Degradation of *p*-Chlorophenol by Advanced Oxidation Processes

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The aim of this paper was to assess the mineralization degree of p-chlorophenol by using photo-Fenton and heterogeneous photocatalytic processes (photocatalysts based on LDH_S - layered double hydroxides). The degradation of p-chlorophenol was assessed by measuring TOC values for samples taken at various intervals. As part of the photo-Fenton method, after 60 min, the mineralization degree was 63.5% under given working conditions. The degradation of p-chlorophenol by heterogeneous photocatalysis set off the beneficial role of sonication in the synthesis of layered double hydroxide-supported photocatalytic systems. The mineralization degrees as resulted from experiments showed that the increase of sonication and stirring times (as part of the conventional method) was not justifiable beyond 60 min. Moreover, the experiments emphasized the role of hydrogen peroxide on the efficiency of heterogeneous photocatalytic degradation. Based on literature, which stated that the mineralization process of organic compounds followed pseudo-first-order kinetics, and the obtained experimental data, the apparent mineralization constants were assessed for all sets of resulted kinetic data.

Keywords: p-chlorophenol, mineralization degree, photo-Fenton, heterogeneous photocatalysis

Statistics within the last years pointed towards the presence of new xenobiotic substances in waters as a consequence of various manufacturing processes. Most of these substances are considered as a priority as they are harmful organic pollutants with not fully known noxious effects. For example, phenolic compounds are common persistent organic contaminants, which show low biodegradability, posing serious risks to the environment once discharged into natural waters. The persistent character of chlorophenols is determined by the stability of C-Cl bond, which is also responsible for the toxicity of these compounds [1,2]. The incapacity of the conventional wastewater treatment techniques to comply with the standards regarding harmful pollutants in waters has increased the need to develop new effective treatment methods. The advanced oxidation processes are considered as a feasible alternative for dealing with contaminated waters with chemicals that are resistant to conventional biologic treatment and also for the treatment and disinfection of potable water [3, 4].

The Fenton method has been studied for its prospective applications in unmanageable wastewater treatment [5-7]. The efficiency of this process is traditionally thought to be due to the generation of hydroxyl radical ($HO^{\cdot}$), which is of a high oxidation potential and can mineralize the organic compounds to water and carbon dioxide. Fenton reaction rates are significantly increased by irradiation with UV/visible light [8-10].

During Fenton process, Fe^{3+} ions build up within the system, depletion of Fe^{2+} ions occurs and the reaction is practically stopped. The photo-regeneration mechanism of ferrous ions by photo-reduction of ferric ions (photo-Fenton method) is based on the following reaction [10]:

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet} \qquad (1)$$

The generated ferrous ions react with H_2O_2 forming $HO^{\cdot}$ radicals and the cycle is repeated.

Over the last few years, the tendency has been to carry out chemical oxidation in the presence of a catalyst that serves as a generator of hydroxyl radicals. Heterogeneous photocatalytic process consists in using UV radiation to photo-excite a semiconductor catalyst in the presence of oxygen [11-13].

The photo-catalytic activity of semiconductors is based on generating electron-positive hole pairs, e^-/h^+, by photon irradiation, hí, of higher energy than the gap band, E_g.

The reactions that describe catalytic heterogeneous processes are as follows [14]:

$$e^- + O_{2\,ads} \rightarrow O_2^- \qquad (2)$$

$$O_2^- + e^- + 2H^+ \rightarrow H_2O_2\,. \qquad (3)$$

$$H_2O_2 + e^- \rightarrow HO^- + HO^{\cdot} \qquad (4)$$

$$h^+ + HO^-_{ads} \rightarrow HO^{\cdot} \qquad (5)$$

$$HO^{\cdot} + RH_{ads} \rightarrow R^{\cdot} + H_2O \qquad (6)$$

$$R^{\cdot} + O_{2\,ads} \rightarrow ROO^{\cdot} \qquad (7)$$

Layered double hydroxides, also known as anionic clays or hydrotalcite-like compounds, have received an increased interest over the last years due to their potential applications as precursors for catalysts. These materials originate from the isomorphous substitution of divalent cations, such as Mg^{2+}, by trivalent cations, such as Al^{3+}, in a brucite-like structure. Both Mg^{2+} and Al^{3+} can be replaced by other di- or trivalent cations giving rise to a wide variety of LDHs having the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]\cdot(A^{n-}_{x/n})\cdot mH_2O$, where M^{2+} and M^{3+} are the divalent and trivalent cations, respectively, and A^{n-} the interlayer anions. Ultrasounds have attracted much attention in the synthesis of inorganic and organic materials, owing to its specific effects on material processing, such as rapid movement of fluids due to the variation of sonic pressure or, formation and collapse of microbubbles (cavitation), creating localized high-temperature and high-pressure conditions [15]. Therefore, the synthesis of LDHs by using sonication can lead to increased catalytic activity due to changes within surface composition of the catalyst.

To develop wastewater treatment technologies based on advanced oxidation processes, it is necessary to set up the conditions that provide advanced mineralization of organic pollutants and formation of harmless final products (CO_2 and H_2O).

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This paper dealt with p-chlorophenol (p-CP) mineralization by photo-Fenton method as compared to heterogeneous photo-catalysis, when new catalysts with layered double hydroxides-like structure (Zn/Al-LDH$_S$) were used. The apparent mineralization constants were determined based on experimental data.

Experimental part

Synthesis of LDH$_S$ - photocatalysts

Preparation of reaction mixtures

The reaction mixtures were prepared based on the co-precipitation at constant *p*H method, described by Cavani et al. [16]. Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_20$) and aluminium nitrate ($Al(NO_3)_3 \cdot 9H_20$) were dissolved in 250 mL distilled water. The mole ratio of the divalent and trivalent metal ions (i.e., Zn^{2+}/Al^{3+}) was set to 3 and the total concentration of metal ions was set to 1M. The synthesis was carried out by slow addition of mixed metal nitrate solution to Na_2CO_3 (2 mM) solution under magnetic stirring at room temperature for 1 h. During synthesis the *p*H was kept constant at 7.5 by adding appropriate volumes of 2M NaOH solution. The reaction mixtures prepared in this way were used as starting slurries for the following syntheses of LDHs.

Syntheses under sonication

Sonic energy was provided by an ultrasonicator (Branson Sonic Power Co., Model 3510E-MTH, output level of 100W) that generated 42 kHz ultrasound waves. Reaction mixtures were exposed to sonication for periods ranging from 30 to 90 min under normal atmospheric conditions without any additional experimental control. Due to the input of sonic energy, the temperature of the reaction mixtures typically increased to about 60° C in 30 min. The resulting catalysts were denoted as S1, S2 and S3.

Syntheses without sonication (conventional method)

As part of this method, 50 mL of reaction mixtures were aged for 30 and 90 min, respectively, under magnetic stirring and heated at 60° C in a temperature-controlled oil bath. The resulting catalysts were denoted as S4 and S5.

All synthesized LDHs were washed with distilled water and dried at 60°C for 12 h.

p- Chlorophenol degradation

p- Chlorophenol degradation by photo-Fenton method

Photo-Fenton degradation of p-CP was carried out in a thermostatic cylindrical reactor with a total volume of 1 L. The reactor was provided with two openings on the top, one as gas vent and the other one for taking samples. One UV immersion lamp (12 W, 254 nm) from Heraeus was placed in the centre of the cylindrical reactor. The temperature was controlled to 25ÚC during the experiments. Fe^{2+} solution was added onto p-CP solution. As soon as hydrogen peroxide was added, the UV lamp was turned on and, at given intervals, aliquots were withdrawn and analysed for the total organic carbon content.

p- Chlorophenol degradation in the presence of Zn/Al-LDH$_S$ photocatalysts

Heterogenous photocatalytic degradation runs were carried out in the experimental setup used for p-CP degradation by photo-Fenton method. For all experiments, p-CP and peroxide hydrogen concentrations were $20\ mg \cdot L^{-1}$ and 5 mM, respectively. In addition, constant stirring provided good dispersion of the catalysts. Before reaction, the suspension containing $0.25\ g \cdot L^{-1}$ photo-catalyst was stirred in dark for 30 min to establish the adsorption/desorption equilibrium between pollutant and catalyst surface. Then the reaction was initiated by turning on the UV lamp and H_2O_2 was added immediately to p-CP solution.

Doubly distilled water was used throughout this study. Hydrogen peroxide excess was removed by adding Na_2SO_3, p.a.

The degradation of p-chlorophenol was assessed by measuring TOC values for samples taken at various intervals during process. The device was TOC Shimadzu – V_{cpn}.

The mineralization degree, X_{TOC}, at various times of the oxidation process was calculated by using the following equation:

$$X_{TOC} = \left(\left(TOC_0 - TOC_\tau\right)/TOC_0\right) \cdot 100 \qquad (8)$$

where:

TOC_0 – initial total organic carbon, $mg\ L^{-1}$;

$TOC_{ó}$ - total organic carbon, at π time, $mg\ L^{-1}$.

Results and discussion

p- Chlorophenol degradation by photo-Fenton method

Photo-Fenton degradation of p-CP was carried out under the following working conditions: p-CP initial concentration: $20\ mg \cdot L^{-1}$; 5 mM H_2O_2; 0,125 mM Fe^{2+}, molar ratio $[H_2O_2]/[Fe^{2+}] = 40$.

Based on literature and the present experimental data, it was noticed that the mineralization process of organic compounds by advanced oxidation processes followed pseudo-first-order kinetics; the rate constant, $k_{ap,TOC}$, can be determined in accordance with the following equation [6]:

$$\ln\left(TOC_0/TOC\right) = -\ln\left(1 - X_{TOC}\right) = k_{ap,TOC} \cdot \tau \qquad (9)$$

Figure 1 shows the mineralization degrees versus time and the linearization that was used to calculate the rate constant of the mineralization process, $k_{ap, TOC}$.

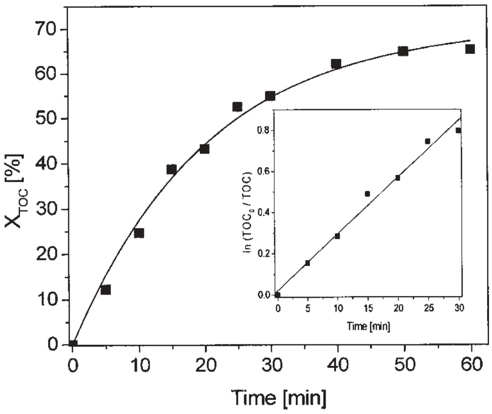

Fig.1. p-chlorophenol mineralization degree vs. time by photo-Fenton method. Working conditions: 5 mM H_2O_2; 0,125 mM Fe^{2+}; $[H_2O_2]/[Fe^{2+}] = 40$; Inset: linearization of eq. (2)

After 60 min, the mineralization degree was 65.3%. The calculated rate constant of the mineralization process was $4.58 \cdot 10^{-4}\ s^{-1}$.

p- Chlorophenol degradation in the presence of Zn/Al-LDH$_S$ photocatalysts

For these experiments two types of photocatalysts were used: S1, S2 and S3 that were synthesized under sonication for 30, 60 and 90 min., respectively and S4, S5 that were synthesized by the conventional method, under magnetic stirring for 60 and 90 min., respectively.

To compare the photo-oxidative effect with the result from p-Chlorophenol degradation by photo-Fenton

Table 1

APPARENT MINERALIZATION CONSTANTS

Parameter	Samples				
	S1	S2	S3	S4	S5
$k_{ap,TOC}$, s^{-1}	$0.92 \cdot 10^{-4}$	$1.22 \cdot 10^{-4}$	$1.11 \cdot 10^{-4}$	$0.77 \cdot 10^{-4}$	$0.79 \cdot 10^{-4}$

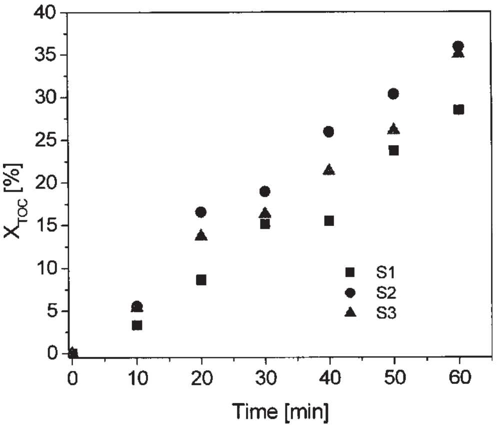

Fig. 2. Comparative evolution of p-chlorophenol mineralization degrees in the presence of S1-S3 catalysts: $C_{p\text{-}CP}$=20 mg·L^{-1}; time for equilibrium to be established -30 min; 5 mM H_2O_2

method, this was monitored for 60 min only, the concentration of catalysts was 0.25 g·L^{-1}.

The photo-degradation experiments by using catalysts synthesized under sonication conditions allowed the calculation of mineralization degree, X_{TOC}. Figure 2 shows mineralization degree vs. time for S1, S2, S3 catalysts.

One observation is that after 60 min of photo-catalysis, the mineralization degrees corresponding to S2 and S3 samples were very close (35.87% for S2 sample and 35.00% for S3 sample) indicating that further sonication up to 90 min was not needed. The mineralization degree was lower (only 28.4% after 60 min) in the presence of S1 sample, which was synthesized under sonication for 30 min. The increase of sonication from 30 to 60 min determined the increase of p-chlorophenol mineralization degree by 7% (35.87%). The absence of plateaux in figure 2 indicated that p-chlorophenol mineralization process was not completed under the given working conditions after 60 min. Higher photocatalytical degradation times would have allowed higher mineralization degrees. In addition, the increase of catalyst concentration might cause significant increase of the mineralization degree.

For the conventionally synthesized catalysts, under magnetic stirring for 60 min (S4 sample) and 90 min (S5 sample), the evolution of mineralization degree vs. time is shown in figure 3.

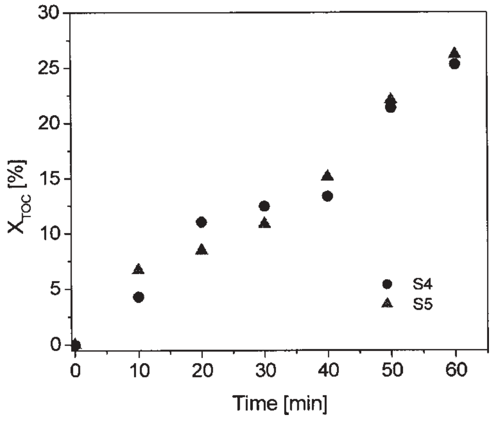

Fig. 3. Comparative evolution of p-chlorophenol mineralization degrees in the presence of S4 and S5 catalysts: $C_{p\text{-}CP}$=20 mg·L^{-1}; time for equilibrium to be established: 30 min; 5 mM H_2O_2

The behaviour of the two samples in the mineralization process was similar. After 60 min photo-catalysis, the mineralization degrees were 25.3% for S4 sample and 26.2% for S5 sample. This finding showed that the increase of aging from 60 to 90 minutes was not necessary as part of synthesis. The absence of plateaux on X_{TOC} vs. time plots indicated that the maximum mineralization degree was not achieved and thus the increase of duration for the mineralization process would have allowed higher mineralization degrees. By comparing the mineralization degrees for S2 - S3 samples as against those for S4 - S5 samples, it was clear that sonication had a beneficial effect on the behaviour of the synthesized photo-catalytic systems used for p-CP degradation and it could be justified as a synthesis method.

Table 1 shows the apparent mineralization constants that were calculated from experimental data based on equation 9.

Although the magnitude order of rate constants was the same for all samples, the mineralization constants of the conventionally synthesised samples, S4 and S5, were lower than those for S1, S2 and S3 samples, which were synthesised under sonication. Thus, as far as kinetics was concerned, the use of sonication could be justified as part of synthesis of LDH catalysts.

To determine the influence of hydrogen peroxide upon mineralization process, two sets of kinetic experiments were carried out on S4 sample in the absence and presence of H_2O_2. The results are shown in figure 4.

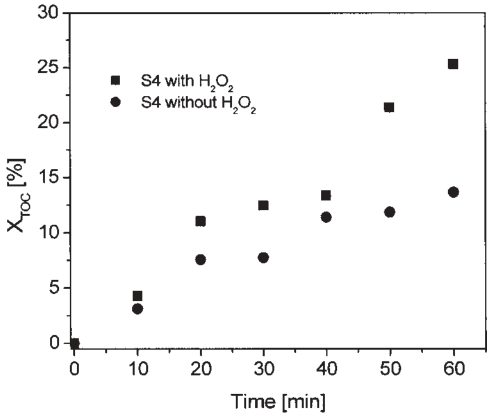

Fig. 4. Evolution of *p*-chlorophenol mineralization degrees in the presence of S4 catalyst and in the absence and presence of H_2O_2: $C_{p\text{-}CP}$=20 mg·L^{-1}; time for equilibrium to be established: 30 min.

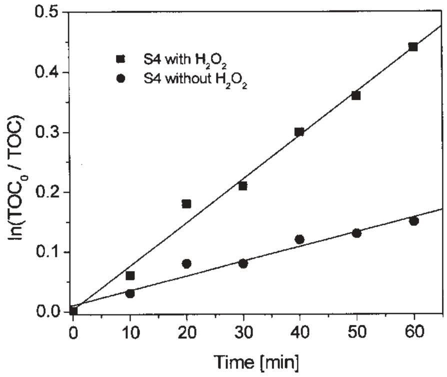

Fig. 5. Determination of the apparent mineralization constants for *p*-chlorophenol degradation (20 mg·L^{-1}) in the absence and presence of H_2O_2.

After 60 min, the mineralization degrees were 13.6% and 25.3% in the absence and presence of H_2O_2, respectively. Practically, at 5 mM H_2O_2 the mineralization degree doubled. The same finding resulted from the kinetic interpretation of the experimental data (fig. 5). The apparent mineralization constants were $0.77 \cdot 10^{-4}\ s^{-1}$ and $0.41 \cdot 10^{-4}\ s^{-1}$ in the presence and absence of H_2O_2, respectively.

Conclusion

This paper assessed the mineralization of *p*-chlorophenol as part of photo-Fenton and heterogeneous photo-catalytic methods, by using new catalysts based on layered double hydroxides, Zn/Al-LDHs.

The efficiency of homogeneous photo-catalysis (photo-Fenton method) was demonstrated by the high mineralization degree (65.3%) that resulted after 60 min photodegradation under the following working conditions: p-CP initial concentration 20 $mg \cdot L^{-1}$; 5 mM H_2O_2; molar ratio $[H_2O_2]/[Fe^{2+}] = 40$.

To study p-chlorophenol mineralization by heterogeneous photo-catalysis, two types of LDH_S photocatalysts were used: S1, S2 and S3 that were synthesized under sonication for 30, 60 and 90 min, respectively and S4, S5 that were synthesized by the conventional method, under magnetic stirring for 60 and 90 min, respectively. After 60 min, the mineralization degrees for S2 and S3 samples were very close; the increase of sonication over 60 min was not justifiable.

The mineralization degrees in the presence of S2 and S3 catalysts (about 36%) were sensibly higher than those for S4 and S5 catalysts (about 25 - 26%). This finding supported substitution of the conventional method (magnetic stirring) for sonication.

The study of the influence of hydrogen peroxide on the efficiency of heterogeneous photocatalytic process showed that the mineralization degree practically doubled after 60 min.

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