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ORIGINAL PAPER

Sonochemical removal of naphthol blue black azo dye: influence of parameters and effect of mineral ions

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Abstract Sonochemical degradation at 278 kHz of naphthol blue black (NBB, a diazo dye widely used in the textile and soap industries) has been investigated. The effects of different parameters and the influence of mineral matrix (bicarbonates ions and phosphates ions) on its sonodegradation have been evaluated. The influence of parameters linked to the pollutant (concentration: 0.50–97.32 µmol L^{-1}), to the technique (power: 20–100 W) and to the natural medium (pH 3–10.8; bicarbonate ions; phosphate ions) has been studied. The decolourisation rate of NBB increases when substrate concentration or ultrasound power increases. Bicarbonate ions at natural medium concentration (2.97 mmol L^{-1}) have a positive influence for low pollutant concentration (0.5–2.0 µmol L^{-1}), due to carbonate radicals. Phosphate ions may also improve the kinetics, but this effect depends on the pH domains. Furthermore, acid pH (pH 3) has a positive effect for high pollutant concentration, whereas basic pH (pH 10.8) has a positive influence at low pollutant concentration.

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Introduction

Coloured wastewater from many industries is a problem in large parts of the world. Due to their relatively high solubility, synthetic dyes are common water pollutants and are likely to be frequently found in industrial wastewater as trace quantities (Crini 2006). The release of those coloured wastewaters in environment is a considerable source of non-aesthetic pollution, eutrophication and chemical reactions, namely oxidation, hydrolysis, complexation and precipitation that take place in the aqueous phase. They are likely to generate metabolites, which are much more toxic than the parent pollutant (Neppolian et al. 2002).

Azo dyes are synthetic organic chemicals widely used in textile, pulp and paper, plastic, pharmaceutical, food, paint and other industries. They are characterized by the presence of at least one nitrogen-to-nitrogen double bond (–N=N–) bearing aromatic rings, and they dominate the worldwide market of dyestuff with a share of about 70 % (Soares et al. 2002). Furthermore, some azo dyes and their dye precursors have been proven or are suspected to be human carcinogens as they generate toxic aromatic amines (Stylidi et al. 2003). Therefore, colour removal has drawn an increasing attention of scientists, as indicated by the multitude of related research reports.

Many physical and chemical methods including adsorption, coagulation, ultrafiltration, reverse osmosis, membrane process and biological treatment have been used for the treatment of azo dyes (Latif et al. 2010). Nevertheless, they are non-destructive techniques since they just transfer organic pollutants from water to another phase, thus causing secondary pollution (retentate, sludge, adsorbent, etc.).

Among the advanced oxidation process (AOP), degradation of dye using high-frequency ultrasound has gained interest in recent years and some articles devoted to this topic have been previously reported by Özen et al. (2005). It is expected that the application of an ultrasound system to degrade the dye shows lots of advantages because this technique prevents the transfer of the pollutant from one part of environment to another, operates at ambient conditions and does not require the addition of any extra chemicals or catalysts (Kritikos et al. 2007).

This process is based on $^{\bullet}$OH radical production mainly through the acoustic cavitation, which is defined as the cyclical formation (nucleation), rapid growth (expansion) and collapse (implosion) of microbubbles in the liquid (Crum 1995; Suslick 1990). Fast collapse of the bubbles adiabatically compresses entrapped gas and vapour, which results in short and local hot spots according to Fitzgerald et al. (1956). At the final step of the collapse, the temperature and pressure inside the residual bubble or in the surrounding liquid are thought to be above 2,000 K and 500 bars, respectively. In this situation, entrapped molecules of dissolved gases, vaporized water and solutes can be brought to an excited state and dissociate. In particular, water and oxygen molecules undergo thermal dissociation and can generate $^{\bullet}$OH and $^{\bullet}$OOH radicals (Eqs. 1, 2) (Mason and Pétrier 2004). These primary radicals of sonolysis can react in three different zones: in the gas phase, at the cavitation bubble interface (recombination and formation of hydrogen peroxide, Eqs. 3, 4) and in the solution bulk (formation of hydrogen peroxide and initiation of oxidation reactions of pollutant P, Eq. 5) (David 2009).

$$H_2O +))) \rightarrow {}^{\bullet}H + {}^{\bullet}OH \quad (1)$$

$$^{\bullet}H + O_2 \rightarrow {}^{\bullet}OOH \quad (2)$$

$$2^{\bullet}OH \rightarrow H_2O_2 \qquad k = 5.5 \times 10^9\,\mathrm{L\,mol^{-1}\,s^{-1}} \quad (3)$$

$$2^{\bullet}OOH \leftrightarrow H_2O_2 + O_2 \quad (4)$$

$$P + {}^{\bullet}OH \rightarrow \text{by-product} \quad (5)$$

The chemical pathway and the rate of elimination depend on the volatility, hydrophobicity and surface activity of the pollutant (Hoffmann et al. 1996). A volatile and hydrophobic molecule will be incinerated inside the bubble of cavitation, while a non-volatile and hydrophilic molecule will be oxidized by the $^{\bullet}$OH radicals ejected from the cavitation bubble (Hoffmann et al. 1996; Pétrier et al. 1998). Finally, non-volatile and hydrophobic molecule will undergo mainly radical attacks at the cavitation bubble interface (Ashokkumar et al. 1997, 1999; Barbour et al. 1999).

Inorganic anions such as bicarbonate ions are usually present in industrial and natural waters. It is reported in literature that the bicarbonate ions in pollutant wastewater have negative effect on several AOPs: TiO_2 photocatalysis, photo-Fenton, UV/H_2O_2, UV/O_3 (Neppolian et al. 2002; Pignatello et al. 2006; Guittonneau et al. 1986; Tanaka et al. 2001). Nevertheless, their effects on sonochemical water treatment processes are controversial. Some papers have shown that the presence of bicarbonate ions does not affect appreciably the sonochemical elimination of organic pollutant (Cost et al. 1993; Gültekin et al. 2008), while other papers have provided evidence that sonolysis of organic substrates can be accelerated by the presence of inorganic anions (Guzman-Duque et al. 2011; Chiha et al. 2011; Minero et al. 2008).

In this study, in order to investigate the sonochemical degradation of dyes, a diazo dye naphthol blue black (NBB) has been chosen as a pollutant model. The effects of some parameters on the sonochemical decolourisation of NBB were evaluated: NBB concentration, ultrasonic power and pH. Therefore, the influence of inorganic species, such as bicarbonates ions, found abundantly in natural water and wastewater, was studied. Finally, the mineralization degree of NBB using ultrasound has been examinated by TOC measurement. This research was conducted both at the University of Grenoble and the University of Yaoundé, from October 2011 to March 2013.

Materials and methods

Chemicals

Naphthol blue black (NBB) was supplied by Sigma-Aldrich Corporation and used without any purification. Potassium iodide (KI) and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}$, $4H_2O$ come, respectively, from Acros Organics and Chimie Plus. Sodium bicarbonate was purchased from Prolabo, as H_3PO_4, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4, to test phosphate effect.

The water used to prepare solutions and clean the reactor and glassware was purified with activated carbon cartridges and then deionized thanks to ion exchange resins, from Fisher Bioblock Scientific.

Apparatus

The power system is a high-frequency generator (Radiocoms Systèmes ULV300A), which delivers a 278 kHz frequency. The impedance of this generator is set at 50 Ω and regulated by an impedance adapter. At the base of the reactor, a piezoelectric disc is fixed (diameter 4 cm) on a Pyrex plate (5 cm diameter) the role of which is to transmit the ultrasonic waves in the solution to be treated.

The cylindrical reactor (400 mL) is double-jacketed in order to maintain the system at a constant temperature (20 ± 1 °C) to avoid thermal fluctuation induced by ultrasound. Temperature is monitored thanks to a thermocouple immersed in the solution. The cooling water is cooled by a cryostat (Heto CB 8-30e).

Analysis

Quantitative analysis of NBB was performed by UV–visible spectroscopy thanks to a Shimadzu UV-mini 1240 spectrophotometer, set at a 618 nm wavelength. For an experiment, about 10 samples (each of them of 1.5 mL) are regularly withdrawn to be analysed.

A Shimadzu TOC-Vcsn analyser was used for total organic carbon (TOC) measures. The instrument was equipped with an automatic sample injector (ASI Oct 1–8). A solution of potassium phthalate was used as the calibration standard. Acidification and stripping were carried out before analyses.

H_2O_2 concentration is analytically determined by the spectrophotometric method, using potassium iodide (1 g L^{-1}) and ammonium heptamolybdate salt as catalyst (10^{-4} mol L^{-1}). Aliquots (1 mL) were taken from the reactor and were immediately added in the sample quartz bowl of the Shimadzu UV-mini 1240 spectrophotometer containing the reagents. Absorbance at a 350 nm wavelength was recorded after 5 min.

Experimental work

This work is devoted to the sonodegradation of naphthol blue black. Kinetics of sonodegradation was conducted in order to examine the influence of operating parameters, including pollutant initial concentration, power and pH. It also studies the presence of two different mineral ions, bicarbonate and phosphate, likely to be present in natural waters. Finally, TOC measurements were carried out in order to estimate the mineralization of the pollutant.

Results and discussion

Effect of concentration

When submitting a solution of NBB to ultrasound at 278 kHz, its concentration decreases exponentially as a function of the irradiation time (Fig. 1). This decrease can be expressed by Eq. (6) derived from a first-order kinetics.

$$C = C_0 \exp(-kt) \quad (6)$$

where C_0 is the initial concentration of pollutant, C is the concentration at the irradiation time t and k represents the rate constant of the first-order kinetics.

In parallel to the process of sonodegradation of NBB, hydrogen peroxide is formed in the solution, at a slightly lower rate than that of distilled water without any chemical target (Fig. 1). It is clear that in the absence of any substrate, the radical species ($^{\bullet}$OH and $^{\bullet}$OOH) formed in the cavitation bubble recombine at the interface bubble/

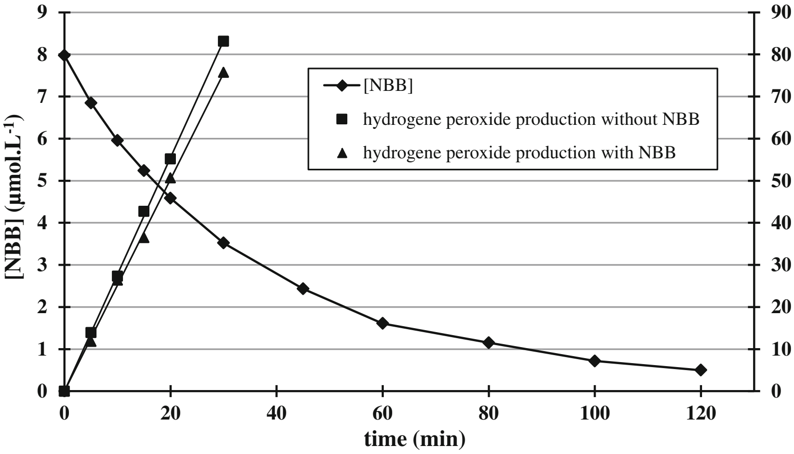

Fig. 1 Sonochemical degradation kinetics of NBB and comparison of H_2O_2 production in absence (*square*) and in presence (*triangle*) of NBB. $[NBB]_0$: 8.1 µmol.L^{-1}, frequency: 278 kHz, power: 100 W, volume: 400 mL, temperature: 20 ± 1 °C

solution to produce hydrogen peroxide, which is then ejected into the solution (Eqs. 3, 4).

The NBB is very soluble in water and nonvolatile. Therefore, its degradation takes place in solution via hydroxyl radicals attacks. Given the very short lifetime of these $^{\bullet}$OH radicals (about 70 ns, Haugland 1996), it is clear that only a small amount could not recombine and is ejected into the solution. There, those radicals react with the pollutant molecules and more specifically near the interface. Méndez-Arriaga et al. (2008) gradually added quantities of H_2O_2 equivalent to those produced by sonolysis in a solution of ibuprofen, mechanical stirred and in the absence of ultrasound. They found that there was no degradation of the pollutant, so hydrogen peroxide is not responsible for the ibuprofen sonochemical degradation, but the $^{\bullet}$OH at the bubble–solution interface are.

In our case, the same experiment as that of Méndez-Arriaga et al. (2008) was performed with a solution of NBB (8.1 μmol L^{-1}). In accordance with their results, it is shown that there is no influence of H_2O_2 on the oxidation rate of NBB (Fig. 1). Under these conditions, the hydrogen peroxide does not play any significant part, which means it would not cause the decolourisation of NBB solution. This action is attributed to $^{\bullet}$OH.

Figure 2 shows the evolution of the initial rate of the NBB decolourisation, V_i, depending on the NBB initial concentration C_0. At low concentration ($C_0 < 8.1$ μmol L^{-1}), it is noticed that the dependence of V_i on C_i is linear, reflecting a first-order kinetics (Luo and Hepel 2001). However, at high concentrations ($C_0 > 32.44$ μmol L^{-1}), the rate increases slightly, indicating the nature of uninsulated sonochemical reactions with the NBB. Also, this behaviour reflects the combined effects of by-products and oxidizing species generated in the solution, as radical species and by-products are known for their competition to react with $^{\bullet}$OH (Méndez-Arriaga et al. 2008). For the whole concentration range (0.50–97.32 μmol L^{-1}), the results show that the initial rate V_i increases with the initial concentration C_i.

However, the kinetic model of such a reaction established by several authors is the controversial subject. Some of them have argued that the degradation of pollutants does not follow first-order kinetics (Torres et al. 2008; Serpone et al. 1994). To test the hypothesis of a first-order kinetics, our results were analysed by applying the Langmuir kinetics law (Eq. 7) and its corresponding linear form (Eq. 8) as follows:

$$V_i = \frac{K'KC_i}{1 + KC_i} \tag{7}$$

$$\frac{1}{V_i} = \frac{1}{k'KC_i} + \frac{1}{K'} \tag{8}$$

where V_i is the initial rate, C_i the initial concentration, k' and K are the rate constant and the equilibrium constant, respectively, deduced from the intercept and the slope.

The respective values of k' and K are 0.73 μmol L^{-1}-min^{-1} and 7.62×10^{-2} μmol L^{-1} (Fig. 3). This kinetic model is similar to the Langmuir type, so the first order, that is in agreement with those reported in the literature (Luo and Hepel 2001). In addition, the NBB is very soluble in water (hydrophilic), and then, sonodegradation occurs mainly in the bulk of the solution. So some models based on a simultaneous degradation of the pollutant at the interface bubble/solution and in the solution cannot be applied, like the kinetic model proposed by Serpone et al. (1994).

Effect of power

From an economic perspective and in order to take into account the energetic cost, power is the most important

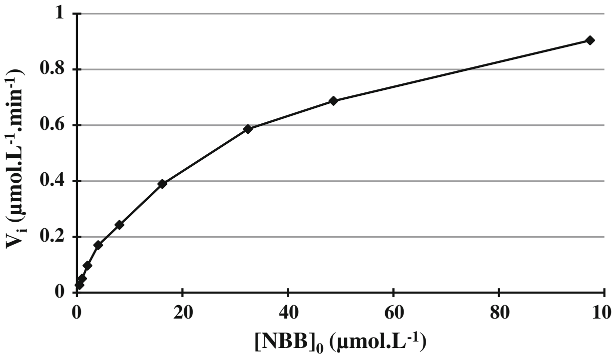

Fig. 2 Influence of initial concentration on initial rate of NBB sonochemical decolourisation. Frequency: 278 kHz, power: 100 W, volume: 400 mL, temperature: 20 ± 1 °C

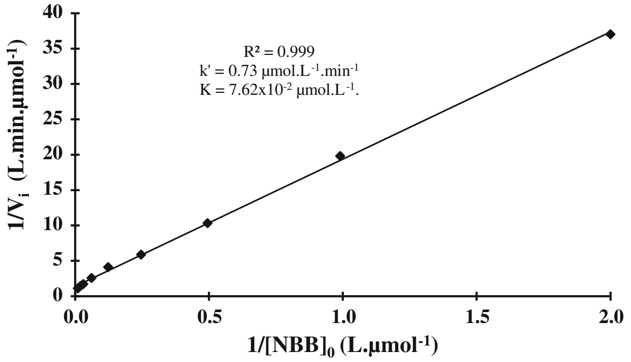

Fig. 3 Langmuir relationship between initial rate of NBB sonochemical decolourisation and initial concentration. $[NBB]_0 =$ 0.5–97.3 μmol L^{-1}, frequency: 278 kHz, power: 100 W, volume: 400 mL, temperature: 20 ± 1 °C

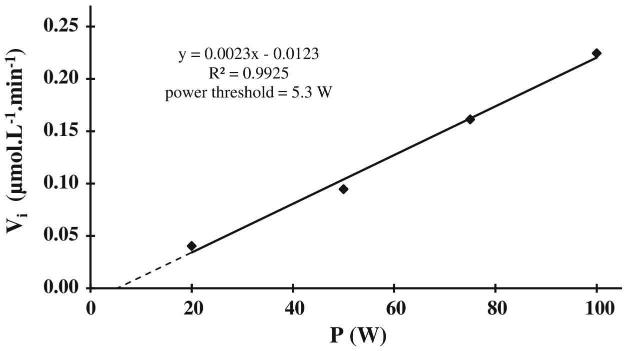

Fig. 4 Effect of power on the initial rate of NBB decolourisation. $[NBB]_0 = 8.1\ \mu mol\ L^{-1}$, frequency: 278 kHz, volume: 400 mL, temperature: 20 ± 1 °C

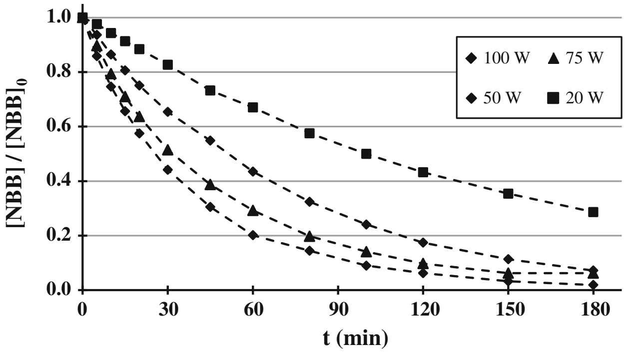

Fig. 5 Effect of power on the NBB sonochemical decolourisation. $[NBB]_0 = 8.1\ \mu mol\ L^{-1}$, frequency: 278 kHz, volume: 400 mL, temperature: 20 ± 1 °C

criterion for choosing a water treatment technique. In sonochemistry, power is one of the parameters responsible for the molecular activation.

At an operating frequency of 278 kHz, different ultrasonic powers (20, 50, 75 and 100 W) were applied. The calorimetric method (Mason et al. 1992) used to measure the power dissipated in the reactor reveals a yield of 58.5 ± 5.3 %.

Figure 4 shows to the decolourisation rate as a function of the applied power. For the power range studied, the decolourisation rate of sonochemical NBB increases linearly with the applied power. This linear dependence of the initial rate of sonochemical degradation versus power has been also reported for other chemicals (Hung et al. 2000). However, the power range is studied in an interval between the cavitation threshold and a maximum power value. Above the maximum power, the sonochemical effects are attenuated (Floger and Barnes 1968) and it is reported that no reaction is observed below the cavitation threshold, which is obtained for a 5.3 W power in our case (Fig. 4).

The effect of power on the degradation rate can be explained by the relationship between the activity of cavitation and the power. Generally, the ultrasonic power affects the cavitation by increasing the population of bubbles, resulting in an increase in $^{\bullet}OH$ as shown by Henglein (1987). As a consequence, the power thanks to the main degradation mechanism (radical attacks) will have a direct impact on the degree of conversion of NBB, as highlighted by Fig. 5 (Jiang et al. 2006).

Influence of mineral ions

Effect of bicarbonate

The physicochemical analyses of water have often revealed the presence of mineral ions, including ions HCO_3^- with levels depending on the nature of the effluent, and the site where the samples are carried out, as mentioned by Chiha et al. (2011). The inhibitory effect of bicarbonate ions on several advanced oxidation processes is well known (Neppolian et al. 2002; Pignatello et al. 2006; Guittonneau et al. 1986; Tanaka et al. 2001; Chen et al. 1997). However, its role in the treatment of these effluents by ultrasound is ambiguous, with contradictory data reported in literature. Recently, some works highlighting the accelerating effect of bicarbonates on the sonodegradation of recalcitrant pollutants at low concentrations were published, for instance by Guzman-Duque et al. (2011).

To have a better understanding of the influence of bicarbonate ions in aqueous medium, solutions of NBB in the presence and in the absence of HCO_3^- were submitted

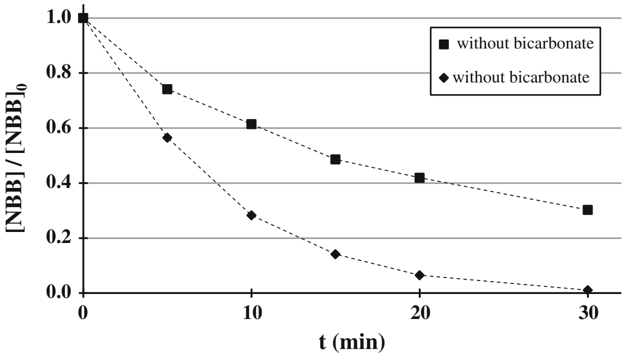

Fig. 6 Effect of bicarbonate ions on the sonochemical decolourisation of NBB (without *square* and with bicarbonates *diamond* ($250\ mg\ L^{-1}$); $[NBB]_o = 2\ \mu mol\ L^{-1}$; frequency: 278 kHz, power: 100 W, volume: 400 mL, temperature: 20 ± 1 °C)

to ultrasound. The 250 mg L^{-1} bicarbonate concentration used is not only in the optimal range of concentration values (Guzman-Duque et al. 2011), but is also mainly found in natural waters (Merouani et al. 2010).

Comparative kinetics of NBB sonochemical decolourisation were performed, in the absence and the presence of bicarbonate ions as a function of substrate concentration. They clearly put in evidence that the presence of HCO_3^- ions increases the rate of decolourisation of NBB, only for low initial NBB concentrations, 2 µmol L^{-1} for instance (Fig. 6). At 0.5 µmol L^{-1}, decolourisation rate of the NBB is four times faster in the presence of HCO_3^- that in the absence. When the initial substrate concentration increases, the effect of bicarbonate ions decreases and appears to stabilize at 32.44 µmol L^{-1} (Table 1). This result agrees with previous work in which the inhibitory effect of bicarbonate ions for high concentrations of the pollutant has been shown (Merouani et al. 2010).

Indeed bicarbonate ions are well known for their inhibitory effect on hydroxyl radicals, they react with them in the cavitation bubble to produce radical bicarbonates, which will migrate towards the bulk solution. Even if they are less reactive than $^{\bullet}OH$ radicals (2.8 V), $CO_3^{\bullet-}$ radicals are oxidant enough (1.78 V), more stable and more mobile (Guzman-Duque et al. 2011), which allows them to react with the hydrophilic NBB molecules in the bulk of the solution, hence increasing its rate of decolourisation (Eqs. 9, 10, 11).

$$CO_2 + HO^- \rightleftarrows HCO_3^- \tag{9}$$

$$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + H_2O \quad k = 8.5 \times 10^6\ L\,mol^{-1}\,s^{-1} \tag{10}$$

$$CO_3^{\bullet-} + P \rightarrow \cdots \rightarrow \text{Products} \tag{11}$$

Effect of phosphate

To evaluate the influence of phosphate on NBB sonodegradation, solutions of NBB (8.1 µmol L^{-1}) were irradiated, with a pH ranging from 3 to 10. pH was adjusted by addition of H_3PO_4, NaH_2PO_4, Na_2HPO_4 et Na_3PO_4 (3 mmol L^{-1}) and, according to the pH value, different anionic species are predominant: $H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-}.

As a result, the rate constant is influenced by the phosphate presence according to the pH (Fig. 7). Maximum effect is obtained at pH 3.1 and pH 8, with a corresponding rate constant of 0,039 and 0,038 min^{-1}, respectively.

In presence of anionic phosphate species, the $^{\bullet}OH$ radicals, created during ultrasound irradiation, are involved in a set of four Eqs. (12–15). Thus, phosphate radicals are produced, as reported by Jiang et al. (2002b): $H_2PO_4^{\bullet}$, $HPO_4^{-\bullet}$

Table 1 Ratio between initial rate of sonochemical decolourisation of NBB in presence and in absence of bicarbonates (250 mg L^{-1})

$[NBB]_0$ (µmol L^{-1})	0.5	1	2.02	4.05	8.1	16.22	32.44	48.66
V_i with HCO_3^-/V_i without HCO_3^-	4.35	3.40	2.40	1.43	1.42	1.25	1.17	1.06

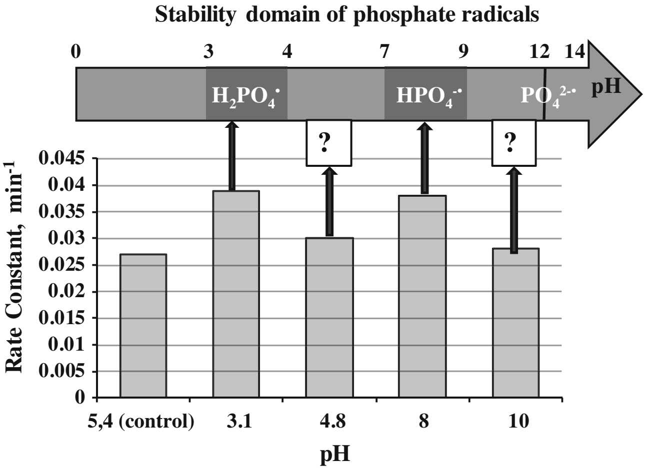

Fig. 7 Effect of phosphate ions on the sonochemical decolourisation of NBB according to the pH. $[NBB]_0 = 8.1$ µmol L^{-1}; $[H_2PO_4^{3-}] = [HPO_4^{2-}] = [PO_4^{3-}] = 3$ mmol L^{-1}; frequency: 278 kHz, power: 100 W, volume: 400 mL, temperature: 20 ± 1 °C

and $PO_4^{2-\bullet}$, corresponding to 3 stability pH zones respectively 3–4, 7–9 and 12 (Maruthamutu and Neta 1977).

Lifetime of phosphate radicals is about some millisecond (Rosso et al. 1998) while lifetime of hydroxyl radicals is very shorter (about 70 ns), so phosphate radicals are more stable. In the literature, these radicals were mentioned to react on organic and inorganic pollutants (Eq. 16), with the following efficiency: $H_2PO_4^\bullet > HPO_4^{-\bullet} > PO_4^{2-\bullet}$ (Maruthamutu and Neta 1978).

$$H_3PO_4 + HO^\bullet \rightarrow H_2PO_4^\bullet + H_2O \quad (12)$$

$$H_2PO_4^- + HO^\bullet \rightarrow H_2PO_4^\bullet + HO^- \quad (13)$$

$$HPO_4^{2-} + HO^\bullet \rightarrow HPO_4^{-\bullet} + HO^- \quad (14)$$

$$PO_4^{3-} + HO^\bullet \rightarrow PO_4^{2-\bullet} + HO^- \quad (15)$$

$$X^\bullet + NBB \rightarrow \cdots \rightarrow \text{Products} \quad (16)$$

pH 3.1 and pH 8 belong to the stability domain of the most oxidant radicals, $H_2PO_4^\bullet$ and $HPO_4^{-\bullet}$, respectively 3–4 and 7–9. So, these radicals improve the kinetics of sonodegradation (Fig. 7). At pH 4.8, these radicals are less stable so the rate constant is lower than at pH 3.1 and pH 8. At pH 10, there are no stable phosphate radicals, so the rate constant is low.

Finally, phosphate ions may have a positive effect on NBB decolourisation thanks to phosphate radicals, but it strongly depends on the pH and the stability domains of these secondary radicals.

Effect of pH

In sonochemistry, pH plays a very important role in the degradation of chemical pollutants, because it changes the physical properties by the ionization of functional groups. Generally, at acidic pH, a hydrophilic pollutant undergoes protonation and therefore increases its hydrophobicity. This protonated form becomes predominant, and its degradation increases under these conditions. On the contrary, in basic medium, the pollutant turns into an ionic form that increases its solubility and finally slows its degradation (Jiang et al. 2002a; Stock et al. 2000).

At high concentration of NBB

The effect of pH on the sonochemical decolourisation of NBB is first tested at high concentration, namely 8.1 µmol L^{-1} (Fig. 8, right abscissa axis). Decolourisation is more pronounced when the pH is acidic, and it respects the following order: pH 3 > pH 5.4 > 10.8.

Furthermore, the molecular size of NBB and the presence of many functional groups in its structure (two sulfonates, amine and hydroxyl attached to the naphthalene) make the highlighting of the pH effect on the sonochemical degradation more complex. Similarly, the lack of information on its pKa does not predict its structural form with ease depending on the pH of the medium. However, the high solubility of NBB provides its decolourisation on the bulk of the solution. At pH 3, the sulphonate groups undergo protonation, which increases the hydrophobicity of the pollutant. Under these conditions, decolourisation of NBB would take place more rapidly in the vicinity of the bubble–solution interface, thereby increasing its conversion rate. At pH 10.8, the molecule of the NBB takes a deprotonated or ionic form, and thus, it becomes more hydrophilic and decolourises less rapidly than in an acid medium.

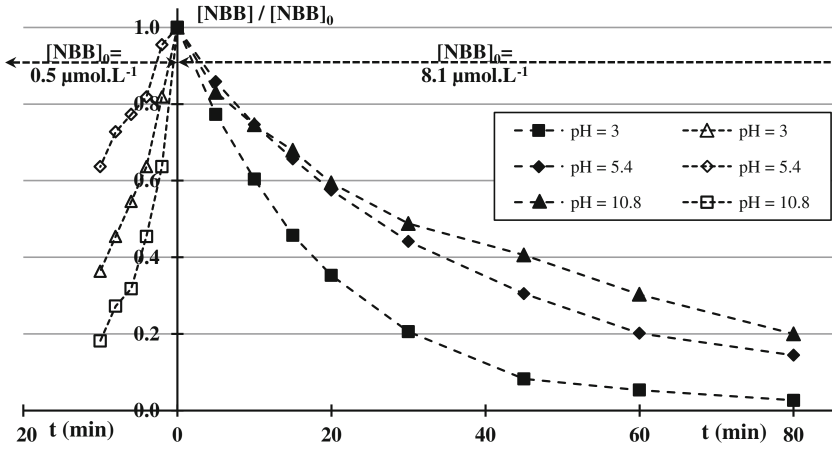

Fig. 8 Effect of pH on the sonochemical decolourisation of NBB. $[NBB]_o = 8.1$ µmol L^{-1} (*closed symbols*) or 0.5 µmol L^{-1} (*open symbols*), frequency: 278 kHz, power: 100 W, volume: 400 mL, temperature: 20 ± 1 °C)

At low concentration of NBB

Contrary to the previous study at high substrate concentration, the order of conversion of NBB at low concentrations (0.5 µmol L^{-1}) according to the pH is the following one: pH 10.8 > pH 3 > pH 5.4 (Fig. 8, left abscissa axis).

The acidic effect (pH 3) on the decolourisation of the pollutant remains unmodified, as previously mentioned for high NBB concentration. Nevertheless, the greatest rate of elimination is obtained at pH 10.8. This behaviour could be explained as follows: at low concentration of NBB and in a basic medium, the dissolved CO_2 would not only bicarbonate by reaction with HO^- anion as previously mentioned (Eq. 9), but also carbonate (Eq. 17) because the pH is higher than the HCO_3^-/CO_3^{2-} pK_a. So, the radicals $CO_3^{-\bullet}$ are likely to be obtained through HCO_3^- as previously mentioned (Eq. 10) and also through CO_3^{2-} (Eq. 18), the constant of which is 100 times much higher. So, there are more $CO_3^{\bullet-}$ radicals in the basic medium, implying a faster decolourisation in this case.

$$HCO_3^- + HO^- \rightleftarrows CO_3^{2-} + H_2O \qquad pK_a = 10.3 \qquad (17)$$

$$CO_3^{2-} + HO^\bullet \rightarrow CO_3^{\bullet-} + HO^- \quad k = 3.9 \times 10^8\ L\ mol^{-1}\ s^{-1} \qquad (18)$$

Mineralization of NBB

The only decolourisation is not enough to talk about the degradation. The mineralization degree of NBB (97.32 µmol L^{-1}) by ultrasound was evaluated by measurement of TOC. This is carried out in the following operating conditions: 278 kHz, 100 W of electric power and at natural pH in the presence of air as the saturating gas. Table 2 shows the TOC removal of 19.9 % after 360 min of treatment. It should be noted that hydroxyl radicals and hydrogen peroxide are oxygen species which are responsible for the sonochemical degradation of micropollutants studied. However, an estimated 80 % of the radicals $^\bullet OH$ and $H^\bullet$ generated by sonolysis recombine, and only a small amount of $^\bullet OH$ escapes and reacts with organic molecules in solution. The low conversion of TOC obtained confirms that the action of ultrasound on organic pollutants leads to very hydrophilic and low volatile intermediates, which migrate to the bulk of the solution where they degrade easily by $^\bullet OH$ radical attack. During the same period and for similar pollutants, Stock et al. (2000) obtained the same removal rate of TOC (50 µmol L^{-1}) after 480 min of ultrasonic irradiation time. However, this study was carried out in different operating conditions (640 kHz, 240 W power supply, V = 500 mL and C_o = 50 µmol L^{-1}).

Table 2 TOC removal for NBB sonochemical degradation

t (min)	TOC (mg L^{-1})	TOC removal (%)
0	41.2	0
180	39.2	4.9
360	33.0	19.9

$[NBB]_0$ = 97.32 µmol L^{-1}, frequency: 278 kHz, power: 100 W, volume: 400 mL, temperature: 20 ± 1 °C

Conclusion

The sonochemical decolourisation of NBB was studied at 278 kHz in aqueous media. The effects of different parameters have been investigated. It appears that the NBB decolourisation takes place in the bulk of the solution by $^\bullet OH$ radical attack, and its rate is influenced significantly by substrate concentration, power supply, pH and mineral ions. For low concentration of NBB, sonochemical decolourisation is enhanced by bicarbonate ions, due to the formation of carbonate radicals likely to migrate in the bulk of liquid and to attack substrate. Moreover, still at low NBB concentration, the same effect is underlined because the decolourisation rate is improved for basic pH, above the pK_a of the couple HCO_3^-/CO_3^{2-}, because CO_3^{2-} is the dominant form of the carbonates species and is a better source of carbonate radicals. Finally, phosphate ions have a positive influence thanks to phosphate radicals, but this effect strongly depends on the pH and the stability zones of these radicals.

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