Combination of Mn oxidation states improves the photocatalytic degradation of phenol with ZnAl LDH materials without a source of O₂ in the reaction system

Getsemani Morales-Mendoza a,*, Mayra Alvarez-Lemus b, Rosendo López b, Francisco Tzompantzi a, Rajesh Adhikari c, Soo Wohn Lee d, Leticia M. Torres-Martínez e, Ricardo Gómez a

a Universidad Autónoma Metropolitana-Iztapalapa, Depto. de Químico, Área de Catálisis, Grupo ECOCATAL, Av. San Rafael Atlixco No. 189, México 09340 D.F., México
b Universidad Júarez Autónoma de Tabasco, División Académica de Ingeniería y Arquitectura, Carretera Cunduacán-Jalpa Km. 1 Col. La Esmeralda C.P.86690, Cunduacán, Tabasco, México
c Institute National De La Research et Scientific-Energy Materials Telecommunication (INRS-EMT), 1650 Boul. Lionel Boulet, Varennes, QC JX1 1S2, Canada
d Research Center for Eco Multi-Functional Nano Materials, Sun Moon University, Asan, South Korea
e Depto de Ecoc materiales y Energía, Facultad de Ingeniería Civil, Universidad Autónoma de Nuevo León, Av. Universidad y Av. Fidel Vélázquez S/N, Cd. Universitaria, San Nicolás de los Garza Nuevo León, 66451 México

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A B S T R A C T

Mn-doped Zn/Al layered double hydroxides (LDH) materials were synthesized by the co-precipitation method. X-ray diffraction (XRD) analysis confirmed the polytype structure of LDH materials obtained as well as the successful incorporation of Mn into the structure. Atomic absorption spectroscopy (AAS) and energy dispersive X-ray spectroscopy (EDS) studies showed a well dispersion of Mn and a good correlation between the nominal and experimental composition. Scanning electron microscopy (SEM) revealed the formation of grains close to 1 μm length. Energy band gap (Eg) of the solids determined by UV–vis diffuse reflectance spectroscopy (DRS) showed high photosresponse in the ultraviolet (UV) region, which was increased with Mn incorporation into the LDH structure. The LDH materials were evaluated in the photocatalytic degradation of phenol in aqueous medium, under UV radiation with and without O₂ source in the reaction system. The results showed that the O₂ is not an effective electron scavenger as usually occurs in TiO₂ photocatalyst. The Mn effect in the photocatalytic activity was notably marked in anaerobic condition however in aerobic or anaerobic conditions the presence of Mn increases the photocactivity. The phenol mineralization reached in anaerobic conditions was 95% (1.5 ppm) of the initial concentration (30 ppm) and it is maintained constant after 6 h of radiation while in aerobic conditions the TOC reaches only 55% (13.5 ppm). The role of Mn as charges separator is discussed and a suitable mechanism is proposed. This study shows that the Mn doped-Zn/Al LDH materials could be a promising photocatalysts under anaerobic conditions for the removal of phenol from aqueous medium.

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1. Introduction

According to the Environmental Protection Agency (EPA), the removal of phenolic compounds from wastewater is a priority problem due to its remarkable toxicity which represents a serious environmental problem even at low concentration. The human health ambient water quality criteria (AWQ) are numeric values for pollutants concentration in ambient water that the U.S. EPA considers as protective limits for the human health. In 2014, a report was published with the updated threshold of phenolic content for consumption of water by humans and organism (as fish) [1]: AWQC = 2 mg of phenol/L. Because of the need to reduce the phenolic content present in the effluents to such small values, it is necessary to search alternatives for the degradation of phenolic pollutants and prevent it from spreading in aqueous media. On this respect, different concentrations can be found in surface water closed to the interval of 0.01–2.0 μg/L in natural water, however have been found concentration of phenol in surface water of

* Corresponding author. Tel./Fax: + 52 5558044669.
E-mail address: getmome@hotmail.com (G. Morales-Mendoza).

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Netherlands of 2.6–5.6 μg/L. In polluted river water with sewage, derived from petrol processing plants, have been found concentrations of phenol over 40 mg/L. In domestic water supply in the USA have been reported levels of 1 μg/L. Also, the phenol can be present in the atmosphere due to the emissions from motor vehicles and as a photooxidation product of benzene exceeding the background levels in air are expected to be low than 1 ng/m³ [2].

Actually in the field of research, the most popular methodology for the oxidation of organic pollutants is the photocatalytic degradation using semiconductors due to its potential application using the solar radiation and the complete destruction of the pollutants. However, recent research employing alternative materials for the phenol degradation have reported non-traditional semiconductor materials as, aluminum oxide (Al₂O₃) [3] and magnesium hydroxides (Mg(OH)₂) [4]. This revolutionary alternative has motivated to employ known materials used in other areas of research as in catalysis. In particular, some non-traditional semiconductors and amply used in catalytic reactions are the layered double hydroxides (LDH). These materials have principally been employed as precursors of photocatalytic mixed oxides [5–8] or as hydroxides lamellar composites [4,9–15], being applied instead of traditional semiconductor for photocatalytic applications [12,16–19]. The LDH are solids with a surface formed and covered by OH anions [20–22] and structurally they are described as brucite-like octahedral sheets separated by anions. The separation of the sheets of the LDH materials is produced by a partial substitution of the metal cations M²⁺ with M³⁺ which occurs during the synthesis; the excess of positive charge on the octahedral layers is balanced by anions arranged between two sheets. Due to the different combination of M³⁺ and M²⁺, several cations are employed as precursor of the LDH materials. Most of the reported photocatalytic LDH materials in the ultraviolet (UV) or visible (vis) region have employed Zn²⁺ and Al³⁺ as cations precursors with a Zn/Al nominal molar ratio close to 2 and synthetized by the precipitation method being the elimination of pollutants their principal application [5,12–19].

According to the proposed mechanism, in photocatalytic reactions for the pollutants degradation using metal oxides like TiO₂ it is reported the use of a source of O₂ which can be adsorbed on the surface of the photocatalyst. The adsorbed O₂ acts as acceptor agent of the photogenerated electrons (e⁻) or electron scavenger [17]. The capture of e⁻ by the adsorbed O₂ help to the charge separation (electron e⁻ and hole h⁺) producing an accumulation of h⁺ which can be recombined with e⁻ from the oxidation of the adsorbed OH⁻ anions on the surface for recover the neutrality of the photocatalysts. The oxidation of the adsorbed OH⁻ by the h⁺ produces the formation of OH* radicals (OH*) which have an adequate potential to produce the degradation of organic compounds [17]. However for LDH materials, the role of the adsorbed O₂ is uncertain and unknown, and now it has been assumed to be analogous to the mechanism of the TiO₂ empirically.

Another strategy to increase the separation of photogenerated charges has been the doping with a metal cation photoactive in the UV–vis region as the transition metals. Manganese (Mn) has been used as a photoactive doping agent [23–27]. In this regard, it has been reported that the doping with Mn increases the UV absorption and it enhances the photocatalytic activity with respect to undoped materials [23–27]. The increase of the photocactivity is attributed to the introduction of available orbitals 3d (3d states) into the band gap which act as charge separators in the photoactive bare materials [24,28]. As Mn can be a dopant that favors the charge separation acting as holes trap in Mn²⁺ state [24,28,29,30] or as electrons trap in Mn³⁺ or Mn⁴⁺ state [26,29,31], this property can be employed as a tool to improve the e⁻ and h⁺ separation into the LDH.

In the present work, we show the ZnAl LDH materials doped with Mn applied as photocatalysts in the degradation of phenol. We discuss the role of Mn in the physicochemical properties of doped LDH materials and the investigation shows that these materials could be a promising option to degrade pollutants in anaerobic conditions. The increase of the photocatalytic activity is related to an improved charge separation that can be produced by the presence of Mn into the LDH structure.

2. Experimental

2.1. Synthesis of photocatalysts

Two LDH (Zn/Al) named ZA2 and (Zn+Mn)/Al named ZAMn1 were prepared at constant pH by the co-precipitation method using Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and Mn(NO₃)₂·6H₂O (J.T. Baker and Aldrich analytical Reagent) as precursors. The Zn/Al and (Zn+ Mn)/Al nominal molar ratio was 2:1, and in ZAMn1 sample the Mn/Zn nominal molar ratio was 0.01. In a typical procedure, stoichiometric amounts of metal precursors were dissolved simultaneously in 1000 ± 1 mL of distilled water and heated at 90 ± 1 °C. As precipitant agent, urea (NH₂CONH₂) was added to the solution and after the urea hydrolysis (decomposition) the pH was adjusted to 10.0 ± 0.1 by adding an alkaline mixture of KOH/NaHCO₃. The formed mixture was vigorously stirred and maintained under reflux during 36 h at 90 ± 1 °C. The resulting precipitate was filtered and washed with hot de-ionized water (90 ± 1 °C), dried at 100 ± 1 °C and for 12 h and finally annealed at 400 ± 5 °C in air.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained with a Siemens D500 diffractometer using a graphite crystal monochromator to select Cu-Kα radiation (λ = 1.541 Å), with a step of 0.03° s⁻¹. A detailed study was made in 55–65° (2θ) region in order to confirm the isomorphous incorporation of Mn in the layer structure. Scanning electron microscopy (SEM) images were obtained with a microscope JEOL model JSM-6490LV with 20 kV, equipped with a detector for energy-dispersive X-ray spectroscopy (EDS) model INCA-Xsight Oxford. The composition of the samples was also analyzed by atomic absorption spectroscopy (AAS) using a S4 Thermo Electron Corporation apparatus. Diffuse reflectance spectroscopy (DRS) was carry out in the UV–vis region with a Labsphere DRA-301 integration sphere (Spectralon®) coupled to a Cary-100 spectrophotometer with resolution of 0.001 nm; the data were processed with the Kubelka–Munk’s (K–M) equation [32].

2.3. Photocatalytic activity

The phenol photodegradation in aqueous medium was carried out in a homemade Pyrex batch open photoreactor containing 0.2000 ± 0.0001 g of annealed solid and 200.0 ± 0.1 mL of a solution with 30 ppm (0.3187 mmol/L) of phenol prepared with water previously boiled to eliminate the dissolved CO₂ (carbonates) and O₂. The suspension formed by the solid and the solution was kept under continuous stirring in the dark for 1 h before starting irradiation in all experiments. The employed light source was an UV lamp (UVP Products), with a UV Pen-Ray power supply (254 nm and 2.8 W respectively) and emission intensity measured from 2.16 to 2.20 ± 0.01 mW/cm². The lamp was placed in a quartz tube and then immersed in the suspension. Aliquots of 5 mL were taken each hour and analyzed by UV–vis spectroscopy with a Cary-100 UV–vis spectrophotometer with resolution of 0.001 nm following the absorption band of phenol at 268 nm. Influence of air bubbling as O₂ source in the photocatalytic test was carried out by mean bubbling air (775.0 ± 0.1 mL/min) during the radiation time and without air bubbling. The determination of the total organic carbon (TOC) was made as function of time using a TOC-Vcsn analyzer.
(Shimadzu) with resolution of 0.001 mg of C/L. After of the photocatalytic test, the samples recovered and dried at 100 ± 5 °C were analyzed by FTIR using a Shimadzu IRAffinity-1 spectrophotometer equipped with an attenuated total reflectance (ATR) accessory of ZnSe crystal in the interval from 650 cm⁻¹ to 4000 cm⁻¹ with resolution of 2 cm⁻¹. For the preparation of reference 200.0 ± 0.1 mg of ZA2 sample was mixed with 30 ± 0.1 mg of phenoland was taken a sample of the mixture to obtain the FTIR spectrum as reference. A detection study of active oxidative species (OH⁻ radicals) generated by the irradiated solids in solution was made by photoluminescence spectrophotometry using a LS-50B Perkin-Elmer spectrometer with resolution of 1 nm and following the methodology of Ishibashi et al. [33]. For this, 0.2000 ± 0.0001 g were placed in 200 ± 1 mL of 5 × 10⁻⁴ M solution of terephthalic acid prepared in 2 × 10⁻³ M solution of NaOH. Aliquots of the solution were then analyzed using an excitation wavelength of 315 nm, and the fluorescence spectrum was collected in the range from 350 to 600 nm.

3. Results and discussion

3.1. Structural study

Fig. 1a shows the XRD patterns of the undoped LDH and Mn-doped LDH solids dried at 100 ± 1 °C, the reflections are characteristic of the LDH materials. The diffractograms can be indexed on basis to a three-layered rhombohedral lattice with the hexagonal unit-cell parameters a = 3.038 ± 0.002 Å and c = 22.446 ± 0.002 Å. The indexing results suggests that the obtained materials correspond to a polytype structure of LDH (designated as 3R1 hydrotalcite) reported by Newman et al. [21]. The reflection that appear in 11.84–11.87° (2θ) interval correspond to the plane (0 0 3) which is associated with materials containing the CO₃²⁻ between the layers. The cell parameters were calculated using the reflections (0 0 3) and (1 1 0), employing the equations c = 3d₀₀₃ and a = 2d₁₁₀; where “a” represents an indirect measure of the average metal-metal distance contained into the plane (1 1 0) of the layer structure. In Fig. 1b, the detailed analysis of the diffraction patterns in the interval from 55 to 65° showed the shift of the peak corresponding to (1 1 0) reflection. This shift toward low values, compared with the reference sample ZA2, suggests the presence of Mn in the structure of the layers [7–11]. The cell parameters values reported in Table 1 show a modification in the average size of the unit cell that is related with the Mn incorporation into the layers.

Memory effect is a well-known property present in LDH materials annealed at T < 500 °C. In our case, the annealed solids at 400 °C were placed into the aqueous phenol solution, recovered and dried at 90 °C and then the DRX patterns obtained. The diffractograms confirm the recovery of the LDH structure by mem-

![Fig. 1. XRD patterns of the solids obtained (a) polytype of LDH, (b) magnification on the 56–63° in 2θ interval of a detailed study for the plane (1 1 0).](Image)

![Fig. 2. XRD patterns of the recovered annealed samples after 12 h in contact with phenol 30 ppm and configurations of adsorbed phenol exclude that could change the interlayer thickness.](Image)

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (±0.02 Å)</th>
<th>c (±0.03 Å)</th>
<th>d₀₀₃ (±0.01 Å)</th>
<th>Average interlayer thickness* (±0.02 Å)</th>
<th>D₀₀₃* (±1 Å)</th>
<th>D₁₁₀* (±1 Å)</th>
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<tr>
<td>ZA2</td>
<td>3.05</td>
<td>22.40</td>
<td>7.46</td>
<td>2.66</td>
<td>242</td>
<td>176</td>
</tr>
<tr>
<td>ZAMn1</td>
<td>3.06</td>
<td>22.50</td>
<td>7.50</td>
<td>2.70</td>
<td>166</td>
<td>208</td>
</tr>
</tbody>
</table>

* The difference between d₀₀₃ and 4.80 Å (the thickness of the brucite-like sheet).
* Calculated using the Scherrer equation.
ory effect. Fig. 2. As can be seen in both cases (doped and undoped materials) a high crystallinity was obtained in the recovered samples with a well-defined LDH structure. Furthermore, the calculated interlayer space in the reconstructed samples suggested no significant changes in this value indicating that the phenol cannot produces an important opening of the sheets by adsorption in the interlayer space. In Fig. 2, are showed two possible accommodations in the interlayer space of the LDH corresponding to 4.17 Å and 5.76 Å [34]. These values are higher than the calculated values in the reconstructed samples in phenol solution which indicates that these arrangements of phenol in the solids are not present. Commonly, it is expected that the molecules are adsorbed in the interlayer space of LDH; however the adsorption capacity depends of the functional group of the molecules being preferably adsorbed molecules with carbonyl group which is not the phenol structure. This suggests that the interaction of phenol with the LDH surface is by mean of weak interactions through Van Der Waals forces (H-bridge bound) decreasing the adsorption capacity of phenol.

3.2. Study of composition

The obtained molar composition for the annealed solids by EDS and AAS techniques are shown in Table 2. A good agreement between experimental and nominal composition of the samples was obtained. The Mn/Zn ratio estimated by EDS was lower than the obtained by AAS indicating that Mn is preferably located into the bulk since it is necessary a digestion of the sample, as in AAS, to detect Mn content fully. For the ZAMn1 sample, the Zn/Al molar ratio was lower (1.47 and 1.87) than the obtained for ZA2 sample (2.05 and 2.01). This could be due to the presence of Mn in other oxidation state (Mn3+ and Mn4+) which could prevent the total Zn2+ incorporation during the synthesis process.

3.3. Study of morphology

Obtained SEM images are showed in Fig. 3. It can be seen that ZA2 and ZAMn1 samples showed conglomerates with nonuniform sizes. In ZA2 sample the average grain sizes were below 1 μm, nonuniform and some with rice-grain shape. In ZAMn1, the presence of Mn leads to increase the average grain size than ZA2, reaching sizes higher than 1 μm. Also, the increase in grain size produced a decrease of the cavities created in the conglomerate. On the other hand, in an elemental mapping of the ZAMn1 sample from SEM image, was observed a high dispersion of Mn which corresponds to a well distribution over the structure, Fig. 3.

### 3.4. Study of optical properties

The UV-vis DRS results for the annealed samples are shown in Fig. 4. These results are interpreted as an optical absorption due to F(R) which is directly proportional to the optical absorptivity coefficient under K–M model [32]. This means that the wavelength at which the F(R) has a high value, the absorption intensity will be the highest. Two strong absorption bands in the UV region around 230 and 270 nm can be observed in both samples. In ZAMn1 sample, the absorption capacity apparently increased and was shifted toward higher wavelengths. The increase of the absorption in the 200–400 nm region can be related to structural modifications due to the insertion of Mn cations into the lattice as it has been reported for other materials [35–37]. The increase of these bands respect to reference ZA2 can be attributed to a superimposed broad band in the 320–380 nm range which it is assigned to the O2− → Mn3+ charge transference in a 3B1g → 5B2g transition of the crystal field [35–37]. There are not reports for an appropriate estimation of the band gap of the LDH materials since the absorption coefficients as well as the transition type are not defined for these materials. K–M graphic, F(R) vs energy (eV), and the extrapolation of the absorption edge in the UV–vis absorption to X axis for (F(R)) equal to zero is generally used methodology to estimate the band gap (Eg) values in the most of the LDH materials reported [7,11,13]. In Fig. 4a is shown the interception of linear fit with the x-axis for the ZA2 and ZAMn1 samples and the calculated values are reported in Table 3. A slight shift toward higher wavelengths was observed in the ZAMn1 sample. The obtained Eg values clearly indicate that photoactivation of the LDH is achieved under UV light. Apparently, the presence of Mn decreases the band gap value compared with the reference (ZA2); however, this shift is due to the overlapping of d → d electronic transition of Mn with the edge of absorption of the ZA and it can be confused wrongly with a shift of the band gap.

Furthermore, UV–vis-DRS spectra can also provide information related to the oxidation states of Mn [35–39]. The d–d transition of Mn2+ and Mn3+ can be identified in the visible region, whereas the transition due to Mn2+ ions of spin- and orbital-forbidden type produces a very weak absorption bands [35–39]. The weak absorption bands observed in the ZAMn1 sample in the 400–600 nm region can be related with the presence of Mn2+ ions, assigned to the transitions 6A1g → 4T2g of the crystal field [35,39]. Additionally, a broad weak shoulder observed in the 690–800 nm region and can be assigned to 5B1g → 4A1g d–d transitions of Mn3+. Therefore, due to the absorption bands in 500–800 nm it could be assumed that Mn is present as Mn2+ and Mn3+. Moreover, it is also possible that Mn4+ can also be present, however the band at 470 nm is overlapped with
the bands described above. A Summary of the principal transition corresponding to Mn states is reported in Table 3.

3.5. Photocatalytic test

The photocatalytic degradation of phenol as a function of the irradiation time was followed by UV–vis spectroscopy. As preliminary evaluation, a photocatalytic test of the dried samples was made. As can be seen in Fig. 5, the characteristic spectrum of phenol significantly did not change after the radiation time and only increase slightly around 220 and 190 nm which suggest the formation of other phenolic intermediaries. Moreover, a considerably content of the phenol remains in the solution after the photocatalytic evaluation with the dried samples as was showed by the band of phenol spectrum centered at 268 nm in Fig. 5. The persistence of phenol can be due to an effect of inhibition of the formation of OH* radicals by the carbonates or nitrates, adsorbed on the surface and between the sheets of the dried samples, acting as hole scavenger. For this reason the samples preferably were evaluated after annealing at 400 °C. Prior to initiating the reaction with the annealed samples, the adsorption test showed that phenol is poorly adsorbed on the surface of the LDH samples even after 26 h in dark. To evaluate the influence of the O2 source in the photocatalytic activity of the samples, the experiments were carried out with and without bubbling air as O2 source. Fig. 6a shows the degradation of phenol with ZA2 sample in presence of O2, and the spectrum suggests that O2 does not participate as an efficient electron scavenger in the photocatalytic process due to a low decrease of the bands 190–220 nm; when the air bubbling was omitted (Fig. 6b), the photodegradation increased, indicating that the O2 source was not necessary. On the other hand, the photocatalytic evaluation of the ZAMn1 sample was performed under the same conditions with and without O2 (Fig. 6c and d). In this results was showed the higher activity of the ZAMn1 sample (Fig. 5c) than ZA2 (Fig. 6a) in aerobic conditions by effect of the Mn incorporation in the LDH material. The Mn effect in anaerobic conditions (Fig. 6d) compared with ZA2 (Fig. 6b) was not notable. The comparison of ZAMn1 with O2 (Fig. 6c) and without O2 (Fig. 6d) showed a small increase of the photoactivity when the O2 source was not employed. The graphical representation of the phenol degradation as a function of time by the LDH materials with and without oxygen is presented in Fig. 7 for a better comparison. To confirm photoxidation in anaerobic conditions, N2 was bubbled through the irradiated solution and it can be observed that the photocatalytic activity with N2 and without O2 exhibited the same behavior. These results suggested that the presence of O2 is not necessary and a significant increase in the photodegradation by effect of the Mn incorporation into the LDH material can be related with the role of Mn as a charge separator.

3.6. OH* radicals detection study

In situ generation of hydroxyl radicals by solids in the reaction medium without O2 was carried-out using terephthalic acid as scavenger of radicals and the fluorescence technique for the detection [33]. Fig. 8, shows a comparison of the fluorescence spectra
corresponding to the 2-hydroxyterephthalic acid formed after the 
reaction of terephthalic acid and OH\(^{\cdot}\) produced by the ZA2 and 
ZAMn1 samples. Higher fluorescence intensity was obtained for the 
solution irradiated in presence of the ZAMn1 sample than the ZA2 
sample. The intensity of the emission band followed at 425 nm was 
associated to the formation the 2-hydroxyterephthalic acid which 
was related with the OH\(^{\cdot}\) production by the irradiated solids in 
dispersion. Unfortunately, after 30 min of radiation the terephthalic 
acid began to be degraded and was not possible follow the radical 
production during all reaction time.

3.7. Kinetic model adjustment study

In the case of the phenol degradation with these LDH materials, 
a first order kinetics under Langmuir–Hinshelwood model (L–H) 
[40], is not the better adjustment of the obtained results. Due to the 
low adsorption capacity of phenol on the LDH surface, the degrada-
tion of phenol fails since it does not follow the L–H model [41–44] 
and therefore, as it has been reported [45–48], no all experimen-
tal data on photocatalytic reactions can be predicted by this model. 
The L–H model is applied to reactions that follow the pathway of (i) 
adsorption of reacting species on the catalyst surface, (ii) reaction 
involving adsorbed species, (iii) desorption of reaction products. In 
our proposal, the phenol oxidation can take place on the exposed 
surface of the solid [45–48].

The LDH materials in aqueous solution are covered by a high 
content of OH\(^{\cdot}\) ions adsorbed on the surface [49]. In a zero kinetics 
order under L–H model, the kinetics parameters can be related with 
the OH\(^{\cdot}\) radicals produced by the solids [30,33,45–48,50]. In solu-
tion, the high and permanent concentration of OH\(^{\cdot}\) adsorbed on the 
surface allows to the system be independent of the concentration of 
OH\(^{\cdot}\) or H\(_2\)O. This is congruent with the condition to generate OH\(^{\cdot}\) 
continuously. Assuming that the generated OH\(^{\cdot}\) react quickly with 
the phenol molecules degrading, the disappearance of phenol can 
be interpreted as an indirect measure of photocatalytic activity of 
the LDH materials due to phenol degradation by means of the OH\(^{\cdot}\) 
produced. Therefore, in the L–H model, the coverage corresponds to 
the OH\(^{\cdot}\) adsorbed on the LDH and the photocatalytic activity is 
the corresponding to the effective OH\(^{\cdot}\) produced that react with phenol 
molecules. The zero kinetic order was the better adjustment with 
a correlation coefficient among 0.98–0.99 for the obtained results. 
The rate constant was obtained from the curves (Fig. 8), according 
to the Eq. (1):

\[
\frac{C}{C_0} = \frac{K_{\text{app}}}{C_0} t + 1
\]

Where, C is the concentration at time t, C_0 is the initial concen-
tration at equilibrium, t is the time and K_{\text{app}} is the apparent 
rate constant. The obtained kinetic parameters are shown in Table 4. 
It can be seen that K_{\text{app}} for the ZA2 sample in the reaction without O\(_2\)
is four times higher than the reaction with O$_2$. A similar behavior was observed with the ZAMn1 sample.

### 3.8. Study of mineralization

TOC results showed a mineralization closed to 90% (28.5 ± 0.1 ppm) of initial concentration of phenol (30.0 ± 0.5 ppm) with the ZAMn1 sample without O$_2$, and 70% (21.0 ± 0.1 ppm) with O$_2$. The ZA2 sample reached a 66% (19.0 ± 0.1 ppm) without O$_2$ and 55% (16.1 ppm) with O$_2$, Fig. 9. Therefore, it showed the Mn effect into the structure improving the oxidation of phenol and this can be related with the produced OH$^-$. The results confirmed the improved mineralization capacity of Mn-doped LDH materials which can be taken into account as alternative for the water treatment reaching the suggested limits for some backed organizations [1].

### 3.9. Proposed mechanism

We proposed a mechanism for the OH$^-$ generation on the LDH surface without O$_2$ and the role of Mn as charge separator, Fig. 10. In ZA2 sample, the absorbed photons excite electrons from occupied state in the O$^{2-}$ or Zn$^{2+}$ atoms that form the layers similarly as in ZnO semiconductor. The photoexcited electrons (e$^-$) can move easily on the layer producing a deficiency of electronic charge in the ground estate of the O$^{2-}$ or Zn$^{2+}$ which compensate with the electrons from the neighboring atoms promoting the charges mobility. This process can be interpreted as an analogous to the process described for the photogenerated charges e$^-$ and h$^+$ in semiconductors. The photogenerated e$^-$ can be transferred toward protons H$^+$ adsorbed on the surface to produce H$_2$, however, the dispersion of LDH materials in aqueous medium after turn on the lamp, change the pH producing a basic medium. This change of pH decrease the H$^+$ concentration reducing the transfer of the e$^-$ toward the H$^+$ which can be responsible of the low photocactivity in ZA2 as result of an inefficient charges separation. In ZAMn1 sample, the photogenerated h$^+$ in the layer can be trapped by the Mn$^{2+}$ or Mn$^{3+}$ [28], inducing momentary change in the oxidation state of the manganese to Mn$^{3+}$ or Mn$^{4+}$ respectively. To recover its original charge, Mn$^{3+}$ or Mn$^{4+}$ oxidizes the OH$^-$ adsorbed on the surface recovering the initial oxidation state Mn$^{2+}$ or Mn$^{3+}$ and producing OH$^-$. Subsequently, the OH$^-$ react with the phenol molecules oxidizing it. On the other hand, it has been reported that the available Mn 3d states act as electron trapping, increasing charge separation [23–31]. Mn$^{3+}$ or Mn$^{4+}$ can capture photogenerated e$^-$ changing to Mn$^{3+}$ or Mn$^{4+}$, favoring the charge separation and producing an accumulation of h$^+$ which can move toward OH$^-$ adsorbed and produce OH$^-$. To recover its oxidation state Mn$^{3+}$ or Mn$^{4+}$, the capture e$^-$ are transfer toward H$^+$ adsorbed on the surface and leading to the formation of H$_2$, analogously as when is employed an organic pollutant as sacrificial molecule for the H$_2$ evolution [51,52]. Recently, we have published a report confirming the presence of the oxidation states Mn$^{4+}$, Mn$^{3+}$ and Mn$^{4+}$ in ZAMn1 sample dried, reconstructed and recovered after photocatalytic reaction [53]. The results confirmed the presence of a mixture of oxidation states and the optimal content of Mn closed to 1% molar ratio. In both mechanisms, for ZA2 and ZAMn1 samples, the capture of photogenerated charges can be used to improve the charges separation independently of the contents of Mn$^{2+}$, Mn$^{3+}$ or Mn$^{4+}$ which favors the OH$^-$ generation to degrade the phenol molecule.

### 3.10. FTIR analysis of the solid recovered after photoreaction

In order to confirm phenol elimination by degradation and not by a possible adsorption on the LDH surface produced by the radiation, an analysis of the recovered samples after the photocatalytic test was performed by FTIR spectroscopy. In Fig. 11, the spectrum of ZA2 + phenol corresponds to a mechanical mixture of 30.0 ± 0.1 mg of phenol with 200.0 ± 0.1 mg of ZA2 dried at 90 °C. The spectrum showed two characteristic bands of phenol (reference), which are assigned to C=C vibrations of the aromatic ring (1499 and 1474 ± 2 cm$^{-1}$) and vibrations of the OH group (1370 ± 2 cm$^{-1}$). In the spectrum of the recovered samples, the phenol vibration bands disappeared indicating the non-adsorption of phenol on the LDH and the phenol elimination. This confirms that the results showed in Figs. 6, 7 and 9 really corresponds to the photocatalytic elimination of phenol by the LDH materials. Also, the dried and annealed samples are included in Fig. 11 denoting that the identified vibra-

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Table 4

Kinetic rate constant obtained for the photocatalytic degradation of phenol 30 ppm (0.3187 ± 0.0001 mM) with and without O$_2$ and degradation percent after 5 h of radiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_0$ (±0.0002 mmol L$^{-1}$ h$^{-1}$)</th>
<th>$\tau$ (min)</th>
<th>% Degraded (±1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA2</td>
<td>0.0508 ± 0.0014</td>
<td>1.2</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>ZAMn1</td>
<td>0.0603 ± 0.0015</td>
<td>1.3</td>
<td>70 ± 1</td>
</tr>
</tbody>
</table>

Fig. 5. Photocatalytic evaluation in the phenol degradation with O$_2$ source of ZA2 and ZAMn1 dried at 100 °C.
Fig. 6. Photocatalytic degradation of phenol at different times using ZA2 and ZAMn1 LDH materials under UV light. Degradation profiles with O2 (a and c) and without O2 (b and d).

Fig. 7. The activity of ZA2 and ZAMn1 obtained for the phenol degradation with and without a source of O2.

4. Conclusions

The synthesis of Mn doped-ZnAl LDH by the co-precipitation method was accomplished and confirmed by XRD results. The experimental molar ratio of the samples determined by EDS and AAS is close to the nominal ratio. The incorporation of Mn in the LDH materials increases the adsorption capacity in the UV region. The weak absorption bands in the visible region indicates the presence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ in the Mn doped-ZnAl LDH. The proposed mechanism for the photocatalytic reaction with ZnAl and Mn-doped ZnAl LDH materials indicates that phenol degradation is produced by OH$. This investigation showed that the photodegradation of phenol can be carried out in anaerobic conditions or without an O2 source, since apparently the O2 is not an efficient electron scavenger on ZnAl LDH materials. The Mn effect in the photocatalytic degradation of phenol with LDH materials is notably marked in aerobic conditions; however Mn increases the photocatalytic activity in both medium, aerobic and anaerobic. The mineralization is improved with the Mn doping in LDH materials and is better in aerobic conditions. Aerobic conditions have not influence in the photocatalytic activity of LDH material and the decrease of the activity under these conditions can be due to the influence of the O2 source into the photocatalytic system as it can be an inefficient distribution of the powder particles in the reactor due to the air bubbling. Also it is probably that the presence...
**Fig. 8.** Fluorescence spectra of the probe molecule employed in the detection of OH• generate by the HDL materials without air bubbling.

**Fig. 9.** The phenol mineralization analysis followed by the total organic carbon (TOC) measured as a function of reaction time.

**Fig. 10.** The mechanism proposed for the photocatalytic degradation of phenol with the ZAMn1 LDH. Mn^{n⁺} (n = 2,3,4) acts as hole trap in Mn²⁺, Mn³⁺ oxidation state or as electron trap in Mn⁴⁺, Mn⁵⁺ oxidation state that produce an increase of charge separation and then the production of OH•.
of O₂ can produce a competition for the adsorption sites with protons in aqueous medium decreasing the electron transfer from the photocatalyst.

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References