Aqueous-Phase Mineralization of s-Triazine Using Pulsed Electrical Discharge

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Abstract- The present study investigates s-triazine mineralization and stability towards hydroxyl radical attack using pulsed electrical discharge in water. This process is an example of an advanced oxidation technology, AOT, capable of mineralizing the s-triazine ring. The Fenton reaction alone gives fairly poor mineralization of s-triazine, but mineralization is increased by a factor of two when the reaction takes place with electrical discharge. In addition to the hydroxyl radicals produced directly by the electrical discharge in water, ferrous salt in combination with hydrogen peroxide (produced by the discharge) is an additional source of hydroxyl radicals. It is further shown that utilization of a platinum high voltage electrode and a ferrous salt electrolyte led to more than 66% s-triazine mineralization within one hour. A simple mathematical model was also developed to describe s-triazine and product concentration profiles with Pt and NiCr electrode materials.

I. INTRODUCTION

S-triazine (1,3,5-triazine) is a six-component heterocyclic ring containing three nitrogen atoms and three carbon atoms (Fig. 1). S–triazine is the basis for a number of herbicides including atrazine, simazine, prometon and propazine. The U.S. Environmental Protection Agency estimated that atrazine is one of the most heavily used herbicides in the United States. Among current methods tested to completely degrade triazine herbicides are the advanced oxidation technologies (AOTs) which all involve the generation of highly oxidative and non-selective hydroxyl radicals. None of the conventional AOTs (e.g., Fenton chemistry [1], UV and ozone [2], ozone with H_2O_2 [3] and radiolysis techniques [4]) are able to completely degrade atrazine, the most studied s-triazine based herbicide, primarily because of low hydroxyl radical concentration and the stability of the heterocyclic ring.

Hydroxyl radicals can eliminate the side chains of atrazine leading to the formation of cyanuric acid as a final product, but can only induce s-triazine ring opening (i.e. degradation of cyanuric acid) at very high concentration and after several hours of operation [5]. Photocatalytic oxidation [6], Fenton system [1], and radiolysis [4] lead to cyanuric acid as the final product of atrazine oxidation without complete mineralization.

High voltage pulsed electrical discharge injects energy into an aqueous solution through formation of plasma-like channels between two submerged electrodes. It has been demonstrated that pulsed high-voltage electrical discharges generated directly in water initiate a variety of physical and chemical processes including the emission of ultraviolet radiation, formation of shock waves, and generation of chemically active species [7]. Emission spectroscopy has shown that the primary species produced by the water discharge are hydroxyl, hydroperoxyl, oxygen and hydrogen radicals [8], and indirect chemical methods have quantified hydroxyl

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radical concentrations and rates of production through utilization of various radical probes [9]. Direct chemical measurements revealed the presence of H_2O_2, molecular hydrogen and molecular oxygen [10]. Electrical discharges in water produced by high voltage pulses have been known to degrade various chemicals such as phenols [11-13], polychlorinated biphenyls (PCBs) [14], organic dyes [15], aniline [16] and monochlorophenols [17, 18].
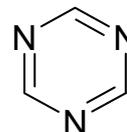
Fig. 1. Structure of s-triazine.

The rates of reaction of OH radicals with a number of substituted s-triazines have been determined to be close to the diffusion limit [19]. The rate constant of s-triazine with OH radicals was determined in pulse radiolysis to be $9.6*10^7 M^{-1}s^{-1}$, i.e., 30 times lower then the reactivity of atrazine with hydroxyl radicals [20]. In a second pulse radiolysis study, a significantly different value of $3.4*10^9 M^{-1}s^{-1}$ [21] was determined. The present study seeks to determine the reactivity of the 1,3,5-triazine ring with OH radicals generated by pulsed electrical discharges in water. Various electrolytes, electrode materials, and zeolites are utilized to determine the optimum conditions for s-triazine mineralization.

II. EXPERIMENTAL SECTION

The chemicals used included 1,3,5-triazine ($C_3H_3N_3$), ferrous sulfate ($FeSO_4*7H_2O$), ferric chloride ($FeCl_3$), hydrochloric acid (HCl), potassium chloride (KCl), sodium hydroxide (NaOH), sodium persulfate ($Na_2S_2O_8$), hydrogen peroxide (H_2O_2, 30%) and sodium thiosulfate ($Na_2S_2O_3$) (all were obtained from Fisher Scientific Inc., Pittsburgh, PA). All chemicals were used as received from the manufacturer. Zeolite Fe-ZSM5 was prepared by solid state ion exchange with ZSM5 (Zeolyst

International, Valley Forge, PA) [22]. Platinum wire (Fisher Scientific Inc., Pittsburgh, PA), nickel-chromium alloy (NiCr) (Consolidated Electronic Wire & Cable, Chicago, IL) wire and stainless steel disk (Washington Alloy Co.) were used as received from the manufacturers. Solutions of $FeSO_4*7H_2O$ (500μM/L), $FeCl_3$ (185μM/L), HCl (0.1mM/L), KCl (0.8mM/L), NaOH (0.8mM/L), $Na_2S_2O_8$ (1mM), H_2O_2 (2mM) and $Na_2S_2O_3$ (0.9mM) of the same conductivity of 130μS/cm were prepared from de-ionized water (<1μS/cm).

Conductivity (Cole-Parmer Model 1484-10 conductivity meter) and pH (Fisher Accumet 950 pH meter) were measured at the beginning and the end of every experiment. The concentration of s-triazine was measured using a Perkin Elmer Series 200 HPLC system with a 5-μm reversed phase Supelcosil LC-18 column (25 cm × 4.6 mm; Supelco). An isocratic program used the Na_2HPO_4 (0.875g/L) and NaH_2PO_4 (0.25g/L) mixture as a mobile phase. The injection loop volume was 300μl. The detection wavelength was 250nm. Experiments were repeated at least twice for each condition and the variability was less than 5%.

All triazine solutions were prepared by dissolving 0.05g of s-triazine in 1L of DI water (0.617mM). In the experiments where 1g or 0.5g zeolite Fe-ZSM5 was used, the conductivity readings were immediately 210μS/cm or 110μS/cm after placing the zeolite inside the reactor most probably due to a release of salt ions from the zeolite. No additional salt was added into the solution for those cases. All the samples from the reactor were centrifuged for 15 minutes and analyzed for total organic carbon (TOC). In the experiment with Fe-ZSM5 possible leaching of the Fe^{2+} from the zeolite was tested by measuring free Fe^{2+} by the 1,10-phenantroline method [23]. The results showed that no Fe^{2+} was initially present in the sample (0min), and after 60min the concentration was 36μM. A control experiment to test the possibility of adsorption of 1,3,5-triazine on zeolite was also performed. After 60 min of electrical discharge, the resulting solution was filtered and the zeolite was collected on filter paper and placed in a glass beaker where 100mL of DI water was added. The solution was stirred over night, centrifuged, and analyzed by UV-vis spectrophotometry. The resulting spectra confirmed the absence of the characteristic s-triazine peak between 240 and 260nm.

In the experiments where ferrous salt was used, samples were taken every 10 minutes from the reactor and OH radicals were quenched by adding 1mL of methanol to the 5mL of the original sample. 1,3,5-triazine degradation with only Fenton reagents (no electrical discharge) was preformed as follows. At the beginning of the experiment, 0.5mM ferrous sulfate was added to 1L of 1,3,5-triazine aqueous solution. The reaction was initiated by adding H_2O_2. Every 5 minutes an aliquot with a specific concentration of the H_2O_2 (corresponding to the amount produced by electrical discharge, i.e. 0.019mL (0.19mM), every 5minutes) was added to the solution. The total sum of H_2O_2 aliquots added during 60 minutes was equal to the total amount of

H_2O_2 produced by the electrical discharge over one hour. H_2O_2 was added in this manner in order to keep experimental conditions of the Fenton reagent experiment without electrical discharge as similar as possible to the electrical discharge experiments where H_2O_2 is produced at a constant rate.

In the experiment where hydrogen gas was introduced into the reactor solution, a fritted glass sparger producing fine bubbles was used. The sparger was placed approximately 3cm from the high voltage (HV) electrode in order to preclude its influence on the discharge. Gas was bubbled 30 min before and throughout these experiments with a gas flow rate of 500mL/min.

Qualitative analysis of saturated aldehydes was performed as described in [24]. A few mL of the sample taken from the reactor was mixed with ~0.5g 2-thiobarbituric acid with the addition of few drops of phosphoric acid. The sample tube containing this mixture was placed in a water bath with a temperature of 80^0C and heated for a few minutes. The formation of orange color indicates the presence of aldehydes.

Measurements of the total organic carbon (TOC) were obtained using a Shimatzu TOC-Vws analyzer. Ion chromatography measurements were performed with an IonPack AS4A anion-exchange column (Dionex, 4500i).

The power supply used to generate the high voltage pulsed electrical discharges of positive polarity is the same as that used previously [25, 9]. The pulse-forming network consists of variable-voltage 0-100kV DC source (Universal Voltronics, Brookfield, CT), storage capacitor of 2nF and a rotating spark gap with pulse repetition frequency of 60Hz. All experiments were conducted with fixed applied voltages of 45kV. A Tektronix P6015A (Tektronix Inc., Beaverton, Oregon) high voltage probe coupled with to a Tektronix TDS 460 fast digital storage oscilloscope along with the P6021 Tektronix current probe were used to record peak voltage and peak current. Pulse energy of approximately 1.0J delivered to the reactor was calculated by integrating the product of the current and voltage.

A jacketed 1L glass reactor with point-to-plane geometry was used. Isothermal conditions were maintained by flowing cooling water through the jacket at 15 °C. A magnetic stirring bar was used at the bottom of the reactor to keep the solution well mixed. The point high voltage needle electrode was made from either platinum or nickel-chromium wire (diameter=0.79mm) and the planar ground electrode was made from a stainless steel disk attached to a stainless steel tube. Both electrodes were immersed in a water solution and separated by a distance of 5cm.

III. RESULTS AND DISCUSSION

A. KINETICS OF HYDROLYSIS OF 1,3,5-TRIAZINE IN MILDLY ACIDIC AND BASIC MEDIA

Experimental observations shown in Fig. 2 indicate that in the pH ranges 3 to 5 and 6 to 10, 1,3,5-traizine undergoes hydrolysis in the absence of the aqueous-

phase electrical discharge. It is clear that at pH=3.5 (HCl) the acid catalyzed 1,3,5-triazine hydrolysis takes place, whereas at pH=10.5 (NaOH) base induced hydrolysis predominates. At pH=5.5 (KCl or FeSO$_4$), 1,3,5-triazine does not hydrolyze. This observation is in agreement with previously reported experiments [26] where the kinetics of the acid catalyzed 1,3,5-triazine hydrolysis were determined. The first order rate constants for acid and base hydrolysis determined in the present study are 1.34×10^{-3} s^{-1} and 5.27×10^{-4} s^{-1}, respectively. The rate constant for pH=10.5 was determined from the slope of the semi-log plot for all experimental data (0-60 min). At pH=3.5, the initial rate during the first 10 minutes was used to determine the first order rate constant since after that time there were significant deviations from first order kinetics. The value of the acid catalyzed 1,3,5-triazine hydrolysis determined here is comparable to the reported value of 2.9×10^{-3} s^{-1} measured in formate buffer solution [26]. Literature data on base catalyzed hydrolysis was not found. The reaction pathway for the acid catalyzed hydrolysis of s-triazine was proposed [10] to be due to nucleophilic attack by a water molecule leading to an open ring product with an amino group and an aldehyde group side chain.
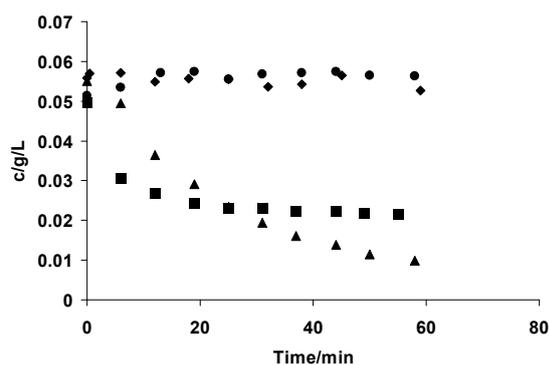
Fig. 2. Hydrolysis of 1,3,5-triazine in aqueous solution at different pH with no electrical discharge. Electrolytes: FeSO$_4$ (♦ pH=5.5), KCl (● pH=5.5), NaOH (▲ pH=10.5) and HCl (■ pH=3.5).

B. SALT EFFECT ON THE 1,3,5-TRIAZINE DEGRADATION

It has been shown that the choice of electrolyte and electrode material [10] have significant effects on organic pollutant removal in aqueous phase pulsed electrical discharge. Therefore, the efficiency of 1,3,5-triazine removal in the presence of electrical discharge was tested by employing various salts and two different electrode materials. Table I shows that for all initial pH and salt compositions (KCl, NaOH, HCl, Na$_2$S$_2$O$_3$ and FeCl$_3$) tested no significant 1,3,5-triazine degradation occurred. Experiments 1-10 are of oxidative nature while experiments 11 and 12 are reductive since the hydrogen gas bubbled in from outside the reactor is activated in the presence of the platinum electrode forming reductive species which may cause degradation [27]. Other organic compounds, including phenol, can be directly degraded and mineralized in pulsed electrical discharge in water by

direct reaction with OH radicals. The large ring stability due to the presence of three nitrogen atoms in s-triazine appears to require very high OH radical concentrations. The predominance of oxidative degradation is confirmed further in the present study where the strong oxidant sodium persulfate was used and with Fenton experiments.

TABLE I
The removal efficiency of 1,3,5-triazine with different electrolytes and two high voltage electrode materials. Applied voltage is 45kV.

Exper. No.	HV electrode	Electrolyte	Initial pH	Initial conductivity	% Triazine removed[*]
1	NiCr	KCl	5.5	130	3
2	NiCr Pt	KCl	5.5	130	7
3	Pt	NaOH	10.5	130	5
4	NiCr	NaOH	10.5	130	2
5	Pt	HCl	3.5	130	2
6	NiCr	HCl	3.5	130	2
7	Pt	Na$_2$S$_2$O$_3$	3.9	130	18
8	NiCr	Na$_2$S$_2$O$_3$	3.9	130	10
9	Pt	FeCl$_3$	3.5	130	10
10	NiCr	FeCl$_3$	3.5	130	8
11	Pt	KCl/H$_2$	5.5	130	8
12	NiCr	KCl/H$_2$	5.5	130	5

* BASED ON THE ONE HOUR OF OPERATION WHERE THE AMOUNT OF HYDROLYSIS IS TAKEN INTO ACCOUNT

Fig. 3 shows the normalized 1,3,5-triazine and TOC removal in the reference reactor with both NiCr and Pt HV electrodes with a sodium persulfate electrolyte. As shown in this figure, at this pH approximately 17% of 1,3,5-triazine undergoes acid catalyzed hydrolysis (without electrical discharge). When the discharge was used with NiCr HV, 40% of 1,3,5-triazine was removed over 1 hr. When the same experimental conditions were used and the NiCr electrode was replaced with Pt, 66% of the triazine was removed over the same length of time. Sodium persulfate is a well known oxidizer which thermally decomposes in aqueous solutions producing two strong oxidants: sulfate radical anion and hydroxyl radical [28]:
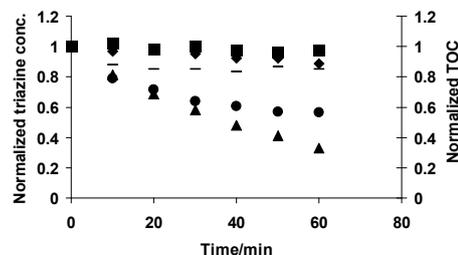
Fig. 3. 1,3,5-triazine degradation in the reference reactor with two HV electrodes and sodium persulfate electrolyte (pH=4.5). (▲=Conc., Pt HV, ●=Conc., NiCr HV, ■=TOC NiCr HV, – = No corona, ♦=TOC, Pt HV)

$$S_2O_8{}^{2-} \xrightarrow{\Delta T} SO_4{}^{\bullet -} \qquad (1)$$

$$SO_4{}^{\bullet -} + H_2O \rightarrow OH^{\bullet} + HSO_4{}^{-} \qquad (2)$$

These strong oxidants can react with 1,3,5-triazine leading to its degradation. TOC measurements shown in Fig. 3 revealed that no mineralization occurs with either of the electrodes (Pt or NiCr).

C. DEGRADATION OF 1,3,5-TRIAZINE WITH A FERROUS(II) SALT IN AN ELECTRICAL DISCHARGE WITH FENTON'S REACTION

Previous work has shown that ferrous sulfate used in the reference pulsed electrical discharge reactor considerably enhances the degradation of various pollutants such as PCBs and phenols [14, 29] due to the additional OH radicals generated via Fenton reaction [30]. In classical Fenton chemistry, hydroxyl radicals are formed in the reaction between Fe^{2+} and H_2O_2 at low pH by:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \qquad (3)$$
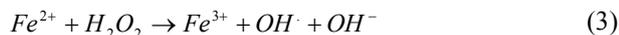
Fig. 4 shows the comparison of 1,3,5-triazine removal in a three different experiments:
1. Electrical discharge w/ Pt HV electrode and $FeSO_4$,
2. Electrical discharge w/ NiCr HV electrode and $FeSO_4$,
3. Classical Fenton reaction (no electrical discharge).
As shown in Fig. 4, in all three cases the 1,3,5-triazine concentration drops to zero within 50 min. In the case of the pulsed electrical discharge, with either Pt or NiCr HV electrodes, the triazine removal is complete after 30 min. whereas the Fenton reaction (no corona) needed an additional 20 min for the same result. These results imply that even when the same initial concentrations of ferrous sulfate and H_2O_2 are present in all three experiments, the electrical discharge produces additional hydroxyl radicals which lead to faster 1,3,5-triazine removal compared to the non-electrical discharge Fenton reagent experiment. It should be mentioned that at this pH, hydrolysis does not play a role in these experiments (control experiment, Fig. 2) and no by-products were observed.
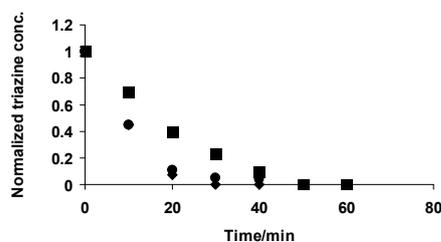
Fig. 4. Normalized 1,3,5-triazine concentration with $FeSO_4$ electrolyte (● Reference reactor with NiCr HV, ♦ Reference reactor with Pt HV electrode,■ Fenton reaction).

Fig. 5 shows normalized TOC removal corresponding to the same experiments presented in Fig. 4. It can be seen that the electrical discharge with a Pt HV electrode leads to the highest TOC removal (64% after 1 hr) while electrical discharge with NiCr HV electrode and Fenton reaction (no electrical discharge) give approximately the same TOC removal (25% after 1 hr). From these data it can be concluded that all three experiments lead to 1,3,5-triazine ring cleavage but to different extents. Since electrical discharge with the NiCr HV electrode and the no-discharge Fenton reagent experiments lead to similar degrees of mineralization, it would be expected that the change in 1,3,5-triazine concentration (Fig. 4) would be the same in both experiments. However, this is not the case because mineralization of the secondary reaction products from s-triazine appears to be rate limiting in comparison to the initial ring opening. The reaction of hydroxyl radicals with s-triazine leads to the formation of intermediate products which are further mineralized to CO_2. Since the Fenton's reaction alone without electrical discharge produces the least amount of hydroxyl radicals, there is slower production of these products (slower decrease in s-triazine removal) then in the case of NiCr HV electrode with Fe^{2+}. Even though both experiments lead to decreases in concentration, the TOC removals are the same because this is the rate limiting step.
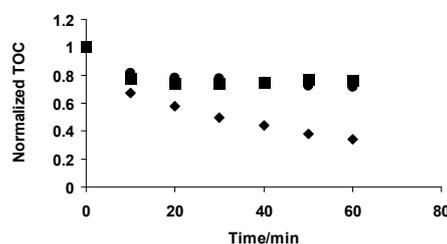
Fig. 5. Normalized 1,3,5-triazine TOC removal with $FeSO_4$ electrolyte (● Reference reactor with NiCr HV, ♦ Reference reactor with Pt HV electrode,■ Fenton reaction)

The reason why the electrical discharge with the Pt HV electrode gives rise to larger TOC removal can be explained based on the results published in previous work [31] where it was shown that the Pt particles emitted by the HV electrode chemically reduce the Fe^{3+} formed by the Fenton reaction back into the Fe^{2+}, thereby producing a catalytic cycle between Fe^{2+} and Fe^{3+}. Molecular hydrogen produced by the discharge adsorbs on the surface of Pt particles where it dissociates into atomic hydrogen which reduces Fe^{3+} to Fe^{2+}. This phenomenon was not observed with the NiCr electrode.

A large majority of the electrical discharge experiments with ferrous sulfate as an electrolyte have shown that the concentrations of targeted pollutant can drop to zero in one hour without any significant TOC removal [32]. This was explained by the fact that within that time, the degradation proceeds via Fenton reaction in which all the Fe^{2+} are oxidized to Fe^{3+}. The reverse reaction, in which Fe^{3+} are reduced to Fe^{2+}, is relatively

slow, mainly because the concentration of reductive species is very low. This is one of the main disadvantages in the Fenton process. The Pt HV electrode can be used to avoid that problem. Of course this advantage comes at the cost of Pt, and particularly of the continual injection of Pt. However, this cost may be avoided by utilizing suspended Pt particles in solution [33]. Once Fe^{2+} is converted to Fe^{3+} by the Fenton reaction, the Pt catalyst will form Fe^{2+} so the Fenton reaction can take place during the entire time of the experiment. This explanation is supported by the Pt HV TOC removal shown in Fig. 5 where it can be seen that the TOC value continuously drops with time. On the other hand, since the NiCr HV electrode and Fenton reagent are not involved in the Fe^{2+} regeneration, once Fe^{2+} is depleted, TOC removal stops in those cases.

In order to clarify the above explanation, a simple mathematical model was developed including the reactions found in Fenton chemistry and the rates of hydroxyl radical and H_2O_2 production measured in aqueous-phase electrical discharge. As shown in Table II, the model assumes the reaction between s-triazine and hydroxyl radicals where product P is formed (reaction 4, Table II). This product further reacts with hydroxyl radicals to form CO_2 (reaction 5, Table II) or it can form directly CO_2 by intramolecular rearrangement (reaction 6, Table II). Reactions 7-10 are typical reactions found in Fenton's chemistry where hydroxyl radicals are formed. Reaction 11 takes place when Pt is used as a high voltage material because it has been found that Pt regenerates Fe^{2+} from Fe^{3+}. This same reaction is zero for the NiCr case. The rate of H_2O_2 production by the aqueous-phase electrical discharge is incorporated in the model. Apart from hydroxyl radicals produced by the Fenton reaction, the electrical discharge produces additional radicals that are included in the model.

Fig. 6 shows the model results for the NiCr case. The triazine shows a good agreement between the model and experiment. On the other hand, the model predicts that the concentration of product formed reaches a maximum after 16min and then stays approximately constant until last 10min of the experiment when it starts to decrease. The model results when Pt is used as electrode material, Fig. 7, show good agreement between model and experiment for the s-triazine concentration. For this case, the product concentration reaches a maximum at 20 min after which it decreases almost linearly. The reason why the product distribution is different for the NiCr and Pt cases lies in the hydroxyl radical concentration. Fig. 8 shows that in Pt case, the OH radical concentration increases with time due to the constant regeneration of Fe^{2+} via reaction 11 in Table II. This is the reason why there is a constant decrease in product concentration, as shown in Fig. 7. In the NiCr case, there is no Fe^{2+} regeneration so the concentration of hydroxyl radicals reaches a maximum in 16 min after which it starts to drop. That is why in Fig. 6 the product concentration reaches a limit without further degradation (in the last 10 min of the experiment there is a slight degradation that is most likely due to Fe^{2+} formed by reaction 10 in Table II).

Fig. 9 shows the Fe^{2+} distribution for the Pt and NiCr electrode materials. It can be seen that in the NiCr case, Fe^{2+} are depleted after 16 min. whereas in the Pt case there is a much slower decrease of Fe^{2+} concentration which actually doesn't reach zero.

TABLE II
Reactions and rate constants used for the mathematical model simulation.

Rxn. No.	Reaction	Rate constant $(M^{-1}s^{-1})$	Ref. No.
4	$s-triazine + OH^{\cdot} \rightarrow P$	$3.4*10^9$	21
5	$P + OH^{\cdot} \rightarrow CO_2$	$1*10^{8,a}$	This work
6	$P \rightarrow CO_2$	$2*10^{-4,a}$	This work
7	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$	76	29
8	$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-}$	$4.3*10^8$	29
9	$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O$	$2.7*10^7$	29
10	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+}$	0.01	29
11	$Fe^{3+} \xrightarrow{Pt} Fe^{2+}$	0 NiCr 0.1^a Pt	This work
12	Rate of H_2O_2 formation	$6.1*10^{-7}$	35
13	Rate of $OH^{\cdot}$ formation	$6.7*10^{-8}$	9

a-FIT TO THE MODEL
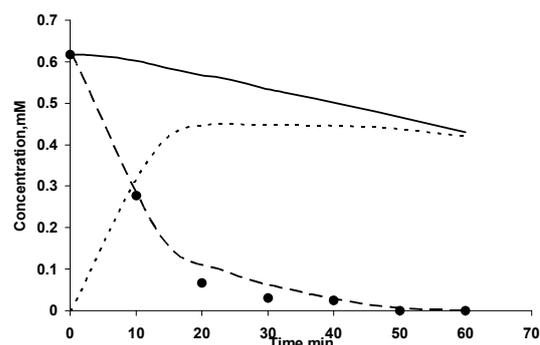
Fig. 6. Concentration profile of s-triazine and product with the NiCr electrode. Model results (Dashed line=Model,triazine, ●=Experiment, triazine, Solid line=Model,triazine+product, Dotted line =Model,product).

Since the sum of product concentration and triazine concentration in time represents TOC removal, it can be seen from figures 6 and 7 that the line representing the sum of product and triazine concentrations is comparable with the TOC removal experimentally measured and shown in Fig. 5. The differences in TOC between figures 6 and 7 and Fig. 5 can be seen in the first 10 minutes of the experiment. Fig. 5 shows much steeper TOC removal in the first ten minutes for both, Pt and NiCr then figures 6 and 7. The model did not account for some other initial intermediate compounds which can lead to the TOC removal.

Since the experiment with the Pt HV electrode and ferrous sulfate electrolyte showed the largest effect on the 1,3,5-triazine TOC removal, the effect of the Fe^{2+} concentration on TOC removal was further investigated.
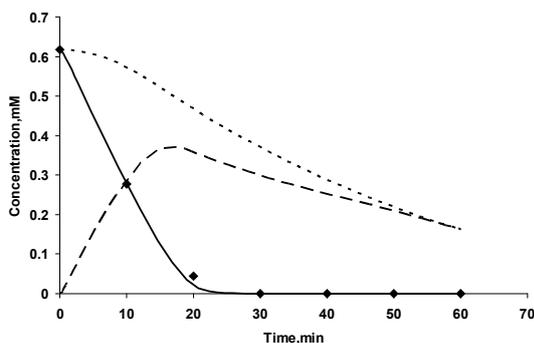
Fig. 7. Concentration profile of s-triazine and product with the Pt electrode. Model results (Solid line=Model,triazine, ♦= Experiment, triazine, Dotted line=Model,product+triazine, Dashed line =Model,product).
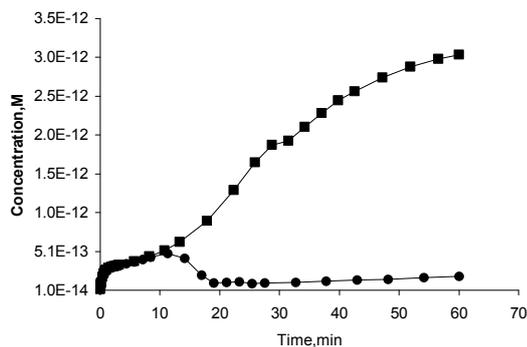
Fig. 8. Hydroxyl radicals concentration profile with Pt and NiCr electrode. Model results (■=Pt, ●=NiCr).

Fig. 9. Fe^{2+} concentration profile with Pt and NiCr electrode. Model results (●=NiCr, ■=Pt).
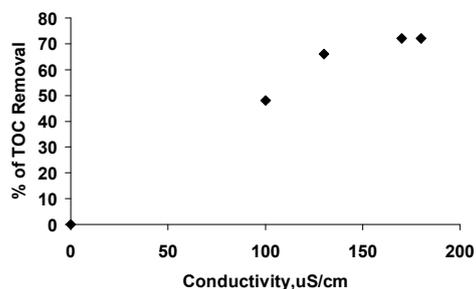
Fig. 10. The effect of the conductivity (Fe^{2+} concentration) on the percentage of the 1,3,5-triazine TOC removal. (%TOC data taken after 60 minutes of experiment, Pt HV electrode).

Fig. 10 shows normalized 1,3,5-triazine TOC removal with the Pt HV electrode in the reference reactor with the different initial concentrations of Fe^{2+}. It can be seen that when conductivity is fixed at 100μS/cm, after 60 min 50% of the TOC removal is observed. An increase in the initial concentration of Fe^{2+} which corresponds to a conductivity of 130 μS/cm leads to an increase in TOC removal to 66 %. Further increases in the initial concentration of Fe^{2+} (conductivity 170μS/cm and 180μS/cm) did not show any additional increase in TOC removal. One possible explanation for this behavior is that an increase in the initial Fe^{2+} concentration leads to an increase in the reaction rate between Fe^{2+} and OH radicals. Table III gives calculated initial concentrations of Fe^{2+} corresponding to the different initial solution conductivities. The reaction between Fe^{2+} and OH radicals with the corresponding rate constant is given as:

$$Fe^{2+} + OH^{\cdot} \rightarrow FeOH^{2+}$$
$$k_4 = 4.3 \cdot 10^8 M^{-1} s^{-1} \tag{14}$$

and the reaction between s-triazine and OH radicals:

$$s - triazine + OH^{\cdot} \rightarrow products \tag{15}$$

The second order reaction rate constant between OH radicals and s-triazine, determined by radiolysis, is k=9.7*10^7 M^{-1}s^{-1}[20]. For the 100, 130 and 170 μS/cm conductivities, the rate of reaction (14) is smaller than the rate of reaction (15). For the 180μS/cm conductivity, rate of reaction (14) is given as:

$$r = k \cdot c(Fe^{2+}) \cdot c(OH^{\cdot}) = 5.4 \cdot 10^4 \cdot c(OH^{\cdot}) \tag{16}$$

For s-triazine concentration of 0.05g/L (0.617m M) the rate of reaction (15) is:

$$r = k \cdot c(s - triazine) \cdot c(OH^{\cdot}) = 5.9 \cdot 10^4 \cdot c(OH^{\cdot}) \tag{17}$$

By comparing the rates of (16) and (17), it is clear that for the Fe^{2+} concentration of 1.258*10^{-4} M, the rate of reaction between Fe^{2+} and hydroxyl radicals becomes very close to the rate between hydroxyl radicals and 1,3,5-triazine. Therefore, the presence of significantly larger amounts of Fe^{2+} is not going to lead to further 1,3,5-triazine degradation but rather to scavenging the hydroxyl radicals [34]. It is also true that even in the case of 100μS/cm conductivity (Fe^{2+}=0.72*10^{-4}M) , the rate of reaction (6) has a similar order of magnitude as the rate at 180 μS/cm (Fe^{2+}=1.258*10^{-4} M). In that case the scavenging effects need to be explained by noticing that H_2O_2 production decreases with an increase in solution conductivity [13, 29]. As reported in [35], at 100μS/cm

the rate of H_2O_2 production is 0.6μmol/Ls whereas at 180μS/cm that same rate is 0.4μmol/Ls.

D.   HETEROGENEOUS   1,3,5-TRIAZINE DEGRADATION

It can be seen from Fig. 11 that the addition of 0.5g/L Fe-ZSM5 zeolite has a small effect on s-triazine mineralization with the Pt HV electrode. Increasing the zeolite concentration to 1g/L TOC led to a twofold increase in removal. The mechanism through which the Fe-ZSM5 zeolite works is very similar to the homogeneous Fenton's reaction where H_2O_2 reacts with Fe^{2+} (in this case bound to the zeolite structure) to produce hydroxyl radicals and Fe^{3+}. In the experiment with 0.5g/L, all the Fe^{2+} in the zeolite structure are converted to Fe^{3+} in the first 10 min so the mineralization stops. Increasing the zeolite concentration to 1g/L, provides more Fe^{2+} so mineralization takes place throughout the entire hour of the experiment. Compared to the Pt HV electrode experiment in which ferrous sulfate was used as an electrolyte, the presence of 1g/L Fe-ZSM5 zeolite showed the same TOC removal after 1 hr. In the first 30 minutes TOC removal was greater in the ferrous sulfate (homogeneous) case (Fig. 5). It is likely that diffusion and mass transfer limitations may limit the rate of s-triazine removal in the case with the porous zeolite particles.
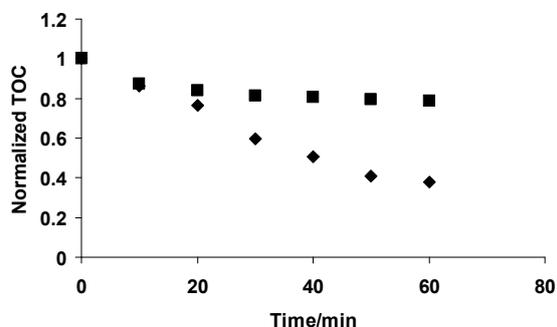
Fig. 11. Normalized 1,3,5-triazine TOC removal with two different amounts of the Fe-ZSM5 zeolite and Pt HV electrode .(♦=1g ,■=0.5g)

One of the benefits of using the Fe-ZSM5 zeolite instead of ferrous salt lies in the possible reuse of the zeolite after filtration. The present study did not test the capacity of the Fe-ZSM5 for reuse. It can also be noted that this zeolite prevents the formation of the yellow color which comes from the Fe^{3+} in the Fenton's reaction and fouling of the reactor glass walls can be avoided.

E. 1,3,5-TRIAZINE DEGRADATION BY-PRODUCTS

In all the above experiments, HPLC chromatograms showed almost no triazine degradation by-products even though it is likely that some hydroxylated products were formed. The retention time of s-triazine, due to a very low melting temperature was too short for analysis, by

GCMS. No other by-products were detected over a longer analysis time of 20 minutes.
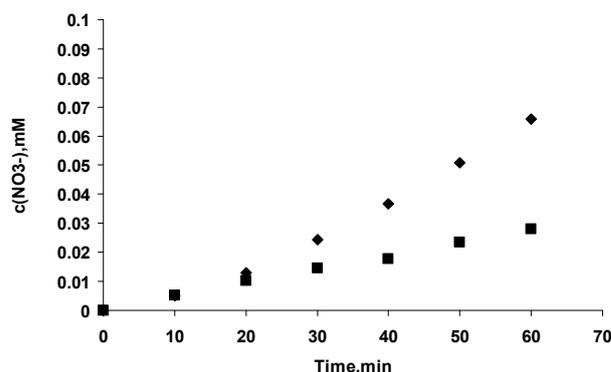
Fig. 12. Nitrate measurements from the experiment with the ferrous sulfate electrolyte and two different electrode materials.(♦=Pt ,■=NiCr)

Degradation of heterocyclic compounds like imidazole [36] suggests that the final ring opening by-products of this type of molecule are nitrate and nitrite ions. Ion chromatography measurements of the nitrate ions resulting from 1,3,5-triazine degradation are given in Fig. 12. These measurements are the result of the experimental conditions where ferrous sulfate was used as an electrolyte, and Pt and NiCr were used as HV electrodes (Fig. 4). It should be mentioned that no nitrite ions were detected (they were most probably oxidized to nitrate ions). As expected and experimentally observed, the Pt HV electrode, which leads to higher triazine degradation, formed 2.5 times more nitrate ions than the NiCr electrode. Assuming that one mole of s-triazine gives three moles of nitrate ions, calculations show that in the case of both electrode materials the final concentrations of nitrate ions are one order of magnitude less then theoretical. This would imply that other final by-products such as ammonium ions are formed which can account for this difference [36].

TABLE III.
Calculated concentrations of Fe^{2+} with different initial conductivities

Conductivity μScm^{-1}	m(FeSO$_4$*7H$_2$O) g	c(FeSO$_4$*7H$_2$O) M	c(Fe^{2+})M
100	0.1	$3.6*10^{-4}$	$0.72*10^{-4}$
130	0.15	$5.4*10^{-4}$	$1.08*10^{-4}$
170	0.17	$6.12*10^{-4}$	$1.224*10^{-4}$
180	0.175	$6.29*10^{-4}$	$1.258*10^{-4}$

The presence of ammonium ions was confirmed by a simple test in which a reactor sample after 60 minutes was mixed with sodium hydroxide giving ammonia as a hydrolysis product. Scheme 1 shows a proposed degradation pathway for s-triazine which is based on imidazole degradation [36]. In this mechanism, the ring opening of s-triazine was caused by a hydroxyl radical attack forming a long chained unsaturated aldehyde. This aldehyde can further be broken directly into carbon dioxide, or it can form nitrogen containing intermediates by an intramolecular rearrangement. By hydroxyl radical attack, nitrogen intermediates can give various products

such as amines and lower molecular weight alkyl aldehydes. Further oxidation leads to the formation of ammonium and nitrate ions as final degradation byproducts. The formation of nitrate ions is supported by the results shown in Fig. 12. The thiobarbituric test (taken after 40 minutes of the experiment) for the unsaturated aldehydes gave a positive result (formation of orange color) thus confirming the presence of aldehydes in solution. This is in the agreement with the scheme 1 where the ring opening product is an unsaturated aldehyde.

SCHEME I.
Proposed degradation pathway of-s-triazine
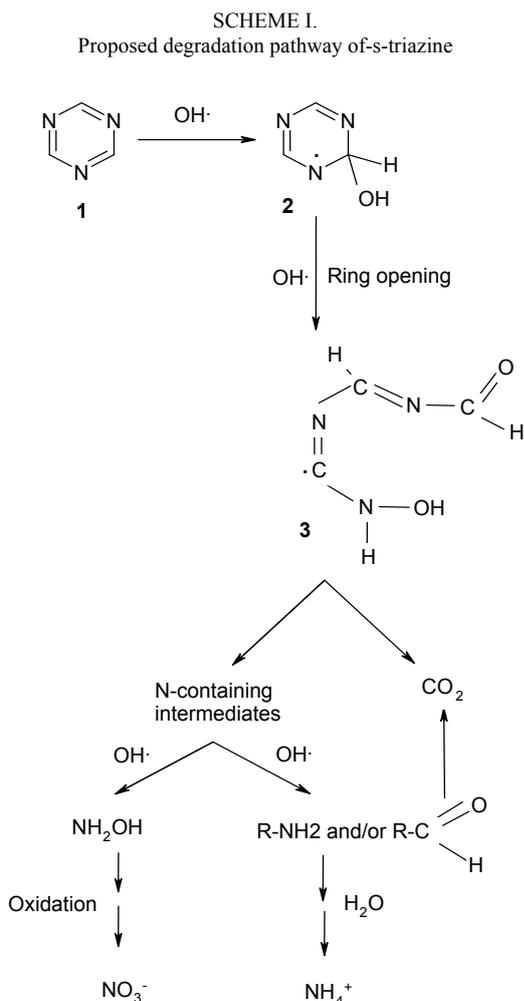
IV. CONCLUSIONS

The present study describes the effects of various electrolytes and electrode materials on the degradation of the s-triazine ring in an electrical discharge in water. It has been shown that triazine hydrolyses in acidic and basic media, and the rate constants of hydrolysis were determined. Also, the hydrolysis ring opening product of s-triazine is of similar structure to the one proposed by the hydroxyl radical attack. The pH dependent hydrolysis is of great importance when the s-triazine degradation by hydroxyl radicals needs to be distinguished from degradation by water molecules in hydrolysis. Salts that are typically effective in the aqueous phase electrical discharge for the destruction of different molecules showed no effect in the triazine degradation (excluding ferrous salts). Sodium persulfate leads to the removal of triazine but the TOC measurements for the same salt revealed no significant degradation (e.g, ring opening). The Fenton reaction without electrical discharge is capable of mineralizing 20% of the triazine after one hour of operation. This percentage of mineralization is completed in the first 10 minutes of the experiment due to the depletion of the Fe^{2+}. A similar result is observed in the case of electrical discharge with the NiCr HV electrode and ferrous sulfate electrolyte. In this case, mineralization of 20% is complete in the first ten minutes. It is likely that the amount of hydroxyl radicals produced directly by the electrical discharge is sufficient to cause a decrease in s-triazine concentration but not to cause further mineralization which is the rate limiting step. The best results were obtained for the case of the Pt HV electrode with a ferrous sulfate electrolyte. This experiment showed that 66% of the triazine can be degraded in one hour of electrical discharge operation. The shape of the TOC removal curve indicates that mineralization would continue for the longer operation times.

The explanation for this large mineralization with the Pt electrode lies in the catalytic activity of Pt to reduce Fe^{3+} into Fe^{2+}, thereby increasing the concentration of hydroxyl radicals through the Fenton's reaction. This same percentage of mineralization can be also achieved with the use of 1g/L zeolite Fe-ZSM5. The proposed mathematical model accurately fit the s-triazine concentration profiles for both electrode materials. The difference in the TOC removal for Pt and NiCr cases was based on the difference in hydroxyl radical concentrations which was also supported by the model. Based on the ions and intermediates detected, a degradation pathway for the s-triazine mineralization was proposed. The most important step in this pathway is ring opening causing formation of aldehydes which break down into fragments forming lower molecular aldehydes and alkyl amines followed by further oxidation to nitrate and ammonium ions. Based on the TOC removal the calculations have shown that the G-value for the s-triazine removal is $6.8*10^{-9}molJ^{-1}$ for Pt electrode and Fe^{2+} electrolyte and $3.5*10^{-9}molJ^{-1}$ for NiCr electrode with Fe^{2+} electrolyte.

REFERENCES

[1] Ventura, G.; Mouet, A.; Bermond and V. Camel," Electrochemical Generation of the Fenton's Reagent: Application to Atrazine Degradation", *Water Res,*, vol. 36, no. 14, pp. 3517-3522, Aug. 2002.

[2] Zwiener, C, "Atrazine and Parathion-Methyl Removal by UV and UV/O₃ in Drinking Water Treatment", *Int. J. Environ. An. Ch.*, vol. 58, no. 1-4, pp. 247-264, 1995.

[3] Beltran J.F.; Garcia-Araya J.F., Alvarez P.M. and J. Rivas., "Aqueous Degradation of Atrazine and Some of Its Main By-products with Ozone/Hydrogen Peroxide", *J. Chem. Technol. Biot.*, vol. 71, no. 4, pp. 345-355, Apr. 1998.

[4] Angelini, G.; Bucci, R.; Carnevaletti, F. and Colosimo, M., "Radiolytic Decomposition of Aqueous Atrazine", *Radiat. Phys. Chem.,* vol. 59, no.3, pp. 303-307, Sep.2002.

[5] Arnold, S.M.; Hickey, W. J. and Harris, R. S., "Degradation of Atrazine by Fenton's reagent: Condition Optimization and Product Quantification", *Environ. Sci. Technol.*, vol. 29, no. 5, pp. 2083-2089, Aug. 1995.

[6] Pelizzetti, E.; Maurino V.; Minero, C.; Carlin, V.; Pramauro, E. and Zerbinati, O., "Photocatalytic Degradation of Atrazine and Other s-Triazine Herbicides", *Environ. Sci.Technol.*, vol. 24, no. 10, pp. 1559-1565, Oct. 1990.

[7] Sunka, P.; Babický, V.; Člupek, M.; Lukes, P.; Simek, M.; Schmidt, J.; Černák, M., "Generation of chemically active species by electrical discharges in water", *Plasma Sources Sci.T.*, vol. 8, no. 2, pp. 258-265, May 1999.

[8] Sun, B.; Sato, M.; Clements, J.S., "Optical study of active species produced by a pulsed streamer corona discharge in water", *J. Electrostat.*, vol. 39, no. 3, pp. 189-202, Jul. 1997.

[9] M. Sahni and B. R. Locke, "Quantification of Hydroxyl Radicals Produced in Aqueous Phase Pulsed Electrical Discharge Reactors", *Ind. Eng. Chem. Res.*, vol. 45, no.17, pp. 5819-5825, Aug. 2006.

[10] Locke, B.R.; Sato, M.; Sunka, P.; Hoffmann, M.;, Chang J-S., "Electrohydraulic Discharge and Non Thermal Plasma for Water Treatment", *Ind.Eng. Chem. Res.*, vol. 45, no. 3, pp. 882-905, Feb. 2006.

[11] Sharma, A.K.; Locke, B.R.; Arce P. and Finney, W.C.," A Preliminary Study of Pulsed Streamer Corona Discharge for the Degradation of Phenol in Aqueous Solutions", *Hazard. Waste Hazard Mat.*, vol. 10, no. 2, pp. 209-219, Spr. 1993.

[12] Hoeben, W. F. L. M.; Van Veldhuizen, E. M. ; Rutgers W. R. and Kroesen, G. M. W., "Gas Phase Corona Discharges for Oxidation of Phenol in an Aqueous Solution", *J. Phys. D: Appl. Phys.,* vol. 32, no. 24, pp.133-137, Dec.1999.

[13] Lukes, P., "Water Treatment by Pulsed Streamer Corona Discharge", Ph.D.Dissertation, Institute of Chemical Technology, Environmental Eng. Program, Prague, Czech Republic, 2001.

[14] Sahni, M.; Finney, W.C. and Locke, B.R.,"Degradation of Aqueous Phase Polychlorinated Biphenyls (PCB) using Pulsed Corona Discharges", *J. Adv. Oxid. Technol.*, vol. 8, no. 1, pp. 105-111, Jan. 2005.

[15] Goheen, S.C.; Durham, D.E., McCulloch, M. and Heath, W.O., "The Degradation of Organic Dyes by Corona Discharge", Chemical Oxidation Technologies for the Nineties, W. W. Eckenfelder, A. R. Bowers, and J. A. Roth, Eds. Basel, CH: Techomoic AG, pp. 356-367, 1994.

[16] Tezuka, M. and Iwasaki, M., "Plasma-induced Degradation of Aniline in Aqueous Solution", *Thin Solid Films*, vol. 386, no. 2, pp. 204-207, May 2001.

[17] Sharma, A.K.; Josephson, G.B.; Camaioni, D.M. and Goheen, S.C.," Destruction of Pentachlorophenol using Glow Discharge Plasma Process", *Environ. Sci. Technol.*, vol. 34, no. 11, pp. 2267-2272, Jun. 2000.

[18] Brisset, J.L., "Removal of Pentachlorophenol from Water by AC Corona Discharge Treatment in Air", *J. Trace Microprobe T.*, vol. 16, no. 3, pp. 363-370, 1998.

[19] De Laat, J.; Chramosta, N.; Doré, M.; Suty, H. and Pouillot, M.,"Rate Constants for the Reaction of Hydroxyl Radicals with Some Degradation Byproducts of Atrazine", *Environ. Techn.*, vol. 15, no. 5, pp. 419-428, May 1994.

[20] Tauber, A. and Von Sonntag, C., "Products and Kinetics of the OH Radical Induced Dealkylation of Atrazine", *Acta hydroch.t hydrob,* vol. 28, no. 1, pp. 15-23, Feb. 2002.

[21] Joseph, J.M.; Jacob, T.A.; Manoj, V.M. and Aravindakumar, T.C.,"Oxidative Degradation of Triazine Derivatives in Aqueous Medium: A Radiation and Photochemical Study," *J. Agr. Food Chem.,* vol. 48, no. 8, pp. 3704-3709, Aug. 2000.

[22] Rauscher, M.; Kesore, K.; Manning, R.; Schwieger, W.; Tissler, A. and Turek, T., "Preparation of a highly reactive Fe-ZSM-5 catalyst through solid-state ion exchange for the catalytic decomposition of N₂O", *Appl. Catal. A-Gen.*, vol. 184, no. 2, pp. 249-256, Aug. 1999.

[23] Furman, N.H., Iron, in: Standard Methods of Chemical Analysis, vol. 1, Van Nostrand, Princeton, pp. 529-555, 1962.

[24] Feigl, F. and E. Libergott, Spot Test for Aromatic and α,β-unsaturated Aldehydes, *Anal. Chem.*, vol. 36, no. 6, pp. 132-140, 1964.

[25] Sahni, M. and Locke, B.R.," Quantification of Reductive Species Produced By High Voltage Electrical Discharges In Water", *Plasma Process. Polym.*, vol. 3, no. 4-5, pp. 342-354, Jul. 2006.

[26] Privman, M. and Zuman, P: "Kinetics of Hydrolysis of 1,3,5-triazine in Mildly Acidic Media", *Heterocycles,* vol. 37 , no. 3, pp. 1637-1644, May 1994.

[27] Krasna, A.I., "The Activation of Molecular Hydrogen by Platinum", *J. Am. Chem. Soc.*, vol. 83, no. 2, pp. 289-293,1961.

[28] Tan, L.C. and House, D.A., "Peroxodisulfate Oxidations .2. Kinetics and Mechanism of Peroxodisulfate-Sulfur (IV) Reaction", *New Zeal. J. Sci.,* vol. 17, no. 3, pp. 319-325, 1974.

[29] Grymonpré, D.R.;Sharma, A.K.; Finney, W.C. and Locke, B.R.,"The Role of Fenton's Reaction in Aqueous Phase Pulsed Streamer Corona Reactors", *Chem. Eng. J.,* vol. 82 , no. 1-3, pp. 189-207, Mar. 2001.

[30] Pignatello, J.J.; E. Oliveros, and A. MacKay, "Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry", *Crit. Rev.Environ. Sci. Tec.*, vol. 36, no. 1, pp. 1-84, 2006.

[31] Međedović, S. and Locke B.R., **"**The Role of Platinum as the High Voltage Electrode in the Enhancement of Fenton's Reaction in Liquid Phase Pulsed Electrical Discharge", *Appl. Catal. B: Environ.*, vol. 67, no. 3-4, pp. 149-159, Oct. 2006.

[32] Grymonpré D.R.,"An Experimental and Theoretical Analysis of Phenol Degradation by Pulsed Corona Discharge", Ph.D. Dissertation, Chem. Eng. Program, FAMU-FSU College of Engineering, Florida State University, Tallahassee, 2001.

[33] Ershov B.G., "The Nature of Colloidal Platinum in Aqueous Solution: Features of Catalytic Reactions", *Russ. Chem. B.,* vol. 50, no. 4, pp. 626-630, Apr. 2002.

[34] Jiju, J.M., Destaillats H., Hung, H-M., and Hoffmann M.R., "The Sonochemical Degradation of Azobenzene and Related Azo Dyes: Rate Enhancements via Fenton's Reactions", *J. Phys. Chem.A*, vol. 104, no. 2, pp. 301-307, Jan. 2000.

[35] Kirkpatrick, M.J. and Locke B.R., "Hydrogen, Oxygen, and Hydrogen Peroxide Formation in Aqueous Phase Pulsed Corona Electrical Discharge", *Ind.Eng.Chem. Res.*, vol. 44, no. 12, pp. 4243-4248, Jun. 2005.

[36] Nohara, K.; Hidaka, H.; Pelizzetti, E. and Serpone, N., "Processes of Formation of NH₄⁺ and NO₃⁻ ions During the Photocatalyzed Oxidation of N-containing Compounds at the Titania/Water Interface", *J. Photoch. Photobio. A*, vol. 102, no. 2-3, pp. 265-272, Jan. 1997.