

Mineralisation of Surfactants using Ultrasound and the Advanced Fenton Process

*Alberto Naldoni¹, Alessandro Schiboula¹, Claudia L Bianchi¹ and David H Bremner^{*2}*

¹ Department of Physical Chemistry & Electrochemistry, University of Milan, Via Golgi 19, 20133 Milan, ITALY.

² School of Contemporary Sciences, University of Abertay Dundee, 40 Bell Street, Dundee, DD1 1HG, Scotland UK

Abstract The destruction of the surfactants, sodium dodecylbenzene sulfonate (DBS) and dodecyl pyridinium chloride (DPC) using an advanced oxidation process is described. The use of zero valent iron (ZVI) and hydrogen peroxide at pH = 2.5 (the advanced Fenton process; AFP), with and without, the application of 20 kHz ultrasound leads to extensive mineralisation of both materials as determined by total organic carbon (TOC) measurements. For DBS, merely stirring with ZVI and H₂O₂ at 20 °C leads to a 51% decrease in TOC, but using 20 kHz ultrasound at 40 °C, maintaining the pH at 2.5 throughout, and adding extra amounts of ZVI and H₂O₂ during the degradation, then the extent of mineralisation of DBS is substantially increased to 93%. A similar result is seen for DPC where virtually no degradation occurs at 20 °C but if extra amounts of both ZVI and hydrogen peroxide are introduced during the reaction at 40 °C and the pH is maintained at 2.5 then an 87% mineralisation of DPC is obtained. The slow latent remediation of both surfactants and the mechanism of degradation are also discussed.

Keywords: mineralisation; surfactants; sodium dodecylbenzene sulfonate; dodecylpyridinium chloride advanced Fenton process; zero valent iron; hydrogen peroxide

1 Introduction

Surfactants are amphiphilic molecules that accumulate at interfaces, decrease interfacial tension and form aggregate structures such as micelles. Due to these properties, surfactants alter interfacial behaviour and impact on the way other molecules behave at interfaces and in solution. Surfactants are used in a number of applications and products in the petroleum, food, pharmaceuticals and

therapeutics, cosmetic, environmental bioremediation, agricultural, and biocatalysis industries (Singh et al. 2007). Although, they are generally not directly toxic, these compounds have intrinsic structural properties which can induce different environmental problems such as: hindering both the dissolution of atmospheric oxygen into natural waters and the sedimentation of floating particles; having potential to disrupt hormonal systems of aquatic organisms and might subsequently alter the ecosystem (Ikehata and El-Din 2004). Surfactants can normally be removed from water using the activated sludge technique but complete elimination cannot be guaranteed. Traditional techniques for such contaminants in soil include landfill, air stripping/carbon adsorption, incineration, biological processing and chemical treatment.

However, incineration, adsorption, and landfill merely transfer the contaminant to another phase or location and produce a potentially dangerous and toxic secondary disposal requirement. Biodegradation is very sensitive to numerous environmental factors, is slow, often produces unpredictable results, and is uneconomical for highly concentrated waste effluents. For these reasons, in the past few decades, Advanced Oxidation Processes (AOPs) have been used as alternative techniques in the degradation of surfactants and, generally, for wastewater treatment. AOPs are based on the generation of the hydroxyl radical (HO•), one of the most powerful oxidants known ($E^0 = 2.73 \text{ V}$), and which are capable of reacting non-selectively with virtually all organic compounds.

Several authors report surfactant remediation experiments using several oxidizing agents (Mendez-Diaz et al. 2009) and AOPs such as photocatalysis supported by TiO_2 (Hidaka et al. 1995; Ohtaki et al. 2000; Zhang et al. 2003; Vohra and Tanaka 2003; Zhang et al. 2004; Horvath et al. 2005), ultrasound (Manousaki et al. 2004; Yim et al. 2002; Yang et al. 2005), Fenton or Fenton-like processes (Lin et al. 1999; Bandala et al. 2008; Amat et al. 2004) and most of these achieve good remediation in short reaction times (a few hours instead of days as happens using conventional wastewater treatment with activated sludge). The classical Fenton oxidation process (Fenton 1894; Haber and Weiss 1934; Barb et al. 1949; Barb et al. 1951a; Barb et al. 1951b) utilizes the reaction of aqueous iron (II) salt with hydrogen peroxide to generate hydroxyl radicals, which are then used to carry out chemical oxidation or to degrade recalcitrant organic pollutants in wastewater treatment (Equation 1). The characteristics and uses of Fenton and Fenton-like processes have been extensively reviewed (Pignatello et al. 2006). The usual Fenton process is applied in the degradation of industrial wastewater treatment and it has also been investigated as a pre-treatment process for surfactants (Wang et al. 2008).



The classic Fenton process has been used extensively for the degradation of organic pollutants (Pignatello et al. 2006) but this methodology suffers from a number of drawbacks. An improvement on the Fenton process is the advanced Fenton process (AFP), which uses zero valent iron (ZVI) instead of expensive iron salts, which need to be removed later in the usual Fenton process. In the AFP, hydrogen peroxide and ZVI in acidic conditions, react to generate hydroxyl radicals and ferric ions (Bremner and Burgess 2004; Namkung et al. 2005). These ferric ions are then recycled back to ferrous ions by further interaction with the ZVI surface in a pseudo catalytic process (Equations 2 and 3). Furthermore, the use of ultrasound in conjunction with AFP activates the catalyst and helps clean the metal surface and also induces cavitation, which enhances the production of hydroxyl radicals.



The degradation of organic pollutants by ultrasound in conjunction with AFP has been described (Bremner et al. 2006; Bremner et al. 2008; Namkung et al. 2008; Zhang et al. 2009; Devi et al. 2009) but to our knowledge there has been no report on the degradation of aqueous surfactants using this methodology. Therefore, in this study, we describe the degradation of two surfactants, sodium dodecylbenzene sulfonate (DBS) and dodecylpyridinium chloride (DPC) using the AFP in combination with ultrasonic irradiation. DBS, an anionic surfactant, is an example of a linear alkylbenzene sulfonate (LAS) which is the major type of surfactant produced industrially. Also studied was the cationic surfactant, DPC, which has bactericidal and fungicidal properties and was chosen for investigation because of its high resistance toward classical wastewater treatment.

The purpose of the present investigation was to examine the effects of operating conditions such as temperature, the presence or absence of ultrasound, the effect of the addition of ZVI and / or hydrogen peroxide, the pH and reaction time. The extent of mineralisation of DBS and DPC was determined by measuring the decrease in total organic carbon (TOC) content.

2 Experimental

2.1 Materials

Sodium dodecylbenzene sulfonate (DBS), dodecylpyridinium chloride hydrate (DPC), zero valent iron powder (ZVI, 325 mesh) and hydrogen peroxide (30% w/w in water) were purchased from Aldrich and were used as received. Water was purified using an Elga Option 3 de-ionizer and was used to prepare all solutions.

2.2 Apparatus

The total organic carbon (TOC) content of the initial surfactant (DBS and DPC) aqueous solution and the samples taken from the reaction medium was measured by oxidation analysis (Model 1020 TOC Analyzer from OI-Analytical). The sono-Fenton experiments were performed in a cylindrical glass reactor making use of a commercial ultrasonic processor (Cole-Parmer, 400W model) equipped with a titanium probe with a 1 cm diameter tip capable of operating either continuously or in a pulse mode at a fixed frequency of 20 kHz. In the present work, the experiments were carried out with the probe working in pulses, 4.0 s on and 2 s off, which allows the system to dissipate some of the heat generated by the ultrasonic waves. The intensity of the irradiation was adjusted to 50% of ultrasonic power amplitude, which corresponds to a calorimetric measurement of 18 W.

2.3 Experimental methodology

In a typical run, the probe was immersed in a 1000 mL cylindrical glass reactor filled with 500 mL of aqueous surfactant stock solution (1 mM is equivalent to $[\text{TOC}]_0$ of DBS = 216 ppm and $[\text{TOC}]_0$ of DPC = 204 ppm). The pH was adjusted to 2.5 with appropriate amounts of H_2SO_4 (1 mM). The temperature was kept constant at $20 \pm 5^\circ\text{C}$ or $40 \pm 5^\circ\text{C}$ during all reactions by an external cooling bath as necessary. The appropriate amounts of hydrogen peroxide (2.38 g/L) and ZVI (0.6 g/L) were added to the reactor just before beginning the reaction. Aliquots of the reaction mixture (10 mL) were removed by syringe every 15 min during the reaction and filtered through 0.45 μm polycarbonate membranes before being analyzed (pH and total organic carbon measurement). Silent experiments were carried out in an identical manner without the input of ultrasound but with an overhead stirrer (250 rpm). All reactions were performed in triplicate and the error bars are shown on the graphs.

3 Results and Discussion

3.1 Sodium dodecylbenzene sulfonate (DBS) degradation with 20 kHz ultrasound

DBS although, relatively benign, can give rise to toxic oxidation products on traditional biological or chemical treatments (Kirmele and Swisher 1977; Beltran et al. 2000). A recent review (Mendez-Diaz et al. 2009) compared the effectiveness of different oxidising agents for removal of DBS but only measured the rates of removal and did not determine the extent of mineralisation. In the current work we wished to examine the effect of the advanced Fenton process on the conversion, by hydroxyl radicals, of DBS into low carbon containing organics as measured by TOC content.

When DBS (1 mM) in 500 mL of de-ionised water, with pH adjusted to 2.5 with dilute sulphuric acid, was stirred at 250 rpm with hydrogen peroxide (2.38 g/L) no decrease in TOC was observed over 60 min. A similar result was obtained when zero valent iron (ZVI; 0.6 g/L) replaced the hydrogen peroxide. The amounts of hydrogen peroxide and ZVI used were based on previous work (Chand et al. 2009) where they were optimised for the degradation of phenol and consequently were chosen at these levels for this investigation. However, when both hydrogen peroxide (2.38 g/L) and ZVI (0.6 g/L) were present (the advanced Fenton process – AFP) (Namkung et al. 2005) at the beginning of the reaction a 51% decrease in TOC was seen after 15 min stirring at 20 °C indicating that stirring alone is reasonably efficient for mineralisation of DBS using the AFP (fig 1). The reaction probably ceases at this time as the hydrogen peroxide which was added initially is used up. Interestingly, around half of the mineralisation occurs in the first 5 min of treatment, and may be even faster than this, as seen from the inset in fig 1.

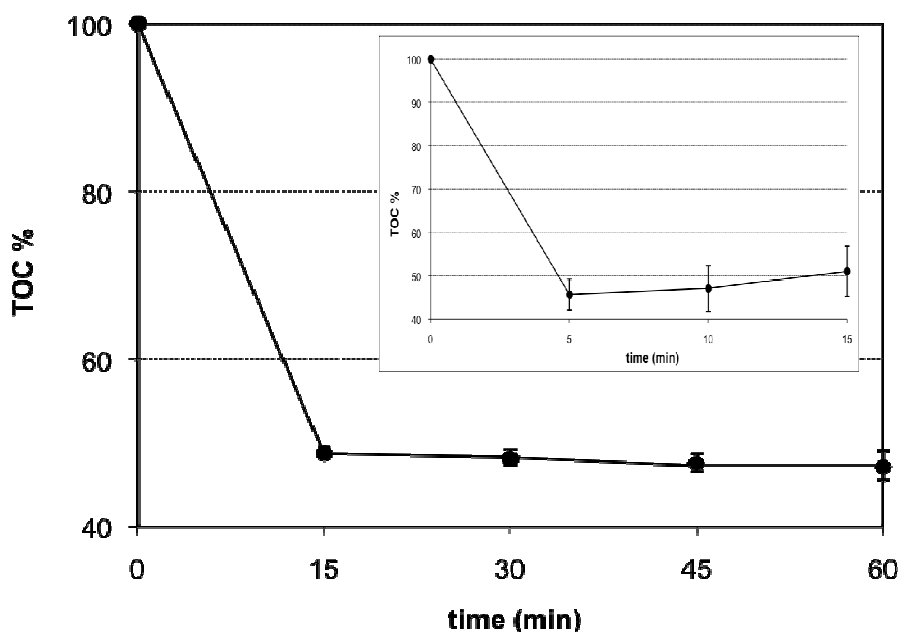


Fig 1: Mineralization of DBS with AFP and stirring at 20 °C; (inset) kinetics in the first 15 minutes of reaction.

The additional effect of introducing ultrasound is illustrated in fig 2 where the reaction was stirred for 60 min at 20 °C and then 20 kHz ultrasound was applied for 4 s on and 2 s off for a further 60 min. After an induction period of about 15 min the TOC content dropped to 50% and remained reasonably constant for the next 45 min. When ultrasound was introduced there was little effect for 10 min but then the TOC dropped to about 40% after 120 min. This increased mineralisation with the addition of US may be due to the generation of additional hydrogen peroxide from sonication of water though generally this is not a very efficient process. However, other effects such as mass transfer and enhanced corrosion of the iron surface cannot be discounted.

In an attempt to increase the amount of mineralisation even further the reaction was carried out at 40 °C and the comparison between the two temperatures is shown in Figure 2. It can be seen that there is a slight difference between the degradation at the two temperatures with the rates being similar but the remaining TOC, after 120 min, was 40% at 20 °C and 35% at 40 °C respectively. At the higher temperature (40°C) there was a significant change in pH going from 2.5 at the beginning of reaction to 4.8 at the end of the degradation (inset fig 2).

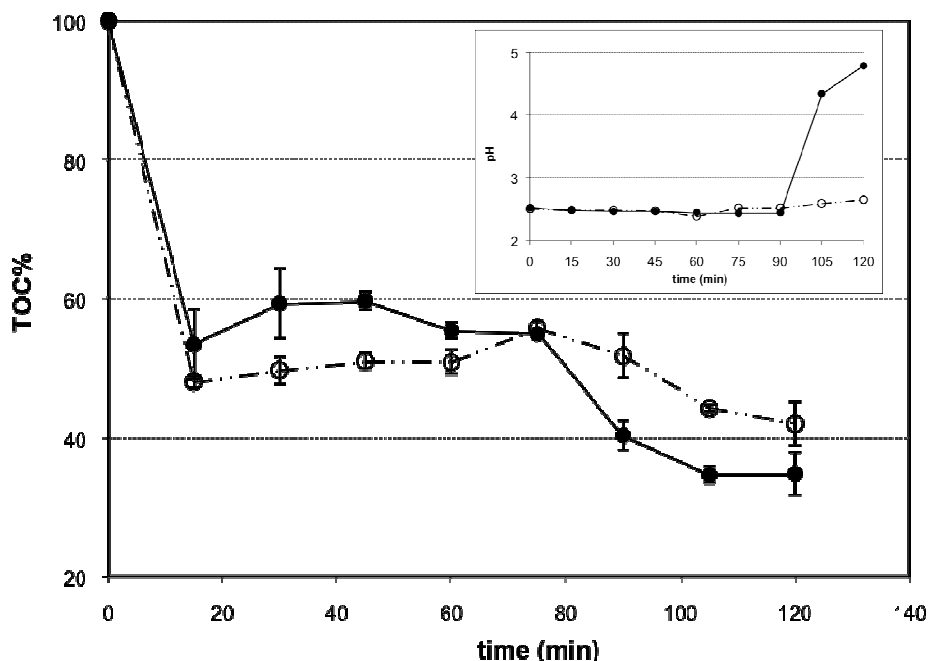


Fig 2: Mineralisation of DBS (dashed line) using the AFP with stirring for 1h then US 1 h at 20 °C; and (solid line) AFP, stirring 1 h then US 1 h at 40 °C; (inset) change of pH.

To obtain high mineralization ultrasound was introduced from the beginning (in combination with AFP) at 40°C and various other reaction conditions were investigated. When the initial amounts of hydrogen peroxide and ZVI were maintained as above but when the pH reached 4, extra

sulphuric acid was added to return the pH to 2.5 (pH control), the extent of mineralisation was 61%. If extra H₂O₂ (1.19g) was added after 75 min with maintenance of pH at 2.5 then the extent of mineralisation increased to 71 % after 120 min. However, if the pH was maintained at 2.5 throughout, and extra amounts of ZVI (0.3 g) and H₂O₂ (1.19g) were both added at 75min and 90 min, then the extent of mineralisation of DBS was increased, substantially, to 93% (Data not shown).

Advanced oxidation processes have been investigated previously for surfactant wastewater treatment using Fenton oxidation (Lin et al 1999; Bandala et al. 2008); electrochemical oxidation (Gu et al 2006); ozone and or/UV irradiation (Amat et al. 2007) and ozone along with powdered activated carbon (Rivera-Utrilla et al. 2006). Beltran and co-workers (2000) have also reported the kinetics of decomposition of DBS with ozone but most of these studies have concentrated on the kinetics of removal of the surfactant rather than the decrease in total organic carbon.

It is well known that hydroxyl radicals are exceptionally powerful oxidants and the oxidative mechanism proceeds by electrophilic attack on the aromatic ring of the substrates. In the case of the model compound phenol there are a number of oxidized aromatic intermediates before the ring is broken open leading eventually to small organic entities such as maleic, acetic and formic acids along with CO₂ and H₂O (Santos et al. 2002; Bremner et al. 2006). In the case of DBS it is expected that the aromatic ring is hydroxylated by HO• several times before ring opening and then further oxidation by hydroxyl radical/hydrogen peroxide will produce β-dicarboxylic acids which will decarboxylate to give mono acids and CO₂ (Fig 3). Continuing oxidation will afford small organic acids and CO₂ which accounts for the residual organic content in the case of the former and a decrease in TOC from the latter. This mechanism is partially supported by the work of Fernandez (2004) who examined the products of photodegradation and ozonation of alkyl benzenesulphonates.

The conditions used in the AFP, merely stirring with H₂O₂ and ZVI produces a reasonable flux of hydroxyl radicals giving a 50 % decrease in TOC. This is augmented slightly by application of US as a result of enhanced mass transfer and possibly sonochemical production of hydrogen peroxide. There is a slight improvement in mineralization by increasing the reaction temperature to 40 °C but this may be due to faster kinetics resulting in hydrogen peroxide being available for a slightly longer time. The increase in pH is noteworthy and is ascribed to production of hydrated iron salts which are no longer capable of taking part in Fenton chemistry but this problem is overcome to a large extent by returning the pH to 2.5 and solubilising more ferrous ion from the ZVI. Addition of extra iron, hydrogen peroxide and maintaining the pH at 2.5 ensures that optimum Fenton conditions are present throughout the reaction and gives an impressive TOC

removal of 93% because of enhanced Fenton production of HO•. Thus it can be concluded that maximum mineralisation of DBS may be obtained when using a pH of 2.5 with addition of extra ZVI and H₂O₂ at a temperature of 40°C. The residual carbon content is probably small organic acids which are notoriously difficult to mineralize.

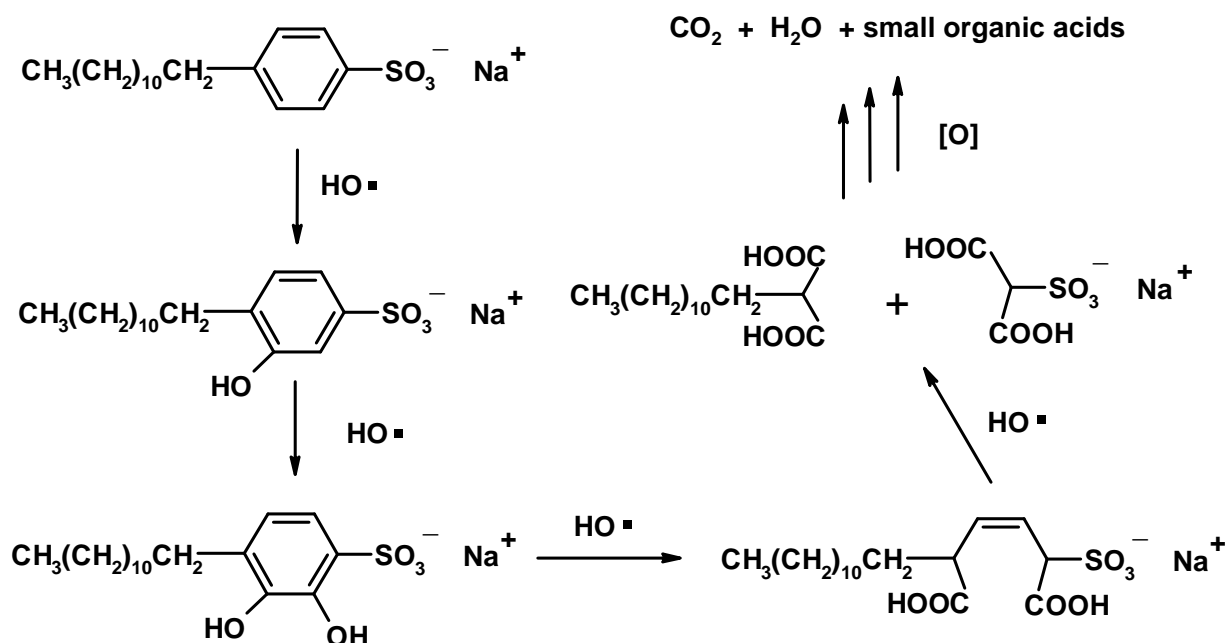


Fig 3: Proposed oxidation route of sodium dodecylbenzene sulfonate by hydroxyl radicals.

3.2 Dodecylpyridinium chloride (DPC) mineralisation with 20 kHz ultrasound

Initially, a DPC solution (500 mL; 1 mM) was prepared and the pH adjusted to 2.5. This solution was stirred separately at 20 °C with only iron (0.6 g/L) and then with hydrogen peroxide (2.38 g/L) alone and no change in TOC measurements were observed indicating that no reaction occurred under these conditions. When the reaction was repeated with stirring but under normal AFP conditions (pH = 2.5; ZVI = 0.6 g/L; H₂O₂ = 2.38 g/L) at 20 °C only 2% TOC removal was observed after 60 min. Surprisingly, when US was introduced after 1 h of stirring at 20 °C the amount of mineralisation of DPC only increased to 45% after a further hour of treatment.

In an effort to increase the extent of mineralisation the AFP reaction was examined at higher temperature. When DPC was stirred at 40 °C with ZVI and H₂O₂ then only 7% mineralisation was observed after 60 min. However, when ultrasound was then applied to this solution the extent of mineralisation increased to 58% (fig 4). As seen from the inset in fig 4 the pH trend was similar, at 20 °C and 40 °C, to that observed previously for DBS.

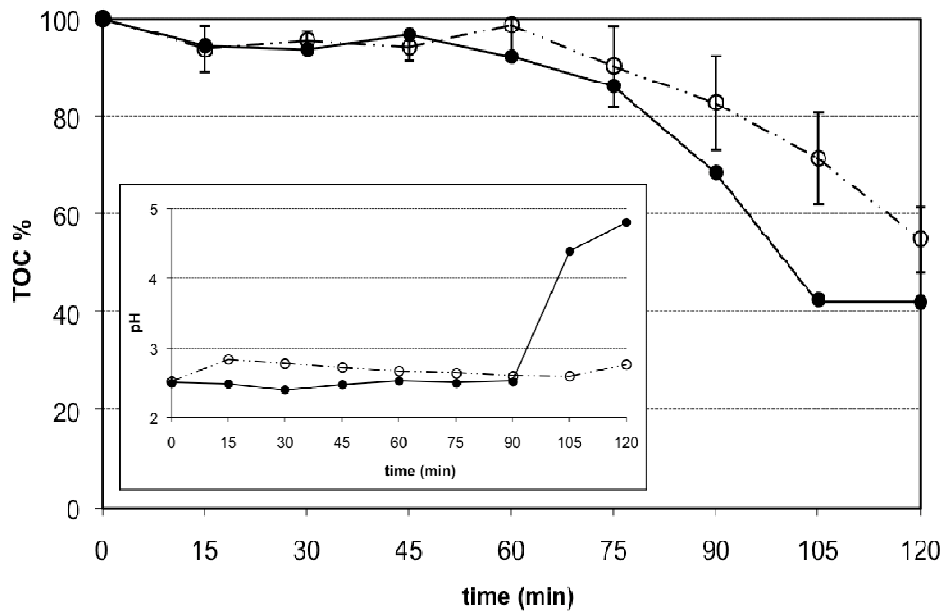


Fig 4: Mineralisation of DPC (dashed line) AFP, stirring 1 h then US 1 h at 20 °C; and (solid line) AFP, stirring 1 h then US 1 h at 40 °C; (inset) change of pH.

When ultrasound, in combination with AFP, was introduced from the beginning at 40°C with pH control then the extent of mineralization was around 50%. If extra H₂O₂ was added at 45 min with pH control then 57% mineralisation was seen (Fig 5). If extra ZVI (0.3 g) and hydrogen peroxide (1.19 g) were introduced at 45, 60, 75, 105 min at 40 °C and the pH was maintained at 2.5 by addition of H₂SO₄ (1 mM) then 87% mineralisation of DPC was observed after 120 min. Thus it can be seen that the addition of all the extra reagents are required to gain this high removal of carbon although these conditions have not been optimised.

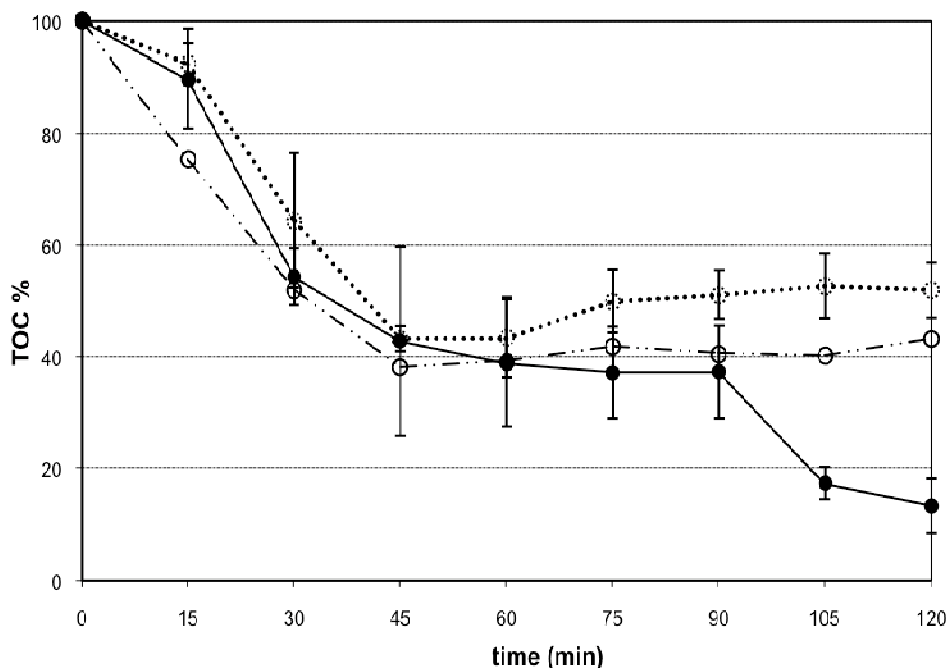


Fig 5: Mineralisation of DPC with AFP and US from the beginning at 40 °C: (dotted line) pH control, (dashed line) pH control and H₂O₂ additions; (solid line) pH control and ZVI / H₂O₂ additions.

Little work has been reported on the oxidation of DPC using hydroxyl radicals. However, it is expected that the reaction will proceed in a similar manner to that describe in section 3.1. In this case little reaction was observed at 20 °C with just stirring with the reagents (unlike for DBS) and only 45% removal of TOC was seen on the additional application of ultrasound. If the full range of excess oxidants, extra ZVI and with stirring and US were used then only 13% TOC remained after treatment at 40 °C. The lack of reaction at 20 °C is a reflection of the relative stability to hydroxyl attack on the positively charged pyridinium ring in DPC compared to the benzene ring in DBS.

3.3 Latent Remediation of DBS and DPC

In order to minimise energy input during the mineralisation process it was decided to investigate the effect of minimal ultrasonic treatment along with silent processing in a process termed Latent Remediation (Chakinala et al., 2009). In this procedure the pollutant is irradiated for a short time with ultrasound in the presence of iron and hydrogen peroxide and then the solution is left silent for 24 h and the TOC content then measured. When DBS was stirred with ZVI (0.6 g/L) and hydrogen peroxide (2.38 g/L) at pH 2.5 for 60 min at 20 °C then 51% mineralisation occurred. If the stirring was stopped after 60 min and the sample left undisturbed with no added reagents for a further 24 hours the amount of mineralisation increased to 83%. A similar result was obtained if the sample

containing ZVI and H₂O₂ stirred for 1h at 20 °C was irradiated with 20 kHz ultrasound for further hour of treatment (58%) and then left for 24 h (77%). Interestingly, performing the same experiment at 40 °C for the first hour and then leaving the solution at room temperature overnight resulted in no improvement mineralisation (65%) possibly due to the higher initial temperature decomposing some of the hydrogen peroxide.

The effect of latent remediation was also examined for DPC. Merely stirring DPC with ZVI and hydrogen peroxide for 60 min at 20 °C resulted in only 2% mineralisation. If the stirring was stopped after 60 min and the sample left undisturbed for a further 24 hours the amount of mineralisation increased to 18%. If the DPC solution was stirred using the usual AFP conditions for 1h and ultrasound applied for further 1 h then 45% mineralisation was seen. If this solution was then left silent for 24 h, the TOC reduced to 70%. Again the higher temperature had a negative effect on the latent remediation: at 40°C the extent of mineralisation observed was constant (58%) after 2h and 24h. Further work on the exact mechanism involved in latent remediation is ongoing.

4 Conclusions

Generally, surfactants are relatively resistant to degradation using conventional oxidation processes. However, when sodium dodecylbenzene sulfonate (DBS) and dodecylpyridinium chloride (DPC) are separately treated with zero valent iron (ZVI) and hydrogen peroxide at pH = 2.5 along with the application of 20 kHz ultrasound extensive mineralisation is observed. DBS is partially decomposed at 20 °C but if the temperature is raised to 40 °C then the extent of mineralisation is increased to 93%. When the oxidation of DPC is attempted at 20 °C, under identical conditions to DBS, it proves to be recalcitrant but at 40 °C, then 87% mineralisation of DPC is obtained. A novel energy saving process (latent remediation) is also described where mineralisation continues even after energy input has ceased and future work will concentrate on establishing the mechanism of this process. Although the concentrations of surfactants used in this study are well above those normally found in water the current work illustrates the high effectiveness of the advanced Fenton process and acts as a model for mineralisation studies. Indeed our previous work has shown that highly dilute solutions of pollutants (as found in wastewater) are even more readily mineralised.

Acknowledgments The authors thank COST D32 and the European Science Foundation for financial support to carry out an STSM.

References

- Amat, A., Arques, A., Miranda, M.A., & Segui, S. (2004). Photo-Fenton reaction for the abatement of commercial surfactants in a solar pilot plant. *Solar Energy*, 77, 559–566.
- Bandala E.R., Pelaez, M.A., Salgado, M.J., & Torres, L. (2008). Degradation of sodium dodecylbenzene sulphate in water using solar driven Fenton-like advanced oxidation processes. *Journal of Hazardous Materials*, 151, 578–584.
- Barb, W.G., Baxendale, J.H., George, P., & Hargrave, K.R. (1949). Reactions of ferrous and ferric ions with hydrogen peroxide. *Nature*, 163, 692–694.
- Barb, W.G., Baxendale, J.H., George, P. & Hargrave, K.R. (1951a). Reactions of ferrous and ferric ions with hydrogen peroxide. Part 1. - The ferrous ion reaction. *Transactions of the Faraday Society*, 47, 462–500.
- Barb, W.G., Baxendale, J.H., George, P. & Hargrave, K.R. (1951b). Reactions of ferrous and ferric ions with hydrogen peroxide. Part 2 - The ferric ion reaction. *Transactions of the Faraday Society*, 47, 591–616.
- Beltran, F.J., Garcia-Araja, J.F. & Alvarez, P.M. (2000). Sodium dodecylbenzenesulfonate removal from water and waste-water. 1. Kinetics of decomposition by ozonation. *Ind. Eng. Chem. Res.* 39, 2214-2220.
- Bremner, D.H., & Burgess, A.E. (2004). US Patent 6,692,632, University of Abertay Dundee.
- Bremner, D.H., Burgess, A.E., Houlemare, D., & Namkung, K.-C. (2006). Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide. *Applied Catalysis B: Environmental*, 63, 15–19.
- Bremner, D.H., Di Carlo, S., Chakinala, A.G., & Cravotto, G. (2008). Mineralisation of 2,4-dichlorophenoxyacetic acid by acoustic or hydrodynamic cavitation in conjunction with the advanced Fenton process. *Ultrasonics Sonochemistry*, 15, 416–419.
- Chakinala, A. G., Gogate, P.R., Burgess, A.E., & Bremner, D.H. (2009). Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced **Fenton** processing. *Chemical Engineering Journal*, 152, 498-502.
- Chand, R., Ince, N.H., Gogate, P.R. & Bremner, D.H. (2009). Phenol degradation using 20, 300 and 520 kHz ultrasonic reactors with hydrogen peroxide, ozone and zero valent metals. *Separation and Purification Technology*, 67, 103-109.
- Devi, L.G., Kumar, S.G., Reddy, K.M., & Munikrishnappa, C. (2009). Photo degradation of Methyl Orange an azo dye by Advanced Fenton Process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism. *Journal of Hazardous Materials*, 164, 459–467.
- Fenton, H.J.H. (1894). Oxidation of tartaric acid in presence of iron. *Journal of the Chemical Society*, 65, 899–910.
- Fernandez, J., Riu, J., Carcia-Calvo, E., Rodriguez, A., Fernandez-Alba, A.R. & Barcelo, D. (2004). Determination of photodegradation and ozonation by products of linear alkylbenzene sulfonates by

liquid chromatography and ion chromatography under controlled laboratory experiments. *Talanta*, 64, 69-79.

Gu, L., Wang, B., Ma, H., & Kong, W. (2006). Catalytic oxidation of anionic surfactants by electrochemical oxidation with $\text{CuO-Co}_2\text{O}_3\text{-PO}_4^{3-}$ modified kaolin. *J. Hazardous Materials*, 137, 842-848.

Haber, F., & Weiss, J. (1934). The catalytic decomposition of hydrogen peroxide by iron salts. *Proceedings of the Royal Society A*, 134, 332–351.

Hidaka, H., Nohara, K., Zhao, J., Pellizzetti, E., & Serpone, N. (1995). Photodegradation of surfactants XIV. Formation of NH_4^+ and NO_3^- ions for the photocatalyzed mineralization of nitrogen-containing cationic, non-ionic and amphoteric surfactants. *Journal of Photochemistry Photobiology A: Chemistry*, 91, 145-152.

Horvath, O., Bodnar, E., & Hegyi, J. (2005). Photoassisted oxidative degradation of surfactants and simultaneous reduction of metals in titanium dioxide dispersions. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 265, 135–140.

Ikehata, K., & El-Din, M.G. (2004). Degradation of recalcitrant surfactants in wastewater by ozonation and advanced oxidation processes: a review. *Ozone Science and Engineering*, 26, 327–343.

Kirmele, R.A. & Swisher, K.D. (1977). Reduction of aqueous toxicity of linear alkylbenzene sulfonate (LAS) by biodegradation. *Water Res.*, 11, 31-37.

Lin, S.H., Lin, C.M., & Leu, H.G. (1999). Operating characteristics and kinetic studies of surfactants wastewater treatment by Fenton oxidation. *Water Research*, 33, 1735-1741.

Manousaki, E., Psillakis, E., Kalogerakis, N., & Mantzavinos, D. (2004). Degradation of sodium dodecylbenzene sulfonate in water by ultrasonic irradiation. *Water Research*, 38, 3754-3759.

Mendez-Diaz, J.D, Sanchez-Polo, M., Rivera-Utrilla, J., & Bautista-Toledo, M.I. (2009). Effectiveness of different oxidizing agents for removing sodium doecylbenzenesulphonate in aqueous systems. *Water Research*, 43, 1621-1629.

Namkung, K.-C., Burgess, A.E., & Bremner, D.H. (2005). A Fenton-like oxidation process using corrosion of iron metal sheet surfaces in the presence of hydrogen peroxide: A batch process. *Environmental Technology*, 26, 341-352.

Namkung, K.C., Burgess, A.E., Bremner, D.H., & Staines, H. (2008). Advanced Fenton processing of aqueous phenol solutions: A continuous system study including sonication effects. *Ultrasonics Sonochemistry*, 15, 171–176

Ohtaki, M., Sato, H., Fujii, H., & Eguchi, K. (2000). Intramolecularly selective decomposition of surfactant molecules on photocatalytic oxidative degradation over TiO_2 photocatalyst. *Journal of Molecular Catalysis A: Chemistry*, 155, 121–129.

Pignatello, J.J., Oliveros, E., & MacKay, A. (2006). Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Environmental Science and Technology*, 36, 1–84.

Rivera-Utrilla, J., Mendez-Diaz, J., Sanchez-Polo, M., Ferro-Garcia, M.A. & Bautista-Toledo, I. (2006). Removal of the surfactant sodium dodecylbenzenesulphonate from water by simultaneous use of ozone and powdered activated carbon: Comparison with systems based on O₃ and O₃/H₂O₂. *Water Res.*, 40, 1717-1725.

Santos, A., Yustos, P., Quintanilla, A., Rodriguez, S. & Garcia-Ochoa, F. (2002) Route of the catalytic oxidation of phenol in aqueous phase. *Applied Catalysis B: Environmental*, 39, 97-113.

Singh, A., Van Hamme, J.D., & Ward, O.D. (2007). Surfactants in microbiology and biotechnology: Part 2. Application aspects. *Biotechnology Advances*, 25, 99–121.

Vohra, M.S., & Tanaka, K. (2003). Photocatalytic degradation of aqueous pollutants using silica-modified TiO₂. *Water Research*, 37, 3992–3996.

Wang, X-J., Song, Y., & Mai, J-S. (2008). Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulphate. *Journal of Hazardous Materials*, 160, 344–348.

Yang, L., Rathman, J.F., & Weavers, L.K. (2005). Degradation of alkylbenzene sulfonate surfactants by pulsed ultrasound. *Journal of Physical Chemistry B*, 109, 16203-16209.

Yim, B., Okuno, H., Nagata, Y., Nishimura, R., & Maeda, Y., 2002. Sonolysis of surfactants in aqueous solutions: an accumulation of solute in the interfacial region of the cavitation bubbles. *Ultrasonics Sonochemistry*, 9, 209–213.

Zhang, T., Oyama, T., Horikoshi, S., Zhao, J., Serpone, N., & Hidaka, H., 2003. Photocatalytic decomposition of the sodium dodecylbenzene sulfonate surfactant in aqueous titania suspensions exposed to highly concentrated solar radiation and effects of additives. *Applied Catalysis B: Environmental*, 42, 13–24.

Zhang, R., Gao, L., & Zhang, Q. (2004). Photodegradation of surfactants on the nanosized TiO₂ prepared by hydrolysis of the alkoxide titanium. *Chemosphere*, 54, 405–411.

Zhang, H., Zhang, J., Zhang, Liu, F., & Zhang, D. (2009). Degradation of C.I. Acid Orange 7 by the advanced Fenton process in combination with ultrasonic irradiation. *Ultrasonics Sonochemistry*, 16, 325–330.