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Reactive dye decolorization using combined ultrasound/H_2O_2

Darinka Brodnjak Vončina[a,*], Alenka Majcen-Le-Marechal[b]

[a]Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia
[b]Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, Slovenia

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Abstract

The decolorization of six vinylsulphone reactive dyes (C.I. Reactive Yellow 15, C.I. Reactive Red 22, C.I. Reactive Blue 28, Remazol Dark Black N 150%, C.I. Reactive Blue 220 and C.I. Reactive Black 5) in aqueous solution was investigated using ultrasound and ultrasound/ hydrogen peroxide degradation. Two different concentration levels of hydrogen peroxide were used. The efficiency of the decolorization was evaluated by measuring the absorbance of the dye solutions. The results show that ultrasound treatment was significantly enhanced in the presence of H_2O_2.

Keywords: Ultrasonic irradiation (US); Hydrogen peroxide; Decolorization; Vinylsulphone reactive dyes

1. Introduction

It is known that reactive dyes form a covalent bond with the –OH groups of cellulosic fibres and the amino groups of wool and amino groups of PA fibres, which is the reason for their good stability during washing. Such properties make reactive dyes popular; however reactive dyes can also react with the –OH groups of water resulting in hydrolysis of the dye. The inability of molecule dye to react with fibres contributes to pollution of the wastewater, as this aesthetic problem becomes global if we take into consideration the fact that dyeing may cause pollution with heavy metals, which are structural elements in some dyes. Decolorization of wastewater, polluted with reactive dyes is closely related to cleavage of the – C=C- and -N=N- bonds or heterocyclic and aromatic rings. The result is that the absorption of light shifts from the visible to the UV or IR region of the electromagnetic spectrum. At present three types of wastewater treatment are known, namely physical, chemical and biological.

Physical methods of treatment include precipitation, adsorption, reverse osmosis and filtration, combustion and incineration and other methods such as distillation and extraction. Chemical methods include oxidation, reduction, complexometric methods and ion exchange methods while biological methods involve aerobic and anaerobic treatments.

Environmental sonochemistry [1] is a rapidly growing area and is an example of an advanced oxidation process (AOP) that deals with the destruction of organic species in aqueous solution. Benzene, for example, well known for its resistance to the action of strong oxidants, succumbs to oxidation under ultrasonication in aqueous media. Concerning the sonochemical degradation of dyes, some attempts have been made which

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* Corresponding author. Fax.: +386-2-252-7774.
E-mail address: darinka.brodnjak@uni-mb.si (D.B. Vončina).

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promoted sonolysis as a feasible method to achieve both decolorization and degradation of the dye. The C.I. Acid Black 1 dye was investigated using a combination of sonolysis and photocatalysis; it was found that sonolysis was effective for inducing faster degradation of the dye, while photocatalysis was effective for promoting degradation [2].

In the present paper we describe a comparative study of the decolorization techniques of six reactive, vinylsulphone dyes using ultrasound and ultrasound/H_2O_2.

2. Theory

2.1. Decolorization using H_2O_2

One of the more popular AOP methods for wastewater decolorization is oxidation with H_2O_2 which, due to its stability in pure form, needs to be activated. Hydrogen peroxide activated with UV light decomposes into OH· radicals [3–8].

Oxidation potential of OH· radicals is much higher then that of hydrogen peroxide. Also, UV irradiation and other activators can be used for H_2O_2, such as Fe (II) salts (Fenton's reagent) and ozone [9]. Recently, ultrasound was described as a possible generator of highly active OH·, HOO·, H· radicals [2,16, 24].

2.2. Fundamentals of ultrasound treatment

The part of the sonic spectrum, which ranges from about 20 KHz to 10 MHz is called ultrasound [10]. Ultrasound waves, like all sound waves, consist of cycles of compression and expansion. Compression cycles exert a positive pressure on a liquid, pushing the molecules together; expansion cycles exert a negative pressure, pulling the molecules away from one another [11].

If a large negative pressure is applied to a liquid (here it is the acoustic pressure on expansion), so that the distance between the molecules exceeds the *critical molecular distance* R (the value R for water is 10^{-8} cm) necessary to hold the liquid intact, the liquid will break down and voids will be created (i.e. cavitation bubbles will form). These bubbles will grow over a few cycles taking in some vapor or gas from the medium (rectified diffusion) to an equilibrium size, which matches the frequency of bubble resonance to that of the sound frequency applied. At this point, the bubble can efficiently absorb energy from the sound field. At 20 kHz, the critical size is ~ 170 μm in diameter. Once a cavity has overgrown, it can no longer efficiently absorb energy from the sound field and can no longer sustain itself and the surrounding liquid rushes in and the cavity violently implodes [11–13].

The dynamics of cavity growth and collapse are strikingly dependent on the local environment. Cavity collapse in a homogeneous liquid is very different from cavitation near a liquid–solid interface [12]. Furthermore, it has been shown experimentally that cavitational collapse creates drastic conditions inside the medium: temperatures of 2000–5000 K and pressures up to 1800 atm within the collapsing cavity have been reposed. There are three different theories about cavitation namely, the *hot-spot*, the *electrical* and the *plasma* theories. According to each theory, there is no doubt that the origin of sonochemical effects is cavitation [11]. The most understandable theory, in a qualitative sense, is the *hot-spot* approach [14] in which each cavitation bubble acts as a localized micro reactor, which, in an aqueous system, generates instantaneous temperatures of several thousand degrees and pressures in excess of 1000 atmospheres [10].

These rather extreme conditions generate highly reactive species (OH·, H·, HO_2·, H_2O_2) when H_2O is the medium, which, potentially, can give rise to radical chain reactions throughout the sonolyzed media. Another phase of potential significance is a shell of supercritical water ($T_c = 374$ °C; $P_c = 221$ bar) surrounding sonochemical *hot-spots* [13].

Sonochemistry is an example of advanced oxidation processes [13]. Destruction or mineralization of organic compounds by these processes is based on oxidative degradation by free radical attack, particularly by hydroxyl radical, which is a far more powerful oxidizing agent than all commonly known oxidants [15].

Sonication improves mass transfer and chemical reaction and is expected to reduce or eliminate chemical usage, resulting in minimum sludge and disposal problems. The coupling of ultrasound with H_2O_2 / O_3 or UV photo catalysis enhances the efficiency of free radical generation through cavitation. It appears that using a combinative AOP approach is certainly a positive step toward achieving quick mineralization (CO_2) and more such studies should be considered in future. Sonochemistry offers the potential for shorter reaction cycles, cheaper reagents and less extreme physical conditions, leading to less expensive and perhaps smaller plants [16–25].

3. Experimental procedures

3.1. Chemicals

The three dyes, namely C.I. Reactive Yellow 15, C.I. Reactive Red 22, C.I. Reactive Blue 28 were all purchased from the producer Bezema. The other three dyes, namely Remazol Dark Black N 150% (no color index), C.I. Reactive Blue 220 and C.I. Reactive Black 5 were commercial products purchased from the producer DyStar. All six dyes were used without purification. Hydrogen peroxide solution (35% w/w, with $\rho = 1.13$ g/ml) of analytical grade was obtained from Belinka. Aqueous solutions were prepared using ultra pure water (conductivity 0.056 μS/cm) obtained from Millipore MilliQ. Absorbances were measured and recorded using a VARIAN CARY 1E UV in 10 mm cells at the λmax of the particular dye in aqueous solution. An Ultrasonic Processor Sonics & Materials VibraCell VCX 600 with a constant frequency of 20 kHz and power 80 W/cm^2; 1 cm^2 titanium direct immersion horn was used for ultrasound decolorization.

3.1.1. Preparation of stock and standard solutions for the calibration curves

Six reactive dyes were used for decolorization, namely C.I. Reactive Yellow 15, C.I. Reactive Red 22, C.I. Reactive Blue 28, Remazol Dark Black N 150%, C.I. Reactive Blue 220 and C.I. Reactive Black 5. The known structures of three dyes are presented in Figs. 1–3. Standard stock solutions of 100 mg/l dyes were prepared by diluting the corresponding mass of dye in milliQ water. The standard working solutions (10 mg/l) were prepared by further dilution of standard stock solutions.

The solutions were prepared for calibration by further dilution of the standard working solutions. The calibration curves were established by measuring a series of the solutions (0.4, 0.5, 1.0, 2.0, 2.5, 5.0 and 10.0 mg/l). A blank signal was obtained using MilliQ water. The measurements were made in replicates. Standard deviation and relative standard deviation were calculated, which means that measurements were kept under continuous statistical control.

The sonolysis experiments were carried out with 20 kHz sonolysis setup of Sonics and Materials VCX600. Fifty millilitres of the dye solution was placed in a cylindrical glass vessel. The horn was immersed into the solution. A cooling bath was used to obtain constant temperature 25±5 °C during irradiation of the samples.

The absorbance of dye solutions was measured at the beginning of the experiment. Samples were taken and measured every hour for 7 h. The concentration of a particular dye solution was calculated from the calibration curves prepared from the corresponding dyes and the measured absorbance at λmax. The percentage of decolorization was calculated according to Eq. (1).

$$\text{Decolorization} \quad \% = \left(1 - \frac{c}{c_0}\right)100 \tag{1}$$

c_o: initial concentration of the dye; c: concentration of the dye after US or US/H_2O_2 treatment.

4. Results and discussion

Our results confirm the suitability of the ultrasound and ultrasound/H_2O_2 process as a reactive dye decolorization. The greatest percentage of decreasing of the dye concentration was established with the C.I. Reactive Black 5 dye solution. It has decreased from 10.0 mg/l to 0.38 mg/l (96.2%) after treating with ultrasound for 7 h. The concentration has been calculated from the corresponding calibration curve by measuring the absorbance at wavelength 598 nm. The concentration of the Remazol Dark Black N 150% has decreased from 10.0 mg/l to 2.51 mg/l (74.9%)

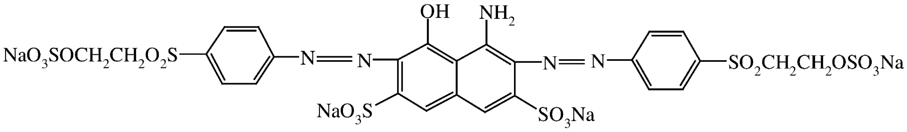

Fig. 1. Chemical structure of the reactive vinylsulphone dye C.I. Reactive Black 5.

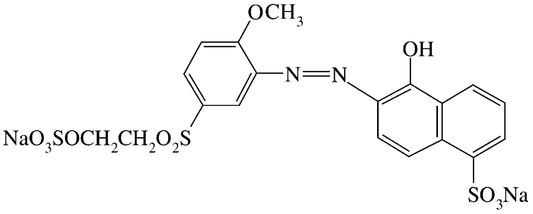

Fig. 2. Chemical structure of the reactive vinylsulphone dye C.I. Reactive Red 22.

after 7 h of ultrasound treatment. The absorbance was measured at two wavelengths, 480 and 597 nm showing the same concentrations from both calibration curves. The concentration of the C.I. Reactive Red 22 dye has decreased from 10.0 mg/l to 1.85 mg/l (81.5%) after treating with ultrasound for 7 h. The concentration has been calculated from the corresponding calibration curve by measuring the absorbance at wavelength 522 nm. The concentration of the C.I. Reactive Yellow 15 dye has decreased from 10.0 mg/l to 0.90 mg/l (91%). The decreasing concentration of all six dyes is presented in Table 1.

The influence of ultrasound on the decreasing concentration of all dyes used in the experiments is evident. The results were evaluated using calibration curves for the corresponding dye. It is important that decreasing of the concentration is established to a great extent using only ultrasound. The cleavage of bonds is performed using only ultrasound, which is the advantage of this method. The influence of ultrasound can be increased by the addition of hydrogen peroxide (Fig. 4). Different amounts of hydrogen peroxide were added.

0.395 g of H_2O_2 (1 ml H_2O_2 35% w/w) was added to 50 ml of the corresponding dye giving the hydrogen peroxide concentration 0.23 mol/l with the same initial dye concentration as in the experiments using only ultrasound.

In the next experiment greater amounts of hydrogen peroxide were added, namely 5.93 g of H_2O_2 (15 ml H_2O_2 35% w/w) to 50 ml of the dye solution of the same concentration as in the previous experiment, giving the hydrogen peroxide concentration 3.49 mol/l.

It is evident that concentrations of the dyes were substantially decreased using ultrasound and hydrogen peroxide (Table 2).

The concentration of C.I. Reactive Red 22, C.I. Reactive Yellow 15 and C.I. Reactive Black 5 were all decreased to a great extent, more than 96%. The concentration of all dyes was decreased more than 91%. The concentrations for some dyes were decreased under the detection limit only after 4 h treatment (Figs. 5 and 6). The influence of hydrogen peroxide addition on decreasing concentration of the dye depends on the type of dye. A greater amount of hydrogen peroxide indicates more hydroxide radicals in the sample solution than can be used for oxidative degradation of the dye molecules.

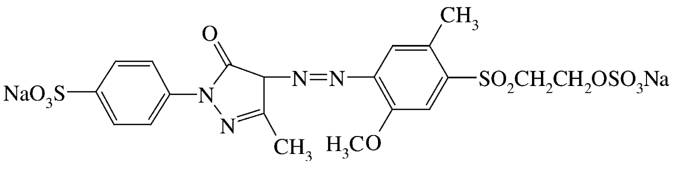

Fig. 3. Chemical structure of the reactive vinylsulphone dye C.I. Reactive Yellow 15.

Table 1
The influence of ultrasound on the decreasing of absorbance and concentration of the dyes after 7 h

Dye	λmax /nm	Absorbance (before US)	Absorbance (after US)	[a]c_o (mg/l)	[a]c (mg/l)	[b]Decolorization (%) $(1-\frac{c}{c_0})$ 100
C.I. reactive yellow 15	415	0.268	0.023	10.0	0.90	91.0
C.I. reactive red 22	522	0.230	0.045	10.0	1.85	81.5
C.I. reactive blue 28	574	0.092	0.0391	10.0	4.26	57.4
Remazol dark	480	0.134	0.030	10.0	2.51	74.9
black N 150%	597	0.137	0.033			
C.I. reactive blue 220	609	0.129	0.039	10.0	2.96	70.4
C.I. reactive black 5	598	0.343	0.016	10.0	0.38	96.2

[a] c_o = initial concentration of the dye solution. c = concentration of the dye solution after US treatment.
[b] Eq. (1).

Table 2
The influence of ultrasound/H_2O_2 (concentration 3.49 mol/l) on the decreasing of absorbance and concentration of the dyes after 4 h

Dye	λmax /nm	[a]c_0	[a]c after 10 min	c after 60 min	c after 120 min	c after 180 min	c after 240 min	[b]Decolorization (%) $(1-\frac{c}{c_0})$ 100
C.I. reactive yellow 15	415	10.0	5.73	1.44	1.14	0.71	0.39	96.1
C.I. reactive red 22	522	10.0	7.68	1.88	1.03	0.70	0.33	96.7
C.I. reactive blue 28	574	10.0	7.55	3.16	2.00	1.06	0.90	91.0
Remazol dark black N 150%	480 597	10.0	8.30	3.42	1.37	0.93	0.78	92.2
C.I. reactive blue 220	609	10.0	7.87	3.58	1.20	0.97	0.66	93.4
C.I. reactive black 5	598	10.0	8.36	3.91	2.91	0.17	0.14	98.6

[a] c_o = initial concentration of the dye solution. c = concentration of the dye solution after ultrasound/H_2O_2 treatment.
[b] Eq. (1).

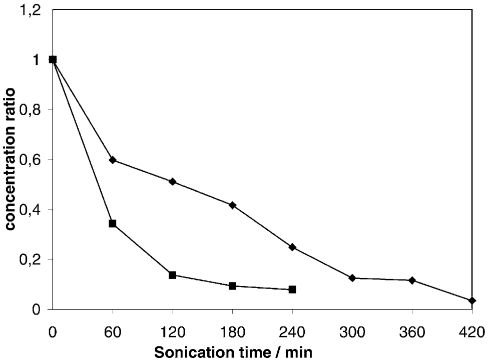

Fig. 4. Degradation of C.I. Reactive Black 5 dye using only ultrasound (◆) and ultrasound/H_2O_2 0.23 mol/l (■).

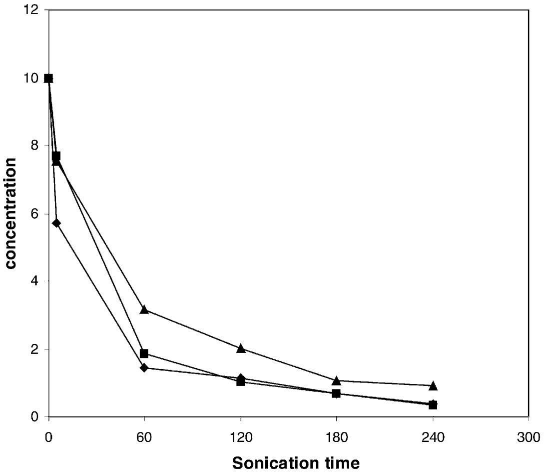

Fig. 5. Sonochemical degradation of reactive dyes using H_2O_2 3.49 mol/l: ◆ C.I. Reactive Yellow 15, ■ C.I. Reactive Red 22, ▲C.I. Reactive Blue 28.

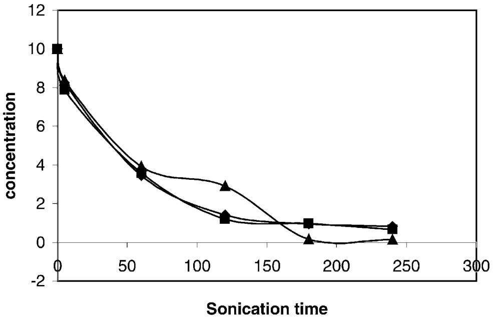

Fig. 6. Sonochemical degradation of reactive dyes using H_2O_2 3.49 mol/l: ▼ Remazol Dark Black N 150%, ■ C.I. Reactive Blue 220 and ▲ C.I. Reactive Black 5.

5. Conclusions

The decolorization of six dye solutions under ultrasound and ultrasound/H_2O_2 conditions was examined. The study has shown that the efficiency of the ultrasound treatment was significantly enhanced if ultrasound and H_2O_2 were used. The rate of color degradation was twice as fast as that accomplished by sonolysis alone. The results have shown that with a dose of 3.49 mol/l H_2O_2 and ultrasound treatment for 4 h the decolorization was higher than for ultrasound treatment with a dose of 0.23 mol/l H_2O_2. Complete color removal was achieved in less than 4 h for C.I. Reactive Black 5. The best results were found using ultrasound/H_2O_2 in a higher concentration level. The proposed combination (ultrasound/H_2O_2 treatment) may be applicable in the management of dye house effluents. In future work we will perform decolorization of industrial textile wastewaters and also follow the mineralization of the dyes.

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