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Degradation of chemical water pollutants using ultrasound

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Abstract

Introduction

The manufacture of Printed Circuit Boards (PCBs) produces a cocktail of chemicals in waste water effluent from inorganic compounds to organic species used as additives in electroless and electroplating solutions. In addition resist strippers can introduce a range of dyes and ink based compounds into the effluent stream. With environmental legislation become ever stricter it is imperative that the industry keeps abreast of new techniques for waste water treatment one of which is the employment of ultrasound.

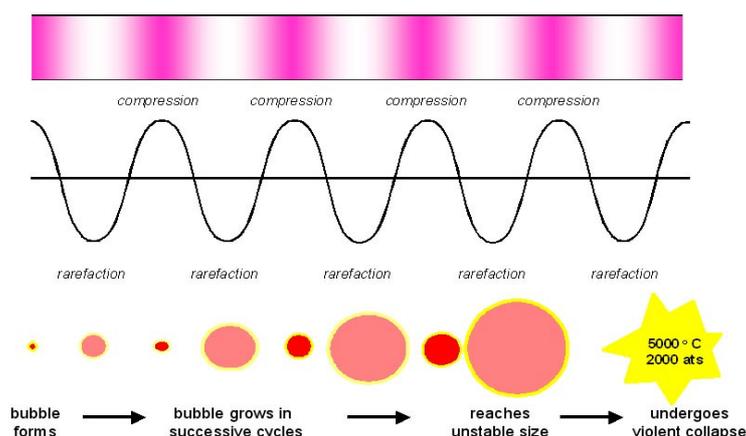
The use of ultrasound to treat industrial effluent is an area which has been relatively unexplored by industry to date. Currently effluent is chemically treated with either high levels of UV light (Oliver 1975), chlorinated using various agents such as sodium hypochlorite, or oxidised via the addition of hydrogen peroxide or a combination of all the above (I.T. Miettinen 1998). Chemical treatment may be combined with biological treatment involving either aerobic or anaerobic metabolism (G Britton 1999).

Advanced oxidation processes (AOPs) using ultraviolet light and oxidizing chemicals such as ozone, hydrogen peroxide and Fenton's reagent (Bains 2003, Yasman 2006, Hulsun 2007) have been found to be extremely effective when used with chemicals that are difficult to degrade. Ultrasound can be used to aid chemical degradation, either as an alternative more environmentally friendly technique to those currently used, or in addition to those techniques thus making the existing processes more effective.

Ultrasound is simply the introduction of high frequency sound to a medium through which it can travel, often this medium is water. There is a common misconception that for ultrasound to work effectively extremely high power low frequency approximating 20 kHz must be employed. In reality however the low power high frequencies of 850 kHz are proving to be the most effective for generation of hydroxyl radical ($\cdot\text{OH}$) and or hydrogen peroxide.

Ultrasound appears to act via the introduction of oxidising free radicals such as the hydroxyl radical ($\cdot\text{OH}$). These radicals can act directly upon the target chemical or may combine to form hydrogen peroxide, itself an extremely efficient oxidising agent. As free radicals such as these are extremely short lived there is no possibility of chemical contamination. As ultrasound moves through a medium, such as water, a series of compression and rarefaction cycles results in the formation of cavities within the solvent. Solvent vapour enters these cavities and, as they become compressed during the next compression cycle, high temperatures and pressures result causing the vapour to undergo homolytic fission, forming free radicals such as the hydroxyl radical ($\cdot\text{OH}$). (Mason 1999)

ACOUSTIC CAVITATION



(taken from Mason (1999) Sonochemistry Oxford University Press)

If the free radicals remain in close proximity to each other they will react to form hydrogen peroxide and this often happens with long cycles such as those at 20 kHz. If the radicals are expelled from the cavity during an extremely short cycle, such as those found with 850 kHz, then these radicals go on to attack the target chemical directly.

To illustrate the effectiveness of using ultrasound to waste treat an aqueous effluent this study investigated the efficacy of the process to degrade a range of chemically persistent dyes. Recently there has been much work investigating the use of ultrasound and its ability to degrade dyes. (Robinson *et al* 2001, Vinodgopal *et al* 1998, Ince and Tezcanlı 2001, Rehorek *et al* 2004) and there is enough evidence to suggest that use of ultrasound to degrade dyes is a viable process on a laboratory scale.

Experimental

The decolourisation of four dyes (Methyl Orange, Reactive Orange 16, Direct Orange 31, Direct Red 81) in aqueous solution was investigated in the presence and absence of sonication. Ultrasonic equipment employed included a 20 kHz probe, 40 kHz bath, 512 kHz bath and 850 kHz bath. The efficiency of the decolourisation was monitored using the change in UV absorbance of the respective dye solutions

Results

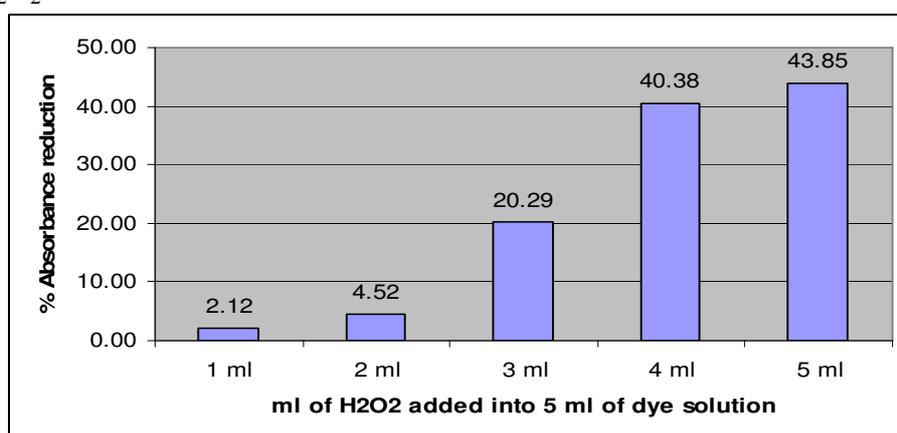
In order to determine whether decolourisation of the dyes under study could be a simple result of thermal degradation or direct degradation from hydrogen peroxide as series of experiments were performed. Thermal degradation was investigated by refluxing the dyes under study for 2 hours and their decolourisation determined. It was found that none of the dyes under study exhibited any thermal degradation.

Degradation via hydrogen peroxide was monitored by the direct addition of a solution of 30% H₂O₂ and the resultant decolourisation monitored using UV. Reactive Orange 16 and Direct Red 81 did not exhibit any decolourisation with hydrogen peroxide. This demonstrated, therefore, that if these two dyes showed any decolourisation with sonication it will not be due to the presence of hydrogen peroxide.

With Methyl orange the addition of a solution containing 30% H₂O₂ resulted in a absorbance peak shift of the λ_{max} with a change in pH, however decolourisation was not observed

When 30% hydrogen peroxide solution was added to a solution of direct orange 31 it appeared to decolourise significantly. Here the degradation mechanism appears to be due to presence of H₂O₂. See Figure 1 below.

Figure 1 : % absorbance reduction of 100 μmol/l direct orange 31 at 430 nm after adding H₂O₂



Ultrasonic Decolourisation of dye

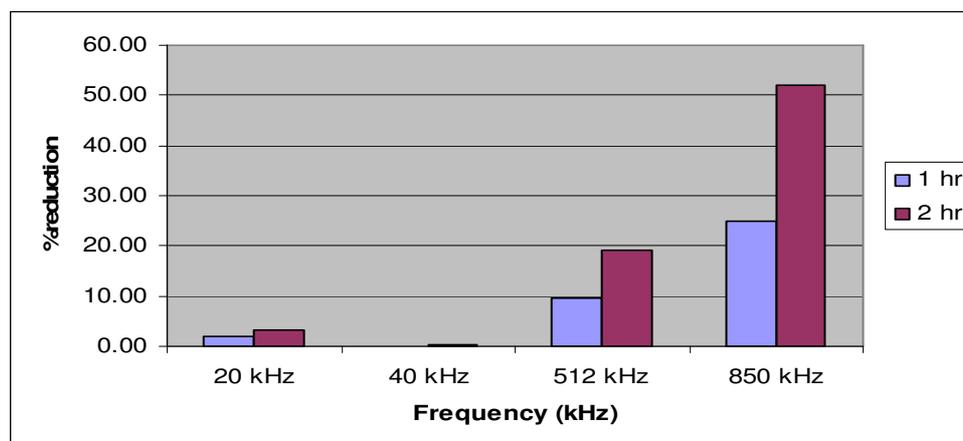
Methyl orange

From Table 1, it can be observed that the 20 kHz ultrasonic probe and 40 kHz bath were not effective in decolourising methyl orange. The 512 kHz Ultrasonic bath was more effective but the most effective, with an 81% reduction in dye colourisation, was the 850 kHz bath. This is thought to be due to the 512 and 850 kHz baths being able to generate more hydroxyl radicals in the bulk solution.

Table % absorbance reduction of 10 μmol/l methyl orange at 464 nm after sonication

Equipment	Freq kHz	Vol (cm ³)	% Dye reduction	
			1 hr	2 hr
Ultrasonic probe	20	100	1.89	3.11
Ultrasonic bath #1	40	100	0.00	0.42
Ultrasonic bath #2	512	500	9.44	19.29
Ultrasonic bath #3	850	200	25.00	51.95

Figure 2 : % absorbance reduction of 10 $\mu\text{mol/l}$ methyl orange at 464 nm after sonication at different frequencies



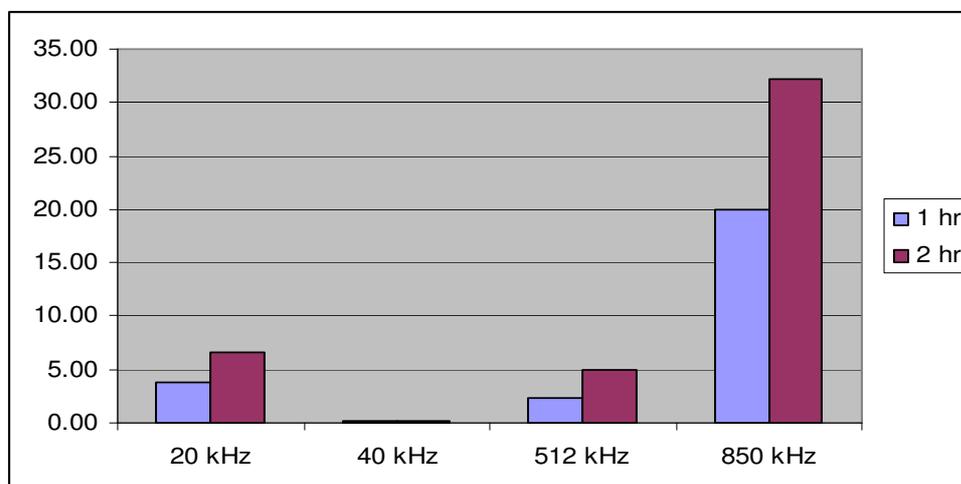
Reactive orange 16

In Table 2 below similar results are observed with the 850 kHz bath again producing the greatest levels of dye decolourisation observed with Reactive Orange 16. Direct Orange 16 is not susceptible to decolourisation with hydrogen peroxide suggesting ultrasonic decolourisation is due to radical attack.

Table 2 % absorbance reduction of 100 $\mu\text{mol/l}$ reactive orange 16 at 494 nm after sonication

Equipment	Freq kHz	Vol (cm ³)	% Dye reduction	
			1 hr	2 hr
Ultrasonic probe	20	100	3.84	6.64
Ultrasonic bath #1	40	100	0.16	0.24
Ultrasonic bath #2	512	500	2.29	4.95
Ultrasonic bath #3	850	200	19.92	32.14

Figure 3 : % absorbance reduction of 10 $\mu\text{mol/l}$ reactive orange 16 at 494 nm after sonication at different frequencies



Direct orange 31

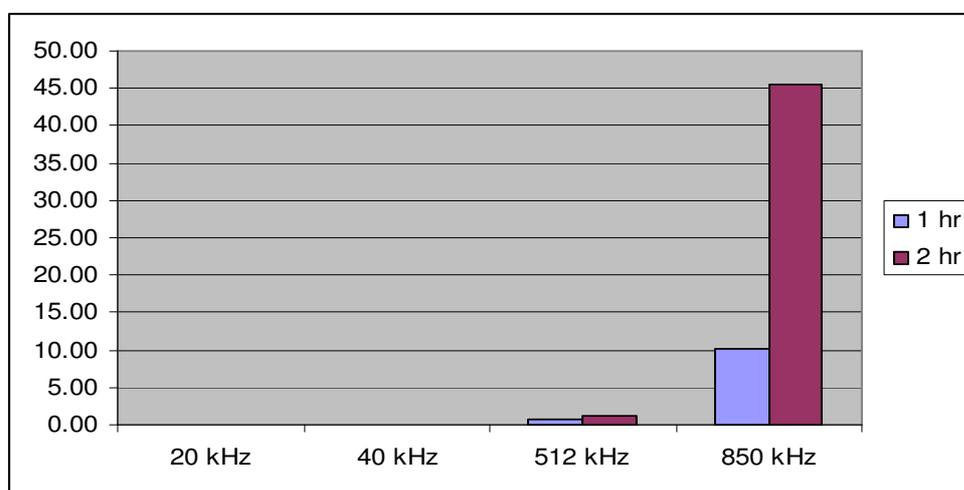
Direct Orange 31 is susceptible to direct decolourisation with hydrogen peroxide. On addition of a 30 % solution of H₂O₂ to a solution of this dye the absorbance reduced by 43.85 % with a ratio of dye solution:H₂O₂ of 1:1 by volume.

The direct orange 31 solution was not bleached either by the 20 kHz ultrasonic probe or 40 kHz bath. The slight increase of the absorbance after sonication for 2 hours may be the result of evaporation although cooling measures were taken to prevent this. Again the highest levels of dye decolourisation were observed with the 850 kHz bath with a 45.43% reduction observed after irradiation for 2 hours.

Table 3. % absorbance reduction of 100 µmol/l direct orange 31 at 430 nm after sonication

Equipment	Freq kHz	Vol (cm ³)	% Dye reduction	
			1 hr	2 hr
Ultrasonic probe	20	100	-0.51	-0.61
Ultrasonic bath #1	40	100	-0.84	-1.36
Ultrasonic bath #2	512	500	0.71	1.23
Ultrasonic bath #3	850	200	10.22	45.43

Figure 4 : % absorbance reduction of 10 µmol/l direct orange 31 at 430 nm after sonication at different frequencies



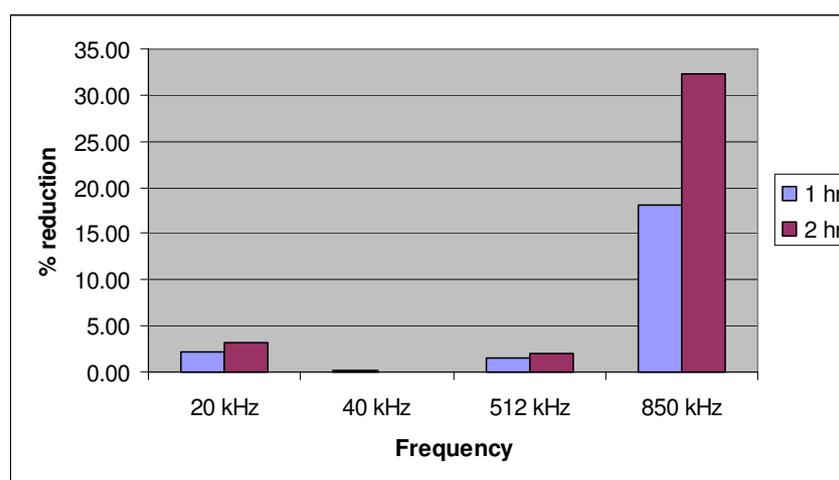
Direct red 81

Direct red 81 not appear to be susceptible to direct decolourisation with hydrogen peroxide and therefore the decolourisation of this dye may be entirely due to the radicals formed by sonication which attack the dye directly rather than the result of any peroxide they may form. Again 850 kHz proved to be the most effective decolourisation frequency.

Table 5. % absorbance reduction of 100 $\mu\text{mol/l}$ direct red 81 at 508 nm after sonication

Equipment	% reduction	
	1 hr	2 hr
Ultrasonic probe	2.23	3.14
Ultrasonic bath #1	0.17	-0.48
Ultrasonic bath #2	1.57	1.94
Ultrasonic bath #3	18.05	32.31

Figure 5 : % absorbance reduction of 10 $\mu\text{mol/l}$ direct red 81 at 508 nm after sonication at different frequencies



Conclusion

Thermal Refluxing of the dye solutions did not result in any decolourisation and addition of hydrogen peroxide decolourised only Direct Orange 31. This suggests that the mechanism for ultrasonic decolourisation is not thermal and is also not due to direct action by hydrogen peroxide in the case of 3 of the dyes investigated. For the dye solutions decolourisation was found to be difficult using ultrasound alone with long treatment times required however at the highest frequency of 850 kHz decolourisation was achieved with ultrasound alone and this opens up the possibility of using ultrasound as part of a water treatment process rather than as a treatment process alone. Large scale ultrasonic equipment is becoming more freely available and if ultrasound acts synergistically to increase the efficiency of decolourisation of dyes, as it has been shown to do in other processes, it may then be possible to achieve dye control at faster processing times but also at possibly lower processing temperatures using fewer environmentally damaging chemicals.

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