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The development and evaluation of electrolysis in conjunction with power ultrasound for the disinfection of bacterial suspensions

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Abstract

There is an increasing incidence in health problems related to environmental issues that originate from inadequate treatment of potable waters. This has compelled scientists and engineers to engage in innovative technologies to achieve a maximum disinfection at affordable costs. Some species of bacteria produce colonies and spores that can agglomerate in spherical clusters and thus protect organisms on the inside of the cluster against biocidal attack. Flocs of fine particles (e.g., clay) can entrap bacteria and this can also protect them against the biocides. Other bacteria have the ability to mutate, thus building up resistance to conventional biocides (e.g., chlorine).

Ultrasound has been shown to be effective in improving the effectiveness of biocides such as chlorine. The aim of this present study was to investigate the effect of electrolysis and power ultrasound as a disinfection treatment and to provide a greater knowledge of the fundamentals of disinfection through the production of hypochlorite in situ from saline solution via electrolysis. The electrode materials investigated were, carbon (felt and graphite), copper and stainless steel rods. The results show that sonication appears to amplify the effect of electrolysis. A combination of both treatments is significantly better than sonication or electrolysis alone.

Keywords: Water disinfection; Biocidal action; Ultrasound; Electrolysis

1. Introduction

We have reported the effect of ultrasonic frequency, acoustic power and exposure time on bacterial kill [1,2] and have now extended these studies to the biocidal effect of ultrasound (40 kHz) in conjunction with electrolysis. Studies were conducted on aqueous suspensions of the indicator organism: *Klebsiella pneumonia* (a member of the family Enterobacteriaceae in physiological saline (0.9% by weight NaCl, pH between 7 and 7.5)). Viable plate count techniques were used as a measure of microbial activity [3].

Common disinfection techniques used in water treatment include chlorination, ozonation and ultraviolet irradiation. Chlorination is still a common technique but unfortunately some species of bacteria have the ability to mutate under the adverse conditions of chlorination. This results in the production of strains that are more tolerant to normal chlorine treatment levels. To combat this it is possible to use higher chlorine levels, but such treatment can result in unpleasant flavours and odours (due to the formation of chlorophenols and other halocarbons) [4]. We have reported that ultrasound substantially improves the effectiveness of chlorination through the effects of acoustic cavitation in water (Fig. 1). As with all of the results quoted in this paper the original plate count measurement is normalized to 100%. On collapse, cavitation bubbles produce enough energy to mechanically weaken or disrupt bacteria or biological cells via a number of processes [5–10]. The initial rise in %CFU caused by sonication and recorded in Fig. 1 as values greater than 100% represents the disruption of bacterial clumps to produce a larger number of colony forming units (CFU).

Sonication alone can provide powerful disinfection but generally this requires very high energy and this is why there is a drive towards the use of power ultrasound

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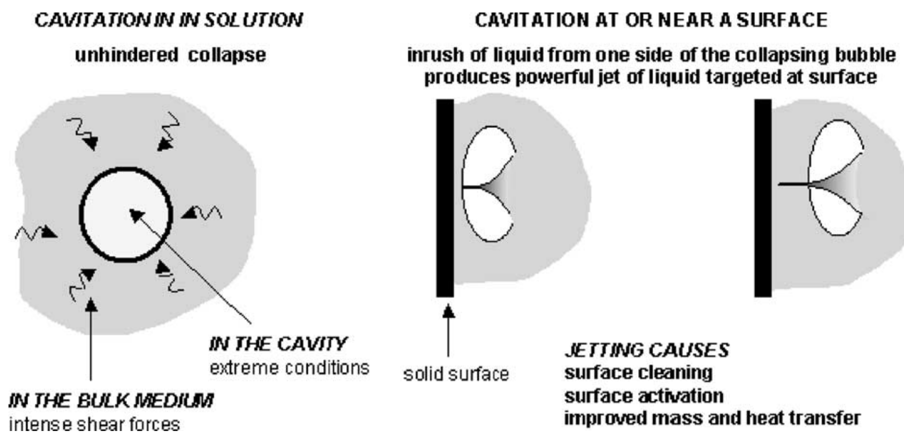

Fig. 1. Effects of acoustic cavitation bubble collapse in bulk solution and near to a surface.

as an adjunct to other techniques (e.g., biocide addition, ultraviolet irradiation and heat treatment [11]). Our current work addresses the disinfection of bacterial suspensions using electrolysis alone (150 mA) and in conjunction with power ultrasound (100 mA together with 40 kHz) to determine the fundamental effects of changes in the electrode material, ultrasonic frequency, power and treatment time on bacterial kill.

The chemistry involved in the electrolysis of saline solution to generate hypochlorite is shown below:

Anode reaction:	$2Cl^- \rightarrow Cl_2 + 2e^-$
Cathode reaction:	$2H_2O + 2e^- \rightarrow 2OH^- + H_2$
In solution:	$Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O$
Overall:	$Cl^- + H_2O \rightarrow OCl^- + H_2$

The equipment used in this study was an electrolytic cell, which consisted of a 600 ml glass beaker either placed on a magnetic stirrer or placed in a 40 kHz ultrasonic bath with a submersible stirrer (Fig. 2). The dimensions of the electrodes used were either rods of 0.95 cm diameter and 23.5 cm long of which 13 cm was submerged in the solution. The carbon felt was 2.5 cm wide and 14 cm long with 13 cm submerged in solution. Over a 15 min experiment using electrolysis alone or with ultrasound the temperature of the reaction mixture increased by only a few degrees and never exceeded 30 °C. Stirring was used in all experiments since electrolysis without mixing resulted in little or no bacterial kill. All experiments were done in triplicate.

2. Results and discussion

2.1. The bioeffects of sonication at 40 kHz (intensity 0.05 W/cm³) on Klebsiella pneumonia suspensions

The results in Fig. 3 indicate that sonication of a 600 ml suspension of coliform bacteria at 40 kHz produces a significant effect. After 60 min sonication a 40% kill is achieved. Sonication at 40 kHz produces an immediate rise in the CFU over the first 10 min followed by a slow

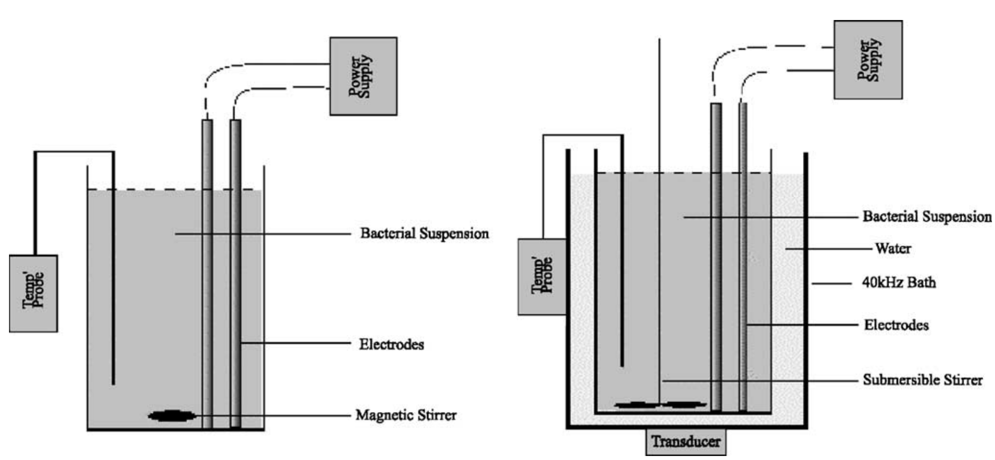

Fig. 2. Schematic diagram of electrolytic cell.

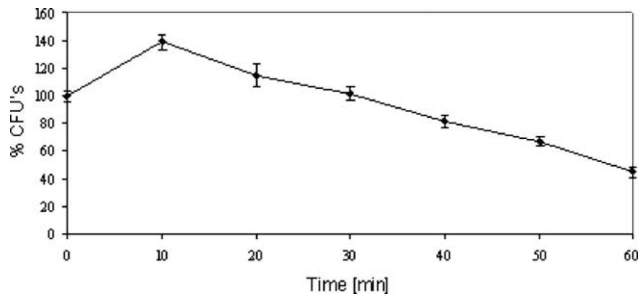

Fig. 3. Plate count monitoring of the bioeffects of sonication at 40 kHz (0.05 Wcm^{-3}).

but steady fall. The results suggest that there is no overall deactivation until after a period of 30 min. This is because the viable plate count technique measures CFU, which reflects the viability of the cells. A CFU may be a single cell or a clump of cells, therefore if ultrasound causes declumping then more CFUs will be formed than were present initially and a period of time will elapse before the apparent overall deactivation falls below the starting level.

2.2. The bioeffects of electrolysis using different electrode materials on Klebsiella pneumonia suspensions at 150 mA

To avoid confusion in Figs. 4–6, the error bars have been omitted, but for each set of results the average error was $<\pm 5\%$. The results in Fig. 4 indicate that there is a significant kill for bacteria in a 600 ml suspension when electrolysed using different electrode materials at 150 mA over a period of 15 min. Although 150 mA current was applied to each system the voltage varied depending on the electrode material used; graphite carbon: ~3.9 V, stainless steel: ~2.2 V, copper: ~2.2 V, carbon felt: ~6.5 V, carbon felt (+) and copper (−): ~3.7 V, and carbon felt (+) and stainless steel (−): ~3.5 V. After 15 min electrolysis 100% kill was achieved using all electrodes except stainless steel, which gave the worst kill, with copper delivering the most effective kill. This is almost certainly due to the fact that copper itself possesses bactericidal properties [12].

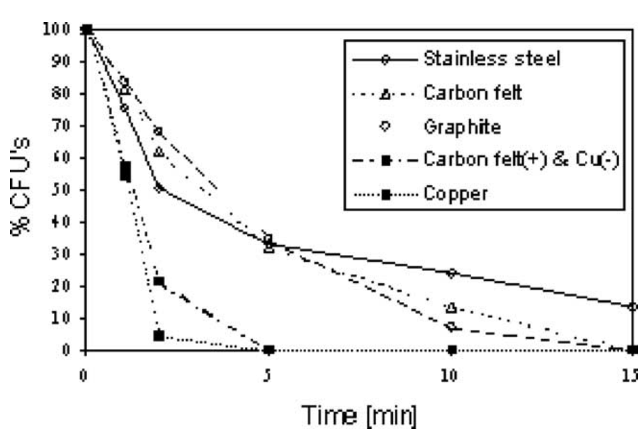

Fig. 4. Plate count monitoring of the bioeffects of electrolysis (150 mA) using different electrode materials on *Klebsiella pneumonia*.

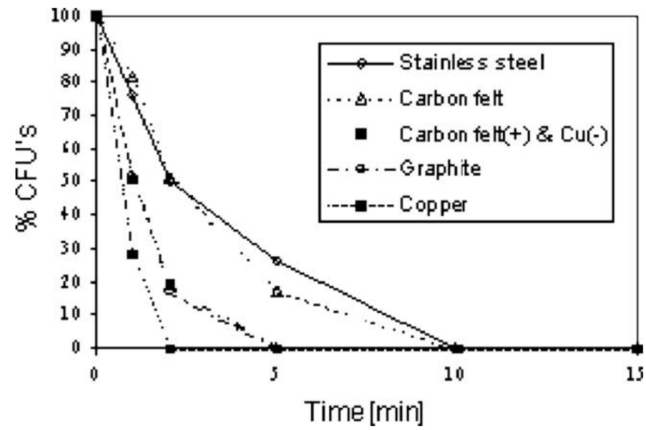

Fig. 5. Plate count monitoring of the bioeffects of electrolysis (100 mA) using different electrode materials in conjunction with ultrasound (40 kHz, 0.05 Wcm^{-3}) on *Klebsiella pneumonia*.

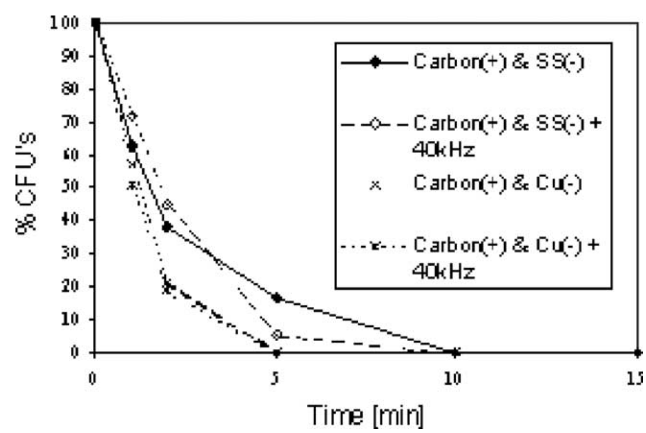

Fig. 6. Plate count monitoring of the bioeffects of electrolysis alone (150 mA) and electrolysis (100 mA) in conjunction with ultrasound (40 kHz, 0.05 Wcm^{-3}) on *Klebsiella pneumonia*.

- When the same electrode material was used for the anode and the cathode (graphite, copper and stainless steel) pitting of the anode surface occurred both in the presence and absence of ultrasound, but was more pronounced in the former. This leads to the production of fine particles in suspension and/or the electrochemical generation of ions with a resultant colour change, i.e. carbon (black), copper (green) and iron (orange/brown), respectively.
- Electrolytic systems in the presence or absence of ultrasound which incorporated carbon felt as anode and either carbon felt, copper or stainless steel as cathode resulted in no precipitation or colour change.
- When carbon felt was used as anode and combined with either copper or stainless steel a more rapid kill

resulted compared with the use of carbon felt for both electrodes.

2.3. The bioeffects of electrolysis using different electrode materials on Klebsiella pneumonia suspensions at 100 mA in conjunction with 40 kHz ultrasound

The results in Fig. 5 indicate that there is a significant kill for bacteria in 600 ml suspensions when electrolysed using different electrode materials at 100 mA in conjunction with ultrasound provided by a 40 kHz ultrasonic bath over 15 min. Although 100 mA current was applied to each system the voltage varied depending on the electrode material used; graphite carbon: ~3.6 V, stainless steel: ~2.4 V, copper: ~1.5 V, carbon felt: ~3.7 V, carbon felt (+) and copper (−): ~2.2 V, and carbon felt (+) and stainless steel (−): ~3.0 V. After 10 min electrolysis 100% kill was achieved using all electrodes, with copper being the most efficient with kill after 2 min and stainless steel the worst with 100% kill reached after 10 min.

2.4. The bioeffects of electrolysis using different electrode materials on Klebsiella pneumonia at 150 mA, and in conjunction with 40 kHz ultrasound at 100 mA

The effect of using a lower current (100 mA) in conjunction with 40 kHz ultrasound provided by an ultrasonic bath was to produce faster kill rates than were achieved with electrolysis alone at the higher current of 150 mA (Fig. 6). When carbon felt was combined with either copper or stainless steel a more rapid kill resulted rather than when carbon felt was used for both electrodes.

3. Conclusions

The effect of electrolysis on bacterial suspensions in saline is minimal unless there is adequate mixing. In the presence of stirring however electrolysis is an effective disinfection treatment and is dependent upon the electrode materials chosen. It has been shown that carbon felt is a suitable material for the anode in that it provides efficient kill and does not appear to suffer from surface pitting or erosion. All of the electrolytic treatments were improved by ultrasound resulting in reductions in treatment time and increased overall kill. Ultrasound also reduced the cell potential, a common effect that has been observed elsewhere in sonoelectrochemistry [13].

The beneficial effect of ultrasound in these processes is probably the result of a combination of several factors:

- Some enhanced mixing of bacterial suspensions in the vicinity of the electrode surface where the hypochlorite is being generated.
- The mechanical action of cavitation on the bacterial cells that will render them more susceptible to attack by hypochlorite either through direct damage or a weakening of the cell wall.
- The cleaning action of ultrasound on the electrode surface that prevents the build up of fouling and thus maintains more efficient electrolysis.

One possible application of this technology in saline solution may be for the treatment of estuary effluent into seawater. We are extending the use of this system to the treatment of raw waters.

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References

[1] E. Joyce, S.S. Phull, J.P. Lorimer, T.J. Mason, The development and evaluation of ultrasound for the treatment of bacterial suspensions. A study of frequency, power and sonication time on cultured *Bacillus* species, in: Proceedings of the 3rd Conference on Applications of Power Ultrasound in Physical and Chemical Processing, Paris, France, 13–14 December 2001, pp. 87–92.
[2] T.J. Mason, E. Joyce, S.S. Phull, J.P. Lorimer, Potential uses of ultrasound in the biological decontamination of water, in: Proceedings of the 3rd Conference on Applications of Power Ultrasound in Physical and Chemical Processing, Paris, France, 13–14 December 2001, pp. 17–22.
[3] J.R. Norris, D.W. Ribbons, Methods in Microbiology—3A, Academic Press, Berkeley Square, London, 1970, p. 203.
[4] J. Mir, J. Morato, F. Ribas, J. Appl. Microbiol. 82 (1997) 7.
[5] C.H. Johnson, J. Physiol. 67 (1929) 354.
[6] F. Schmitt, B. Uhlemeyer, Proc. Soc. Exp. Bio. Med. 27 (1930) 626.
[7] P. Hughes, N. Nyborg, Science 138 (1962) 108.
[8] H. Allinger, Am. Lab. 10 (1975) 75.
[9] P. Reisz, Free radical generation by ultrasound in aqueous solutions of volatile and non-volatile solutes, in: T.J. Mason (Ed.), Advances in Sonochemistry, Vol. 2, JAI Press, 1991, pp. 23–64.
[10] Applications of ultrasonics in the water industry, FWR-Research Report, 1995.
[11] S.S. Phull, T.J. Mason, J.P. Lorimer, A.P. Newman, B. Pollet, Ultrasonics 4 (1997) 157.
[12] J.G. Black, Microbiology Principles and Explorations, fourth ed., Prentice Hall, 1999.
[13] D.J. Walton, S.S. Phull, Sonoelectrochemistry, in: T.J. Mason (Ed.), Advances in Sonochemistry, Vol. 4, JAI Press, 1996, pp. 205–284.