Synergistic integration of sonochemical and electrochemical disinfection with DSA anodes

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Abstract

This work focuses on the disinfection actual urban wastewater by the combination of ultrasound (US) irradiation and electrodisinfection with Dimensionally Stable Anodes. First, the inactivation of *Escherichia coli* (*E. coli*) during the sonochemical disinfection was studied at increasing ultrasound power. Results showed that it was not possible to achieve a complete disinfection, even at the highest US power (200 W) dosed by the experimental device used. Next, the electrodisinfection with DSA anodes at different current densities was studied, finding that it was necessary a minimum current density of 11.46 A m^{-2} to reach the complete disinfection. Finally, an integrated sonoelectrodisinfection process was studied. Results showed a synergistic effect when coupling US irradiation with DSA electrodisinfection, with a synergy coefficient higher than 200% of the disinfection rate attained for the highest US power applied. In this process, hypochlorite and chloramines were identified as the main reagents for the disinfection process (neither chlorate nor perchlorate were detected), and the presence of trihalomethanes was far below acceptable values. Confirming this synergistic effect

with DSA anodes opens the door to novel efficient disinfection processes, limiting the occurrence of hazardous disinfection by-products.

Keywords: Ultrasound, dimensionally stable anode (DSA), electrodisinfection, wastewater reclamation, integrated process.

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1. Introduction.

In recent years, electrochemical disinfection has attracted the interest of several researchers, being the main target the development of economic and safe disinfection technologies which prevent the occurrence of hazardous disinfection by-products (Cotillas et al., 2015; Haaken et al., 2014; Mezule et al., 2013). One of the milestones of these studies has been the applicability of diamond (BDD) anodes for the treatment of synthetic wastewater polluted with *Escherichia coli* (*E. coli*) (Cui et al., 2013; Gusmão et al., 2010; Lacasa et al., 2013; Li et al., 2010). These anodes are classified into the group of non-active electrodes and exhibit high performance in disinfection and in the removal of several type of pollutants (Garcia-Segura et al., 2015; Marselli et al., 2003; Martínez-Huitle et al., 2012; Panizza, 2014).

Unfortunately, the electrochemically-assisted disinfection with BDD anodes favours the generation of chlorates and perchlorates (Bergmann, 2010; Bergmann and Rollin, 2007; Vacca et al., 2011) which are known to be harmful for human health. This fact limits the maximum value of current density and electric charge applicable in disinfection processes (Llanos et al., 2014). Opposite to electrolysis with diamond coatings, production of chlorate and perchlorate is expected to be limited with the well-known Dimensionally Stable Anodes (DSA) based on RuO_2, widely used in chlor-alkali industry for the production of hypochlorite from concentrated brines (Kiros et al., 2006; Mohaddes, 2008).

Another novel technology that may exhibit good features for disinfection of urban wastewaters is the application of ultrasound irradiation (Antoniadis et al., 2007). Disinfection can be achieved by different mechanisms: 1) the production of free radicals in the bulk (Juretic et al., 2015); 2) shearing forces produced by ultrasonic cavitation (Drakopoulou et al., 2009); 3) breakage of bacteria agglomeration, what favours the

72 reaction between oxidants species and microorganisms and therefore, the disinfection
73 processes (Hughes and Nyborg, 1962).
74 In this context, in a previous research it was found that ultrasonic cavitation
75 dramatically increases the efficiency of the inactivation of *E. coli* working with BDD
76 anodes and low current densities (in order to prevent the formation of chlorate and
77 perchlorate) (Llanos et al., 2015). This improved performance was explained in terms of
78 a more efficient production of oxidants and to the promotion of the dispersion of
79 agglomerated cells, favouring the attack to microorganisms.
80 Thus, the aim of the present work is to study the potential synergistic effect of coupling
81 ultrasound irradiation and electrolysis with DSA anodes to the disinfection of actual
82 effluents from municipal wastewater treatment plants (WWTP). This study would
83 widen the application of the combined sono-electrodisinfection process to higher values
84 of current densities and applied electric charges, limiting the formation of hazardous
85 disinfection by-products as chlorate. In a first approach, the efficiency of single
86 sonodisinfection and electrodisinfection processes was studied, evaluating the influence
87 of the applied ultrasound power and current density on the process performance. Next,
88 US irradiation was coupled with the electrochemical disinfection with DSA anode in
89 order to evaluate the potential synergies of both techniques.
90

91 **2. Material and methods.**

92 **2.1 Analytical techniques.**

93 Faecal coliforms were estimated using the most probable number (MPN) technique
94 (APHA-AWWA-WPCF, 1998). Microorganism counts were carried out by the
95 multiple-tube-fermentation technique (24 h of incubation at 44 °C) using 5 tubes at each
96 dilution (1:10, 1:100, and 1:1000).

Nitrogen and chloride inorganic anions (NO_3^-, NO_2^-, Cl^-, ClO^-, ClO_2^-, ClO_3^-, ClO_4^-) were measured by ion chromatography using a Shimadzu LC-20A equipped with Shodex IC I-524A column; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1.0 mL min^{-1}). The peak of hypochlorite interferes with that of chloride; therefore, the determination of hypochlorite was carried out by titration with As_2O_3 in 2 M NaOH. The same ion chromatography equipment (Shodex IC YK-421 column; mobile phase, 5.0 mM tartaric, 1.0 mM dipicolinic acid and 24.3 mM boric acid; flow rate, 1.0 mL min^{-1}) was used to measure the nitrogen inorganic cation (NH_4^+).

Inorganic chloramines were measured following the DPD standard method described in the literature (APHA-AWWA-WPCF, 1998).

Occurrence of trihalomethanes ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$) was followed by gas chromatography with an electron capture detector (ECD). The column used was a SPB 10 column (30 m x 0.25 mm; macroporous particles with 0.25 µm diameter). The flow rate was 50 ml min^{-1} and the initial temperature was 50ºC during 5 minutes until reach a final value of 150ºC (6ºC min^{-1}). Injection volume was set to 1 µL during 5 minutes and hydrogen was used as carrier gas.

2.2 Experimental setup.

The sonodisinfection, electrodisinfection and sono-electrodisinfection processes were carried out in a single-compartment electrochemical cell. Dimensionally Stable Anode (DSA) based on RuO_2 (Tianode, India) was used as anode and stainless steel (SS) (AISI 304) (Mervilab, Spain) as cathode. Both electrodes (anode and cathode) were circular with a geometric area of 78.5 cm^2 and the electrode gap was 10 mm.

Wastewater was stored in a glass tank (2.5 dm^3). The ultrasound generator (UP200S, Hielscher Ultrasonics GmbH, Germany) is equipped with a horn (40 mm diameter, 100

mm length, 12 Wcm^{-2}, 24 kHz) that is located inside the glass tank. The maximum power of ultrasound irradiated is 200 W and the output can be continuous or pulsed with duty cycle ranging from 10 to 100%.

The system works in total recirculation mode, with a peristaltic pump (JP Selecta Percom N-M328) continuously recycling the target wastewater. The power supply is a Delta Electronika ES030-10. Temperature of the system is kept constant by means of a thermostatised bath (JP Selecta, Digiterm 100) and a heat exchanger. A schematic of the experimental set-up has been described elsewhere (Llanos et al., 2015).

2.3. Experimental procedure.

Bench-scale electrolyses and sonoelectrolyses of 2,000 cm^3 of wastewater were carried out under galvanostatic conditions. The current density applied ranged from 6.37–11.46 A m^{-2}. The cell voltage did not vary during electrolysis, indicating that RuO_2 layers did not undergo appreciable deterioration or passivation phenomena. Prior to use in galvanostatic electrolysis assays, the electrode was polarized for 10 min in a 5,000 mg dm^{-3} Na_2SO_4 solution at 150 A m^{-2} to remove any kind of impurity from its surface.

Sonochemical disinfection of 2,000 cm^3 was carried out at ultrasound power ranged from 0-200 w.

2.4. Target effluents.

The target wastewater used in this study is the effluent of the secondary clarifiers of the municipal WWTP of Ciudad Real (Spain). The WWTP treats the wastewater produced in an average-sized town (75,000 p.e.) located in the centre of Spain. The influent is domestic wastewater without a significant industrial contribution. However, the effluent obtained after the treatment presents high concentration of microorganisms and prevents

144 the direct reuse of treated wastewater. The average characteristics of the samples used in
145 this work are shown in Table 1.

146

147 **3. Results and discussion.**

148 **3.1. Single sonochemical and electrochemical disinfection processes for the**
149 **treatment of urban treated wastewater.**

150 Fig. 1a shows the changes in concentration of *E. coli* with the irradiation time during
151 several sonochemical disinfection tests, in which different US power are applied to
152 wastewater. As it can be observed, the concentration of microorganisms decreases with
153 irradiation time until it reaches a final value from which it remains constant. This fact
154 has to be explained in terms of the different processes that occur when ultrasound waves
155 come into contact with a liquid, in particular: 1) shear forces generated for ultrasonic
156 cavitation; 2) generation of free radicals or hydrogen peroxide (Eqs. 2-5) (Adewuyi,
157 2005; Antoniadis et al., 2007).

158 $$H_2O +))) \rightarrow {}^{\cdot}OH + H^{\cdot} \quad (2)$$

159 $$^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2 \quad (3)$$

160 $$^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}O \quad (4)$$

161 $$^{\cdot}O + {}^{\cdot}O \rightarrow O_2 \quad (5)$$

162 The occurrence of these processes depends on the frequency of the ultrasonic radiation
163 applied. In this context, ultrasound irradiated is typically classified in two general
164 groups: low frequency (20-100 kHz) and high frequency (100 kHz-10 MHz). The main
165 difference between these two groups is related to the production of radicals. At low
166 ultrasound frequencies, the bubbles formed are mainly bigger and their implosion

occurs after some cycles of compression/expansion. This behaviour could facilitate the recombination of the radicals formed (Eqs. 3-5) and therefore, it could hinder their transference to the liquid. On the other hand, when the frequency is increased, the generation of free radicals can be favoured due to the short time of the expansion step (Thompson and Doraiswamy, 1999).Hence, high frequency UV irradiation is much more efficient than low frequency. The frequency of the ultrasound used in this work is 24 kHz (low frequency). Thus, the decrease observed in the concentration of *E. coli* should be mainly related to the shear forces produced from the collapse of bubbles during the cavitation and to the recombination of hydroxyl radicals to form hydrogen peroxide, rather than to the direct action of the radicals formed.

Comentado [MARR1]: Supongo que lo habréis sacado de algun sitio. La realidad es que la energía que se transmite y llega a especies que pueden ser precursores de radicales no es suficiente como para romper las moleculas

Comentado [MARR2]: Hubises estado bien medir oxidantes para ver si hay agua oxigenada

Furthermore, it can be observed that the higher the US power irradiated, the higher the inactivation of microorganisms. In order to evaluate the rate of the process, the data obtained in the first stage (corresponding to the decrease in the E. Coli population) were fitted to a first order kinetics (Eq. 6). The disinfection kinetic constants calculated in this stage are shown in Fig. 1b.

$$\text{Ln}\,(E.\ coli\ /\ E.\ coli_0) = -\,k \cdot t \qquad (6)$$

As it can be seen, the disinfection rate increases with the ultrasound power (a trend previously described in literature (Antoniadis et al., 2007)), reaching a maximum value of 0.016 min^{-1} for a power of 200 W (maximum value supplied by the equipment used). However, results indicate that there is a recalcitrant amount of *E. coli* that is not inactivated by the application of US irradiation. This result does not agree with others published in literature that reported a high efficiency in the inactivation of faecal coliforms by US irradiation (Drakopoulou et al., 2009). Nevertheless, the low specific US power irradiated in the present work (1,500 W L^{-1} in Drakopoulou et al. vs. 100 W L^{-1} in the present work) help to explain this residual concentration of *E. coli* that is not

192 inactivated by the application of US irradiation. At this point, it is important to take in
193 mind that even the energy applied in our work is huge for an efficient treatment and
194 hence lower doses of US should be applied in order to study feasible technologies.
195 Finally, it is important to note that the pH was remained constant during the
196 sonochemical process at a value around 8.

197 The next step of this research consisted in the study of electrochemical oxidation with
198 DSA anodes of the same target wastewater. Fig. 2a shows the changes in the
199 concentration of *E. coli* with the applied electric charge during the electrodisinfection
200 tests carried out at different current densities.

201 As it can be observed, the concentration of microorganisms decreases with the applied
202 electric charge, reaching the total disinfection of the effluent (within the duration of the
203 test) only at the highestcurrent density evaluated (11.46 A m^{-2}). Fig. 2b shows the
204 disinfection constants obtained when experimental data are fitted to a first order model
205 (Eq. 6).

206 The disinfection rate increases exponentially. . The most probable mechanism of
207 disinfection is based on the action of disinfectant species electrochemically generated
208 from the ions naturally contained in wastewater (Cotillas et al., 2015), mainly chlorine
209 species as hypochlorite (Eqs. 7-9) (Cotillas et al., 2013; Lacasa et al., 2012b).

210 $$2\ Cl^- \rightarrow Cl_2 + 2e^- \quad (7)$$

211 $$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \quad (8)$$

212 $$HClO \leftrightarrow ClO^- + H^+ \quad (9)$$

213 In this context, Fig. 3a shows the concentration of free chlorine with the applied electric
214 charge during the electrodisinfection at different current densities. As it can be
215 observed, hypochlorite concentration increases with the applied electric charge due to
216 the electrooxidation of chloride. At low current densities (6.37 A m^{-2}), this species

Comentado [MARR3]: Solo hay tres puntos!!!!!. No se sabe que ocurre a j mayores a esta. Es especulación

Comentado [MARR5]: Esto, conjuntamente con lo de las cloraminas se conto en lo de anaid

increases until reaching a final value around 0.04 mmol Cl dm^{-3}. However, from current densities of 8.91 A m^{-2}, hypochlorite behaves as a reaction intermediate, with maximum concentrations of 0.024 and 0.058 mmol Cl dm^{-3} at 8.91 and 11.46 A m^{-2}, respectively. Hypochlorite generated in the cell can be involved in different reaction pathways. First, it can inactivate *E. coli* cells resulting in the disinfection of the effluent. In addition, the reaction of hypochlorite with ammonium may lead to the production of combined chlorine compounds (Eqs. 10-12). Although the initial concentration of ammonium is low, it is important to highlight that the electrochemical reduction of nitrates over stainless steel cathodes is a very efficient process which develops at a high rate during the electrolysis of nitrate-containing solutions like the wastewater samples used in this work (Lacasa et al., 2012a). This reduction produces the source of ammonium for the production of chloramines and, obviously, its effect is expected to be higher at higher current densities.

$$ClO^- + NH_4^+ \rightarrow NH_2Cl + H_2O \quad (10)$$

$$NH_2Cl + ClO^- \rightarrow NHCl_2 + OH^- \quad (11)$$

$$NHCl_2 + ClO^- \rightarrow NCl_3 + OH^- \quad (12)$$

Fig. 3b shows the concentration of chloramines as a function of the current density applied during the electrodisinfection tests. As expected, chloramines increase with the applied electric charge but different trends can be described. At low values (6.37 A m^{-2}), the formation of chloramines is still not heavily favoured, reaching a maximum final value of 0.004 mmol Cl dm^{-3}. However, when current density increases above values of 8.91 A m^{-2}, higher concentrations of chloramines are obtained due to the reaction between hypochlorite and ammonium (j = 8.91 A m^{-2}, chloramines = 0.037 mmol Cl dm^{-3}; j = 11.46 A m^{-2}, chloramines = 0.060 mmol Cl dm^{-3}).

241 Chlorine species at higher oxidation state (chlorite, chlorate and perchlorate) were not
242 detected at the current densities studied. This fact was somehow expected because
243 electrolysis with DSA anodes requires current densities higher than that used in this
244 work to promote this chlorine speciation (Neodo et al., 2012).
245 According to the data obtained during chlorine speciation, it is important to highlight
246 that it is required concentrations of free and combined chlorine species higher than 0.05
247 mmol Cl dm^{-3} and current densities of 11.46 A m^{-2} to reach the total disinfection of
248 urban wastewater within the reaction time used in this work (XX minutes). Likewise,
249 pH remained constant in values around 8, favouring the formation of hypochlorite anion
250 and chloramines (mainly monochloramine).

Comentado [MARR6]: Las líneas de tendencia de las cloraminas son muy feas. Probablemente se deban al efecto envolvente de las tres cloraminas. Esto hay que ponerlo y hacer un línea más bonita en el gráfico

251 Regarding the formation of trihalomethanes during the electrodisinfection (data not
252 shown), it has been found a negligible concentration of these species for all the current
253 densities studied. The maximum concentration generated was 0.1832 µmol dm^{-3} at the
254 highest current density. This concentration is far below the most restrictive values found
255 in environmental regulations.

Comentado [MARR7]: Comentar valores

256 **3.2. Integrated sonoelectrodisinfection process for the treatment of urban treated**
257 **wastewater.**

258 Once the sonodisinfection and electrodisinfection processes were assessed for the
259 inactivation of microorganisms, the goal of this section is to evaluate an integrated
260 sono-electrodisinfection process. The current density chosen to evaluate the
261 performance of this coupled process was 8.91 A m^{-2}, a value at which the complete
262 disinfection was not reached with the electrodisinfection process during the length of
263 the tests carried out. Fig. 4 shows the changes in the concentration of *E. coli* during the
264 sono-electrodisinfection process at increasing US power applied (8-200 W).

As it can be observed, the effluent is efficiently disinfected during the duration of the test (xx minutes) when applying ultrasound power over32 W and E. Coli is completely depleted. Likewise, it is worth noting that it is possible to carry out the disinfection of urban wastewater at lower current densities (8.91 A m^{-2}) than those necessary during the electrochemical process (11.46 A m^{-2}) for the complete removal of pathogens within the test.

As inthe single electrodisinfection process, free and combined chlorine compounds (represented in Fig. 5) play a key role in the disinfection process.

As it can be observed, hypochlorite (Fig. 5a) behaves as a reaction intermediate, as it was the case of electrodisinfection process. When profiles of hypochlorite generation of electro- and sonoelectro- disinfection processes are compared, it can be observed that the irradiation of US increases the production of hypochlorite. Nevertheless, the maximum concentration of hypochlorite follows two different trends depending on the range of US power applied. Within the range 8-72 W, the maximum concentration of hypochlorite increases with US power. On the contrary, from 72 W to 200 W, the maximum concentration detected decreases with US power applied. This dissimilar evolution of the detected hypochlorite can be explained by considering the two overlapped effects that can be observed when US irradiation and electrolysis processes are integrated. Thus, on the one hand, it has been described that coupling both techniques leads to an enhanced production of oxidants due to the generation of hydroxyl radicals by water sonolysis (Eqs. 1-2), as it is the case of the production of hypochlorite from chloride according to Eq. 13 (Souza et al., 2014).

Comentado [MARR8]: No estoy sguro. A 24 khz no es cierto. Si podría ser descomposición de agua oxigendaa generada en el catodo

$$Cl^- + {}^{\cdot}OH \rightarrow ClO^- + H^+ + e^- \quad (13)$$

Furthermore, it has been described that the application of US can suppress the agglomeration of microorganisms and thus increases the disinfection rate by an

enhanced mass transfer of disinfectant species to *E. coli* cells (Jin et al., 2013; Llanos et al., 2015). As commented previously, one of the main routes of hypochlorite reduction is the disinfection process itself, so an increased mass transfer (higher US power applied) can lead to a lower concentration of hypochlorite detected. In this case, the lower hypochlorite concentration measured is due to the higher rate of hypochlorite reduction and not to a lower formation rate.

On the other hand, the concentration of chloramines (Fig. 5b) increases with the applied electric charge and with ultrasound irradiated. This increase is explained by the higher hypochlorite concentration and by the enhanced mass transfer, which facilitate reactions of chloramines formation (Eqs. 10-12). In addition, it is worth mentioning that chlorate and perchlorate were not detected, so it can be stated that the production of these hazardous disinfection by-products is avoided by the use of DSA anodes.

Finally, a synergy coefficient (%) is used to evaluate the rate increase when coupling both processes. The calculation of this synergy coefficient is based on the constant rates previously calculated in the sono- (SD), electro- (ED) and sonoelectro- (SED) disinfection processes (Eq. 14).

$$\text{Synergy coefficient (\%)} = \frac{k_{SED} - k_{SD} - k_{ED}}{k_{SD} + k_{ED}} \cdot 100 \qquad (14)$$

These synergy coefficients are gathered in Fig. 6. As it can be observed, the synergy coefficient increases for higher US power applied, reaching a maximum value of 236% for a US power of 200 W. These synergistic effects are partly explained by the higher amount of hypochlorite measured in the combined process. Furthermore, as previously commented the application of US irradiation produces the suppression of agglomeration of *E. coli* cells in wastewater (Hughes and Nyborg, 1962), enhancing the attack of disinfectants to microorganisms. This synergistic effect was described in a previous

work in which sono-electrolysis with diamond electrodes was assessed (Llanos et al., 2015), although the constant rates obtained with that anode material were higher to those measured for DSA. However, it is worth noting the importance of confirming this behaviour with active anodes as commercial DSA, with which it would be possible to operate at higher current densities without the generation of hazardous chlorine compounds such as chlorate or perchlorate. This fact, together with the lower cost of DSA, would lead to compact, economic and smart devices with improved disinfection capacity.

4. Conclusions

The main conclusions that can be drawn from the present manuscript are:

-The disinfection rate of a sonochemical process increases with ultrasound power irradiated. However, it is not possible to achieve the complete disinfection of the effluent in the range of US power applied in the present work.

- Electrochemical disinfection with DSA anodes is an efficient technology to inactivate the microorganisms in wastewater. It is necessary a minimum current density and applied electric charge to completely disinfect the effluent.

- Synergies higher than 200% of disinfection rate are found when coupling ultrasound irradiation and electrodisinfection with DSA anodes. Chlorate and perchlorate were not detected, being hypochlorite and chloramines the main responsible of the disinfection process.

- Ultrasound enhances mass transfer processes and therefore, it improves the production of disinfectant species in the bulk. Likewise, ultrasound favours the suppression of the agglomeration of *E. coli* cells in the bulk, allowing an efficient attack of disinfectant species to microorganisms. The result obtained allow designing efficient disinfection devices that avoid the production or hazardous disinfection by-products.

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