites activated with different Mg/Al ratio, it can be observed that on possessing a higher amount of Al³⁺, the catalysts are photocatalytically more active. This is due to the displacements of Mg²⁺ by Al³⁺, which produces electrons (e⁻) on the surface, causing the gradual hydroxylation of the material. The increase in catalytic activity is also associated with the increase of the specific area (ranging from 175 to 341 m²/g), as well as a change in the value of E_g (ranging from 3.38 to 4.85), because of the amount of aluminum in the calcined hydrotalcite sheets, due to the fact that MgO and Al₂O₃ have wide banded energies [18, 19].

Figure 6(a) depicts the degradation-rate behavior of 2,4,6-trichlorophenol as a ratio of the amount of degraded molecules per unit time. Highest degradability was that of the HT-1 catalyst, which reached degradation values of 2,4,6-trichlorophenol of 94.2%, followed by the HT-2 catalyst with 92.5% and so on, decreasing this capacity for HT-4, HT-5, and HT-7 solids up to 63.9%, where the decrease in the degradation capacity is associated with the physicochemical properties of the materials (low specific surface area, size of the crystal, and the Mg/Al molar ratio), the latter crucial for the formation of hydroxyl radicals. In addition, this can also be attributed to its crystallographic properties, especially crystal size. This is because larger sizes of glass inhibit the proper separation of electronic charges charged with the recombination of the electron pairs and voids, thus avoiding the formation of superoxide radical (O₂⁻) and hydroxyl radicals (OH·), initiators of advanced oxidation processes, compared with HT-1 and HT-2 [20]. In addition, the analysis of TOC is shown in Figure 6(b), where it can be observed that the degradation of 2,4,6-trichlorophenol is nearly completely reduced to mineralization in the first 90 min.

As mentioned previously, the catalyst that exhibited the greatest efficiency in photocatalytic degradation is HT-1 500°C of Mg/Al ratio=1, because it reached 94.2% degradation of the 100 ppm of 2,4,6-trichlorophenol. This higher catalytic activity is attributed, on the one hand, to the fact that it has a greater specific area, therefore, a higher and better interaction with 2,4,6-trichlorophenol molecules. On the other hand, it can also be explained as due to the mechanism proposed in the literature, in which authors indicate that, when calcining the hydrotalcite and exposing it to contact with water, it interacts with

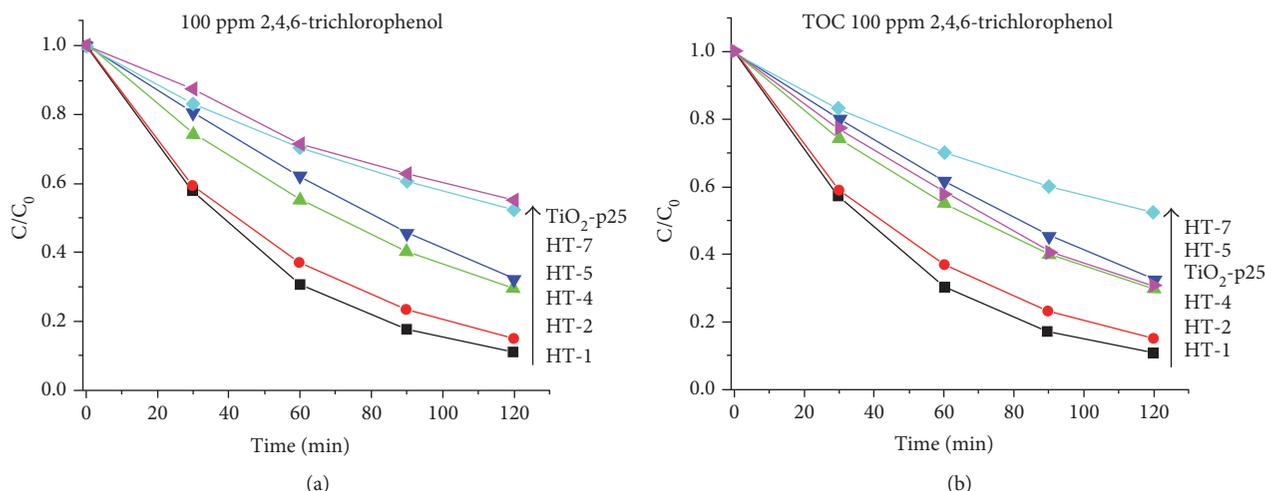


FIGURE 6: (a) Relative degradation rate of 100 ppm of trichlorophenol. (b) Relative concentration of total organic carbon (TOC) against time.

the catalyst, causing hydroxylation of the catalysts. This is because the synthesis of materials containing Mg^{2+} and Al^{3+} cations gives rise to the production of materials with semiconductive properties, whereby the irradiation of UV light gives way to the generation of electron-hole pairs, with the electron delocalized toward the electrodefficient charge of Al^{3+} . The latter generates a gap, which will interact with the water to cause the generation of OH radicals, which will be the main degrading agents in the reaction [21, 22]. Thus, the mixed oxide with the highest amount of Al is the most active; mixed oxides HT-1, HT-2, HT-4, HT-5, and HT-7 demonstrate a tendency from higher to lower, which is linked directly with the increase in the Mg/Al ratio present in the catalyst structure.

Additionally, Figure 6 shows a lower photodegradation with the TiO₂-p25 catalyst, as is the case with TOC quantification; however, in the TOC, a greater decrease is observed, and this could be associated to the formation of different intermediary species during use of the different photocatalysts, and said species or reaction by-products are not possible to be quantified by UV-vis spectroscopy. Consequently, the TOC studies are more conclusive, and TiO₂-p25 is found to be in the fourth position of the behavior during the 2,4,6-trichlorophenol mineralization, mineralizing approximately 40%. On the other hand, the catalyst HT-1 has succeeded in mineralizing 90% of the 2,4,6-trichlorophenol at 120 min of the reaction initiated.

Figure 7 presents the kinetic study of 100 ppm photodegradation of trichlorophenol with Mg/Al different ratio catalysts. As can be observed for all cases, the kinetic studies adjust to a pseudo-first order reaction in $(C_0/C) = Kt$, after least squares linearization with a correlation coefficient of 0.99. The results show a maximal apparent-velocity constant of sample HT-1 ($k_{app} = 0.0186 \text{ min}^{-1}$) and a minimal apparent-velocity constant for the HT-7 sample ($k_{app} = 0.0054 \text{ min}^{-1}$).

Table 2 illustrates the data obtained for the calculation of degradation kinetics, such as half-life, rate constants,

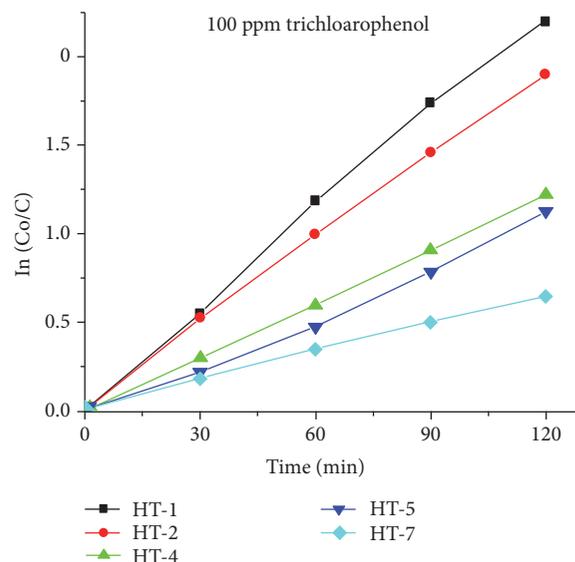


FIGURE 7: Kinetic behavior of 2,4,6-trichlorophenol photodegradation with mixed oxide catalysts at 500°C.

and removal percentage, of 2,4,6-trichlorophenol, in which it can be observed that photocatalyst HT-1500°C is the most active, in that it has the shortest half-life (37.27 min) and an elimination rate of 94.18%. As the Mg/Al molar ratio increases, the constant decreases and the half-life increases that, for the HT-7 catalytic converter, requires a 3-fold longer half-life to reach an elimination of a little more than two-thirds less in relation to the HT-1 catalyst, due to the amount of aluminum present in the sheet structure.

4. Conclusions

Hydrotalcites calcined at 500°C possess E_g values ranging from 3.38 to 4.85, which are values close to TiO₂, rendering

TABLE 2: Kinetics of degradation.

Catalyst	k (min^{-1})	$t_{1/2}$ (min)	Degradation (%)
HT-1 500°C	0.0186	37.27	94.18
HT-2 500°C	0.0158	43.87	92.49
HT-4 500°C	0.0102	67.96	86.15
HT-5 500°C	0.0094	73.74	84.25
HT-7 500°C	0.0054	128.36	63.89

them viable as photocatalytically active materials. Hydrotalcites calcined at 500°C with different Mg/Al molar ratios were tested in the photodegradation of 2,4,6-trichlorophenol, showing good photocatalytic activity, presenting degradation efficiencies of 2,4,6-trichlorophenol on an order 94.18% HT-1 500°C > 92.49% HT-2 500°C > 86.15% HT-4 500°C > 84.25% HT-5 500°C > 63.89% HT-7 500°C in less than 2 h. Degradation was practically complete when mineralization reached values of >90%. The most active catalyst is HT-1 500°, which has a Mg/Al=1 ratio, in that this catalyst contains a greater amount of segregated aluminum in the amorphous structure of the spinel, related with the generation of hydroxyl radicals, responsible for the photodegradation verified with the characterization of the catalysts before and after photodegradation.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

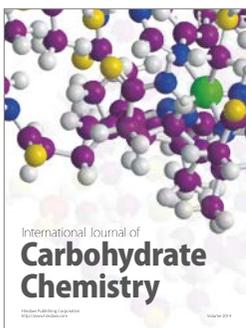
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