COMPARATIVE STUDY OF DEGRADATION OF ISOPROTURON (3-(4-isopropylphenyl)-1,1dimethylurea) PHOTOINDUCED BY FE(III) AND FE(III)-PHOTOINDUCED SONOCHEMICAL IN AQUEOUS SOLUTION

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Résumé

The La dégradation de l'isoproturon 3-(4-isopropylphényl)-1,1dimethylurée photoinduite par les sels de Fe(III) en solutions aqueuses a été étudiée. Les taux de la dégradation dépend de la concentration en $Fe(OH)^{2+}$, La plus réactives espèce en terme de formation des radicaux ·OH. Les radicaux ·OH sont capable de dégrader l'isoproturon jusqu'à minéralisation totale. La formation des Fe(II) en solution irradiée a été évaluée. La dégradation sonophotochimique de l'isoproturon (IP) dépend de l'intensité de sonolyse. La combinaison des ultrasons et de la photochimie a été utilisée pour dégrader l'isoproturon en solution aqueuse. La dégradation de IP en solution aqueuse a été réalisée à 500 kHz en présence de Fe(III), ainsi que sous irradiation ultrasonore et photoinduction par Fe(III) simultané. Le couplage des ultrasons et de la photolyse pour la dégradation de IP a été étudiée. La constante de vitesse de la décomposition photosonochimique est plus grande que la somme des deux procédés séparés. Les produits de dégradation ont été analysés par CG/MS d'ionisation par impact électroniques à 70 eV en plein mode de balayage. Les produits de dégradations ont été identifiés et un mécanisme réactionnel a été proposé pour les deux procédés.

Mots clés : Isoproturon, Photolyse, Photoinduction, Sonochimie

Abstract

The degradation of isoproturon 3-(4-isopropylphenyl)-1,1dimethylurea photoinduced by Fe(III) in aqueous solution has been investigated. The rate of degradation depends on the concentration of $Fe(OH)^{2+}$, the most photoreactive species in terms of ·OH radical formation. These ·OH radicals are able to degrade isoproturon until total mineralisation. The formation of Fe(II) in the irradiated solution was monitored. The sonophotochemical degradation of isoproturon has been found to be dependent on the intensity of sonication. The combination of ultrasound and photochemistry has been used to degrade an aqueous solution of Isoproturon (IP). The degradation of IP in aqueous solution was investigated under sonolysis at 500 kHz and in the presence of Fe(III), as well as under simultaneous sonolysis and photoinduced Fe(III). Coupling photolysis with ultrasound for degradation of IP has been developed. The photosonochemical decomposition rate constant is greater than the additive rate constants of the two processes. Degradation products were analysed by CG/MS performed in the electron-impact (EI) mode, at 70 eV potential using full scan mode. Degradation photoproducts were identified and a mechanism of degradation is proposed for two processes.

Keywords: Isoproturon, Photolysis, Photoinduction, Sonochemistry

ملخص.

لقد تمت دراسة الهدم الضوئى للإزوبروتيرون المحفز بأملاح الحديد الثلاثي. هدم الإزوبروتيرون يتعلق بتركيزشوارد هيدروكسيل الحديد الثلاثي الأكثر فعالية من حيث تكوين الهيدروكسيل القادرة على تفكيك الإزوبروتيرون حتى المعدنة الكلية. تم تتبع تكون تركيزشوارد الحديد الثنائي في المحاليل المشععة. تفكيك الإزوبروتيرون عن طريق الكمياء الضوئية و الأمواج الفوق صوتية يتعلق بشدة هذه الأخيرة. استعمل الجمع بين الكمياء الضوئية و اللأمواج الفوق صوتية لتفكيك الإزوبروتيرون في المحاليل المائية. تم تفكيك الإزوبروتيرون في المحلول المائي تحت 500 كيلوهرتز في وجود الحديد الثلاثي و كذا الإشعاع الفوق صوتي والضوئي المحفز بالحديد الثلاثي. دراسة تفكك الإزوبروتيرون عند الجمع بين الأمواج الفوق صوتية والضوئية بينت أن ثابت التفكك أكبر من مجموع ثابتي التفكك للنظامين كل على حدى. تم تحليل المركبات الوسطية بواسطة مطيافية الكتلة المزدوجة إلى كروماتوغرافيا الطور الغازي حيث تم التعرف على المركبات الوسطية وإقتراح آلية التفاعل من أجل النظامين**.**

<u>الكلمات المفتاحية</u>: إزوبروتيرون، كمياء ضوئية، كمياء صوتية، تحفيزضوئي**.**

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Introduction :

Isoproturon 3-(4-isopropylphenyl)-1,1dimethylurea is a selective herbicide used to control weeds in agricultural and non-agricultural sectors. It is selective herbicide acting by inhibition of photosynthesis. This molecule can be transferred from soil to the aquatic environment by leaching and run-off [1]. Its persistence leads to high pollution levels and therefore European Union recently restricted its usage. In surface water Isoproturon can be biodegraded or subjected to abiotic transformations. Many reports stated that the photodegradation can occur either through direct exposure [2-6].

The use of UV/Fe^{3+} has been given a lot of interest because Fe^{3+} is one of the most ubiquitous metal ions in natural water and wastewater streams. Depending on the nature of the pollutant, the beneficial effect of Fe^{3+} can be highlighted via different photoprocesses [7]. Many authors have studied photodegradation of organic substrates in aqueous solutions containing Fe (III), such us: atrazine [8], monuron [9], asulam [10].

Sonochemical techniques use ultrasound to produce an oxidative environment via acoustic cavitations due to the formation and subsequent collapse of microbubbles from acoustical wave which induced compression/rarefaction. The collapse of the bubbles induces localized extreme conditions (high temperature and high pressure). It has been reported that the gaseous contents of a collapsing cavity can reach temperatures as high as 5200 K and pressures higher than 1000 atm inside the collapsing cavity, and about 1900 K in the interfacial region between the solution and the collapsing bubble [11-14]. The destruction of organic pollutants occurs via several mechanisms. The organic pollutant inside the cavity and in the interfacial region (cavity-liquid) can undergo thermal degradation (pyrolysis or combustion reactions if oxygen is present during the implosion) [14, 15]. The consequences of these extreme conditions are the cleavage of water molecules into ·H radicals, ·OH radicals and dissolution of oxygen molecules.

Ultrasonic degradation efficiency of organic pollutants in aqueous medium can be improved by combination of ultrasound application with advanced oxidation processes (AOPs). One of the promising AOPs is the photochemical treatment in the presence of UV radiation [16].

The aim of this study was the comparison of degradation kinetics of US/ Fe(III) with UV Fe(III) systems and their combination.

2- MATERIALS AND METHODS
2-1-Reagents

All reagents used in this work were analytical reagent grade and used without any further purification. High-purity Isoproturon purchased from Riedel-de Haën. No impurity was detected by HPLC chromatogram at λ= 240 nm. Acetonitrile, HPLC grade product, was purchased from ACROS ORGANICS (99.9%). Water was purified by Milli-Q system (Millipore) and controlled by its resistivity (18 MΩ cm^{-1}). Solutions and mobile phase are filtered on a filter of 0.45 μm before the use. Ferric perchlorate ($Fe(ClO_4)_3$, 9 H_2O) (>99.0%) from Carlo Erba. Chlorhydric Acid (25 %) from Merck. perchloric acid (70%) was purchased from Fisher Scientific. potassium iodide (>99.0%) from Fisher Chemicals and ammonium heptamolybdate (>99.0%) from ACROS.

2-2- Reactor

Sonolysis experiments were performed at an ultrasound frequency of 500 kHz with a variable electric output power. Ultrasonic waves introduced from the bottom of the solution through a plane Pyrex surface holding the piezoelectric disk (diameter 4 cm). The cylindrical sonochemical reactor was thermostated by a water jacket. The temperature inside the reactor was kept constant (25°C ±2°C). Ultrasonic energy dissipated in the reactor was set at specific powers using calorimetric method [17]. The power output on generator for all the experiments was 40 and 70W. The effective calorimetric power [18] delivered to the solutions was 16 and 22W respectively. The volume of solutions sonicated was 200 mL. Ultraviolet irradiations were carried by a CPS+ ATLAS Suntest simulator, equipped with a Xenon lamp (irradiance between 290 and 800 nm). An average irradiation intensity of 750W/m^2 was maintained throughout the experiments. The cylindrical sonochemical reactor was thermostated by a water jacket.

2-3- Analysis

The disappearance of substrate and formation of products were monitored by HPLC on a WATERS chromatograph equipped with two pumps (WATERS 515) and a photodiode array detector (WATERS 996). The column was SunFire C18 (3μm, 250 mm x 4,6 mm). The eluent was a mixture of 50/50 (V/V) acetonitrile - water acidified with chlorhydric acid to pH=3, with a flow rate of 1 mL.min^{-1} and a detection wavelength of 240 nm. Hydrogen peroxide concentrations were determined using the iodo-metric method [19]. The iodide ion (I$^-$) reacts with H_2O_2 to form the triiodide ion (I^{3-}) that absorbs strongly at 352 nm (ε=26000 M^{-1}.cm^{-1}). Sample taken from the reactor were added to a mixture containing potassium iodide (0.1 M) and ammonium heptamolybdate (0.01 M). The mixed solutions were allowed to

stand for 5 min before absorbance was measured in the quartz cuvette of spectrometer.

The Shimadzu GC was equipped with a SE30 (L=25 m x 0,25 mm) capillary column, used at the following chromatographic conditions: injector temperature 250°C , column program of temperatures (10°C/min), initial temperature was de 70°C for 3 min and final temperature was 280°C for 5 min. Helium was used as a carrier gas. Qualitative analyses were performed in the electron-impact (EI) mode, at 70 eV potential using full scan mode.

UV-Visible spectra were recorded on Varian, Cary 50 spectrophotometer. A pH-meter Crison Basic was used to measure the pH of solutions.

3- RESULTS AND DISCUSSIONS
3-1- Effect of ultrasonic power
3-1-1- Water degradation

Water molecules degrade releasing $OH^.$ and $H^.$ radicals (Eqs. (1)-(7)).

$$H_2O \leftrightarrow H^. + OH^. \quad (1)$$
$$2H^. \rightarrow H_2 \quad (2)$$
$$2OH^. \rightarrow H_2O_2 \quad (3)$$
$$2OH^. \rightarrow O^. + H_2O \quad (4)$$
$$2O^. \rightarrow O_2 \quad (5)$$
$$O^. + 2H^. \rightarrow H_2O \quad (6)$$
$$O^. + H_2O \rightarrow H_2O_2 \quad (7)$$
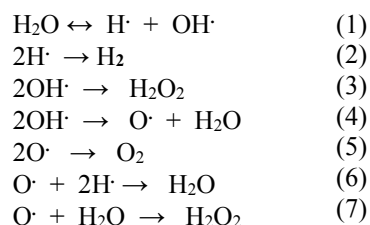
In the case of water degradation, the hydrogen peroxide concentration plots for 60 min of ultrasonic irradiation, using the system of 500 kHz, were showed in **Fig.1**. The concentration hydrogen peroxide produced during sonication increases linearly versus time showing apparent zero-order kinetics. The amount of hydrogen peroxide production after 60 min was 46.8 μM and 72.7μM, for 16 W and 22 W input powers, respectively.
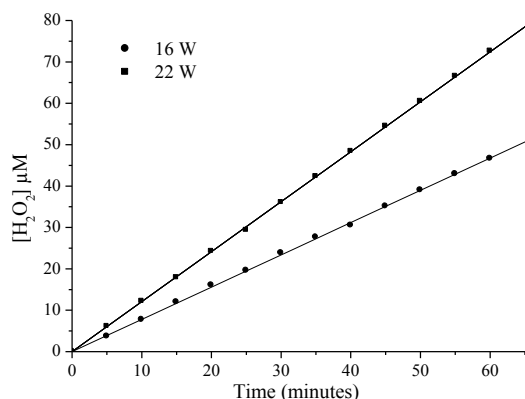

Fig.1: Production of hydrogen peroxide during water sonolysis.

The influence of intensity on the ultrasound efficiency is an important optimisation factor.

3-1-2- IP solution degradation

In general, the hydrogen peroxide concentrations in IP solution during the ultrasonic irradiation were lower than those for water (**Fig. 2**). This is probably due to the consumption of some radicals for IP degradation, resulting in fewer radicals for water degradation. **Table 1** shows difference between production of hydrogen peroxide resulting from 16 W and 22 W input powers during 60 minutes of irradiation.

Table 1: Production of hydrogen peroxide resulting from 16 W and 22 W input powers during 60 minutes of irradiation.

Input power (W)	16	22
$[H_2O_2]$ (μM) in water	46.8	72.7
$[H_2O_2]$ (μM) in IP solution	27.0	45.5

To investigate the power effect on sonication of IP (10^{-4} M), two different powers, 16 and 22 W were tested. **Fig. 2** shows the results of the ultrasonic energy dissipation in IP solution or in water.
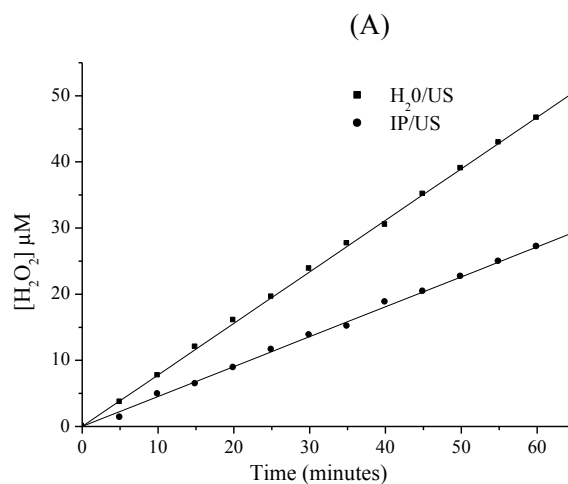
(A)

Fig. 2: Production of hydrogen peroxide during sonolyse; (A): 16 W, (B):22 W.

Fig. 3 shows that ultrasound IP reduction occurs as pseudo-first-order reaction kinetics, a stepwise increase of k_{app} values from 0.022 min^{-1} to 0,026 min^{-1} was observed with the increase of ultrasonic input power from 16 W to 22 W (**Fig. 3**). It is obvious that improvement of US input power has a positive effect on the degradation rate of IP. It is widely accepted that reactions would be remarkably affected by ultrasound input power at a fixed output frequency (500 kHz). Generally, the improvement of input power means that higher

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ultrasound intensity was introduced into the reactor, which would accelerate the reactions.

The effect of acoustic power on the sonodegradation of IP may be explained in terms of cavitational activity. High levels of acoustic power increase the number of cavitational events and consequently the opportunities for free radicals to be generated and thus, enhancing degradation [20, 24]. Suzuki et al. [25] confirmed that the degradation rate is dependent on the acoustic power, because acoustic power may lead to more extensive acoustic cavitation.
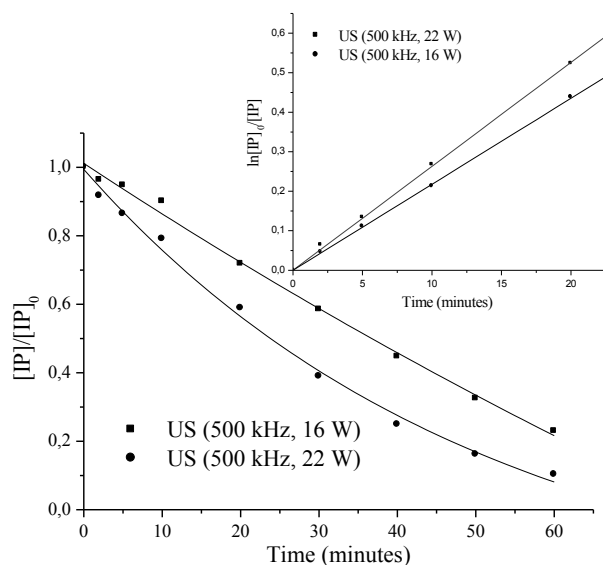

Fig. 3: Sonochemical degradation of (10^{-4} M) at different ultrasonic powers at 500 kHz.

3-2- Effect of iron salts addition to IP/US system

To investigate iron salts addition effect on sonication of IP (10^{-4} M), ultrasonic degradation was carried out in presence of 3×10^{-4} M of ferric perchlorate iron. **Fig. 4** shows the reduction of IP following pseudo-first-order reaction kinetics.

In this study, as shown in **Fig. 4,** no effect on sonochemical degradations kinetics rate of IP was observed. Our results are not in agreement with hose reported by Zhang et *al.* [26]. They studied degradation of C.I. orange Acid 7 by ultrasound at 20 kHz, in presence of goethite, they noted that degradation kinetics depends on goethite added concentration in the range: 0.2 g.L^{-1} to 0.4 g.L^{-1}.
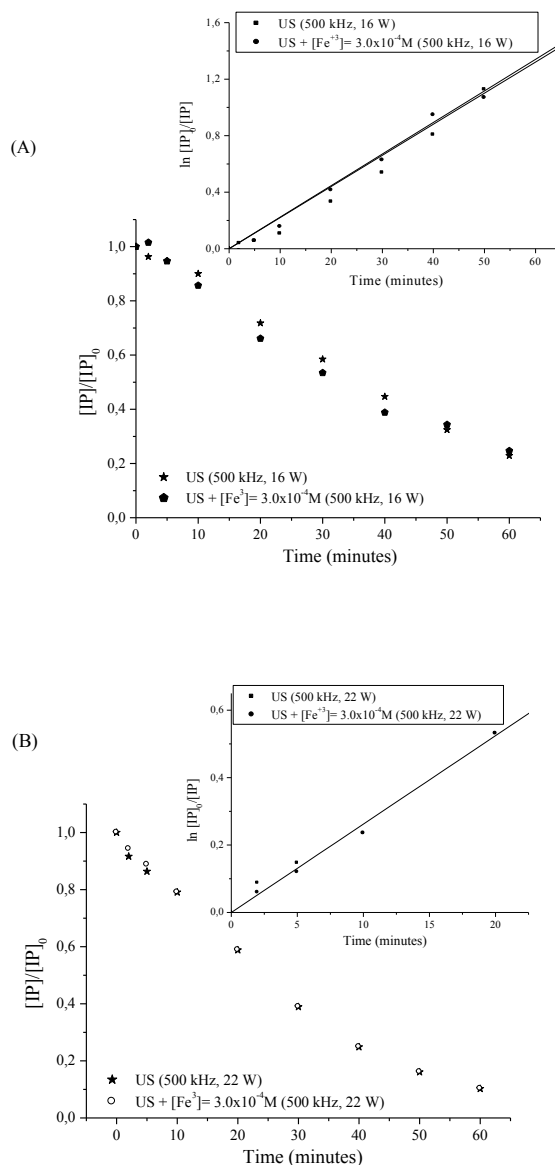
Fig. 4: Effect iron (III) salts (3×10^{-4} M) on IP (10^{-4} M) sonochemical degradation.

3-3- Effect of pH

The effect of pH was investigated for the three solutions: the aqueous IP (10^{-4} M) solution with a free pH of 5.8, the same solution in presence of iron salts (3×10^{-4} M) with a pH of 3.4 and the first solution with a pH of 3.4 imposed with perchloric acid. Sonochemical degradation of IP was carried out under acoustic power of 16 and 22 W. The disappearance of IP follows pseudo-first-order reaction kinetics, with a half-lifetime of 31.5 and 26.5 min for 16 and 22 W respectively. The results suggest that no effect of pH on the rate of the sonochemical degradation of IP for the two pH values. No difference in reactivity at these two pH values arises from the unchanged molecules forms of IP. The effect of pH on the degradation rates is

dependent on the state of the pollutant molecule, whether the pollutant is present as ionic species or as a molecule such as for 4-CP [27] and 4-NP.

3-4- IP photodecomposition by UV radiation alone and combined with iron (III)

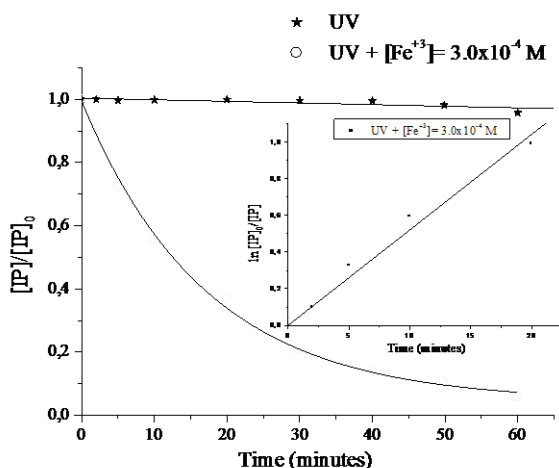The IP (10^{-4} M) decomposition by UV radiation alone was investigated at initial pH = 5.8.

Fig. 6: Kinetic degradation of photolysis of IP (10^{-4} M), $290 \leq \lambda_{irr} \geq 800$ nm.

Fig. 5 shows the results obtained for IP concentration decay with reaction time. IP concentration decreased according to a first order rate, in presence of Fe (III) (3×10^{-4} M), up to 93% after 1h. The pseudo-first order kinetics rate constant k_{app} is 0,052 min^{-1} with a time of half-lifetime equal to 13.5 minutes. Direct photolysis of IP is negligible under our experimental conditions.
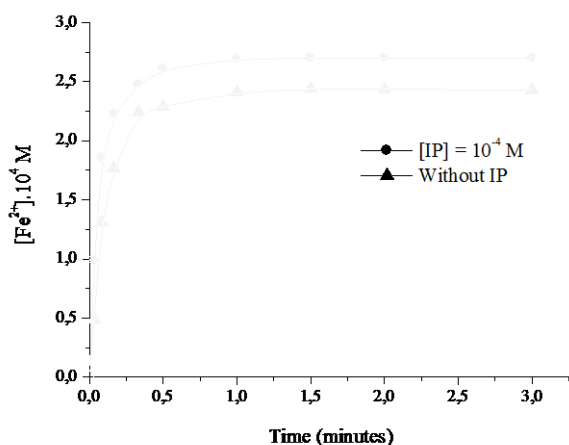

Fig. 7: Fe(II) formation upon irradiation at 365nm of Fe(III) ($3.0 \cdot 10^{-4}$ M).

In this set of experiments, the concentration of Fe(II) was also measured all along the transformation. In all cases Fe(II) was formed, its concentration quickly rose and then reached a plateau value upon continued irradiation. The Fe(II) concentration at the plateau is a positive function of the initial concentration of $Fe(OH)^{2+}$. In solution without pollutant, Fe(II) is formed too, but the concentration at the plateau is lower in the presence of IP(fig.7). In this case, the reaction of oxidation of Fe(II) by ·OH radicals becomes important: Fe(II) appears to be the major sink of ·OH radicals (Eq.8) [28].

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + {}^{-}OH \qquad (8)$$
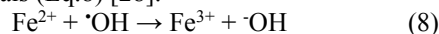
3-5- IP degradation by different system

Ultrasonic degradation efficiency of IP in an aqueous medium can be improved by combination of ultrasound application with advanced oxidation processes. One of the promising advanced oxidation processes is the photochemical treatment in the presence of UV radiation in presence of Fe(III) [9]. Degradation kinetics of IP were shown in **fig.5**. The disappearance of IP in different system follows pseudo-first-order reaction kinetics **(Fig.6)**. It is better in combined system UV/Fe(III)/US than in each system only: UV/Fe(III) or US/Fe(III). **Fig. 9** shows that the pseudo-first order kinetics rate constant k_{app} in combined system (0.087 min^{-1}) is higher than the sum of the pseudo-first order kinetics rate constant k_{app} in the two other separate systems.
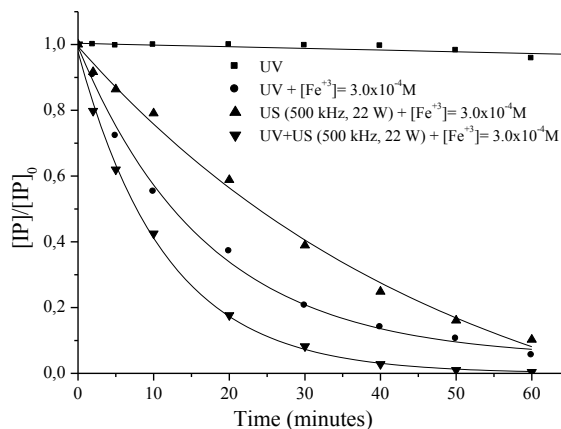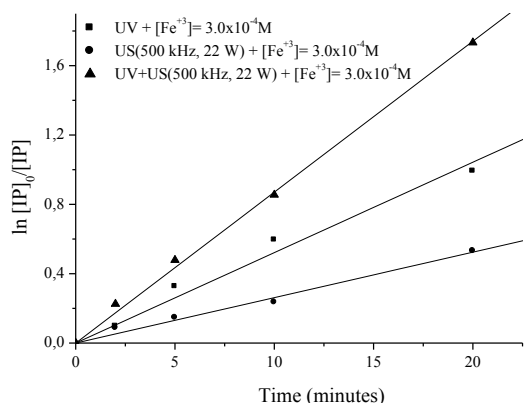

Fig.8: Comparison of IP (10^{-4} M) degradation kinetics in presence of Fe(III) salts (3×10^{-4} M) and with combination to ultrasound or/and ultraviolet.

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Fig. 9: Determination of the first-order rate constants for the transformation of IP (10^{-4} M) in presence Fe(III) salts (3×10^{-4} M), by different systems.

Shirgaonkar and Pandit [29] detected that the combined system UV/US gives a better degradation with 2,4,6-trichlorophenol at 22 kHz. Later a similar result was reported [30] during the sonochemical photodegradation of fenitrothion in presence of Fe (III) and oxalate at 20 kHz.
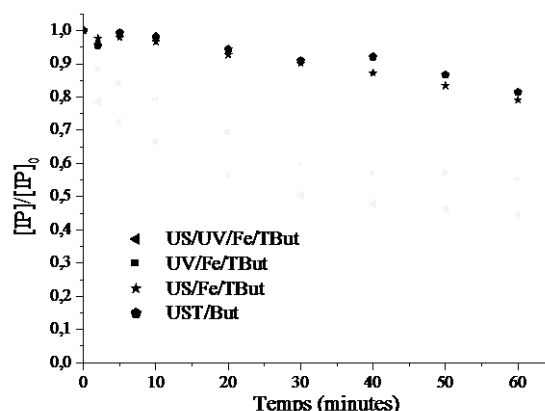
3-6- Effect of tert-butyl alcohol

Further evidence of the role of OH radicals as a primary oxidant can be established by carrying out the sonolysis in an aqueous solution of the IP containing 10^{-2} M tert-butyl alcohol. We expect t-butyl alcohol to scavenge hydroxide radicals under these experimental conditions (**Eq. 8**).

$$(CH_3)_3COH + {\cdot}OH \rightarrow {\cdot}CH_2(CH_3)_2COH + H_2O \quad (8)$$
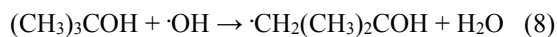
Extensive work on the sonochemistry of tert-butyl alcohol has been reported by Tauber et al [27]. They determined that the alcohol is pyrolized in the bubble via a free radical induced pyrolysis reaction mechanism. The tert-butyl alcohol is able to scavenge OH radicals in the bubble and prevent the accumulation of OH radicals at the interface of the bubble. In the present work, by maintaining higher concentrations of t-butanol, it should be possible to selectively scavenge the OH radicals, there by impeding the degradation of IP. Degradation kiniticks of IP following sonolysis in such an aqueous t-butanol solution is shown in **Fig. 8**.

It is apparent from fig. 8 that degradation has drastically slow down. This provides compelling evidence for the role of ${\cdot}$OH as the primary oxidative agent for the breakdown of IP. The degradation was effectively quenched, but not completely, by the addition of tert-butyl alcohol, suggesting that the main mechanism of IP destruction is chemical oxidation by hydroxyl radicals. This low degradation suggests that the

degradation takes place at the interface of liquid-gas bubbles where it is oxidized by hydroxyl radicals formed within the cavitation bubbles as a result of the sonolysis of water. Another factor that also affects the rate of IP degradation is the formation of degradation that accumulate inside the bubble. Such volatile products decrease the temperature inside the bubble, which, in turn, slow down the sonolytic reactions [27]. Muruganandham et al. [31] also it is observed that t-butanol addition decreases the degradation rate of Direct orange 39 notably in the ultrasound/goethite/H_2O_2 system.

Fig. 10: Effect of tert-butyl alcohol (10^{-2} M) on IP degradation through different systems.

3-6- Identification of degradation products and mechanisms of reaction

The characterization of the products was achieved by using chromatography (GC), coupled with mass spectrometry (MS) technique. The main intermediate products were identified by mass spectroscopy and represented in Table 2. A reaction mechanism was proposed (schema 1).

IP_1: demethylation of urea function can probably be initiated by OH radicals attack yielding CH_3OH in presence of electron and proton. The radical formed gives P_1.

IP_3: the primary stage is hydrogen atom abstraction

from a methyl group of the dimethylurea by ${\cdot}$OH followed by O_2 fixing on the radical formed (peroxy radical). After rearrangement then dehydration, an electron and a proton are fixed on the radical to give IP_3. IP_8: the first step of

mechanism is formation of ${\cdot}$OH adduct IP…OH followed by molecular oxygen oxidation. IP_2 is obtained by the same pathway from adduct formation IP_3…OH.

IP_4, IP_5, IP_6, IP_7, IP_9: was formed by IP, their pyrolysis products and recombination of two radicals.

Table 2: Structure and mass spectra of the main intermediate products

N	Tr (min)	m/z	Structure
IP$_1$	9.0	191, 16, 146	
IP$_2$	11.3	236, 221, 193, 178, 165, 151	
IP$_3$	11.6	220,205,193, 177,14949	
IP$_4$	14.1	327 , 326, 295, 283, 269, 255, 149	
IP$_5$	14.6	326, 236, 43 59	
IP$_6$	15.8	296, 266	
IP$_7$	15.9	298, 267, 255, 241 , 213	
IP$_8$	16.0	279, 264, 222, 207, 193, 180, 149, 137	
IP$_9$	16.2	285, 241, 227, 227, 167	

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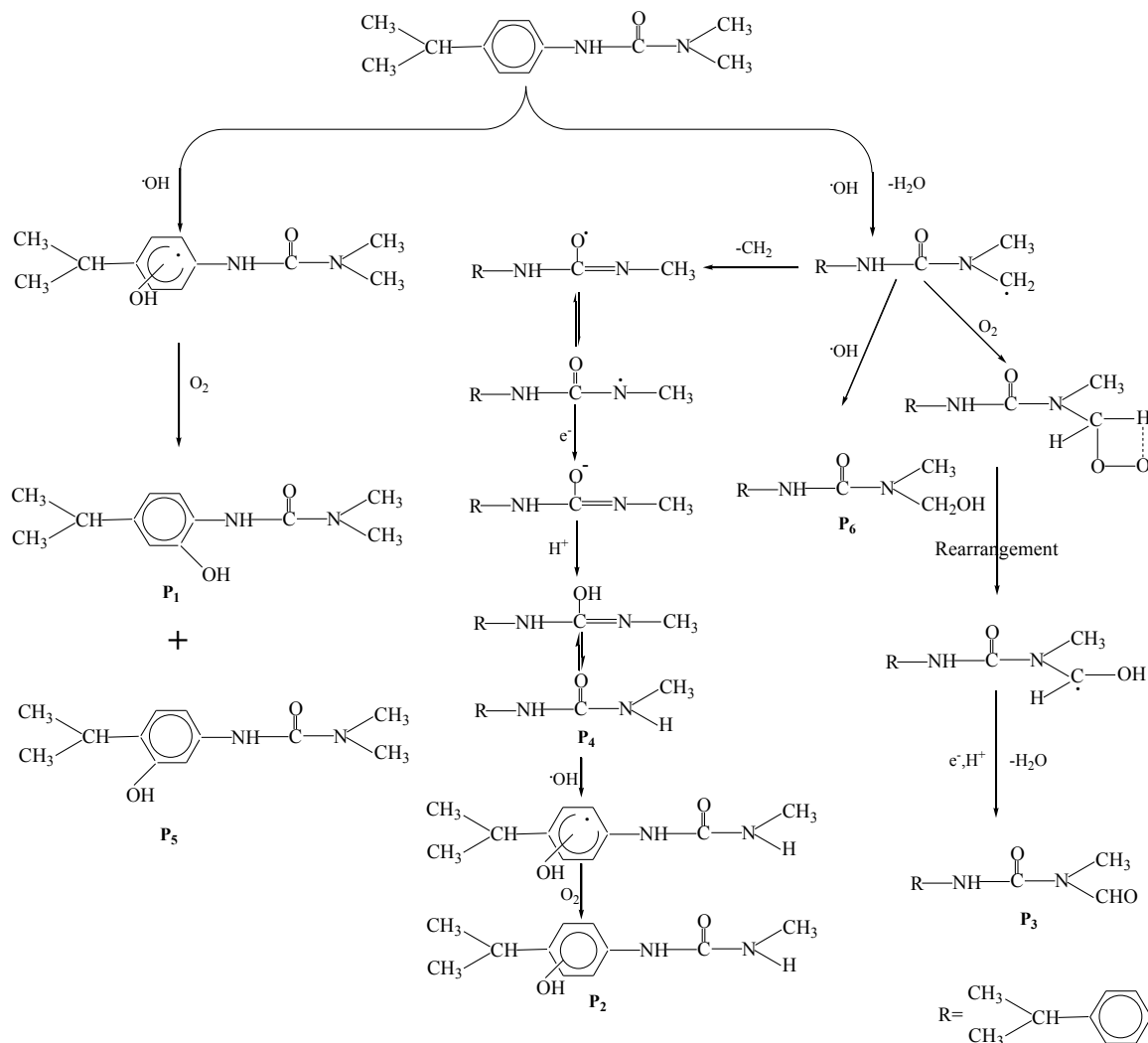
Schema 1: Mechanism of reaction

CONCLUSION

The present study has shown that IP can be degraded by high frequency ultrasonic irradiation (500 kHz) in aqueous solutions.

For the case of different present ultrasound powers, the system using 16 W of actual power, showed a low concentration of radicals, and consequently, low degradation rates. The 22 W system produced high degradation rates, therefore, the generation of hydrogen peroxide show a linear increase.

IP degradation in presence of Fe(III) under ultrasonic or UV irradiation and by combination of the processes was investigated. No improvement of the sonolytic degradation kinetics with addition of Fe(III) (3×10^{-4}M) whereas the degradation rate for US/Fe(III)/UV processes averred the highest amongst the three systems .

The principal intermediate products are the hydroxylation of aromatic ring demethylation and methyl oxidation to obtain the formyl compound in addition to the pyrolysis products.

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