Impact of Fenton and ozone on oxidation of wastewater containing nitroaromatic compounds

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Abstract

Fenton and ozone treatment was investigated at laboratory scale for the degradation of aqueous solutions of nitrobenzene (NB). Effects of reactants concentration (O_3, H_2O_2, and Fe(II)), temperature, and pH on NB degradation were monitored. Reaction kinetic of these processes was also assessed. A rapid reaction took place for Fenton process at higher initial concentration of H_2O_2, higher temperatures, and more acidic conditions (pH 3). Similarly, ozonation reaction exhibited rapid rates for higher ozone dose, higher temperatures, and more basic conditions (pH 11). Complete NB degradation in 65 min was achieved using Fenton process. The conditions of complete elimination of 100 mg/L of initial NB concentration, were 250 mg/L of H_2O_2 concentration, pH 3, and 10 mg/L of Fe(II) concentration. Under these conditions, 55% organic carbon elimination was achieved. Total organic carbon mineralization was attained in 240 min reaction time by Fenton process with 900 mg/L of H_2O_2 concentration, and 30 mg/L of Fe(II) concentration. Fenton reaction showed a pseudo-first order kinetic; the reaction rate constant was ranged from 0.0226 to 0.0658 min^{-1}. Complete NB degradation was also achieved for an ozone dose of the order of 2.5 g/L. The ozonation was studied at different ozone doses, different initial pH (7–11) and at different temperatures (15–35°C). NB ozonation kinetic was represented by a bi-molecular kinetic model which was reduced to pseudo-first order kinetic. The pseudo-first order reaction rate constant was determined to increase at 20°C from 0.004 to 0.020 min^{-1} as the used ozone increased from 0.4 to 1.9 g/L.

Key words: nitro-aromatics; chemical oxidation; organic matter content

Introduction

Nitroaromatic compounds have quickly risen in infamy as important water contaminants that threaten human health (EPA, 2002). Nitrobenzene (NB) was introduced into the environment, in general, from industrial uses, it can also be formed in the atmosphere through nitration processes. Nitroaromatic compounds are used in the manufacture of pesticides, dyes and explosives. As a result of its wide use, these compounds are often detected in industrial effluents, ambient freshwater, ambient environments, and atmosphere (Lipczynsks, 1992). Nitroaromatics have high toxicity to humans and can provoke serious health problems, e.g., blood dyscrasia, eyes and skin irritations, and affect the central nervous system (George *et al*., 1991).

Conventional biological treatments are usually the most feasible treatment options (Contreras *et al*., 2003). However, biological treatment systems removal efficiencies can be greatly reduced because of sudden spills of nitroaromatic compounds entering the treatment system (Makris and Banerjee, 2002); the low and high pH stresses taking place in the treatment system (Yu and Mohn, 2002); and

the presence of poorly biodegradable organic substances (Gamal El-Din and Smith, 2001, 2002). Nitroaromatics have been reported to go through the biological treatment systems without being removed (Rodriguez *et al*., 2000).

Among nitroaromatic compounds, NB is the common pollutant. NB has been used for the production of aniline, aniline dyes, explosives, pesticides, paint solvent, and drugs (Aysegul and Mirat, 2003). Available information indicated that NB is moderately toxic and suspected carcinogenic to humans (Rodriguez *et al*., 2000; Aysegul and Mirat, 2003). As NB in aqueous form does not bind well to soil, it can move through the ground and enter groundwater. Furthermore, the presence of NB in municipal wastewaters in a concentration between 20 and 100 mg/L has been detected (Contreras *et al*., 2003). Studies on NB stability in water have been estimated that its half-life varies from one day for natural channels to 3.8 d in an aerated lagoon (Zoeteman *et al*., 1980; Davis *et al*., 1983). NB is considered as hardly biodegradable compound and inhibitory for activated sludge (Contreras *et al*., 2003).

Previous studies have demonstrated that chemical and physical processes like coagulation, adsorption, and precipitation can readily remove organic compounds from wastewater (Kang and Chang, 1997; Sheng and Cheng,

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1999). However, these processes merely transfer the form of waste, from liquid to solid waste and consequently the residue need further disposal (Al-Momani *et al.*, 2004). Recently, there have been considerable interests in utilization of advanced oxidation processes (AOPs) for destruction of organic compounds (Bidga, 1995; Beltran *et al.*, 1999; Benitez *et al.*, 2003). Advanced oxidation processes are based on the formation of high reactive hydroxyl radicals. These radicals attack non-selectively the organic matter leading to degrade it into other smaller compounds (Oussi *et al.*, 1997; Al-Momani *et al.*, 2001; Chamarro *et al.*, 2001; Contreras *et al.*, 2002; Rodriguez *et al.*, 2002; Al Momani *et al.*, 2004). Different combinations used to produce hydroxyl radical were reported elsewhere (Heinzle *et al.*, 1995; Chamarro *et al.*, 2001; Ben Abderrazik *et al.*, 2002; Al Momani *et al.*, 2004). Among these processes, Fenton process and ozone oxidation can be used efficiently for aromatic removal. A successful removal of NB by Fenton, ozone, and O_3/UV was recommended in different studies (Akata and Gurol, 1992; Lipczynska, 1992; Glaze *et al.*, 1992; Bidga, 1995; Kang and Chang, 1997; Beltran *et al.*, 1998). The predominant mechanism for NB removal, in these processes, was the reactions of generated free radicals with NB molecule. The individual effect of direct ozonation was proposed to be very slow. The works performed by other researcher (Zepp *et al.*, 1987; Zepp *et al.*, 1992; Hoigne, 1997) suggested that the reactivity of NB with the generated free radicals is high.

Kinetic of any chemical process is very important argument, from both theoretical and practical point of view. Proper kinetics data is the best way to achieve optimum operational conditions, economic reactor design, helpful process control, and economical capital and operational cost. The effect of different operational conditions (reagents, contaminants, pH, and temperature) are also important treatment parameters.

Accordingly, this study was carried out to investigate the degradation of NB by Fenton and ozone. The specific objectives of this study included: (1) to further our fundamental understanding of chemical oxidation of NB by AOPs; (2) to determine the effect of important parameters such as reagents doses, pH, and temperature on the removal of NB in both processes; (3) to verify the predominant mechanism for NB removal; (4) to measure the kinetics rate constant for degradation of NB by Fenton and ozone.

1 Materials and methods

1.1 Reagents

Nitrobenzen (> 98%, Merck), H_2O_2 (30%, Merck), iron sulphate 7-hydrate $FeSO_4·7H_2O$ (98%, Panreac), sodium hydrogen sulphite solution (40% *W/V*, Panreac), potassium permanganate (99%, Probus), acetonitrile (99.8%, isocratic grade for HPLC, Merck), phosphoric acid (85.5%, Probus), potassium dichromate (99%, Probus), mercury sulfate (98%, Probus), silver sulfate (98%, Probus), and sulfuric acid (95%–98%, Fluka) .

1.2 Analytical methods

NB concentration was determined by reverse-phase high performance liquid chromatography (HPLC). HPLC analysis was performed with a Shimadzu liquid chromatograph (Shimadzu, Japan) equipped with Shimadzu pumps (model LC-10 AT) and a UV-Vis detector (model SPD-10A). The reverse-phase column was a C_{18} Bondapak, (3.9 mm ID x 300 mm length, Waters, USA). The mobile phase mixture of water and acetonitrile was (65%/35%) isocratically delivered to the column by a pump at a flow rate of 1 ml/min. The wavelength of the UV absorbance was set at 277 nm when using the UV-Vis detector. Under these conditions, the retention time for NB was 13 min. To ensure reasonable measurements, the prepared standard solution and the measurements of tested concentration were repeated for 5 times. The obtained results were averaged and tested to give a maximum of 5% standard deviation of the mean value.

The dissolved organic carbon was measured using a TOC analyzer with potassium phthalate solution as a calibration standard. Each sample was tested for three times to ensure reproducibility. Measurements were averaged and the average value was used in preparing figures. The observed precision in TOC measurements was in the range of ±1 mgC/L.

1.3 Installation

The Experiments were conducted using the setup shown in Fig.1. The setup consists of a mixing tank in which a 100 mg/L of NB solution was prepared with water. Solutions were perfectly mixed to guarantee that all NB was dissolved. For Fenton experiments, the required concentrations of iron salt $FeSO_4·7H_2O$ were added to the mixing tank. A jacketed continuous stirred tank reactor (CSTR) equipped with magnetic bar and base agitator was used for perfect mixing and reaction. The reaction temperature was maintained at a pre-set temperature and regulated by circulating water using a thermostatic water bath. A neutralization tank was used to neutralize the treated solution if required. An ozone generator was used for supplying ozone that will be used in the ozonation reaction of NB solution. The ozone was supplied to the CSTR via plastic tubes and was distributed in the water solution using a diffuser (Fig.1). Peristaltic pumps were used to transfer the solutions from one tank to the other.

1.4 Procedure

1.4.1 Fenton experiments

The Experiments were carried out in batch mode. In each experiment a NB and iron ion were prepared with water in mixing tank. After that, the reactor was filled with the solution, and was mixed for 5 min. A 30% aqueous hydrogen peroxide solution was injected into the reactor at different initial concentrations and start timing. During the experiments, samples were withdrawn from the reactor at several time intervals (0, 10, 20, 30, 40, 50, and 65 min), tested for H_2O_2 consumption with Quantofix® test sticks and quenched with sodium hydrogen sulphite to avoid
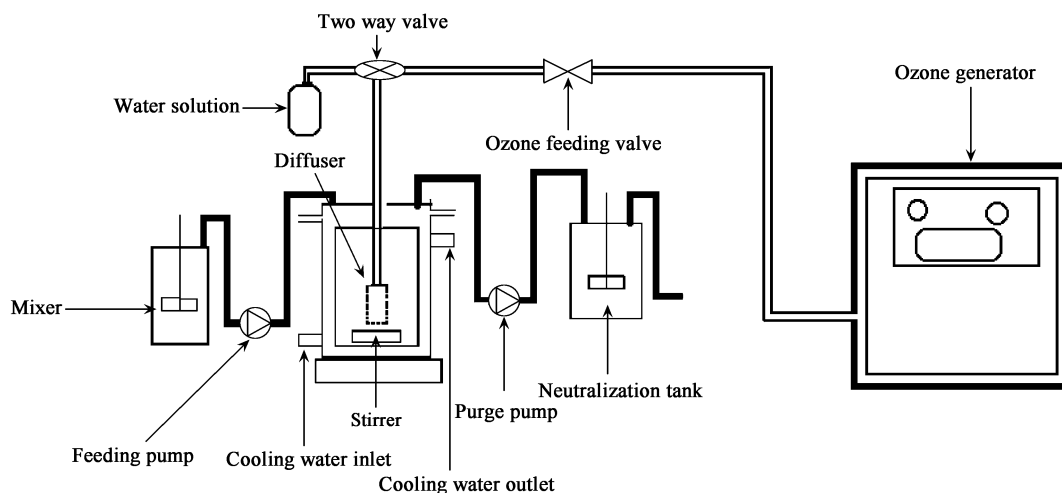
Fig. 1 Experimental installation.

further reactions. The withdrawn samples were used later for TOC analysis.

1.4.2 Ozonation experiments

Experiments were carried out in batch mode. The NB was dissolved in water, and mixed in the mixing tank. The solution was transferred to the CSTR and mixed for 5 min. After an initial sample was taken. The ozone generator was switched on at specific production rate. To assure constant ozone production rate throughout the experiment, ozone generator was switched on 15 min in advance. Then, ozone was introduced to the reactor via the two way valve and timing was started. The dissolved ozone in the reactor and residual ozone concentrations were determined using two analytical methods: (1) a spectrophotometric measurement (ozone maximum absorbance is 260 nm); (2) indigo method according to the procedure stipulated in standard methods (APHA-AWWA-WEF, 1992).

2 Results and discussion

First, a BOD test was performed with 100 mg/L NB aqueous solution, BOD_5 and BOD_{21} were 0. It means that the substrate was completely non-biodegradable. And conventional biological treatment is not an efficient method for treating such wastewater. Volatility at 45°C and stripping at 25°C were also tested. For both tests, less than 9% of compound losses were detected after 2 h treatment (data are not shown). Accordingly, two types of advanced oxidation processes–Fenton process and ozonation were used as a chemical treatment to treat wastewater containing NB.

2.1 Degradation of NB by Fenton process

It is known that the degradation efficiency of Fenton process is related to the amount of hydroxyl radical produced during the oxidation process. The chemistry of Fenton process shows that hydroxyl radical can be produced via two ways: (1) the degradation of two molecule of hydrogen peroxide to produce one hydroxyl radical (Eq.(1)); (2) the oxidation-reduction reaction between iron ion and

hydrogen peroxide (Eq.(2)). Accordingly, it was decided to follow the effect of both reagents (H_2O_2 and Fe(II)) on NB degradation efficiency.

$$2H_2O_2 \longrightarrow H_2O + OH^\bullet + HOO^\bullet \qquad (1)$$

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + OH^\bullet + OH^- \qquad (2)$$
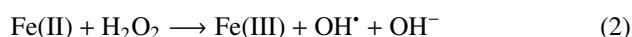
Figure 2 illustrates the evolution of NB concentration as a function of Fenton reaction time at three different initial concentrations of hydrogen peroxide. Presented results are the average of three identical experiments performed at the same condition and maximum standard deviation was 9%. Initial Fe(II) concentration used in experiments was 10 mg/L. Significant effect of H_2O_2 initial concentration on NB degradation efficiency was observed throughout the reaction, as H_2O_2 initial concentration was increased from 65 to 250 mg/L and NB degradation efficiency was increased from 75% to 100%.

The NB elimination efficiency is shown in Fig.3. The results are obtained at different initial concentrations of hydrogen peroxide and fixed initial Fe(II) concentration of 10 mg/L. The results show that NB could be efficiently degraded under Fenton conditions. A complete NB degradation was achieved in 65 min reaction time when 250 mg/L of H_2O_2 was used.
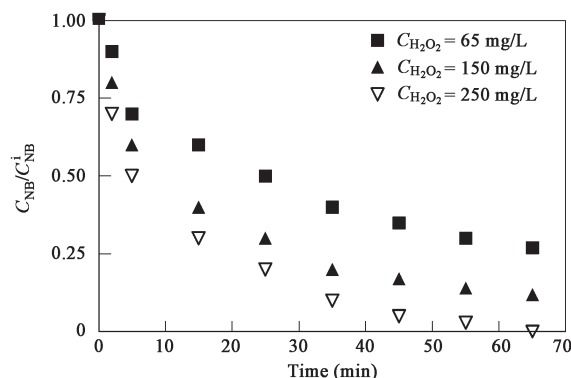

Fig. 2 Evolution of nitrobenzene (NB) as function of reaction time in Fenton process at different initial concentrations of hydrogen peroxide. Conditions: Initial Fe(II) concentration 10 mg/L; temperature 25°C; pH 3.
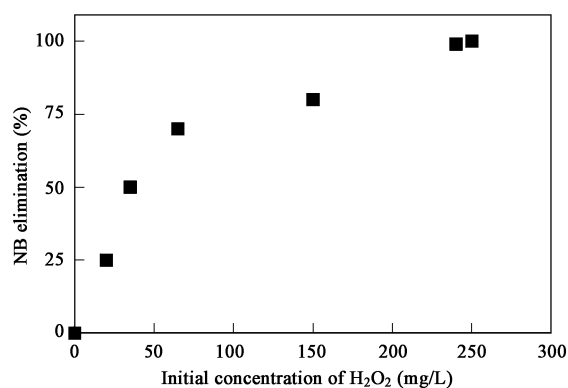
Fig. 3 NB elimination efficiency as function of initial H_2O_2 in Fenton process reaction. Conditins: initial Fe(II) concentration 10 mg/L; temperature 25°C; pH 3; reaction time 65 min.

The change in total organic matter content of the treated solution was followed. Fig.4 shows the organic mater evolution as a function of reaction time during Fenton reaction. During NB degradation, varying initial hydrogen peroxide concentration was led to change of TOC in the water solution. The organic mater mineralization rate was increased by 20%, when increasing the initial H_2O_2 from 65 to 250 mg/L.

Another set of Fenton experiments were carried out changing the initial concentration of Fe(II) with fixed initial concentration of H_2O_2 of 65 mg/L (Fig.5). Increasing the initial concentration of Fe(II) led a slight increase in NB elimination rate. In the contrary, at higher initial Fe(II), a decrease in the degradation efficiency was noticed. The observed tendency can be attributed to the scavenging effect of Fe-ion present in the solution (Murphy *et al.*, 1989; Ghaly *et al.*, 2001).

Figure 6 shows TOC results with respect to elimination tendency. It was also observed that, the elimination tendency follows the same tendency as NB elimination, a slight increase in TOC removal at low initial Fe(II) concentration and a low removal at higher initial Fe(II) concentration.

As the previous experiments were carried out at acidic pH (pH = 3), it was decided to study the effect of initial solution pH on the Fenton process degradation efficiency. The effect of initial solution pH at Fenton process is presented in Fig.7. A maximum NB degradation was
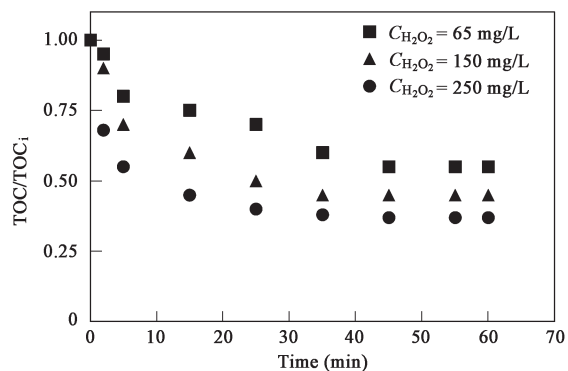

Fig. 5 NB elimination as function of initial Fe(II) in Fenton process. Conditions: initial H_2O_2 concentration 65 mg/L; temperature 25°C; pH 3; reaction time 65 min.

Fig. 6 Evolution of TOC as of reaction time at different initial Fe(II) concentration in Fenton process. Conditions: initial H_2O_2 concentration 65 mg/L; pH 3; temperature 25°C ; reaction time 65 min.

obtained at acidic pH (pH = 3). Low degradation efficiency was observed at higher pH value. As the solution pH was increased from 3 to 9, the NB elimination efficiency was decreased from 75% to 55%. Iron ions precipitating as hydroxide can be a result of such a tendency.

The effect of operational temperature on NB degradation was discussed. Increasing the operational temperature increase in Fenton process degradation efficiency. NB elimination efficiency increased from 65% up to 80% when the temperature changed from 15 to 30°C. TOC removal

Fig. 4 Evolution of total organic carbon (TOC) throughout Fenton process at different initial concentration of H_2O_2. Initial Fe(II) concentration 10 mg/L; temperature 25°C, pH 3; reaction time 65 min.
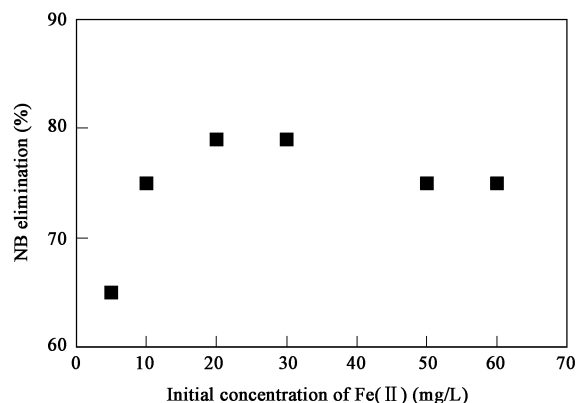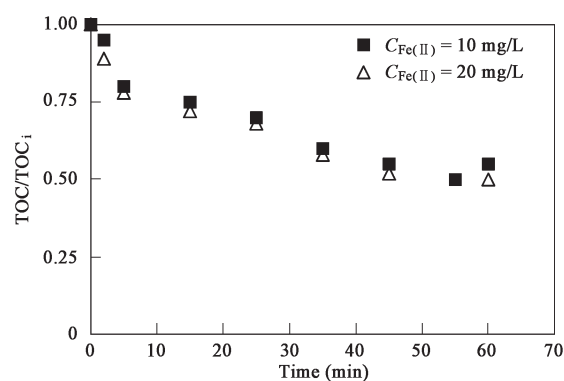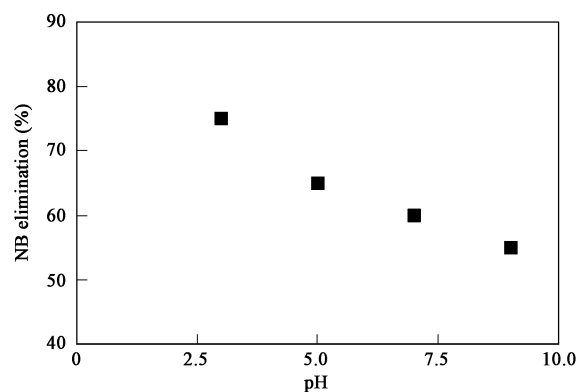

Fig. 7 NB degradation as function of pH. Conditions: initial H_2O_2 concentration 65 mg/L; initial Fe(II) concentration 10 mg/L; temperature 25°C; reaction time 65 min.

rate was also increased by 10% under the same operational temperature.

As Fenton process showed effective oxidation efficiency for NB solution, the ability of this process in mineralization of the total organic matter contained in the solution was examined. In these experiments, TOC measurements were used to follow the organic matter content. Fig.8 shows organic matter elimination in Fenton reaction at different initial concentrations of H_2O_2 and Fe(II). Fenton reaction is an effective method for total NB mineralization. Manipulating the initial reagents concentrations (H_2O_2 and Fe(II)) led to effectively remove the total organic carbon content within reasonable reaction time. A hydrogen peroxide initial concentration of 900 mg/L and initial concentration of Fe(II) of 30 mg/L was sufficient to eliminate all the contained organic matter.

2.2 Kinetic study of Fenton process

Understanding the chemical oxidation kinetics of the treatment process is very important theme, from both theoretical and practical point of view, for achieving higher treatment levels. With the proper kinetics data, optimal operational conditions and reactor design, effective process control, and economical capital and operational cost can be achieved. As hydroxyl radical is the main oxidants responsible on organic matter attack in Fenton reaction, the oxidation reaction can be represented by Eq.(3).

$$\frac{dC_{NB}}{dt} = kC_{NB}^{\alpha}C_{\cdot OH}^{\beta} \tag{3}$$

where, C_{NB} (mol/L) is concentration of NB at time t, $C_{\cdot OH}$ (mol/L) is concentration of hydroxyl radical at time t, α is the reaction order with respect to NB, β is the reaction order with respect to hydroxyl radical, and k is overall oxidation rate constant.

As the life time of hydroxyl radical is short, it is difficult to be measured and considered as constant at specific time. Eq.(3) can be rewritten in the form:

$$\frac{dC_{NB}}{dt} = k_0C_{NB}^{\alpha} \tag{4}$$

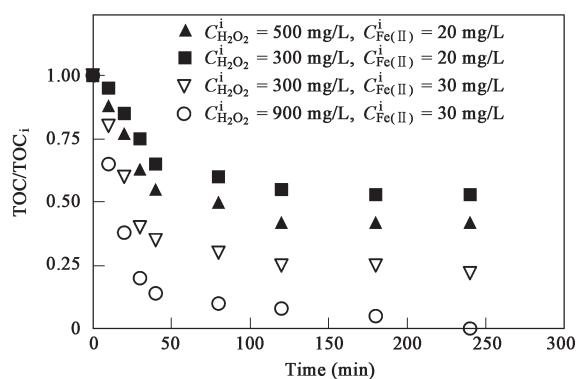where, k_0 is pseudo first-order NB degradation rate constant, i.e., apparent rate constant (min^{-1}). It is known that the oxidation kinetic of Fenton reaction can be modeled as a second order, with first order in each concentration of hydroxyl radical and pollutant (Glaze and Kang, 1989). Accordingly, Eq.(4) can be reduced to:

$$\frac{dC_{NB}}{dt} = k_0C_{NB} \tag{5}$$

If Eq.(5) is integrated with initial condition $C_{NB} = C_{NB}^i$ at $t = 0$, it will be resulted in:

$$\ln(\frac{C_{NB}^i}{C_{NB}}) = k_0t \tag{6}$$

According to Eq.(6), a plot of $\ln(C_{NB}^i/C_{NB})$ versus time must lead to a straight lines. Table 1 presents the kinetic data obtained during the oxidation of NB solution (presented data are the average of 5 experiments performed at the same conditions). A good correlation of the experimental points to a straight line ($R^2 > 0.90$) confirms the validity of the proposed model. Table 1 provides the k_0 values and half-life time for experiments performed at different initial concentrations of H_2O_2 and Fe(II) (between brackets, R^2 values).

Table 1 Kinetic data obtained during the oxidation of NB solution by Fenton reaction

Run	$C_{H_2O_2}^i$ (mg/L)	$C_{Fe(II)}^i$ (mg/L)	K_0 (min^{-1}) (R^2)	$t_{1/2}$ (min)
A1	65	10	0.0226 (0.90)	25
A2	150	10	0.0384 (0.90)	10
A3	250	10	0.0658 (0.97)	5
B1	65	5	0.0200 (0.90)	35
B2	65	20	0.0231 (0.92)	22
B3	65	30	0.0233 (0.89)	20
B4	65	50	0.0238 (0.93)	21
B5	65	60	0.0239 (0.95)	22

As it can be noticed, the effect of H_2O_2 on the kinetic constants are stronger than Fe(II) effect. As the initial concentration of H_2O_2 was increased from 65 to 250 mg/L, initial Fe(II) concentration was fixed at 10 mg/L, the pseudo first-order rate constant (k_0) was increased from 0.0226 to 0.0658 min^{-1}, and the half-life time was decreased from 25 to 5 min.

As mentioned previously, initial concentration of Fe(II) has a minor effect on NB degradation. This tendency was also observed by the obtained kinetic data; increasing the initial Fe(II) concentration from 5 to 60 mg/L, at the same initial H_2O_2, cause the increasing of pseudo first-order rate constant (k_0) from 0.0200 to 0.0239 min^{-1}. Similar tendency was observed with respect to half-life time.

2.3 Degradation of NB by ozonation process

The degradation of NB by ozone was studied over a temperature range of 15–35°C and at initial pH values of 7, 9, and 11. Fig.9 shows the experimental results for the ozonation of NB at various time of the reaction (initial NB concentration was 100 mg/L). At each set of operating conditions, at least 10 experimental runs were accomplished to insure that the experimental results are reproducible. The reaction of NB with ozone was very effective. The

Fig. 8 TOC reduction as function of reaction time for 100 mg/L NB. Temperature 25°C; pH 3.

concentration of NB was decreased progressively as a result of degradation by ozone oxidation reaction. Used ozone dosage of 2.6 g/L was sufficient during 180 min reaction time to abate 100 mg/L of aqueous solution of NB. Fig.10 also presents important kinetic data concern ozonation reaction. For most operational conditions half-life of NB in order of 50 min was observed.

The influence of operational pH on ozonation reaction was also studied. Fig.10 shows the experimental results obtained for the decay of the NB concentration as a function of reaction time during ozonation at three experimental pHs (7, 9, and 11). It is clearly seen, when the pH was increased the NB degradation rate was increased, simultaneously.

The positive influence of pH on the reaction rate could be attributed to the formation of high power oxidative radicals such as hydroxyl radical. As it is well known, ozone reacts with the organic matter in water via two pathways (Hoigne and Bader, 1976; Staehelin and Hoigne, 1983; Benitez *et al.*, 2003): with a direct attack of the solute of molecular ozone, or through a variety of derived oxygen radicals especially hydroxyl radical, which can act as secondary oxidants. In the first pathway, this direct attack is followed by an electrophilic aromatic substitution and undergoes very selective reactions. The second pathway is constituted by the action of radical species generated from the ozone decomposition, main hydroxyl radicals. The result is very fast reactions occurred with or-

ganic compounds with overall second order rate constants. Ozone decomposition is accelerated rapidly by the increase in the pH, especially in alkaline solutions. Therefore, these hydroxyl radical reactions would play an important role in oxidation reactions taking place in basic solutions. Based on experimental results, it might be conclude that NB is more reactive with hydroxyl radical than ozone itself.

The effect of operational temperature on ozonation reaction efficiency was investigated. It was noted that, at all experimental conditions, there was a modest trend indicating a significant increase in the NB degradation efficiency by increasing reaction temperature. At fixed ozone dose (1.4 mg/L), as the temperature increased from 15 to 30°C, the degradation efficiency of NB was increased from 65% to 85%. Similar trends were observed with experiments carried out with different used ozone dose.

2.4 Kinetic study of ozonation process

As presented previously, ozone reacts with organic matter via two pathways (Hoigne and Bader, 1976; Staehelin and Hoigne, 1983; Benitez *et al.*, 2003). Thus, its kinetic at different operational pH can be represented by:

$$-\frac{dC_{NB}}{dt} = k_1^* C_{NB} C_{O_3} + k_2^* C_{NB} C_{\cdot OH} \tag{7}$$

where, C_{O_3} (mol/L) is concentration of ozone at time t, $C_{\cdot OH}$ (mol/L) is concentration of hydroxyl radical at time t. C_{NB} (mol/L) is concentration of NB, k_1^*, and k_2^* are kinetic rate constants for direct molecular ozone oxidation and radicals oxidation, respectively. The units of k_1^* and k_2^* is $mol^{-1}s^{-1}$, i.e., second order kinetic, this indicates that both the direct (ozone) and indirect (hydroxyl radical) concentrations, and the NB concentration affect the reaction kinetic. As it is known that under basic conditions ozone decomposes to produce main hydroxyl radicals ($\cdot OH$). Thus, under the experimental conditions, Eq.(7) can be reduced to:

$$-\frac{dC_{NB}}{dt} = (k_1^* C_{O_3} + k_2^* C_{\cdot OH})/C_{NB} \tag{8}$$

the terms could be replaced by a constant, k_0:

$$-\frac{dC_{NB}}{dt} = k_0 C_{NB} \tag{9}$$

The previous assumption could be valid for three reasons: (1) the presence of sufficient concentrations of ozone and hydroxyl radicals; ozone was continuously bubbled in the aqueous solution; (2) ozonation reaction is known to behave as second overall kinetic with first order for each of the reactants (Trapido *et al.*, 1997); (3) under all the operational pHs, both oxidation pathways (direct and indirect) are important (Langlais *et al.*, 1991). However, a limiting step determines the global kinetic. Moreover, it is important to confirm that although ozone and hydroxyl radicals are the most important oxidants in the solution, other different types of radicals such as $\cdot OH$, $O_2^{\cdot -}$, $HO_2^{\cdot}$, $CO_3^{\cdot -}$, $HCO_3^{\cdot}$ can be detected in the reaction medium (Langlais *et al.*, 1991). At pH > 7, the ozonation mechanism showed that the free-radical initiating is the
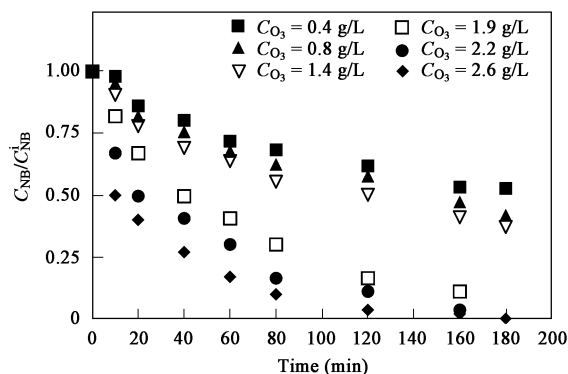

Fig. 9 Evolution of NB as function of reaction time in ozonation reaction at different used ozone concentrations. Temperature 25°C; pH 7.
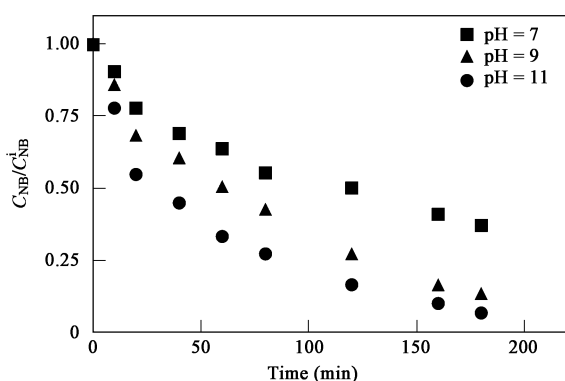

Fig. 10 Evolution of NB as function of reaction time in ozonation reaction at different operational pH. Temperature 25°C.

rate-determining step in the reaction (Trapido *et al*., 1997). Thus, a unique global reaction rate constant could be achieved.

Table 2 presents the averaged pseudo-first order rate constant (k_0) obtained at different experimental conditions for the oxidation reaction of NB with ozone. Reported values illustrate the effects of used ozone dose, operational pH and temperature on the averaged pseudo-first rate constant (k_0). A good relationship of the experimental data to the proposed model ($R^2 > 0.90$) confirms the validity of the proposed model.

Table 2   Kinetic data obtained during ozonation of NB at different used ozone dose

Run	ΔO_3 (g/L)	pH	Temperature (°C)	k_0* (min^{-1})	R^2	$t_{1/2}$ (min)
O1	0.4	7	25	0.004	0.94	158
O2	0.8	7	25	0.005	0.95	130
O3	1.4	7	25	0.006	0.92	120
O4	1.9	7	25	0.020	0.97	40
O5	2.2	7	25	0.015	0.98	20
O6	2.6	7	25	0.027	0.95	10
O7	1.4	9	25	0.011	0.99	60
O8	–	11	25	0.015	0.97	20
O9	1.4	7	15	0.003	0.98	–
O10	1.4	7	20	0.005	0.98	133
O11	1.4	7	35	0.013	0.97	40

* Average of five experiments were carried out at the same conditions.

At 25°C, increasing the solution pH from 7 to 11 caused an increase in pseudo-first order rate constant (k_0) from 0.006 to 0.015 min^{-1}. From the obtained kinetic values, it can be noticed that, the pseudo-first order rate constant (k_0) at basic conditions (pH 11) is higher than at acidic conditions. This tendency verifies the previous hypotheses that ozonation reaction is more effective at basic pH than in neutral and acidic pH (i.e., indirect pathway reacts more efficiently than direct pathway).

3 Conclusions

Advanced oxidation processes (Fenton and ozone) were studied for NB degradation. The studied processes efficiently degraded 100 mg/L NB in aqueous solution. The degradation rate of NB was strongly accelerated by the both processes. The degradation rate was influenced by many factors, such as initial ozone concentration, initial hydrogen peroxide concentration, initial iron-ion concentration, initial pH and temperature. Fenton and O_3 processes could be used successfully to achieve total NB degradation. Total NB degradation was obtained by the Fenton process in only 65 min of reaction time, and with initial reactant concentrations of 250 mg/L H_2O_2 and 10 mg/L Fe(II). The same degradation efficiency (100%) was obtained by ozonation reaction with used ozone dose of 2.6 g/L.

Reaction kinetics data is very important within the treatment process for optimal treatment operation conditions, feasible process control, and economical fixed capital cost. The kinetic experiments in aqueous solutions were performed. Fenton oxidation reaction was modeled to be

pseudo-first order. Different operational condition (initial reagent concentrations, pH, and temperature) on the rate constant was assists. Significant effect of initial H_2O_2 concentration on rate constant was observed. Increasing the initial H_2O_2 concentration from 65 to 250 mg/L led to increase the pseudo-first order constant from 0.0226 to 0.0658 min^{-1}. The reaction between ozone and NB was found to take bi-molecular rate expression representing ozonation reaction pathways (direct and indirect). At the same time, this rate expression was successfully reduced using to a pseudo first-order kinetics model. At pH of 11, the pseudo-first order reaction rate constant varied from 0.003 to 0.013 min^{-1} in the temperature range of 15–35°C. As the pH decreased from 11 to 7, the reaction rate also decreased. The half-life time for both processes (Fenton and ozone) were followed according to the decay in NB apparent concentration. At the pH of 3, reagent concentrations of 65 mg/L for H_2O_2 and 10 mg/L for Fe(II), a half-life time of 25 min was obtained for the Fenton reaction.

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