

Case study of the sonochemical decolouration of textile azo dye Reactive Black 5

Simona Vajnhandl*, Alenka Majcen Le Marechal

University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, Slovenia

Received 3 April 2006; received in revised form 30 June 2006; accepted 4 July 2006

Available online 8 July 2006

Abstract

The decolouration and mineralization of reactive dye C.I. Reactive Black 5, a well-known representative of non-biodegradable azo dyes, by means of ultrasonic irradiation at 20, 279 and 817 kHz has been investigated with emphasis on the effect of various parameters on decolouration and degradation efficiency. Characterization of the used ultrasound systems was performed using calorimetric measurements and oxidative species monitoring using Fricke and iodine dosimeter. Experiments were carried out with low frequency probe type, and a high-frequency plate type transducer at 50, 100 and 150 W of acoustic power and within the 5–300 mg/L initial dye concentration range. Decolouration, as well as radical production, increased with increasing frequency, acoustic power, and irradiation time. Any increase in initial dye concentration results in decreased decolouration rates. Sonochemical decolouration was substantially depressed by the addition of 2-methyl-2-propanol as a radical scavenger, which suggests radical-induced reactions in the solution. Acute toxicity to marine bacteria *Vibrio fischeri* was tested before and after ultrasound irradiation. Under the conditions employed in this study, no toxic compounds were detected after 6 h of irradiation. Mineralization of the dye was followed by TOC measurements. Relatively low degradation efficiency (50% after 6 h of treatment) indicates that ultrasound is rather inefficient in overall degradation, when used alone.

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Keywords: Ultrasound; Textile reactive dye Reactive Black 5; Decolouration kinetics; Degradation; Oxidizing species

1. Introduction

Azo dye containing effluent has been a desirable target for environmental distribution studies over the past 20 years. Azo dyes, with the exception of few simply structured dyes, are known to resist biodegradation under aerobic conditions. On the other hand, azo bond is vulnerable to reductive cleavage and its degradation products include colourless aromatic amines which are known to be toxic and potentially carcinogenic. At this stage the final environmental fate of aromatic amines, derived from the azo bond cleavage of water soluble dyes, is more or less unknown [1]. Over the last few years there have been a lot of reports using different advanced-oxidation processes, and their combinations, for destroying either partial or full varieties of textile dyes, especially azo dyes, with the aim of providing non-toxic and stable end-products [2–5]. In recent years, considerable interest has

been shown in the application of ultrasound for the destruction of textile dyes [6–10].

Sonochemical reactions are induced upon high-intensity acoustic irradiation of liquids at frequencies that produce cavitation (typically in the range 20–1000 kHz). Cavitation is a phenomenon of micro-bubbles formation, and their growth and implosion in the irradiated liquid. The extreme temperature and pressure released during adiabatic bubble collapse causes the fragmentation of those gas molecules trapped in the micro bubbles into radical species. These radical species can either recombine or react with other gaseous molecules within the cavity or in the surrounding liquid, after their migration. Pyrolytic reactions inside or near the bubble and radical reactions in the solution are the two major pathways for sonochemical degradation. A detailed description of acoustic cavitation and its chemical and physical effects is described elsewhere [11–13].

It is generally believed that hydrophilic and non-volatile compounds mainly degrade through hydroxyl radical mediated reactions in the solution, while hydrophobic and volatile species degrade thermally inside or in the vicinity of the bubble [7].

* Corresponding author. Tel.: +386 2 220 7936; fax: +386 2 220 7990.
E-mail address: simona.vajnhandl@uni-mb.si (S. Vajnhandl).

Reactive azo dyes are non-volatile, water soluble compounds and their passage into the gas cavity is unlikely. Hence, oxidative radical reactions in the bulk solution are expected to be the major route for their destruction.

The aim of our work was to study the decolouration and degradation of Reactive Black 5 by low (20 kHz) and high frequency (279/817 kHz) ultrasonic irradiation, without the addition of any oxidant. Emphasis was given to the effect of different operating conditions on radical formation rate, decolouration and degradation efficiency, as well as on the toxicity profile of such treatment. Reactive Black 5, a well-known representative of non-biodegradable azo dyes, which has found widespread use in Slovene textile dye houses, was selected as a model dye.

2. Experimental procedure

2.1. Chemicals

Reactive azo dye C.I. Reactive Black 5 (RB 5) was obtained from DyStar and was used as supplied. The chemical structure of the dye is presented in Fig. 1. No information was provided by the company about any impurities.

High purity reagents (>99%) were used for the sample solutions preparation; KI (Itrij-Kropa), NaCl (Merck), 2-(HO₂C)C₆H₄CO₂K; potassium hydrogen phthalate (Chemica Fluka), (NH₄)₆Mo₇O₂₄·4H₂O (Kemika Zagreb), NaOH (Merck), Fe(NH₄)₂(SO₄)₂·6H₂O (Merck), FeCl₃·6H₂O (Chemica Zagreb). Hydrogen peroxide solution (30%, w/w) was obtained from Belinka and H₂SO₄ (density 1.84 g/mL) from Merck. All solutions were prepared with deionised water (conductivity of 0.5 μS/cm).

2.2. Ultrasound equipment and decolouration experiments

Irradiations were performed using two different types of ultrasound equipment:

- high-frequency plate type URS 1000 L-3 communications system ELAC Nautik consisting of an AG 1006 LF generator/amplifier (200 W maximum output) and USW 51 ultrasonic transducer capable of operating at two different frequencies, namely 279 and 817 kHz with an active acoustic vibration surface area of approximately 25 cm², max working volume 500 mL, and a
- 20 kHz low-frequency probe system from Sonics & Materials with tip diameter 13 mm, capable of working in continuous and pulse mode, and a max working volume 250 mL.

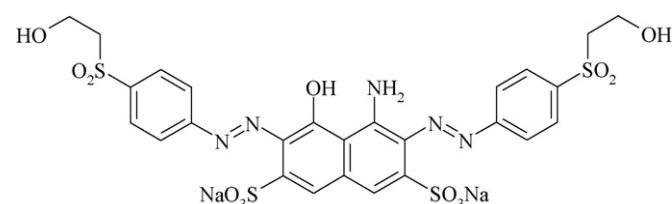


Fig. 1. Structure of C.I. Reactive Black 5 (hydrolysed form).

All kinetic experiments were performed in the batch mode at 25 °C. Solutions were continuously purged with Ar (purity > 99.99%) at a gas flow rate of 3 mL min⁻¹, to overcome degassing and to enhance cavity formation.

A stock solution of RB 5 was prepared by dissolving 1 g of the dye in 1 L of deionised water. The solution was heated to 60 °C, after pH adjustment to 11.0, and maintained for 6 h to allow complete hydrolysis, since azo dyes are found in wastewaters in the hydrolysed form. As determined spectrophotometrically the visible absorption band remained invariant within the pH range of 2–10.5. Increasing the pH above 10.5 resulted in a bathochromic shift in the characteristic absorption band of RB 5 within the visible spectrum of 595–613 nm.

For azo dyes the azo-hydrazone tautomerism has been observed [14]. Some authors attribute this shift in maximum absorption to the ionization of the hydrazone tautomeric form of the dye at high pH values [15–17]. But it is also known that at high pH values the phenolic –OH is transformed in phenolat (ArO⁻) which can also be the origin of bathochromic shift.

The absorption spectra (300–700 nm) of the test solutions were recorded at equal intervals, using a Varian Cary 50 UV–VIS spectrophotometer.

2.3. Calorimetry

The transducer's efficiency for electrical to sound conversion is generally limited and due to that fact the real power dissipating into the liquid (in sonochemistry this is called acoustic power) was determined by calorimetry. Electric power entering the ultrasound system was measured by a high-precision wattmeter on the electrical input line. The power consumed by the generator from ELAC Nautik without load was constant (=100 W).

During the calorimetric measurements the cooling jacket was empty to minimize heat losses. For the selected operational parameters of ultrasound, the temperature (*T*) was recorded against time (*t*) at 10 s intervals using a thermocouple placed in the reactor. From the *T* versus *t* data, the temperature rise (*dT/dt*) was estimated by fitting the data to a polynomial curve. The dissipated power was determined according to the equation [18]:

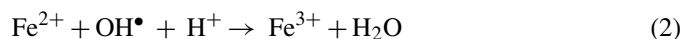
$$P_{\text{diss}} = \left(\frac{dT}{dt} \right) mc_p \quad (1)$$

where *c_p* is the heat capacity of the water, *m* the mass of water, and *dT/dt* represents initial slope of the temperature rise versus time.

2.4. Oxidizing species determination

Hydrogen peroxide concentrations were determined iodometrically: aliquots of the irradiated sample were added in the 1 cm quartz cuvette containing an equal mixture of the solutions A and B. Solution A (33 g of KI, 1 g of NaOH, 0.1 g of (NH₄)₆Mo₇O₂₄·4H₂O in 500 mL of water) and solution B (10 g of potassium hydrogen phthalate in 500 mL of water) were prepared by a procedure described by Klassen et al. [19]. Absorbance was recorded at the maximum wavelength of the formed I₃⁻ (351 nm).

OH• radicals were determined using Fricke dosimetry. The Fricke solution was prepared with Fe(NH₄)₂(SO₄)₂ (1 mM), H₂SO₄ (0.4 M), and NaCl (1 mM). The concentration of Fe³⁺, formed during irradiation by this simplified reaction scheme, was measured by the spectrophotometer (Varian Cary 50) at a maximum wavelength 304 nm:



TOC was measured using a DC 190, Dohrmann apparatus.

2.5. Toxicity measurements

The toxicity of the dye solutions was determined by a Microtox Model 500 analyzer, which utilizes freeze-dried bacteria (*Vibrio fischeri*) as test organisms. The test system is based on the principle of bacterial cellular activity inhibition (in the presence of toxic compounds) resulting in a reduction in the degree of luminescence.

3. Results and discussion

As irradiation with ultrasound can be considered as a special type of energy input into a system, the efficiency of sonochemical processes is closely related to the quality of energy conversion in an ultrasonic device towards the desired effects, in our case radical production. For this reason, the first set of experiments comprised characterization of the used irradiation systems by means of electricity to sound conversion efficiency and radical formation.

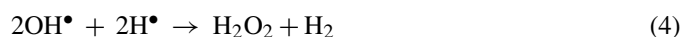
Table 1 presents the economic profile for the ELAC Nautik high frequency ultrasound system. The electrical yield for the whole emission system ($\eta = P_{\text{diss}}/P_{\text{el}}$) varies from 13 to 41% depending on the performance of the generator but, in all cases, was lower than 50%. Residue from the input electric power is transferred into secondary effects, e.g. streaming, heating, and also into useless effects such as emitter and reactor surface erosion and the creation of noise. Measurements also indicate that any increase in generator performance to a critical level does not always correlate with any increase in acoustic power but leads to unnecessary loss of energy, and possible injury of the transducer (this limit was found for 279 kHz).

The ultrasonic density (expressed as acoustic power per working volume in W/mL) and intensity (expressed as acoustic

power per surface of emitter in W/cm²) are considered as important factors [20]. In many papers these parameters are not always well defined. However, the input electric power is not always informative when indicating the real acoustic power, because the energy conversion of ultrasound is transducer-dependent.

3.1. Oxidative species production

The generation of oxidizing species during the sonolysis of aqueous solutions is initiated by the homolytic cleavage of water molecules by pyrolytic reactions as follows:



After the initial splitting of H₂O, further reactions depend on other species present in the gas phase of the bubble. H₂O₂ is formed mainly by the recombination reactions of the produced OH• radicals [21]. Both, OH• and H₂O₂ are strong oxidants with reduction potentials of 2.8 and 1.77 V, respectively. Their production rates depend on the final temperature and pressure at the time of bubble collapse, as well as the bubble's lifetime, while frequency has a significant influence on their reactivity [8]. In addition, higher collapse temperatures support radical production. The most extreme transient temperatures and pressures are obtained if we use gases of high solubility and low thermal conductivity.

In our experiments Ar was used as saturating gas due to relatively high water solubility (0.0336 L/L at 20 °C) and low thermal conductivity (0.01772 W/m K at 25 °C).

However, chemical dosimeters, namely Fricke and an iodine dosimeter, were used for the monitoring of oxidative species, OH• radicals and their recombination product H₂O₂. Emphasis is given on the effect of two different irradiation systems (probe and plate type), frequency (20, 279 and 817 kHz) and acoustic power (50, 100, and 150 W) on radical production rate.

Fig. 2 displays radical rate formation as a function of frequency and type of irradiation system at a calorimetrically determined acoustic power of 50 W. Comparison of frequency effect on reaction rate is valid, only when all other experimental conditions are the same. First, experiments were performed at a volume of 250 mL without Ar. The results vary significantly between low frequency (20 kHz) probe type and high frequency (279, 817 kHz) plate type transducer. The apparent kinetics is

Table 1
Economic profile

Frequency (kHz)	Setting on the generator (%)	Electric power (W)	Dissipated power (W)	Electrical yield (%)	Intensity (W/cm ²)
20	60	–	50	–	37.6
	50	380	50	13	2
279	65	380	100	26	4
	75	380	150	39.5	6
	80	400	130	32.5	5.2
817	60	380	50	13	2
	70	380	100	26	4
	85	380	150–155	39.5–41	6–6.2

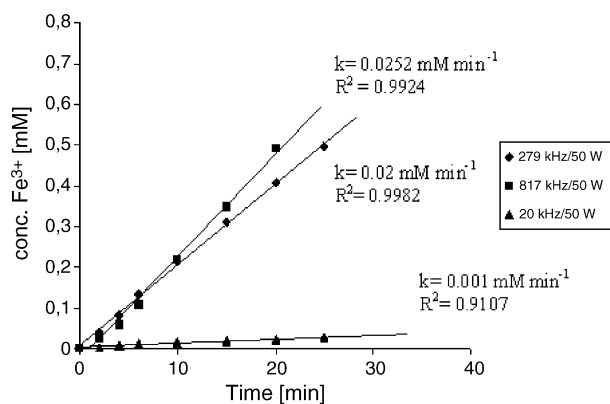


Fig. 2. Effect of frequency and type of transducer (probe, plate) on Fe³⁺ formation at fixed acoustic power of 50 W and working volume of 250 mL.

zero-order, with the observed rates ranging from 1 $\mu\text{M min}^{-1}$ for 20 kHz to 25.2 $\mu\text{M min}^{-1}$ for 817 kHz. In addition, after 30 min of irradiation at 20 kHz, a decrease was observed in the formation of Fe³⁺. This decrease in the concentration can be attributed to degassing effect since this frequency is normally used for degassing liquids at industrial scale. For 279 and 817 kHz no degassing was observed before 60 min of irradiation. We can assume that after a certain irradiation time, dissolved gas or small gas bubbles already present in the liquid were expelled, which causes a decrease in cavitation events since these gas bubbles act as nuclei for successful cavitation. In order to maintain uniform cavitation, further experiments were conducted purging the system continuously with Ar.

Radical formation rates were three-fold higher with the observed rates 72 $\mu\text{M min}^{-1}$ for 817 kHz and 56 $\mu\text{M min}^{-1}$ for 279 kHz under Ar and no degassing effect was observed, even after 120 min of irradiation (linear increase in concentration of Fe³⁺ ions).

Influence of frequency on radical formation (Fig. 2) clearly shows a 20–25 fold higher radical rate for the 279 and 817 kHz plate type transducer in comparison to the 20 kHz probe type.

It is well documented that frequency has a significant influence on whole bubble dynamics [12]. In general, lower frequencies result in a greater degree of vapour-phase pyrolysis, while higher frequencies favour radical production. At higher frequencies the bubble's lifetime is shorter and collapse occurs very quickly, thus enhancing the possibility of the radicals' ejection before they undergo recombination reactions inside the bubble [22,23].

In general, an increase in acoustic power results in an increase in the observed reaction rate [11]. However, when a chemical reaction takes place, an optimum acoustic power exists that provides maximum reaction rate since at high acoustic intensities a great number of cavitation bubbles are generated. They then act as a barrier for the successful transfer of acoustic energy through the entire liquid [24].

Fig. 3 displays zero-order apparent kinetics for hydrogen peroxide formation at 279 and 817 kHz under Ar and selected acoustic powers. Substantial increase in hydrogen peroxide formation with increasing acoustic power was observed at both frequencies.

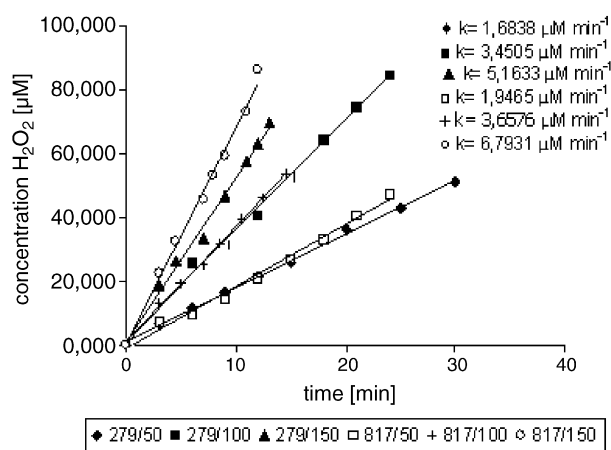


Fig. 3. The formation of hydrogen peroxide as a function of acoustic power under Ar, working volume was 500 mL.

3.2. Decolouration and mineralization experiments

Decolouration experiments were performed with dye solutions of initial concentration from 5 to 300 mg/L, which is in according to Gottlieb et al. [25], within typical effluent dye concentration range (5–1500 mg/L). In the light of this, we studied the effect of pH, initial dye concentration and the operational parameters of irradiation systems on decolouration efficiency, TOC, conductivity and toxicity profile.

3.3. Effect of pH

Ultrasound irradiations of 20 mg/L dye solution were carried out at various pH (2–10). Fig. 4 shows the effect of the initial pH within the range of 2–10, on the decolouration efficiency. As can be seen, acidic conditions accelerate decolouration. This acceleration is probably associated with the effect of protonation of negatively charged $-\text{SO}_3^-$ groups in acidic medium and, obviously, the hydrophobic character of the resulting molecule enhances its reactivity under ultrasound treatment. On the contrary, the inhibition of colour decay under alkaline conditions could be attributed to hydrogen loss from the protonated sites ($-\text{SO}_3\text{H} \rightarrow -\text{SO}_3^-$; $-\text{NH}_3^+ \rightarrow -\text{NH}_2$; $\text{Ar}-\text{OH} \rightarrow \text{Ar}-\text{O}^-$), resulting in enriched hydrophilic characteristics. Moreover, under extreme alkaline conditions, OH^\bullet scavenging effects become more significant.

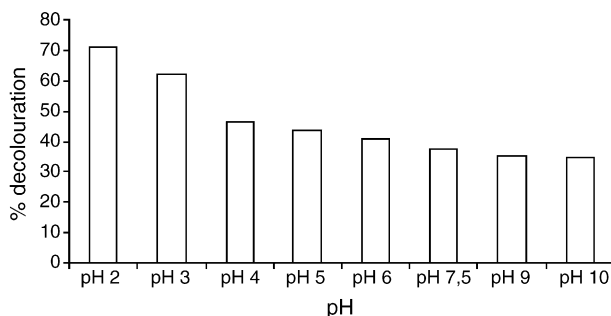


Fig. 4. The effect of pH on decolouration efficiency after 1 h of ultrasound treatment.

In all cases we attained quite an enviable gauge of decolouration after 1 h of ultrasound treatment, without the addition of any other oxidising agent.

3.4. Effect of initial dye concentration

In some previous studies, the sonochemical degradation of various classes of organics was found to obey a pseudo-first-order or zero-order kinetics [2,3,7]. Fig. 5 shows the effect of initial dye concentration on decolouration rates at 817 kHz and 100 W of acoustic power under Ar and slightly acidic conditions (initial pH from 5.8 to 6.1), which was found to enhance decolouration. The decolouration kinetic seems to fit reasonably well into simplified pseudo-first-order rate expression, for the concentration range used in this study:



where the rate constant k' can be determined by

$$-\frac{d[\text{dyestuff}]}{dt} = k'[\text{dyestuff}][\text{OH}^{\bullet}] \quad (6)$$

Eq. (6) can be simplified and k' takes the form of an apparent pseudo first-order constant k if we assume that the concentration of very reactive OH^{\bullet} radicals takes on a steady-state value during the process:

$$-\frac{d[\text{dyestuff}]}{dt} = k[\text{dyestuff}] \quad (7)$$

However, as expected, the apparent decolouration rates decreased with increasing initial dye concentration. Even though, low concentrations of the dye solutions were readily decolourized (decolouration efficiency was 78%, 73%, 63% and 52% for 5, 20, 40 and 70 mg/L) after 1 h of irradiation without the addition of other oxidants.

3.5. Decolouration as a function of operational parameters

Fig. 6 displays the observed decolouration rates as a function of working frequency and acoustic power. The greatest overall decolouration of Reactive Black 5 is observed at 817 kHz

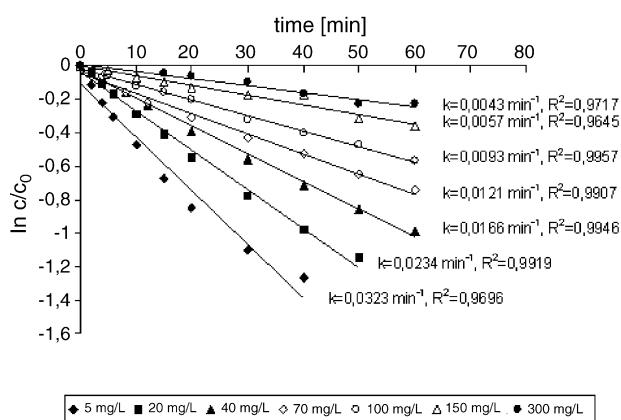


Fig. 5. The apparent decolouration rate constants at various initial dye concentration and experimental conditions 817 kHz, 100 W, under Ar, pH 5.8–6.1.

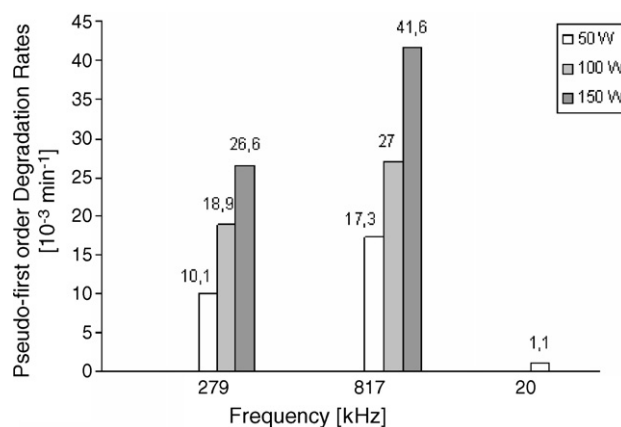


Fig. 6. Rate constants of Reactive Black 5 decolouration at initial dye concentration of 20 mg/L under Ar without pH control after 1 h of treatment.

and 150 W. The rate enhancement is significant with increasing acoustic power. An almost 10-fold rate decrease in dye decolouration rate was observed at 20 kHz, in comparison to 279 kHz. From other oxidative species monitoring, as well as decolouration efficiency measurements, we can conclude that under the experimental conditions being considered, the frequency of 817 kHz provides better decolouration in comparison to 279 or 20 kHz.

Entezari et al. [26] and Kruus et al. [27] extensively studied the influence of frequency and intensity at a constant acoustic power, on the reaction rates of carbon disulphide and chlorobenzene. They claimed when the rate determining process occurs inside the collapsing bubble (in the case of carbon disulphide) the reaction rate is greater at lower frequencies with a smaller surface area of sonicator (consequently the intensity is greater). On the contrary, when the rate determining process are secondary radical reactions in the solution following cavity collapse and diffusion of oxidative species, higher frequencies and a larger surface area of sonicator (lower intensity) increase reaction rate.

The results obtained from hydroxyl radical monitoring and decolouration experiments on RB 5 are in line with the observations of Entezari et al. [26] and Kruus et al. [27]. 2-methyl-2-propanol is known to actively scavenge OH^{\bullet} radicals and thus rendering the advanced oxidation processes less efficient. The influence of radical scavenger on decolouration efficiency was studied in order to confirm the radical oxidative degradation pathway.

Sonolysis of 20 mg/L dye solution containing 5.3 and 2.7 M 2-methyl-2-propanol as scavenger at 817 kHz and 100 W, results in significant inhibition of the decolouration (observed decolouration rates were only 3.2×10^{-3} and $2.1 \times 10^{-3} \text{ min}^{-1}$ instead of $23.4 \times 10^{-3} \text{ min}^{-1}$, respectively). It is, therefore, reasonable to conclude that the initial step in the decolouration mechanism is attack by the hydroxyl radicals.

3.6. Toxicity measurements

Oxidative degradation processes might produce organic intermediates which are more harmful than the parent molecule.

Table 2
Decolouration and degradation efficiency after prolonged time of irradiation

Time of irradiation	Absorbance	TOC (mg/L)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Decolouration (%)	Degradation (%)
0	0.598	5.4	7.0	168.6	–	–
1	0.147	5.3	6.6	179.6	75	1.8
2	0.057	4.8	6.1	181.5	90.5	11.1
3	0.021	4.2	5.9	189.3	96.5	22.2
4	0.009	3.5	5.3	193.9	98.5	35.2
5	0.008	3.2	4.9	197.7	98.7	40.7
6	0.008	2.7	4.6	201.4	98.7	50

It is well documented that sonochemical oxidation is effective in reducing the toxicity of various hazardous pollutants [28,29]. It is believed that azo dyes themselves are non-toxic compounds, while little is known about AOP degradation reaction by-products and degradation pathways. So we decided to investigate the effects of the lengthy exposure of RB 5 solution to ultrasonic treatment, on the subsequent toxicity to marine bacteria *V. fischeri*. Inhibition of luminescence was measured every hour.

Gottlieb et al. [25] reported that a hydrolysed form of Reactive Black 5 at 500 mg/L of initial concentration shows slightly greater toxicity than non-hydrolysed form. In our case no toxicity was detected at the original hydrolysed dye solution of 20 mg/L of initial concentration. Under the conditions employed in this study (817 kHz, 100 W, under Ar) no change in toxicity profile was observed, even after 6 h of ultrasound treatment.

3.7. TOC, pH, and conductivity profile

Degradation of the dye should be evaluated as an overall degradation process, involving the ultimate mineralization of both the parent dye and its intermediates. The most common way of estimating this overall process is to monitor the reduction in total organic carbon (TOC).

The 20 mg/L of Reactive Black 5 was irradiated at 817 kHz and 100 W for 6 h. TOC, absorbance, pH and conductivity followed. The decolouration and degradation efficiencies are presented in Table 2.

Although 75% of decolouration was achieved after 1 h of irradiation, without the addition of any other oxidant, TOC remained almost unchanged. Results obtained from absorbance and TOC measurements indicated that decay of the chromophore in the dye molecule is a relatively fast process (disappearance of chromophore peak in the visible spectra) but overall degradation is not. A defined part of the organic carbon still remained as intermediates refractory to further oxidation, some of them in the form of organic acids. The formation of the later could be the reason for decrease of pH from neutral to slightly acidic. On the other hand, substantial increase in conductivity suggests the formation of ions such as nitrate or sulphate. The presence of both, and some others such as metanoate, nitrite, oxalate, was confirmed in preliminary experiments using ion chromatography. Identification of the final products and intermediates arising from the sonochemical treatment of Reactive Black 5, are still in progress.

4. Conclusions

Ultrasound, like other advanced oxidation processes, works on the principle of generating free radicals, and their subsequent attack on the contaminant molecules. The aim is either, completely mineralizing the contaminants or converting it into less harmful or lower chain compounds, which can then be treated biologically.

In addition to simple manipulation, the advantage of ultrasound is also the fact that sonochemical treatment typically operates under ambient conditions and a defined part of an oxidising agent is generated 'in situ'.

However, sonochemistry has not yet received much attention as an alternative for large-scale chemical processes, probably because ultrasound, when used alone, is relatively energy consuming, since not all of the cavitation energy produces chemical and physical effects. In addition, further work is needed to improve the efficiency of energy conversion, as well as radical generation for a given energy input [8].

The conclusions drawn from this study can be summarised as follows:

- (i) ultrasound alone is capable of Reactive Black 5 decolouration but the extent of conversion strongly depends on the operating conditions employed such as frequency, acoustic power, type of transducer, solution pH, initial dye concentration;
- (ii) ultrasound, when used alone, is quite inefficient in mineralization of the dye (50% degradation efficiency was attained after 6 h of treatment);
- (iii) no toxic degradation by-products could be detected using *V. fischeri* as test organisms under the conditions employed in the study.

Acknowledgement

This research was supported by the Ministry of Education, Science and Sport of Slovenia.

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