I-O-5. ADVANCED DEGRADATION OF 4-CHLOROANILINE FROM WATER IN UV/TiO_2/H_2O_2 SYSTEM

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Abstract

Chlorinated aniline belongs to the anilines family, which are common pollutants, being frequently used as intermediates for the chemical synthesis in polymer, rubber, pesticide, pharmaceutical and dye industries. Due to their high toxicity and persistence in aquatic environments, they are classified by European Water Framework Directive 2000/60/EC as the priority pollutants and are strictly regulated in EU countries. Since their presence in water bodies is risky for human health and aquatic life, developing powerful, modern treatment methods like advanced oxidation processes (AOP`s) are needed in order to assures pollution mitigation. If properly applied, TiO_2-based photocatalysis can be regarded as an environmentally friendly and cheap treatment option.
In the present study, solutions with (0.14-14.2) x 10^{-4} M 4-CLA content were photo-oxidized in the following working conditions: pH=4; [TiO_2] = 50-500 mg/L; [H_2O_2] = (0.1-10)x10^{-3}M; τ_{irr} = 5 – 180 minutes.
Pollutant degradation pathway by three possible routes was proposed, according to organic intermediates identified by gas-chromatography coupled with mass spectrometry-screening method. The first route consists of OH radical attack on target pollutants with amino group substitution and 4-chlorophenol (4-CP) formation. The second degradation route represents OH radical attack on aromatic ring by hydrogen abstraction with aniline-radical formation, that is subsequently stabilized by dimerization to 4,4'-dichloroazobenzene (DCAB), which is further oxidized to 4-chloronitrobenzene (4-NCB). The third route of pollutant degradation takes place by a heterolytic mechanism consisting of hydrogen and chloride atoms release as HCl, and aniline (A) formation, which is oxidized to 4-aminophenol (4-AP) by OH radicals addition to the aromatic ring. The secondary intermediates (4-CP, 4-AP, 4-NCB) are subsequently hydroxilated to hydroquinone that is also oxidized to benzoquinone leading to carboxylic acids by its ring cleavage under OH radical attack.
Based on experimental results can be concluded that after 90 minutes of irradiation, 4-CLA was complete degraded. Mineralization yields of organic chlorine and nitrogen were around 81% and 85%, respectively for prolonged irradiation (180 min.). These results are consistent with presented degradation pathway that proposed as intermediates, aromatic compound like 4-CP, A, 4-NCB and 4-AP. The presence of these intermediates in irradiated samples is also supported by 82.4% TOC removal yield obtained at prolonged irradiation.

Keywords: photocatalysis, UV/TiO_2/H_2O_2 system, 4-chloroaniline degradation

1. Introduction

There are few studies in the literature on chloroaniline degradation through AOP`s. Mailhot et al. 2004 [1] investigated the iron (III)-photoinduced degradation of this pollutant in acidic aqueous solution. The degradation mechanism is initiated by OH radicals generated by photoexcitation of $Fe(OH)^{2+}$. The major intermediates detected are 4-CLA radical cations and OH radical aducts. The decay of radical cations is accelerated by the Fe(III) presence, suggesting the possibility of an oxidative interaction leading to p-benzoquinone imine, which plays a key role in the formation of major oligomeric species detected in the photoproducts study. Hussain et al. 2012 [2] investigated the degradation of 4-CLA by persulfate activated with zero-valent iron and obtained complete pollutant degradation in 12 minutes at pH=4 and $50^{\circ}C$ at. Sarasa et al. 2002 [3] treated 4-CLA aqueous solutions with ozone at basic pH and identified 4-chloronitrobenzene, 4,4`-dichloroazobenzene and 4-chloro-2-pyridine-carboxilic acid as main oxidation by-products, which are less toxic than parent pollutant.

Over the past 20 years, numerous publications recommended semiconductor photocatalysis as an effective method for the removal of toxic pollutants from contaminated waters [4-6]. If properly optimized, TiO_2-based photocatalysis is an environmentally friendly and cheap treatment option since the technology could be carried out by solar energy. The heterogeneous photocatalysis involving TiO_2 was successfully applied for degradation of several aniline derivatives under various experimental conditions [7-9].

By irradiation of a semiconductor with wavelengths of energy *h*_≥*E*g (band gap), an electron e^- is promoted in the conduction band (CB), a positive hole h^+ remaining in the valence band (VB); both the electron and the hole migrate towards the particle surface. After the absorption of UV light corresponding to *E*g = 3.2 eV in the case of TiO_2 (anatase), the primary processes are starting and the oxidizing species $^{\bullet}OH$ and $O_2^{\bullet -}$ are generated [10-12]. These radicals are immediately involved in secondary processes in which the pollutant RH adsorbed on the TiO_2 surface is oxidized. The use of inorganic oxidants in UV/TiO_2 system could increase the degradation efficiency either by inhibiting electron-hole pair recombination through scavenging conduction-band electrons at the surface of photocatalyst or offering additional oxygen atom as an electron acceptor to form the superoxide radical ion or reactive radical intermediates [5,8,13].

In the present study, 4-CLA photooxidation in $UV/TiO_2/H_2O_2$ system has been examined. A wide range of H_2O_2 dosage was studied and degradation pathway of 4-CLA was proposed according to identified organic intermediates.

2. Experimental

The following reagents were used**:** 4- chloroaniline (Aldrich) of 99% purity; TiO_2 (Merck) as anatase form; hydrogen peroxide solution (Merck) reagent-grade 30wt. % solution; Na_2SO_3 (Merck) 98wt.% purity used for the removal of unconsumed H_2O_2 from irradiated samples; KI (Merck) 99wt. % purity and

$Na_2S_2O_3$ (Fluka) 0.1N used for iodometric determination of H_2O_2; n-hexane and CH_2Cl_2 (UniSolv) GC grade was used for 4-CLA and its degradation intermediates extraction from aqueous samples.

The photodegradation experiments were carried out in a laboratory scale UV reactor - Heraeus system using a medium-pressure mercury lamp which emits in the UV – VIS range (λ = 300-500 nm). The lamp equipped with a quartz water cooling jacket is immersed in the center of the reactor containing the pollutant solution. The photon's flow of the emitted radiations was determined by ferrioxalate actinometry and a value $I_0 = 6x10^{-6}$einstein s^{-1} was found. Solution with (0.14-14.2) x 10^{-4} M 4-CLA content was photo-oxidized in the following working conditions: pH=4; $[TiO_2]$ = 50-500 mg/L; $[H_2O_2]$ = (0.1-10) x 10^{-3}M; τ_{irr} = 5 – 180 minutes.

In order to establish the yields of 4-CLA degradation, organic carbon, chlorine and nitrogen mineralization, the initial and irradiated samples were analyzed for 4-CLA, total organic carbon, Cl^-, $NH_4^+$and NO_3^- concentrations by gas-chromatography (GC), total organic carbon (TOC) and ion chromatography (IC) respectively. For irradiated samples, the GC and IC analyses were performed after sample pretreatment by dosage of Na_2SO_3 in order to remove the unconsumed oxidizing agent (concentration determined by iodometric method).

4-CLA concentration was analyzed by GC-MS using an Agilent 7890A gas chromatograph coupled with an Agilent 240 Ion Trap Mass Detector. TOC was determined by using an MULTI N/C 3000 analyzer (Analytik Jena). Mineralization products (Cl^-, NH_4^+, NO_3^-) were determined using a Dionex ICS-3000 Ion Chromatograph, with separate anions and cations columns and suppressed conductivity detectors. GC/MS, screening method was applied for qualitative identification of 4-CLA degradation intermediates solved in CH_2Cl_2 by coupling Agilent 6890N with DB5MS capillary column to mass spectrometer 5975 BinterXL with electron ionization (70 eV). All experiments were duplicated to assure data quality.

3. Results and discussions

The experimental results obtained during the photocatalytic degradation of 4-CLA in $UV/TiO_2/H_2O_2$ at pH=4 are presented in Fig.1. In the pH selection was taken into consideration that H_2O_2 becomes highly unstable and itself-decomposition occurs in alkaline medium. In this context H_2O_2 molecule loss its characteristic as oxidant and mostly important is not acting as OH radicals generation source, due to its rapidly brake down into water and oxygen:

$$2H_2O_2 \rightarrow H_2O + O_2 \qquad (1)$$

The pollutant degradation reaction rate was therefore reduced significantly at higher pH levels as was also shown by Chu et al. 2007 [5] in the case of 2-CLA photocatalysis in $UV/TiO_2/H_2O_2$ system.

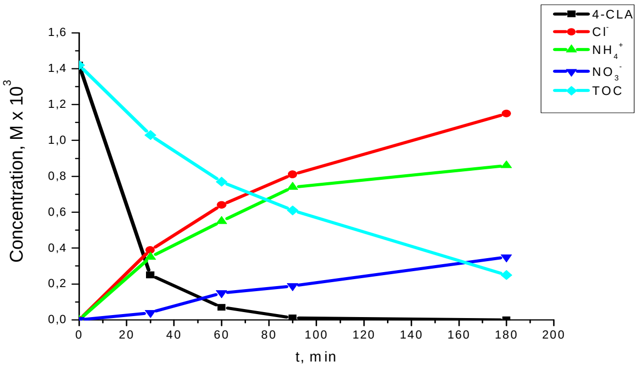

Fig.1. Time profiles of 4-CLA and its degradation products: $[4\text{-CLA}]_0 = 1.42 \times 10^{-3}$M, $[TiO_2]$=150 mg/L, $[H_2O_2]=1 \times 10^{-4}$ M

The experimental data indicated that after 90 minutes of irradiation, 4-CLA was complete degraded. Mineralization yields of organic chlorine and nitrogen were around 81% and 85%, respectively for prolonged irradiation (180 min). In the first 90 min. organic nitrogen is released as NH_4^+ ions which are further oxidized to NO_2^-. Such results suggest that both organic chlorine and nitrogen are still contained by degradation intermediates which are more resistant to oxidation. The presence of these intermediates in irradiated samples is supported by 82.4% TOC removal yield obtained at prolonged irradiation. The kinetic curves (Fig.1) were linearized by the pseudo-first-order kinetic equation in respect to 4-CLA degradation as well as to the mineralization products formation. From the slopes of the linear plots were calculated the pseudo-first-order rate constants k_I with the following values: $k_I^{4\text{-CLA}} = 8.71 \times 10^{-4} s^{-1}$; $k_I^{TOC} = 1.59 \times 10^{-4}$ s^{-1} ; $k_I^{Cl-} = 1.52 \times 10^{-4}$ s^{-1}; $k_I^{NH4+} = 1.35 \times 10^{-4}$ s^{-1}; $k_I^{NO3-} = 0.26 \times 10^{-4}$ s^{-1}

Effect of catalyst dose

Experiments were carried out at pH=4 with different dose of TiO_2 at 1.42×10^{-3}M constant pollutant concentration, without addition of oxidant. In order to prevent excessive photocatalyst dose it was studied the influence of this parameter on the pollutant photodegradation efficiency. Fig.2. illustrates the effect of various TiO_2 concentration (50-500 mg/L) on the pollutant initial degradation rate (v_0), calculated for the first 5 minutes of irradiation.

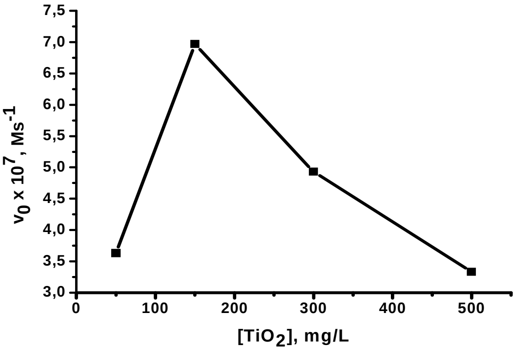

Fig.2. Concentration of TiO_2 versus 4-CLA initial degradation rate (v_0): pH=4; $[4\text{-CLA}]_0 = 1.42 \times 10^{-3}$M; 5 minutes irradiation.

The obtained values indicated that between 50-150 mg/L TiO_2, v_0 increased with TiO_2 amount due to the number of active sites of the catalyst increased too. At higher concentration in the range of 150-500 mg/L, v_0 decreased. The decreasing of initial pollutant degradation rate may be explain by excess catalyst addition, that makes the solution more turbid and retard light penetration. The addition of surplus catalyst also results in the deactivation of photoexcited TiO_2 molecules by collision with ground state molecules. Therefore we selected 150 mg/L TiO_2 as optimum catalyst concentration which shows the maximum value of initial pollutant degradation rate (v_0=6.096 x 10^{-7} Ms^{-1}). For this catalyst concentration, the pollutant degradation and organic chlorine mineralization efficiencies after 60 minutes irradiation were 85,5% and 27,9%, respectively.

Effect of H_2O_2 addition

H_2O_2, as electron acceptor, was added into 4-CLA solution in order to improve pollutant degradation efficiency by enhancing hydroxyl radical concentration and also inhibiting electron/hole pair recombination. Thus, experiments were conducted at various concentrations of H_2O_2 between $1x10^{-4}$-$1x10^{-2}$M, at fixed pH=4, TiO_2 dose 150mg/L and pollutant concentration $1.42x10^{-3}$M. Pollutant degradation and organic chlorine mineralization in absence or presence of various H_2O_2 concentrations follow pseudo-first order kinetics. The calculated values of rate constants are presented in the following table:

Table1. The influence of H_2O_2 concentration on the pseudo-first-order rate constants of 4-CLA degradation and organic chlorine mineralization

$[H_2O_2]$ x 10^4, M	k_I^{4-CLA} x 10^4, s^{-1}	k_I^{Cl-} x 10^4, s^{-1}
-	5.50	0.88
1	8.71	1.52
10	11.94	1.97
100	11.32	1.96

Increasing H_2O_2 concentration between $1x10^{-4}$- $1x10^{-3}$ M has a positive effect on pollutant degradation, values of k_I^{4-CLA} and k_I^{Cl-} increasing too. Further addition of H_2O_2 does not modify pollutant photocatalytic degradation rate, because, when electron acceptor is overdosed ($1x10^{-2}$ M in the present study), the excess H_2O_2 molecules scavenge the valuable hydroxyl radicals and generate a much weaker hydroperoxyl radicals. These ones can further react with the remaining strong hydroxyl radicals to form oxygen and water. In addition, the pollutant photocatalytic oxidation could be inhibited when the excess H_2O_2 reacts with oxidative holes on catalyst surface [5,14]. Based on obtained experimental results it was found that optimum H_2O_2 concentration is $1x10^{-3}$ M, which assures after 180 minutes irradiation, 99,99% pollutant degradation and 88% organic chlorine mineralization.

Kinetics

The photocatalytic reaction rate of most organic compound is described by pseudo-first order kinetic which is rationalized in terms of the Langmuir-Hinshelwood model, modified to accommodate reaction occurring at a solid/liquid interface [15,16].

$$\frac{1}{r_0}=\frac{1}{k_r}+\frac{1}{k_r K_{ad} c_0} \qquad (2)$$

in which r_0 is 4-CLA initial degradation rate, c_0 is pollutant initial concentration, K_{ad} the equilibrium constant of 4-CLA adsorption on TiO_2 particles and k_r the reaction rate of pollutant oxidation which reflects the limiting reaction rate at maximum coverage for the experimental conditions. In Fig. 3 is plotted the equation (2) at different 4-CLA initial concentrations.

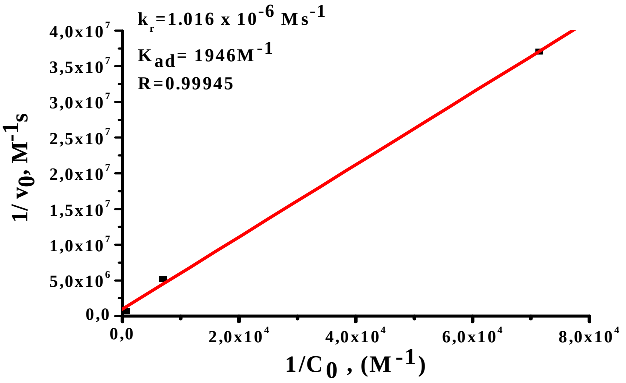

Fig.3 Langmuir-Hinshelwood equation for 4-CLA degradation under $UV/TiO_2/H_2O_2$ process

The linearity obtained shows that the reaction occurs at TiO_2 surface where the pollutant is adsorbed as well as the •OH radicals generated by catalyst UV irradiation. From the intersection of this straight line with the ordinate results $1/k_r$ and the value of the reaction rate is k_r=1.01 x 10^{-6} Ms^{-1}. From the slope of this line we calculated the adsorption equilibrium constant K_{ad} =1237 M^{-1}.

The rate constants k_{4CLA} calculated from the slopes of the typical linear plot characteristic to the pseudo-first-order reaction for various initial pollutant concentrations are presented in the following table:

Table 2 Pseudo-first order rate constant k_{4CLA} of pollutant photocatalytic degradation at different initial concentration:

$[4\text{-}CLA]_0$ x 10^4, M	$k_{4\text{-}CLA}$ x 10^3, s^{-1}
0,14	1,97 ±0,002
1,44	1,75 ±0,002
14,12	1,21 ±0,002

The experimental results revealed decreasing of pseudo-first order rate constants with the increasing of 4-CLA initial concentration. This behavior is due to the competition for •OH radical consumption between the parent pollutant and its degradation byproducts, the last acting as scavengers of radicals.

The identification of organic intermediates and 4-CLA degradation mechanism

Several organic intermediates like aniline (AL), 4-aminophenol (4-AP), 4-chlorophenol (4-CP), 4-chloronitrobenzene (4-CNB), 4,4’-dichloroazobenzene (4,4’DCAB) were identified by GS-MS method, during 4-CLA photocatalytic degradation in UV/TiO_2/H_2O_2 system. In order to obtain information on subsequent intermediates behavior, the influence of irradiation time on their concentrations was investigated. The specific peak of each intermediates from total chromatogram registered for different irradiation time were superposed and obtained results were plotted. Taking into account that peak area of any compound is directly related to its concentration, assessment of concentration versus irradiation time revealed the following information:

- increase of irradiation time leads to 4-CLA and some of its degradation intermediates (4-CP, 4-AP, DCAB) concentrations decrease, emphasizing that these are subsequently involved in other reactions;
- an opposite behavior is registered in the case of A and 4-CNB which are accumulated in the system because are hardly oxidized in the tested working conditions ($[H_2O_2] = 10^{-4}$ M, irradiation time = 30-120 min);
- the evolution of DCAB and 4-CNB concentrations confirmed that the second one is the decomposition product of halogenated diazobenzene derivative;
- 4-AP concentration is almost neglectable compared with 4-CP, after 60 min of irradiation, suggesting that halogenated phenol derivative is hardly degraded; in addition 4-CP concentration is almost constant between 60 and 120 min showing that its generation rate is higher than its subsequently degradation.

Based on previously presented results it was proposed a reaction sequence for the generation of the main intermediates identified during the photocatalytic degradation of 4-CLA, as it is presented in Fig.4.

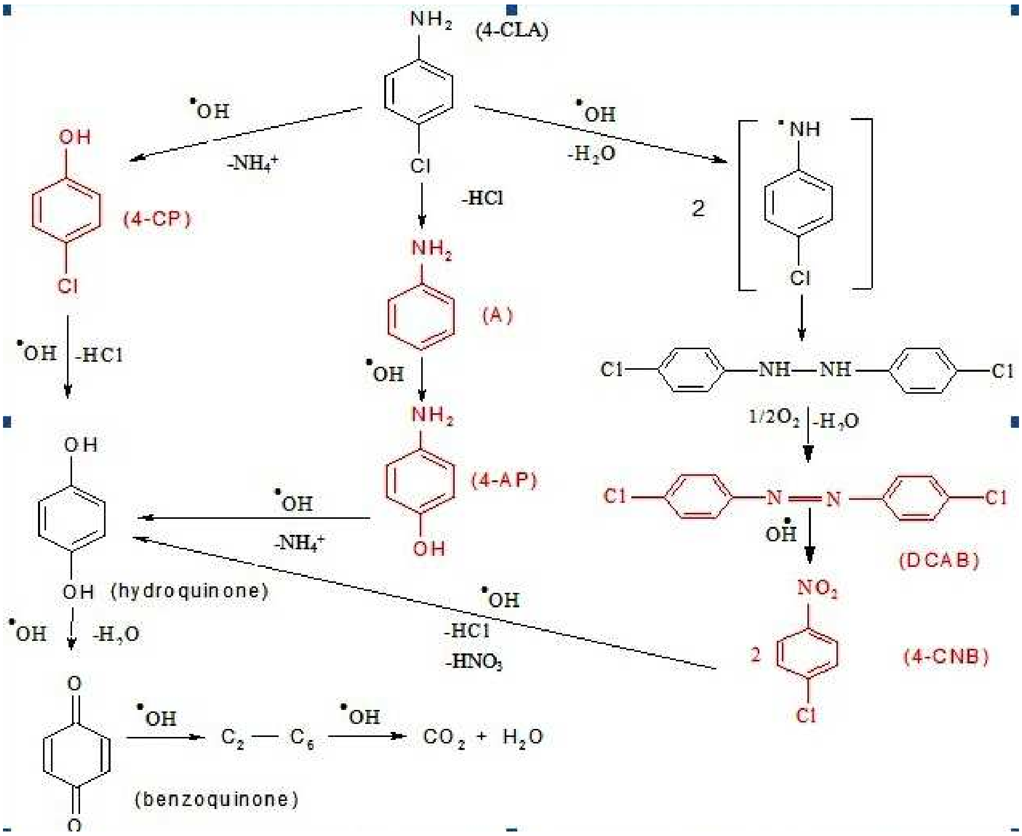

Fig.4. Proposed photocatalytic degradation pathway of 4-CLA

The proposed mechanism pathway showed three possible pollutant degradation routes. The first one consists of OH radical attack on target pollutants with replacement of the amino group and 4-CP formation. The substitution of halogen atom is a difficult reaction because OH radicals and chlorine have similar electronegativity. The OH radical attack on aromatic ring can take place also by hydrogen abstraction with aniline-radical formation, that is subsequently stabilized by dimerization to DCAB as Mathur and Kumar [17] showed. The attack of OH radical on diazo group of DCAB leads to 4-NCB. The third route of pollutant degradation can be dechlorination with intermediate formation of A, that is converted into 4-AP by OH radicals addition to the aromatic ring, in accordance with Canle et al. [7]. The secondary intermediates (4-CP, 4-AP, 4-NCB) are subsequently hydroxilated to hydroquinone [18]. This photoproduct is oxidized also to benzoquinone that leads to C_2-C_6 acids by ring cleavage under OH radical attack. The carboxylic acids are mineralized at prolonged irradiation time. Beside CO_2, final degradation products included also Cl^-, NH_4^+, NO_2^- resulted in different steps of proposed degradation routes, as it is presented in Fig.4. The formation of unchlorinated intermediates like A, 4-AP and hydroquinone are in accordance with experimental results which show the liberation of the organic bound chlorine as HCl, during irradiation. On the other hand our finding that $k_{4\text{-}CLA} > k_{Cl^-}$ demonstrate that Cl^- ions liberation does not take place simultaneously with the attack of •OH radicals on target pollutant, but in a further stage, oxidizing the 4-CP and 4-NCB to hydroquinone. The lower values of k_I^{NO3-} compared with k_I^{Cl-} and k_I^{NH4+} suggest that pollutant degradation route by hydrogen abstraction is less probable to occur.

4. Conclusion

In the degradation of 4-CLA under $UV/TiO_2/H_2O_2$ process, the aromatic intermediates have been detected. The degradation was mainly initiated by OH radicals attack and the pathway was proposed accordingly. Although different intermediates were formed, all of them can be eventually oxidized to benzoquinone, which can be subsequently transform into carboxylic acids through ring cleavage. Ionic products like Cl^-, NH_4^+, NO_3^- are also formed. H_2O_2 dosing was proven useful for further improvement of 4-CLA degradation process. It was found that $1x10^{-3}$ M H_2O_2 concentration assures 99,99% pollutant degradation and 88% organic chlorine mineralization after 180 minutes irradiation,.

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