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Ibuprofen Degradation by a Metal-Free Organic Optoelectronic Synthesized TTA as a Highly Efficient Photocatalyst

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Research Article

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ABSTRACT

There is a growing need to develop new materials for applications in optics, electronics and photocatalytics. Organic molecules play a main role in these advances, through their structural and functional varieties in the conversion of solar energy which is inexhaustible and free to chemical energy. We report in this work a simple and an easy method to synthesis a new organic optoelectronic (donor-acceptor system) (N-(4-(6-(4-aminophenyl)-1, 2, 4, 5-tetrazin-3-yl) phenyl)-N-phenylbenzenamine « TTA») which is composed by the s-tetrazine group was chosen as an acceptor group for its high electron affinity, and the triphenylamine as a donor group for its low ionization potential. The compound was characterized by thermo gravimetric analysis, Fourier transform infrared spectroscopy, UV spectrophotometer and fluorescence photometer. On the basis of UV-visible and fluorescence spectroscopy, the strong absorption and photoluminescence properties were found in visible wavelength region. Furthermore, photocatalytic experiments indicated that the TTA might possess relatively well-done photocatalytic property towards the degradation of IBP in aqueous solution under visible light irradiation. These results indicated that the prepared TTA might work as a potential photo catalyst for treating the organic pollutants efficiently.

INTRODUCTION

Environmental protection has thus become a major economic and political issue. All the countries of the world are concerned with the safeguarding of fresh water resources, either because they lack water, or because they pollute it. The disparity between the needs and the availability of water requires imagining new means of transport and treatment to increase the availability of resources.

Water treatment has always been done in a biological way. Based on the natural self-purification of water, humans then built increasingly sophisticated biological treatment systems. However, that last's stations cannot treat difficultly biodegradable or toxic substances. Currently, due to the small range of *in situ* treatment technologies available for the treatment of effluents containing between 1 and 10 $g.L^{-1}$ of COD, a large quantity of industries cannot treat wastewater properly. Simple and inexpensive solutions are therefore strongly required so that they can fulfill the required conditions [1]. The search for alternative or complementary methods for treating wastewater has led in recent years to the emergence of new technologies. Among these technologies, so-called advanced oxidation (POA) processes such as direct photolysis, UV irradiation in the presence of ozone, Fenton reagent and TiO_2 as a photocatalyst are booming [2]. These technologies are based on the production of non-selective oxidizing reactive species that will allow the oxidation of a large number of organic pollutants. The most widely used oxidant is the hydroxyl radical due to its high reactivity ($E°=2.73$ V) [3]. In a photochemical transformation two cases can arise depending on the nature of the pollutant. Indeed, it can be: Direct: if the pollutant absorbs part of sunlight which will initiate degradation or Induced: if other compounds present in the medium absorb sunlight and intervene in the process of degradation of the pollutant [4].

Different types of materials such as semiconductors, zeolites doped with noble metals, metal complexes etc. have been explored for artificial photosynthesis [5]. A new path is to develop ecological and efficient photocatalysts with structural regularity and synthetic ease provide photoactivity under irradiation in the visible range, the synthesis and uses of novel Charge-Separated (CS) organic compounds have been attractive areas of research within the study of organic photoelectronic materials. Their uses in photocatalytic activities for the degradation of organic compounds were significantly efficient [6]. Among photoactive organic materials family, metal-free organic semiconductors have attracted remarkable attention because of their advantages of unique electron delocalization, flexibility, and proper optoelectronic properties [7,8]. As he has already known that most conjugated organic molecules have a high affinity to absorb visible light and have a very stable character due to the delocalization of electrons on all of the conjugated π bonds because of Intermolecular Charge Transfer (TIC) effects were useful in regulating energy levels and optical band gap [9,10].

S-tetrazines are strongly electron withdrawing groups rich in π bond which have favorable properties of strong light absorption and high photochemical stability [11,12]. They have reported that the introduction of optoelectronic molecules containing strong electron donor units such (triphenylamine) and strong attractor such tetrazine into organic solar cells can improve the absorption of sunlight [13-16]. Recently many efforts are to develop ecological and efficient photocatalysts optoelectronic compounds with their structural regularity and synthetic ease provide a significant supply to respond to photodegradation [17]. Optoelectronic with the aim of combining chemical stability and photoactivity under irradiation in the visible field, this work aims at the design of new materials active in photocatalysis and chemically stable. Recent efforts on photodegradation in wastewater treatment using composite organic photocatalysts obtained by π-π^* interactions as catalysts have been deployed on 7, 7, 8, 8-tetracyanoquinodimethane and perylene tetracarboxylic have shown high efficiency for degradation of phenol under visible light. In this work, an easy and simple method was developed for the synthesis of a metal-free organic optoelectronic molecule (called TTA) consisting of a central tetrazine group and two terminal units of a diphenylamine and aniline group). Tetradecylthioacetic Acid (TTA) has been applied to the photocatalytic degradation in aqueous solution of a pharmaceutical product under visible irradiation light. Intermediates and reactive species for photo degradation of IBP have been studied, which allows us to propose possible mechanisms as well as the use of the combined system with strong oxidants such as hydrogen peroxide that used to improve the efficiency of this support.

MATERIALS AND METHODS

Chemicals

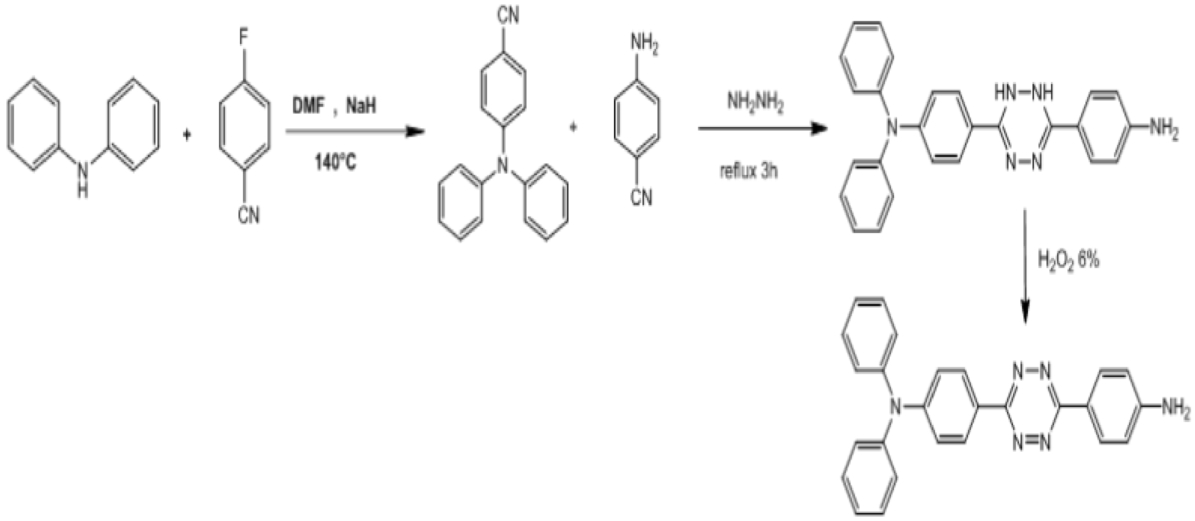
The active principle IBP, 2-(4-(2-methylpropyl) phenyl) propanoic acid, was purchased from a pharmaceutical industry and analyzed by NMR to test its purity prior to use it.

The products used for the synthesis are therefore: diphenylamine, 4-fluorobenzonitrile and DMF. All other reagents were of the purest commercially available grade and used without further purification. The solutions were prepared using ultrapure water. Chloroform (99%), sodium hydroxide (98%), sodium acetate (99%) and sulfuric acid (96%) were supplied by Prolabo. Isopropanol (99.8%) was purchased from Scharlau. Dihydrogénophosphate of sodium (Na_2HPO_4) 99%, Merk. Peroxyde d'hydrogène (H_2O_2) 30%, VWR Prolabo. Acide perchlorique ($HClO_4$) 98%, VWR Prolabo. Hydroxyde of sodium (NaOH) 98%, Carlo Erba Reagent, Acetonitrile 99% grade HPLC, VWR Prolabo.

Chemical synthesis

A simple method was developed for the synthesis of TTA as shown in Figure 1.

Figure 1. Synthesis of TTA.



The synthesis of this compound went through two stages, the first consisted in carrying out the developed of triphenylamine according to the Hartwing-Buchward coupling between triphenylamine and 4-fluorobenzonitrille with a yield of 78%. [18-20], the 2nd consists on the synthesis of dihydrotetrazine where a direct preparation is followed by the action of a mixture of hydrazine hydrate and sulfur [21]. According to the synthetic co-conditions described above: this new way to synthesis of organic materials optoelectronics for energy needs shows a potential characteristics for industrial production in the fields of consumption and conversion of energy by a simple and very efficient method.

Materials characterization

The Raman shift was recorded by using a Bruker Senterra spectrometer with excitation wavelength of 532 nm and power of 0.2 mW. Thermal analysis was carried out on Shimadzu Thermogravimetric Analyzer (TGA) at a heating rate of 10°C .min^{-1} in nitrogen atmosphere. IR samples were prepared by disc obtained from a 200 mg aliquot of the mixed powder (KBr: TTA I=100:1) desiccated for 30 min and the spectra were obtained from Nicolet Magna 550 II FT-IR spectrophotometer in the wavelength range of 4000-400 cm^{-1}. UV/Vis absorption spectroscopy was performed with a Hitachi U-3010 spectrophotometer. For the electrochemical study an electronic assembly: allowing tracing the curves of cyclic voltammetry includes a potentiosat/galvanosates Volta Lab PGZ301 assisted by a computer and measuring cell.

Photocatalytic activity

The reactivity of the optoelectronic material was tested for the degradation of Ibuprofen in aqueous solution. The test was carried out at room temperature using a Pyrex reactor (diameter of 2 cm and a 50 ml capacity), with a cooling water jacket, placed in an elliptical room. The reaction mixture was stirred continuously with a magnetic bar. The tests were carried out in an isothermal reaction system (20 ± 1°C) maintained with a water bath. The sample solution was irradiated with a fluorescent lamp (Philips 15 W TL-D) which emits dominant radiation at 365 nm polychromatic. The distances between the lamp and the wall of the reactor are 10 cm. 5.10^{-5} Mof Ibuprofen was prepared, then 100 mg/L of TTA was added with a magnetic stirrer for 30 min in the dark to establish an adsorption-desorption equilibrium. 4 mL was withdrawn at selected time intervals from the reaction mixture and centrifuged immediately to remove the photocatalyst; the supernatant solution was analyzed by High Liquid Chromatography Performance (HPLC) Shimadzu LC-20C system, equipped with a Supelco HC-C 18 column (5 μm × 4.6 mm). The mobile phase is a mixture of acetonitrile and ultra-pure water with a 60/40 ratio. The flow rate used during the analysis is 1.0 ml min^{-1}. The detection wavelength was set at 222 nm.

RESULTS AND DISCUSSION

Characteristics of Ibuprofen

(2-(4-isobutylphenyl) propanoic acid) named Ibuprofen (IBP) is a No Steroidal Anti-Inflammatory, Antipyretic and Analgesic Steroid (NSAID) which is widely used for the treatment of inflammatory disorders such as rheumatoid arthritis as well as to relieve pain. The chemical and physical properties of an IBP are shown in Table 1.

Table 1. Physico-Chemical properties of IBP.

Chemical properties					Physical properties		
Brute Formula	Molar mass(g/mol)	pka	Wave length(nm)	e(L.mol^{-1}.cm^{-1})	T $_{fusion}$(°C)	Solubility(mg.L^{-1}) 25 °C	Volumic mass(g.cm^{-3})
$C_{18}H_{18}O_2$	206.28	4.52	222	8800	75a77.5	21	0, 2a 0, 6

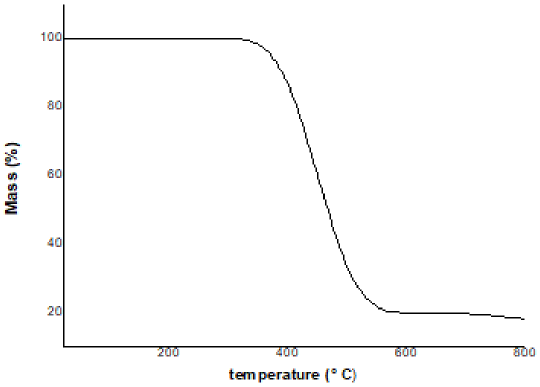
Synthesis and characterization of the organic optoelectronics material TTA

A simple method was developed for the synthesis of TTA as shown in Figure 1. The synthesis of this compound went through two stages; the first consisted in carrying out the synthesis of triphenylamine according to the Hartwing-Buchward coupling between triphenylamine and 4-fluorobenzonitrille with a yield of 78%. The 2nd synthetic step consists of the synthesis of dihydrotetrazine where a direct preparation is followed by the action of a mixture of hydrazine hydrate and sulfur [22]. According to the synthetic co-conditions described above: this new way of synthesizing organic materials optoelectronics for energy needs shows characteristics of a potential for industrial production in the field of energy needs shows characteristics of a potential for industrial production in the fields of consumption and conversion of energy by a simple method and very efficient.

Thermal property, optical absorption, and electrochemical behavior of TTA

The Thermogravimetric Analysis (TGA) curve showed that the compound was stable towards oxygen moisture, and almost insoluble in common organic solvents, such as $CHCl_3$, MeOH, MeCN and DMF (Figure 2).

Figure 2. Thermo gravimetric curve of TTA; the spectrum of TGA has shown that this material is stable up to 500°C while beyond this temperature the molecule decomposes.



To estimate the TGA about TTA the organic optoelectronics compound this last was heated in a temperature range of 20 to 800°C in a nitrogen gas circuit. The weight loss of this material was observed in the range up to 500°C, when the major weight loss could be ascribed to the decomposition of the TTA (observed, 79.83%; calculated, 80 %) implying that the TTA molecules have high thermal stability until 500°C. The UV-visible spectra were recorded from 5 × 10^{-4} $mol.L^{-1}$ concentration solutions in DMSO. The fluorescence spectrum of TTA was carried out on a more dilute solution with a concentration of 5 × 10^{-5} $mol.L^{-1}$. The absorption spectra (Figure 3) of s-tetrazine derivatives both showed two absorption bands characteristics of the tetrazine nucleus.

The first, in the UV-visible range around 447.3 nm, Corresponds to the n-π* transition of the tetrazine nucleus. It is responsible for the color of its derivatives (red rose) and has a low molar absorption coefficient [23] (of the order of a hundred $l.mol^{-1}.cm^{-1}$). Studies have shown that this band is unaffected by the various substituent carried by the nucleus. The second absorption band is the UV range and corresponds to π-π* transition of the tetrazine ring [24]. The associated molar absorption coefficient is higher, in the order of 1000 to 5000 $L.mol^{-1}.cm^{-1}$. Unlike the first absorption band, it depends enormously on the substituents grafted on the nucleus: in fact, the more electrons-withdrawing the substituent, more hypsochromic displacement tetrazine nucleus. Indeed, there is an extinction of fluorescence for molecules exhibiting a tetrazine-carbon bond. The absorption characteristics are given in the following (Table 2).

Figure 3. Ultraviolet visible spectra of TTA; the UV-visible spectrum of this molecule showed that it absorbs light in an intense wave length located at 447.3 nm and apparently the latter is located in solar spectrum; the fluorescence emission spectrum TTA fluoresces in the red with a maximum at 447.3 nm with a high light intensity which is best observed for cyclic and rigid molecules with of π bonds it is increased by the presence of electron-donor groups and reduced with the electron-withdrawing groups. Note: (——) ultraviolet visible spectra TTA; (——) Solar spectrum and also spectrum fluorescence of TTA

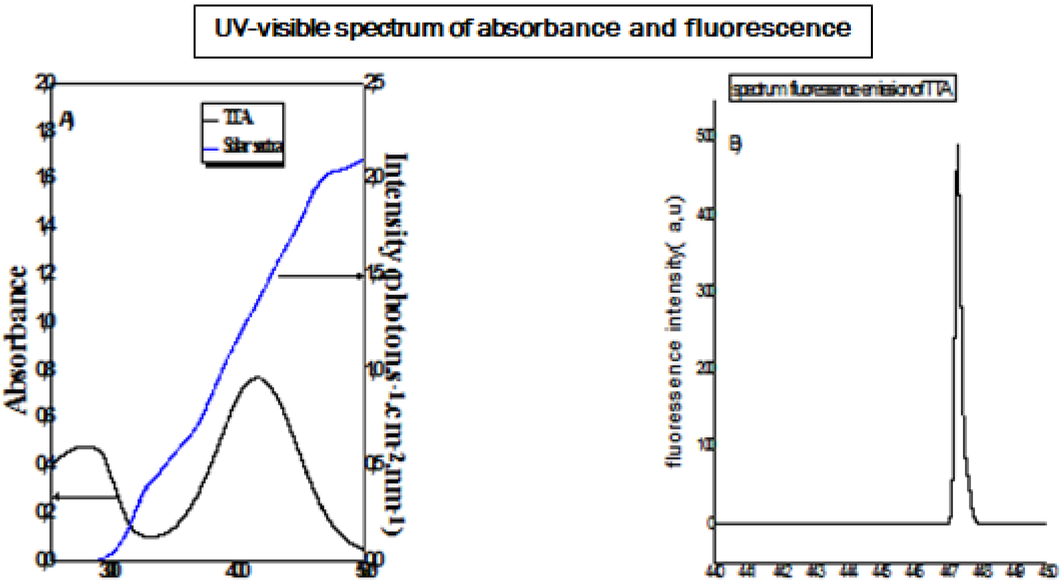


Table 2. UV-visible absorption Characteristics of TTA.

	ε_{max} ($10^4 M^{-1}.cm^{-1}$)	γ_{max} (nm)	γ_{onset} (nm)	Eg-op (eV)
TTA	0.154	417	485	2.55

From these values, we calculated the Eg-op optical gap, for the TTA which is based on the value of the material absorption band threshold wavelength according to the following formula Egap=hc/λ. Fluorescence properties (present or non-existent) are very dependent on atoms directly linked to the emission, TTA fluoresces in the red with a maximum at 447.3 nm with a high light intensity which is best observed for cyclic and rigid molecules with of π bonds it is increased by the presence of electron-donor groups and reduced with the electron withdrawing groups. To check the activation of the holes and the electrons of the semiconductor, the latter is placed by an oscilloscope and the results are shown in Figure 4.

According to figure, electrons have constant higher scattering from holes leading to less excess electrons at the center compared to the holes. Finally, structure characterizations led us to find that this compound absorbs in the solar spectrum, at energy levels consistent with the photo catalytic effect, is capable of correctly transporting excitants and holes. Could increase the photo response by introducing conjugated building blocks the band gap of 1.39 eV. This showed that TTA exhibited excellent visible absorption properties. The Electrochemical and Theoretical Study of TTA was studied (Figure 5) and the results showed, the frontier orbitals of TTA were measured by the Gaussian 9 program to demonstrate the calculations of the energies of frontier orbitals as well as their energy gap and the values of the highest occupied molecular [25-29].

Figure 4. The change in excess carriers with increasing light intensity at the center of a TTA semiconductor; electrons have constant higher scattering from holes leading to less excess electrons at the center compared to the holes.

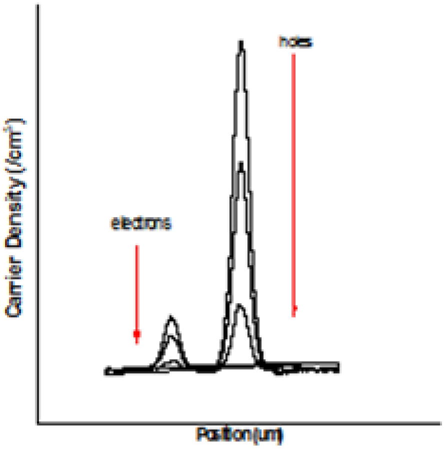
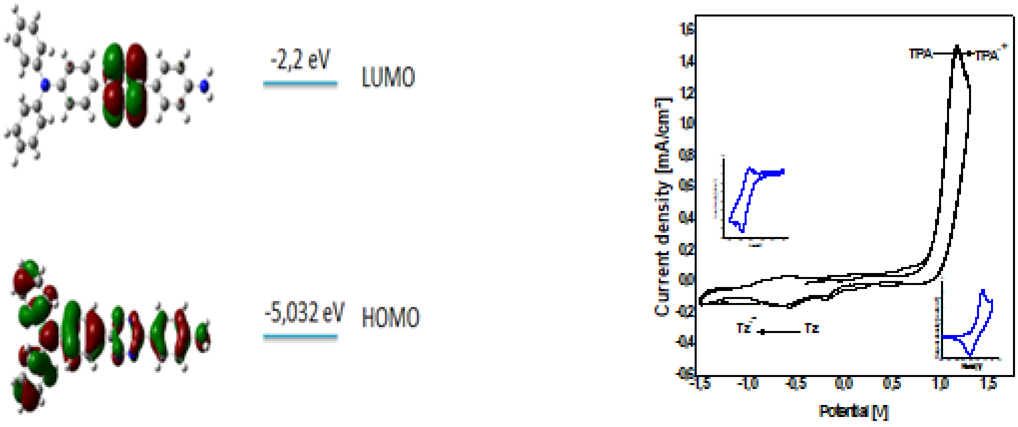
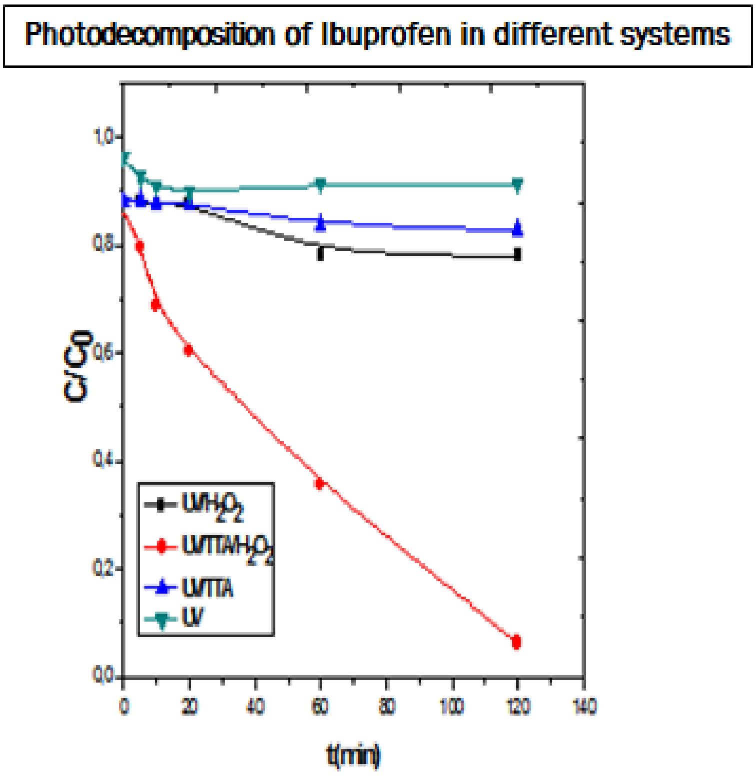


Figure 5. Electrochemical and theoretical study of TTA, the optimization of the geometry is performed by the DFT method using the Gaussian 09 program. The function we used is the B3LYP, The energy values of HOMO and LUMO, allowed us to know if this molecule is suitable as a semiconductor or not. The preliminary observation shows that the frontier orbitals of this molecule allow a transfer of electrons and holes. For the electrochemical study has shown that this molecule exhibits the electrochemical characteristics specific to triphenylamine and tetrazine. It is a compound which is both donor and acceptor.



Molecular modeling calculations have made it possible to better understand the influence of the atom bound to the tetrazine nucleus by determining the nature of the highest occupied (HOMO-5.032 eV) and LUMO lowest vacant (LUMO -2.2 eV) molecular orbitals [30]. We thus determine that the LUMO is always a π^* orbital developed only on the nucleus and weakly dependent on substituents. In the other hand, HOMO changes nature depending on the substitution of the nucleus: when the substituents have a strong donor mesomeric character, the nature of orbital is n, when the substituents are only weakly donor mesomers (or else withdrawing mesomers) [31]. We can thus conclude that a fluorescence emission is observed only in the case where the HOMO orbital is of nature n. These properties can in particular be appreciated in representing the frontier orbitals HOMO and LUMO calculation energy. To emphasize the electrochemical Figure 6 characteristics of the TTA, a donor acceptor group (triphenylamine-s-tetrazine), study by cyclic voltammetric was carried out to define the redox properties.

Figure 6. Photodecomposition of Ibuprofen in different systems; Disappearance of IBP (5.10^{-5} mol. L^{-1}) with the TTA (1 g.L^{-1}) pH = 4.5, T= 25°C under 365 nm irradiation; it is found that the degradation activity is better for the synthesized catalyst. For a time of 240 min, we see a 21.9% degradation of IBP. Note: (—■—) UVH$_2$O$_2$; (—●—) UVTTA H$_2$O$_2$; (—▲—) UVTTA; (—▼—) UV



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Voltammogram showed that our compound is bipolar with a nearly-reversible reducible system better than oxidation while the oxidation peak is significantly higher than the reduction peak. One of the characteristics of the tetrazine ring is its electrodeficiency, which can be explained in particular by the replacement of 4 CH groups by 4 nitrogen atoms, which are more electronegative than the carbon atom. The tetrazine derivatives are therefore reduced to relatively high potentials. The professor Audebert's team has shown that the reduction of tetrazine derivatives substituted by heteroatoms or by strongly electron donor or by aryl, in organic solvents is a reversible phenomenon [32]. During this reduction, an anion radical is formed which is all the more stable as it is substituted by an attractor group [33-34]. It is also possible to observe the formation, which is non-reversible in the scanning back with a protic species to restore the starting tetrazine after oxidation. In our case, the presence of two strongly electron-withdrawing groups (notably in the case of triphenylamine and aniline) increases the electro efficiency of the tetrazine nucleus, exacerbating its reactivity towards aromatic nucleophilic substitutions [35]. This study has shown that this organic optoelectronic molecule can be used as a semiconductor on one side and on the other side their spectrum showed that it absorbs light in UV-visible fields as well as their gap which is between 2 and 5 eV; all these results confirms that the latter can be considered as a photocatalyst in photochemistry for the degradation of organic pollutants.

Photodecomposition of Ibuprofen in different systems

The photo catalytic processes for the degradation of Ibuprofen under different conditions are shown in Figure 6. These processes, with TTA and H_2O_2 (with or without UV) showed higher activities than direct photolysis in UV, UV/H_2O_2 and UV/TTA systems. The photocatalytic power of TTA in the presence of H_2O_2 leads to a significant concentration reduction of ibuprofen a conversion of 93.7% after 120 min of reaction; the pseudo first order reaction rate constant K is 0.79 min^{-1} (R2=0.96), with a half-life of around 35.5 hours.

Common and green oxidizing agent, hydrogen peroxide (H_2O_2) is to act the electron acceptor generating the hydroxyl radicals •OH under irradiation. The reaction happens with the hydroxyl radicals produced from the reaction between the hydrogen peroxide and the surface of TTA (Eqs. (1) - (4)).

$$TTA + h\nu \rightarrow hvb+ + ecb- \qquad (1)$$

$$H_2O_2 + h\nu \rightarrow 2 \bullet OH \qquad (2)$$

$$H_2O_2 + 2ecb- \rightarrow 2 \bullet OH \qquad (3)$$

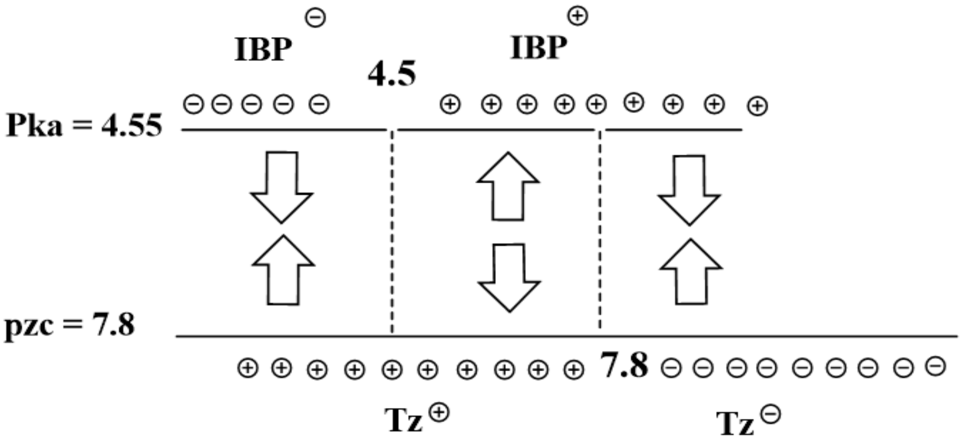
$$H_2O_2 + ecb- \rightarrow \bullet OH + -OH \qquad (4)$$

The scavenger to extinguish the •OH radicals with the isopropanol at low concentrations (2%) and that some •OH radicals would recombine to form H_2O, leading to a partial inhibition. The absence of H_2O_2 in analogous reaction condition led to a conversion of 21.9% after 2 h and a K value determined to be $8.99.10^{-4}$ min^{-1} (R2=0.65). The oxidation performed with the addition of H_2O_2 alone led to a conversion of 17.35% after 2 h (K=3.10^{-4} min^{-1}, R2=0.99). In the system UV/H_2O_2 hydrogen peroxide does not have a significant influence on the photolysis at 365 nm. This process requires a long time, due to the low absorption of the Ibuprofen and the hydrogen peroxide in the emission zone of the lamp (365 nm).The reduction of IBP concentration rates obtained with H_2O_2 alone and TTA alone are negligible compared with H_2O_2/UV processes, and required a longer periods of time.

Effect of initial pH value

The effect of medium pH on the photo catalytic degradation of ibuprofen in the presence of TTA was examined. For this, we irradiated solutions of IBP (5.10^{-5} $mol.L^{-1}$) containing 1 $g.L^{-1}$ of TTA at different pH. The pH was adjusted with a few drops of perchloric acid and NaOH. Ph is the main influencing factor to the ionization state of the surface of TTA and IBP were photocatalytic process take place the according to the Figure 7.

Figure 7. Ionization of TTA surface as a function of the pH, pka of IBP=4.5, Pzc TTA=7.8; the ionization of TTA showed that the catalyst can be profoundly affected in his surface charge negatively up to pzc=7.8 and positively under this value.



The experiments of the effects of pH value (Figure 8) indicated higher rate constant in basic pH, this may be due to the strong adsorption of IBP at basic pH and the formation of hydroxyl radicals, which can occur by the reaction between hydroxyl ions and electron holes at basic pH, hydroxyl radicals are considered as the predominant species at neutral or high pH levels while the positive holes are considered as the major oxidation species at low acidic pH [36, 37].

Effect of hydrogen peroxide concentration

Hydrogen peroxide concentration was also crucial for the production of OH radicals. The influence of H_2O_2 concentration on the Ibuprofen degradation by the UV/H_2O_2 reaction with TTA is shown in Figure 9.

The increase and decrease of pH values would cause the decrease of photo oxidation efficiency (Table 3).

Increasing the concentration of hydrogen peroxide to 10^{-2} mol.L^{-1}, an appreciable acceleration of the degradation kinetics of IBP is then obtained. As we know the increasing of the concentration of H_2O_2 increases the production of hydroxyl radicals.

$H_2O_2 + hv \longrightarrow 2\ OH$ (5).

However, higher increasing in the concentration of H_2O_2 (10^{-2} M) can slow down the degradation process. Excess H_2O_2 could act as a scavenger for HO. Radicals resulting in the generation of HO_2, that is less reactive species [38-41].

$H_2O_2 + OH \longrightarrow HO_2 + H_2O$ (6).

$OH + HO_2. \longrightarrow O_2 + H_2O$ (7).

Figure 8. Effect of pH in the degradation of IBP (5.10^{-5} mol.L^{-1}) with TTA (1 g.L^{-1}), T=25 ° C under 365 nm irradiation; The results show that the rate constant is higher in basic pH, this can be explained by the ionization phenomenon of the catalyst and the dissociation of the pollutants. Note: (–■– , ■) IBP (5.10^{-5} M) +TTA (1 g.L^{-1})/UV/pH=8.9;(–●–, ●) IBP (5.10^{-5} M)+TTA (1 g.L^{-1})/UV/pH=2.8; (✚ , ▲) IBP (5.10^{-5} M)+TTA (1 g.L^{-1})/UV/pH=4.7; (✚) IBP (5.10^{-5} M)pH=8.9; (✚)IBP (5.10^{-5} M)pH=2.8; (✚) IBP (5.10^{-5} M)pH=4.7

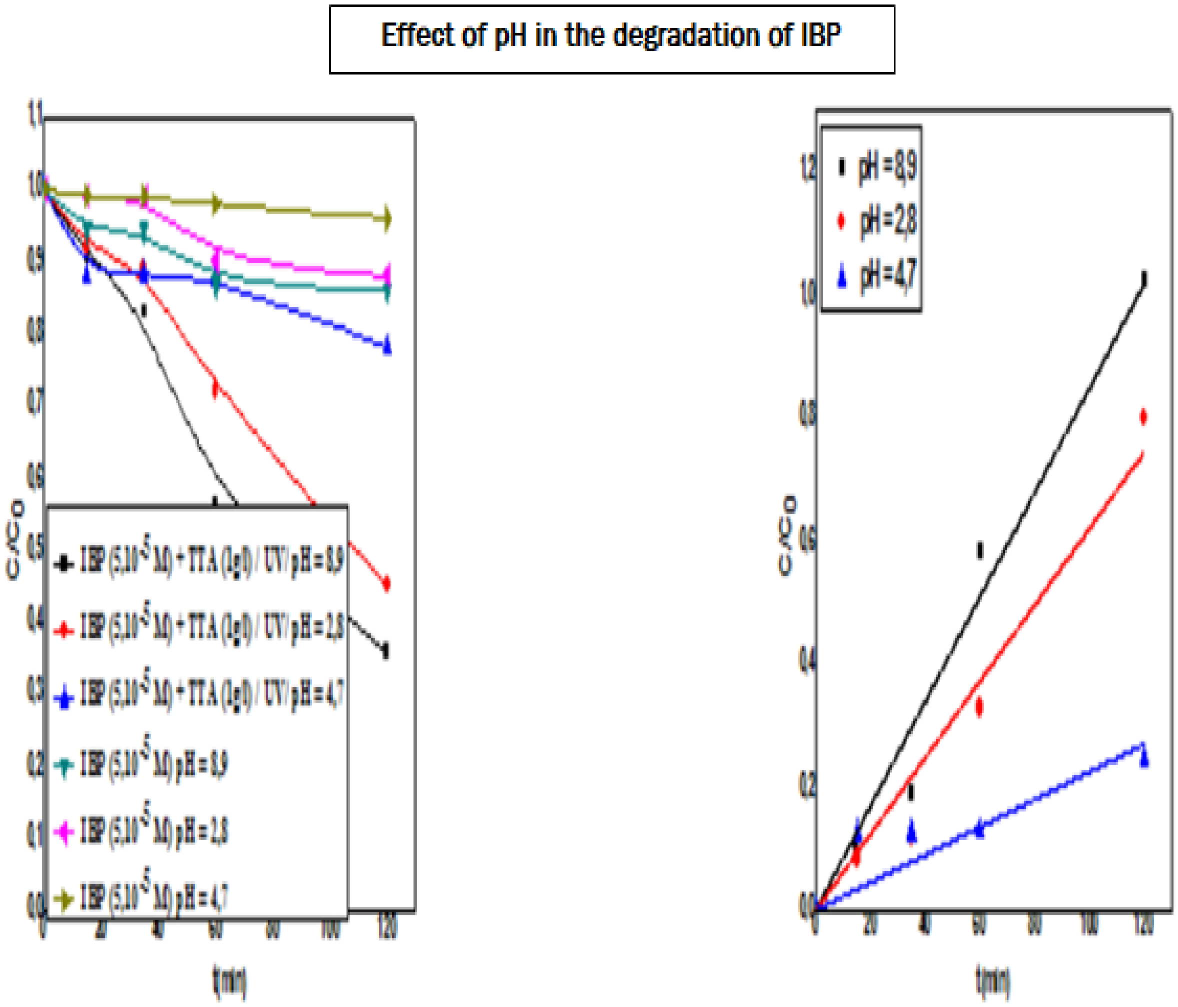
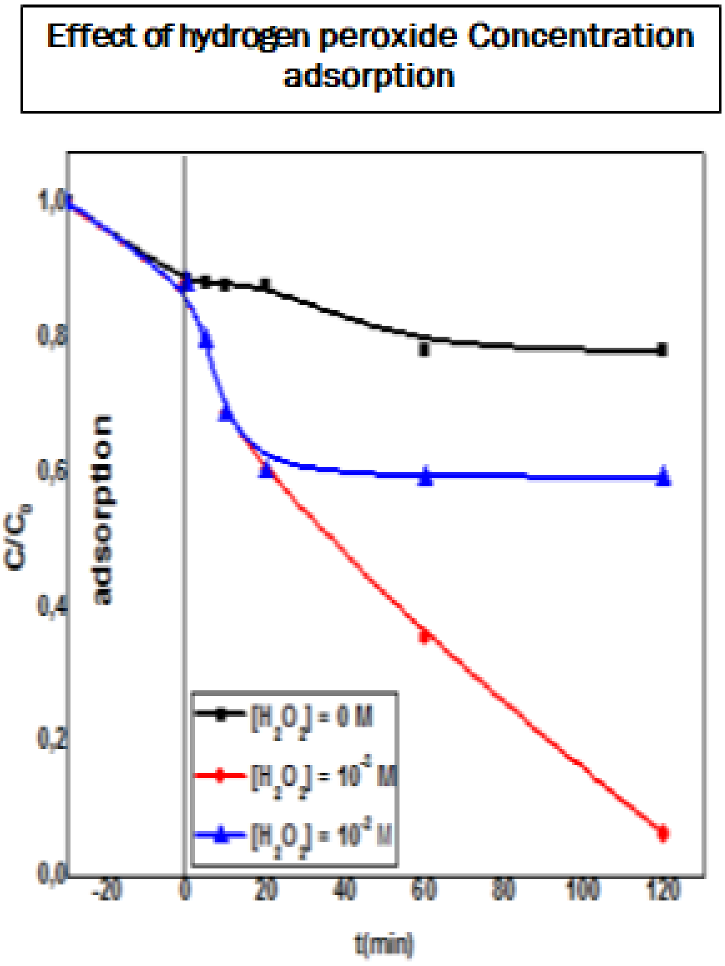


Table 3. Average values of the luminous intensity of sunlight.

Times	1st Day	2nd Day	3rd Day
Light intensity (mw.cm^{-2})	2.149	2.432	1.542

Figure 9. Effect of hydrogen peroxide Concentration; increasing the concentration of hydrogen peroxide to 10^{-2} mol.L^{-1}, an appreciable acceleration of the degradation kinetics of IBP is then obtained. Note: (━■━) H_2O_2=0 M; (━✚━) H_2O_2=10^{-3} M; (━▲━) H_2O_2=10^{-2} M



Effect of the solar irradiation

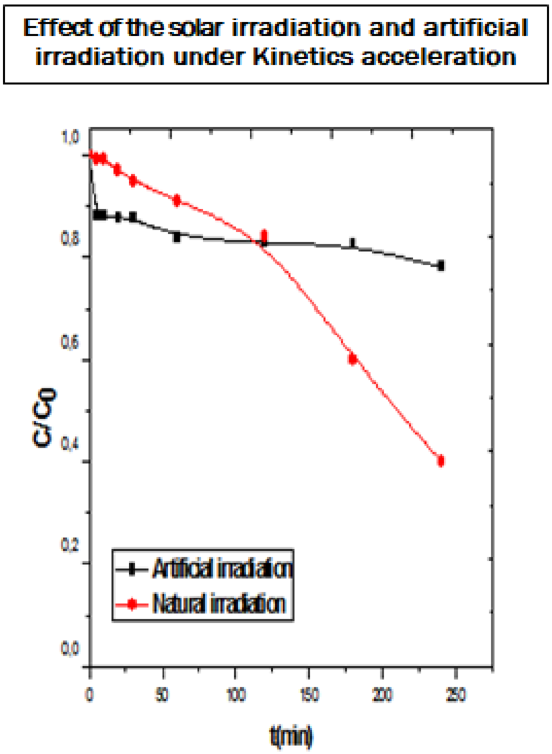
To get closer to natural conditions, an important step in our study concerned monitoring the degradation of IBP under solar irradiation. The experiments were carried out at the level of the LSTE laboratory platform in Constantine (Figure 10).

The light intensity characterizing the period of the experiment was measured at different time intervals. The mean values of the intensities grouped together.

Examination of the different Kinetics obtained showed an evolution similar to that observed under artificial irradiation with a more accelerated rate (Figure 11).

Figure 10. LSTE laboratory platform of sun light in Constantine. The experiments of the effects of sun light were carried out at the level of the LSTE laboratory platform in Constantine.

Figure 11. Effect of the solar irradiation, Examination of the different Kinetics obtained showed an evolution similar to that observed under artificial irradiation with a more accelerated rate. Note: (—+—) Artificial Irradiation; (—◆—) Natural Irradiation



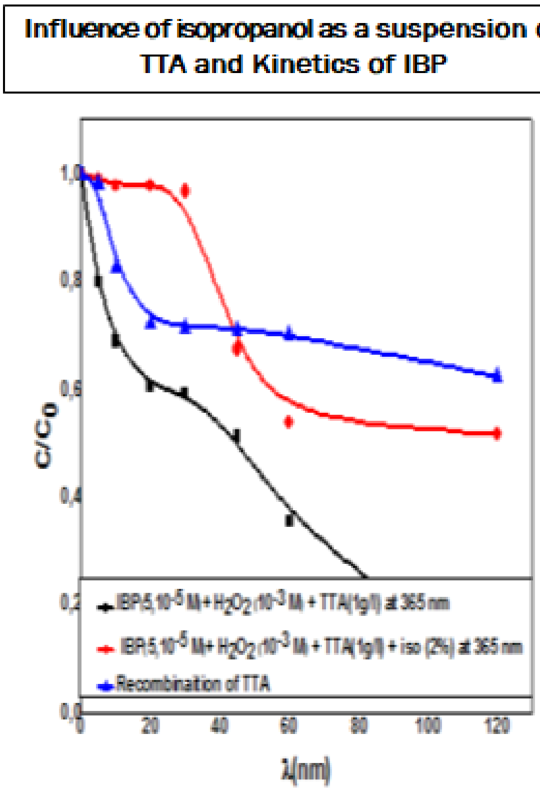
However, it turns out that the rate of degradation is faster under natural irradiation, is explained by the existence of photo products from irradiations at different wavelengths contained in solar radiation.

The effect of isopropanol

In order to know better the role of OH radicals. During the IBP degradation process, 2% of isopropanol was added to the IBP-TTA-H_2O_2 mixture (5.10^{-5} mol.L^{-1}; 1 g.L^{-1}; 10^{-3} mol.L^{-1}; pH=4.3).

Isopropanol is a well-known scavenger of hydroxyl radicals, significantly, it can be seen that the kinetic of disappearance of Ibuprofen in presence of 2.0% of isopropanol was similar to the kinetic of disappearance obtained from direct photocatalysis of Ibuprofen. The added scavenger (Figure 12) reduced partial rate in the chemistry to solely the direct photocatalysis.

Figure 12. Influence of isopropanol (2%) and the holes on the disappearance Kinetics of IBP (5.10^{-5} mol.L^{-1}) in the presence of a suspension of TTA (1 g.L^{-1}), H_2O_2 (10^{-3} mol.L^{-1}) at pH=4.3, T=25 °C under 365 nm irradiation; we use the isopropanol as a scavenger of OH radicals and the method of kepller for snatch the holes, the results show at first 30 min OH radicals responsible for the phenomenon of degradation while after this period we observed another mechanism. Note: (—■—) IBP 5.10^{-5} M+ $H_2O_2 10^{-3}$ M + TTA (1 g.L^{-1}) at 365nm; (—◆—) IBP 5.10^{-5} M+ $H_2O_2 10^{-3}$ M + TTA (1 g.L^{-1}) + iso (2%) at 365nm; (—▲—) Recombination of TTA


Influence of isopropanol as a suspension of TTA and Kinetics of IBP

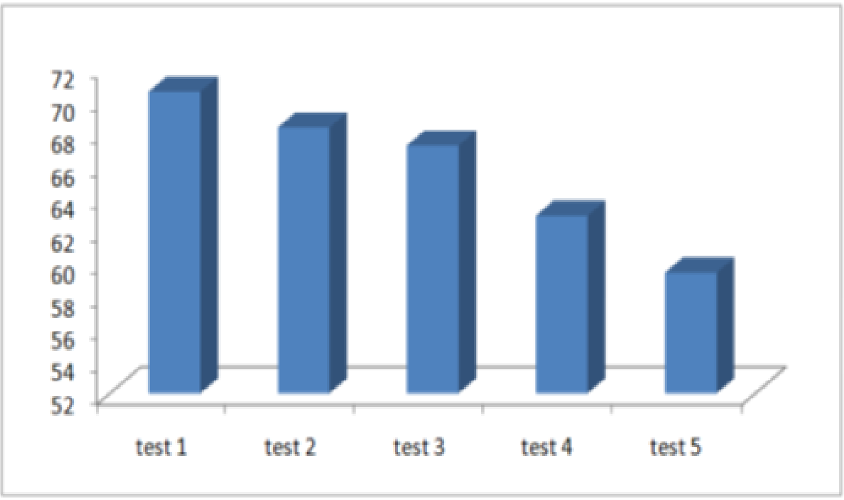
From these results the photo degradation reaction of IBP induced by the organic optoelectronic TTA compound is linked to hydroxyl radicals in the first phase until 30 min. This can be explained by the excess of H_2O_2 which can react with the scavenger to form OH radicals, and the other one have been recombined to form H_2O leading to decrease in the oxidation capacity during the process of photo degradation, in addition the molecules of H_2O_2 entrain with the IBP in adsorption and diffusion at the active sites of the TTA at concentration of H_2O_2 which leads a decrease in degradation based on previous results [42,43]. The rate of degradation reaches almost 50% of the pharmaceutical product up to 60 min then we observe another inhibition can be explained by the decrease in the penetration of the active sites of the accessible surface. To understand this phenomena and known the other spices responsible for the degradation of IBP we, try to scavenger of the holes using the Kepler method [44]. From the pace of the kinetics it can be concluded that the degradation phenomenon before the first 30 min is carried out from the holes are all constant and the adsorption phenomenon is completely unaffected. The comparison of the trapping Kinetics oh holes and OH radicals showed the presence of other species responsible for photodegradation so another mechanism can be seen.

Stability and reuse of TTA

The recyclability of TTA was evaluated with a series of successive degradation experiments of IBP in the TTA-H_2O_2 system. The reuse of the solid was evaluated under identical oxidation conditions. In order to know the number of times the support can be used as an adsorbent, the following experiments were carried out. At the end of the oxidation process, the solid is removed from the reactor by filtration and dried in an oven at a moderate temperature (50°C). The recovered adsorbent (from the test) was added to a new solution of (IBP-H_2O_2) (5.10^{-5} mol.L^{-1}; 10^{-3} mol.L^{-1}) and the percentage of degradation was obtained after 60 minutes of reaction (test 2). Then, the adsorbent which is used in the previous section was separated and added to a new solution of ibuprofen and the percentage of degradation was calculated (run3) and so on.

The results presented in the Figure 13 showed that the solid could be reused for five cycles, and the percentage of degradation of IBP was estimated at 70.5%, 68.3%, 67.2%, 62.9%, and 59.4% after one reaction time for the five cycles respectively.

Figure 13. Stability and reuse of TTA; we can conclude that the specific surface of TTA is large enough to be able to use it several times in the degradation of the pollutant IBP.



It is essential to note that for the last test the quantity of the solid has greatly decreased, hence the decrease in its effectiveness. From these results it can be seen that the reused catalyst retained a catalytic activity almost as effective as the fresh material, it is therefore concluded that the support could be effectively recycled. The excellent stability of the solid during the oxidation cycles.

DISCUSSION

Mineralization study

Mineralization means that the pollutant has completely transformed into mineral carbon. We followed the mineralization of IBP through the Chemical Oxygen Demand (COD) of the IBP-TTA-H_2O_2 mixture (5.10^{-5} mol.L^{-1}; 1 g.L^{-1}; 10^{-3} mol.L^{-1}) as a function of the time artificial and natural irradiation for 12 hours. We have chosen to work at free pH which is acidic. It is important to note that the chemical oxygen demand decreases more slowly regardless of the irradiation (Figure 14).

Figure 14. Abatement of COD during irradiation of the mixture (IBP)=5.10^{-5} mol.L^{-1}, (TTA)=1 g.L^{-1}, (H_2O_2)=10^{-3} mol.L^{-1}, pH=4.3 and T=46°C under 365 nm irradiation; The COD reduction percentages under artificial and natural irradiation successively is 77% , 92% after 12 hours. This therefore implies the need for a longer time to complete the full mineralization. Note: (-■-) Artificial Irradiation; (-♦-) Natural Irradiation

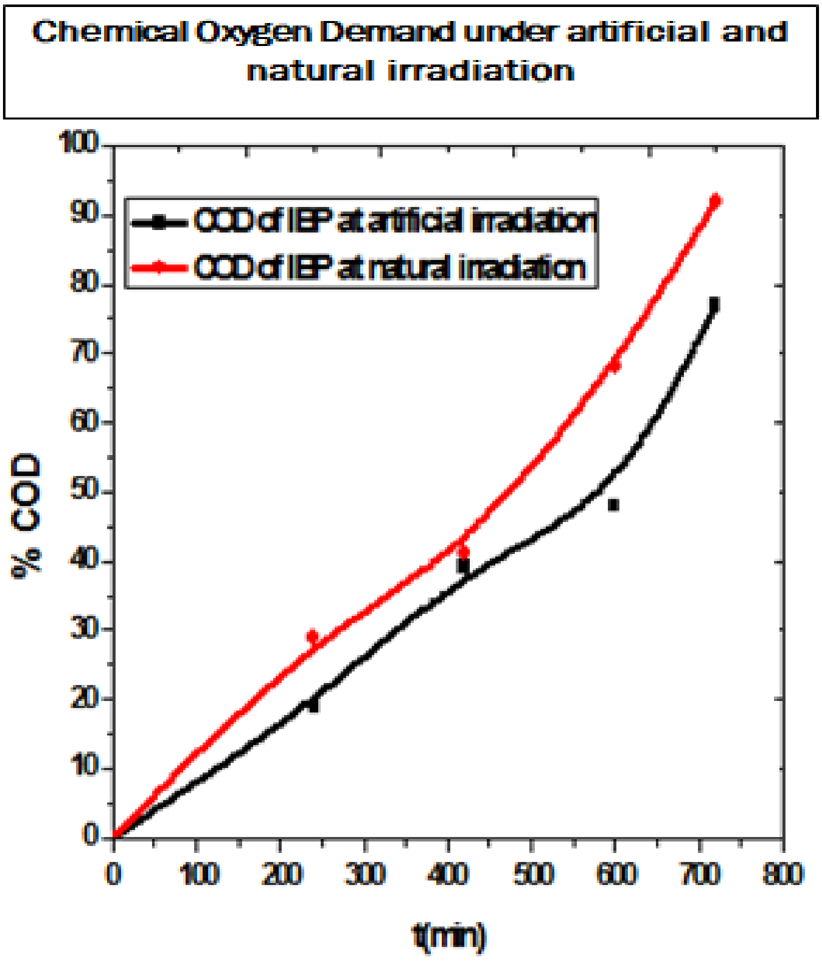
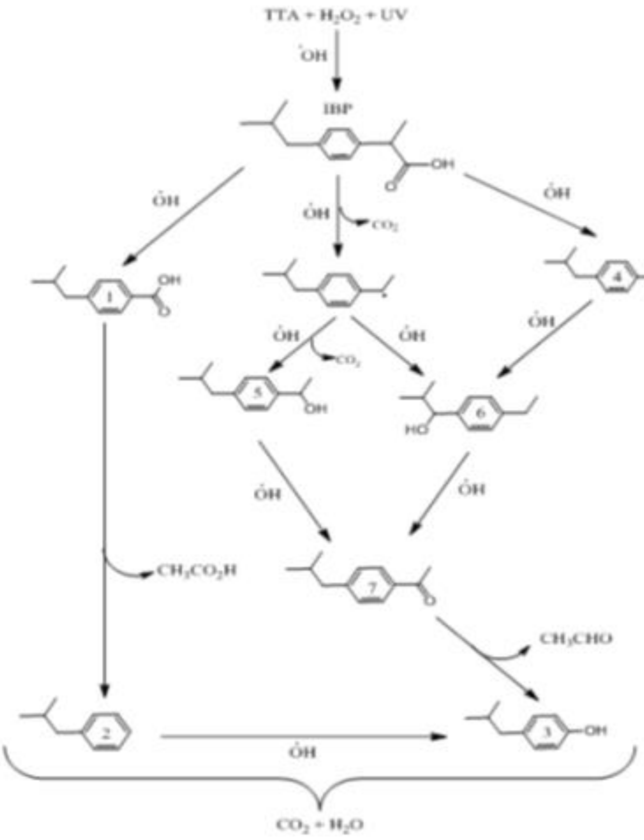


Figure 15. The results found have been grouped together.



The COD reduction percentages under artificial and natural irradiation are successively 77%, 92% after 12 hours. Such poor removal efficiency is attributed to the formation of transformation photoproducts that are more refractory to degradation than TTA/IBP/ H_2O_2 mixture, thus needing more time to be mineralized.

Identification of by-products and degradation mechanism

In order to have a better understanding about the Ibuprofen degradation by the UV/H_2O_2/TTA process, the main photoproducts were analyzed [45]. Four intermediates were identified in a 30 min irradiated solution. The previous study showed that the degradation is done mainly by OH radicals, for that we have proposed a degradation mechanism using this radical for this phenomenon. The results found have been grouped together in the Figure 15.

CONCLUSION

In summary, we've synthesized a new Metal-Free Organic Optoelectronic Molecule exhibiting photo catalytic properties for the degradation of organic pollutants. The synthesis of TTA is carried out with a simple method and its spectroscopic and electrochemical properties have been studied. During this study, the degradation of IBP photo induced by an optoelectronic organic compound in aqueous solution was demonstrated, under polychromatic irradiation at 365 nm and natural irradiation, shown that the degradation of IBP is slow. However, it accelerated with the addition of H_2O_2 hydrogen peroxide at an optimized concentration at 10^{-3} mol.L^{-1}. This is linked to the production of .OH radicals responsible for the faster oxidation of organic matter with a reduction rate of 59% after 60 min of exposure. The involvement of OH radicals was evidenced by the addition of 2% of the isopropanol to IBP/TTA/H_2O_2 suspensions. Therefore, appears effective in the treatment of wastewater and in general in the depollution process.

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