Proceedings of 20th International Congress on Acoustics, ICA 2010

23-27 August 2010, Sydney, Australia

Degradation of water pollutants using ultrasound

L Paniwnyk (1), O. Larpparisudthi (1), T J Mason (1)

(1) The Sonochemistry Centre at Coventry University, Faculty of Health and Life Sciences, Coventry, UK

PACS: 43.35VZ, 43.35WA

ABSTRACT

Water can contain many different types of pollutants of a chemical and also of a biological nature and therefore must be treated prior to subsequent use. Textile effluents contain waste dyestuffs which are sometimes difficult to treat by conventional processes which often involve biological and chemical methods. Due to their toxicity, the treatment efficiency of chlorophenols by general biological treatment systems is normally low and fairly inefficient. Pollution by various bacterial organisms and algae is also become more common place with large scale problems occurring worldwide. Treatment using conventional methods can be difficult and in some cases ineffective. In order to treat water more efficiently advanced oxidation processes must be employed. Ultrasound is considered to be such an advanced oxidation process. Its ability to generate hydroxyl radicals at low temperatures has generated interest in the treatment of dye decolourisation and also in the oxidation of chlorophenols. In this study the decolourisation of several dyes in aqueous solution was investigated in the presence and absence of sonication at varying frequencies with the most effective being 850 kHz. Treatment of aromatic chlorophenols also produced degradation at 850 kHz. However biological systems appear to operate in a different manner with the most effective frequency being 20 kHz which is primarily a frequency used for disruption of cells rather than $^{\cdot}OH$ radical generation.

INTRODUCTION

There is a growing worldwide problem over the lack of available clean (potable) water as populations increase and natural water sources diminish due to climate change. Most of the fresh water *tends* to be tied up in glaciers or is inaccessible deep underground. As a result there is a need to treat water prior to it being available to the public for drinking. There are many methods available to remediate water with the one of the most common being the use of chlorine and chlorination agents or the use of UV radiation to degrade contaminants.

There are however contaminants that resist such treatment resulting in water that appears slightly mis-coloured or people claiming that it has an odd odour or taste. There is also a worry that incomplete degradation of such contaminants may result in the formation of harmful side products that also require further treatment. These resistant contaminants require further treatment in order to achieve their complete breakdown and degradation. Further treatment may include the use of hydrogen peroxide, Fentons reagent or even electrochemical treatment [1,2]. These additional processes are often called advanced oxidation processes and one such process is the use of ultrasound [3]. The use of ultrasound in potable water treatment is an emerging technology which offers an environmentally friendly (little or no toxic chemicals are used or produced), low cost, and compact alternative to conventional water treatment.

Two common types of chemical pollutants in waste water are azo dyes and chlorophenols. Often effluent from textile factories contains waste dyestuffs and these are sometimes difficult to treat by conventional processes involving biological and chemical methods. When such materials are discharged into rivers or streams without adequate treatment, the contaminants can be transported over long distances and may form carcinogenic end products through hydrolysis or anaerobic metabolization [4]. Chlorophenols present problems in the effluent streams from many industries e.g. pulp bleaching, hydrolysis of herbicides and oil refining. The treatment efficiency of chlorophenols by general biological treatment systems is normally low and fairly inefficient due to their toxicity.

In terms of biological contamination Coliform bacteria, algae and cyanobacteria toxins (produced by blue-green algae), are commonly found in water bodies. Human activity that produces pollution such as agricultural and road runoff together with inadequate sewage treatments has led to excessive fertilisation (eutrophication) of many water sources. These environmental conditions result in disproportionate proliferation of coliform bacteria, and in particular algae and cyanobacteria in fresh water. Water treatment processes such as filtration can remove some of the microorganisms and pathogens in water however this still does not meet the safe levels required. As a result further treatment processes are required to control the numbers of microorganisms and pathogens. Ultrasonic treatment provides a green alternative to conventional disinfection through reducing the chemical requirement and this has been examined for the inactivation of coliform bacteria. Treatment methods also include the use of UV radiation and ozone [5].

Ultrasound is known to produce hydrogen and hydroxyl radicals from the sonolysis of water at high frequencies. Due to the shorter life time of the cavitation radicals at high frequencies these radicals are often expelled into the bulk liquid where they go on the degrade any chemical contaminants or attack bacteria cell walls. Radicals can also re-combine to for

hydrogen peroxide which is itself a highly oxidising agent [6]. As result ultrasound has the great potential of becoming a method for treating a wide variety of water contaminants both of a chemical and also a bacteriological nature.

EXPERIMENTAL

Dye solutions

100 µmol/l solutions of a range of azo dyes namely methyl orange, reactive orange 16, direct orange 31, direct red 81, each prepared in aqueous solution, were investigated in the presence and absence of sonication at approximately 20°C. Any loss of colour for each dye was followed for 2 hours by removing aliquots at regular intervals and subjected them to UV/Visible spectroscopic analysis at the appropriate absorbance wavelength for the particular dye. The process was repeated at several different frequencies: 20 kHz probe, 40 kHz bath, 512 kHz bath, 850 kHz bath.

Chlorophenol Solutions

100 mg/l solutions of various chlorinated phenols 4-chlorophenol, 2-chlorophenol and 2,4-dichlorophenol were each prepared in aqueous solution and investigated in the presence and absence of sonication at approximately 20°C. The loss of the chlorophenol was followed over 2 hours by removing aliquots at regular intervals and subjecting them to HPLC analysis. The HPLC conditions used were acetonitrile:water solvent ratio of 60:40 the analytical column was a C18 ODS Hypersil with a flow rate of 1 ml/min and UV detector set at 280 nm. The process was repeated at several different frequencies : 20 kHz probe, 40 kHz bath, 512 kHz bath, 850 kHz bath and a multifrequency bath (380, 1000 and 1176 kHz).

Bacterial solutions

Stock agar plates of bacteria (*Enterobacter cloacae*, *Citrobacter freundii* and *Enterococcus faecalis*) were prepared. The number of bacteria in suspension was determined using the turbidity method by measuring the optical density of the suspension using a CORNING colorimeter. Bacteria cell suspensions were prepared at OD of 0.4 at 440 nm in 0.9% sterile saline water. Bacteria were analysed by using standard plate counts. Ultrasonic treatment was achieved by adding bacteria suspension into the treatment vessel (either directly into the bath or into a conical flask). Temperature was monitored by a thermocouple. 1 ml of sample was taken at 5, 10, 15, 20, 30, 40, 50 and 60 minutes of sonication and analyzed by standard plate counts method. Sonication was applied using a 20kHz probe and 40kHz, 380, 512, 850, 1000 or 1176 kHz ultrasonic baths.

RESULTS

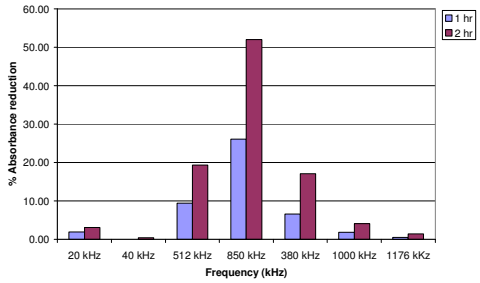
Ultrasonic Decolourisation of dyes

Decolourisation of methyl orange

Fig 1 below shows that neither the 20 kHz ultrasonic probe nor the 40 kHz bath were effective in decolourising methyl orange. The 512 kHz ultrasonic bath was more effective but the 850 kHz bath was the most effective with a 50% reduction in dye colourisation in 2 hours. This is thought to be due to the 512 and 850 kHz baths being more able to generate hydroxyl radicals in the bulk solution (see above).

Methyl orange is not susceptible to decolourisation by addition of hydrogen peroxide (REF). In this case sonochemical decolourisation is due to hydroxyl radical attack.

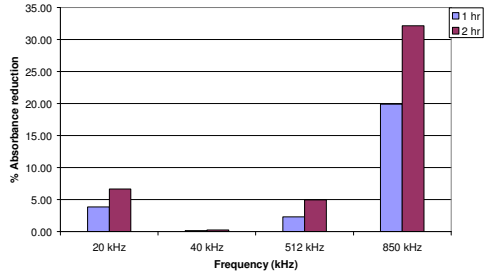
Figure 1 - % absorbance reduction of 100 µmol/l methyl orange at 464 nm after sonication



Decolourisation of reactive orange 16

In Fig 2 below similar results are observed with the 850kHz bath again producing the greatest levels of dye decolourisation observed with reactive orange 16. Since direct orange 16 is not susceptible to decolourisation with hydrogen peroxide this must be also due to hydroxyl radical attack.

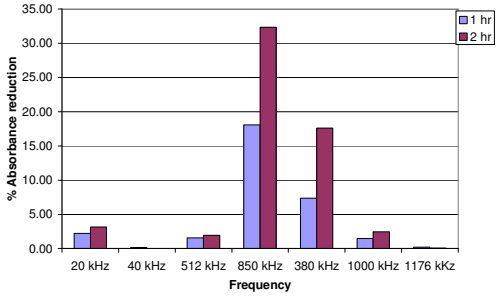
Figure 2 - % absorbance reduction of 100 µmol/l Reactive Orange 16 at 494 nm after sonication



Decolourisation of direct red 81

As for the two previous dyes the sonochemical degradation of direct red 81 may be entirely due to attack by hydroxyl radicals with 850 kHz again the most effective frequency.

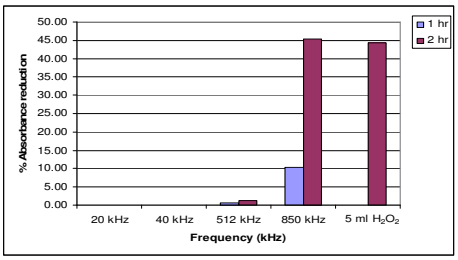
Figure 3- % absorbance reduction of 100 µmol/l Direct Red 81 at 508 nm after sonication



Decolourisation of direct orange 31

Unlike the other three dyes direct orange 31 is susceptible to direct decolourisation with hydrogen peroxide. The direct orange 31 solution was not decolourised either by the 20 kHz ultrasonic probe or 40 kHz bath, (Table 5). The slight increase of the absorbance after sonication for 2 hours may be the result of some slight evaporation although cooling was applied in order 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.

Figure 4 - % absorbance reduction of 100 µmol/l Direct Orange 31 at 430 nm after sonication

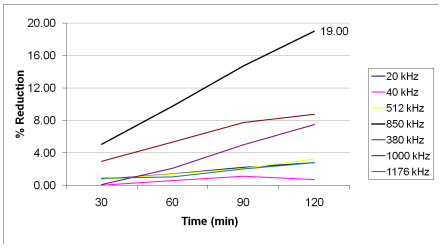


Ultrasonic degradation of chlorophenols

Ultrasonic Degradation of 2, 4, and 2,4-chlorophenol

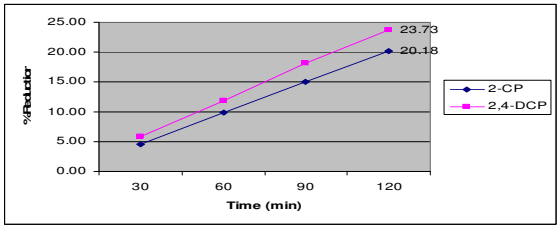
The degradation of 4-chlorophenol was attempted using the same range of ultrasonic frequencies as used for the dyes and the most effective was again identified as 850kHz .

Figure 5 – Degradation of 4-chlorophenol



To determine if 850kHz has the same effects on other similar pollutants chlorophenol (2CP) and 2,4-dichlorophenol (2,4-DCP) were sonicated. The results shown below indicate that 20% of 2-CP and 23.73% of 2,4-DCP were degraded after 2 hour sonication.

Figure 6 –Degradation of 2-chlorophenol and 4-chlorophenol at 850kHz

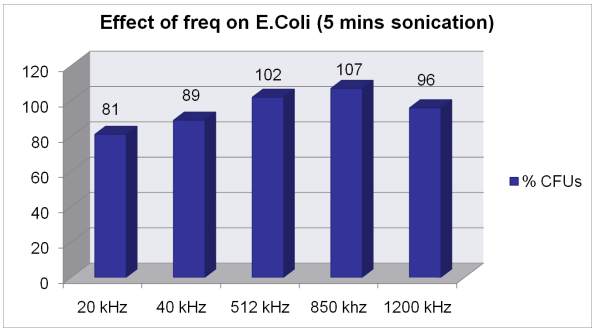


Effect of ultrasound on bacteria

Effect of Frequency on E.Coli

The initial concentration of *Enterobacter cloacae* suspension was prepared at optical density (OD) of 0.4 at 440 nm. The average number of colony forming units (CFU) per volume (ml) of *Enterobacter cloacae* suspension after sonication at different frequencies is shown in Fugure 7 below. It can be clearly seen that it is only the 20 kHz probe that shows a significant reduction of the cells. The rise in CFU scan be attributed to the declumping/deagglomeration of bacterial cell clumps which are disturbed in the first few moments of sonication.

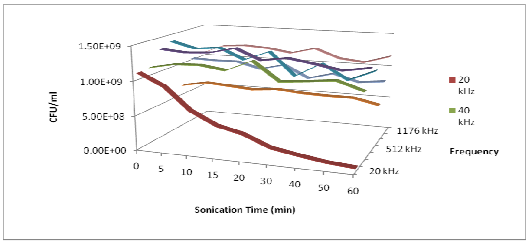
Figure 7- % colony forming units of E Coli remaining after 5 minutes sonication of varying frequencies



Effect of Frequency on E.Cloacea

The deactivation of bacteria by ultrasound is the result of both mechanical and chemical effects. Ultrasound may damage bacteria cells by shear force as a mechanical effect or by the attack of hydroxyl radicals and the reaction with hydrogen peroxide as a chemical effect. These result in the rupture of the cell membrane and lead to a leakage of intracellular content [7]. In this study, the greatest deactivation of *Enterobacter cloacae* was obtained by the 20 kHz probe. At high frequency there was no significant reduction of surviving cells.

Figure 8 - Average log CFU/ml of *Enterobacter cloacae* suspension after sonication at varying frequencies over time



CONCLUSION

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

hydrogen peroxide in the case of 3 of the dyes studied. 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. In the case of degradation of aromatic chlorophenols the highest level of degradation of 4-chlorophenol was also found to be at a frequency of 850 kHz with about 19% of 4-chlorophenol degraded after 2 hour. Similar rates were also observed for 2-chlorophenol and 2,4-dichlorophenol. For bacteria the story appears to be different with the most successful kill rates achieved at a low frequency of 20kHz with poor results at the higher frequencies and at 850kHz, the opposite of that required for chemical degradation. Successful chemical degradation can therefore be achieved using ultrasound with an optimal frequency of 850 kHz however best results for bacterial decontamination appear to be at 20kHz. This means that for future scale up and industrial applications of this technology frequency is a variable which must be considered and is dependent upon the contaminants to be treated.

REFERENCES

1. Yasman. Y, Bulatov.V, Rabin.I, Binetti.M, Schechter.I, (2006) Ultrasonics Sonochemistry, 13, 271–277.
2. Hulsun.J, Sun.S.P, Sun.R.S, Hong Fan. M, (2007) Ultrasonics Sonochemistry, 14, 761
3. T.J.Mason and C.Petrier, (2004) Ultrasound Processes, Advanced Oxidation Processes for Water and Wastewater Treatment, 185-208, IWA Publishing
4. Faust. S.D, Aly.O.M, (1998), Chemistry of water treatment, Washington Lewis publishers
5. Metcalf and Eddy, Inc. (2004) revised by Tchobanoglous, G., Burton, F. L. and Stensel, H. D. *Wastewater Engineering: Treatment and Reuse.* 4th edn. New York: McGraw-Hill Companies, Inc.
6. Gonze, E., Fourel, L., Gonthier, Y., Boldo, P. and Bernis, A. (1999) 'Wastewater pretreatment with ultrasonic irradiation to reduce toxicity'. *Chemical Engineering Journal* 73 (2), 93-100
7. Koda, S., Miyamoto, M., Toma, M., Matsuoka, T. and Maebayash M. (2009) 'Inactivation of *Escherichia coli* and *Streptococcus mutans* by ultrasound at 500 kHz'. *Ultrasonics Sonochemistry* 16(5), 655-659