Electrocoagulation-UV Irradiation Process for Urban Wastewater Reuse

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This work presents a promising process to carry out the reclamation of urban treated wastewaters that consists of the application of UV irradiation to an electrocoagulation process with aluminium electrodes (photo-electrocoagulation). Results show that it is possible to perform the simultaneous removal of the microbiological content and turbidity in wastewater by applying low current densities. During the photo-electrocoagulation process, coagulant species are formed by the electrodissolution of the anode material (aluminium), causing the removal of turbidity in wastewater. The nature of these coagulant species will mainly depend on the pH and the metal concentration. In this context, the pH during the process remained constant around 8, a value that favours the formation of insoluble aluminium hydroxides and therefore, a sweep flocculation as main coagulation mechanism. On the other hand, it has been observed the presence of disinfectant species in wastewater during the process, specifically, free and combined chlorine disinfectants. Urban wastewater present significant concentration of chlorides in their composition and these species are susceptible of being oxidized on the anode surface favouring the generation of hypochlorite. In addition, the electrogenerated hypochlorite can react with the ammonium typically present in wastewater to form chloramines. Both species have noticeable disinfectant capacity and they are the main responsible of the elimination of *E. coli*. Finally, the application of UV radiation during the process favours the elimination of microorganisms due to the interaction of the light on the cell membrane of *E. coli*. Likewise, the application of UV light during the electrocoagulation promotes the formation of free radicals from the oxidizing species previously formed. These radicals not only increase the process performance in terms of *E. coli* removal but also favour the chemical dissolution of the sacrificial electrode and therefore, there is an increase in the turbidity removal performance.

1. Introduction

Electrochemical technologies have been widely studied over recent years for the treatment of industrial wastewater (Sáez et al., 2013; Zongo et al., 2009; Panizza and Cerisola, 2006). One of the most popular techniques that have exhibited great results for the treatment of different wastewaters is the use of boron doped diamond anodes for electrooxidation. This process is commonly known as "Conductive-Diamond Electrochemical Oxidation (CDEO)". During CDEO of industrial wastewaters, the production of significant concentrations of hydroxyl radicals has been reported. These radicals have a high oxidant capacity and make it possible the complete mineralization of different organic compounds. Due to these good results obtained during the treatment of industrial wastewater, the potential use of CDEO has been tested on the production of oxidizing species (Cotillas et al., 2011; Cañizares et al., 2009a) or most recently, on the electrochemical disinfection of urban treated wastewater (Cano et al., 2012; Llanos et al., 2014). However, the use of diamond electrodes for the reclamation of urban wastewaters is limited by the electrochemical production of chlorine compounds in high oxidation state, which are harmful to human health. For this reason, other electrodes materials such as Dimensionally Stable Anodes (DSA) have been tested in order to avoid the generation of these species in wastewater (Cotillas et al., 2013).

On the other hand, electrocoagulation has been proven efficient on the removal of anions, emulsions or colloids. During the process, coagulant species are formed by the electrodissolution of a sacrificial anode (usually aluminium or iron). These species are the responsible of the removal of different pollutants, being the coagulation mechanism will depend on the nature of the pollutant and coagulant species. In the case of urban wastewaters, electrocoagulation has been tested on the removal of turbidity as alternative to chemical coagulation using aluminium electrodes (Rodrigo et al., 2010). In addition, it has been checked the removal of *E. coli* during the process obtaining that electrocoagulation is less efficient than CDEO because only achieves a removal of microorganisms but no a complete disinfection. For this reason, it is necessary to improve the electrocoagulation process in order to obtain reclaimed water using an efficient technology. In this context, the application of UV radiation could contribute to improve the electrocoagulation process with aluminium electrodes in terms of *E. coli* elimination. This process (photo-electrocoagulation) has been tested by the authors for the treatment of urban wastewater by using iron electrodes (Cotillas et al., 2014), obtaining that very low current densities and UV light allow the simultaneous removal of turbidity and a complete disinfection of wastewater.

With these backgrounds, this work focuses on the application of UV irradiation to an electrocoagulation process using aluminium electrodes for the reclamation of urban treated wastewater from a municipal WWTP.

2. Experimental

2.1 Analytical techniques

Turbidity was measured using a 115 Velp Scientifica turbidimeter, according to a standard method described in the literature (Standard methods). Total aluminium concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian) according to a plasma emission spectroscopy Standard Method (APHA-AWWA-WPCF, 1998). To evaluate the total metal concentration, samples were diluted to 50:50 (v/v) using 4 N HNO3 to ensure total solubility of the metal.

Faecal coliforms were estimated using the most probable number (MPN) technique (APHA-AWWA-WPCF, 1998). Microorganism counts were carried out by the multiple-tube-fermentation technique (24 h of incubation at 44 °C) using 5 tubes at each 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 a 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 corresponding to hypochlorite interferes with that of chloride; therefore, the determination of hypochlorite was carried out by titration with As_2O_3 in 2.0 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^+).

Chloramines were measured following the DPD standard method described in the literature (APHA-AWWA-WPCF, 1998)] and occurrence of trihalomethanes (THMs) was evaluated by gas chromatography using a SPB 10 column (30 m x 0.25 mm; macroporous particles with 0.25 µm diameter). Injection volume was set to 1 µL.

2.2 Experimental set-up

Photo-electrocoagulation test was carried out in a bench-scale single-compartment electrochemical reactor equipped with an aluminium plate as anode and perforated stainless steel (SS) plate as cathode. Both electrodes were circular with a diameter of 94 mm (anode area of 69.4 cm2). The electrode gap between anode and cathode was 6 mm and the internal volume of the electrocoagulation cell was 60 ml. A power supply (0-30V, 0-10A) was used to apply current in experiments (Delta Electronika ES030-10).

For coupling UV irradiation to electrocoagulation, one of the cover plates of the electrochemical cell was made of quartz and a UV lamp VL-215MC (Vilber Lourmat), λ = 254 nm, intensity of 930 µW/cm^2 and energy 4.89 eV irradiated 4 W directly to the quartz cover.

Wastewater was stored in a glass tank (5 dm^3). The system works in total recirculation mode, with a peristaltic pump (JP Selecta Percom N-M328) continuously recycling the target wastewater.

2.3 Experimental procedure

Actual wastewater was collected daily at the secondary clarifiers of the wastewater treatment plant (WWTP) of Ciudad Real (small town at the centre of Spain with 80,000 inhabitants). The influent of this municipal WWTP is domestic wastewater without a significant industrial contribution. Composition of the effluent sampled in terms of chemical parameters was very uniform. The average chemical composition of the samples is shown in Table 1.

Table 1: Composition of target wastewater

Parameter	Value
pH	8.14
Conductivity ($\mu S\ cm^{-1}$)	1390
Chloride ($mg\ dm^{-3}$)	172.27
Nitrate ($mg\ dm^{-3}$)	14.59
Sulphate ($mg\ dm^{-3}$)	321.78
Ammonium ($mg\ dm^{-3}$)	37.43
Turbidity (NTU)	7
Total suspended solids ($mg\ dm^{-3}$)	9
Total organic carbon ($mg\ dm^{-3}$)	15.39
E. coli ($CFU\ 100ml^{-1}$)	310

Bench-scale electrolysis tests of 4 dm^3 of actual wastewater were carried out under galvanostatic conditions. The current density applied was 17.3 A m^{-2}. Prior to use in galvanostatic electrolysis assays, the electrode was cleaned for 10 min in a 4% HCl solution to remove any kind of impurity from its surface.

3. Results and discussion

Figure 1a shows the total aluminium concentration electrodissolved with the applied electric charge during the photo-electrocoagulation of urban wastewater. In this Figure, the theoretical values expected according to Faraday´s Law are also represented. As it can be observed, the metal concentration increases linearly with the applied electric charge. However, the experimental values obtained during the process are higher than that predicted by Faraday´s Law. This behaviour is related to different mechanisms that are involved in the dissolution of the metal: chemical and electrochemical dissolution (Cañizares et al., 2005).
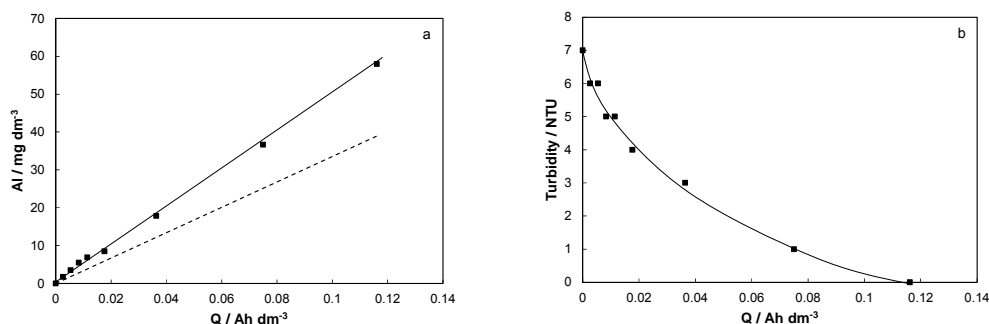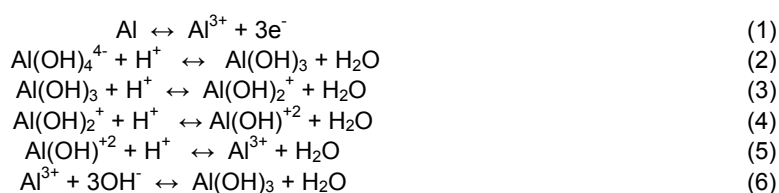

Figure 1: a. Variation of aluminium concentration with the applied electric charge during the photo-electrocoagulation of urban wastewater (■) experimental data; (--) theoretical values predicted by Faraday´s Law. b. Evolution of turbidity with the applied electric charge during the photo-electrocoagulation of urban wastewater. (j: 17.3 A m^{-2}; T: 25ºC; anode: aluminium; cathode; stainless steel).

The chemical dissolution takes place when there are species in wastewater that are capable to attack the aluminium sheet. These species can be free radicals generated during the process or anions such as chloride. In this context, the presence of chloride has been detected in wastewater and therefore, improves the chemical dissolution of the sacrificial anode. On the other hand, the electrochemical dissolution occurs when applied current intensity to the electrochemical cell. This is the main mechanism of generation of soluble and insoluble aluminium species (Eqs. (1)-(6)) in electrocoagulation processes.

$$Al \leftrightarrow Al^{3+} + 3e^- \tag{1}$$
$$Al(OH)_4^{4-} + H^+ \leftrightarrow Al(OH)_3 + H_2O \tag{2}$$
$$Al(OH)_3 + H^+ \leftrightarrow Al(OH)_2^+ + H_2O \tag{3}$$
$$Al(OH)_2^+ + H^+ \leftrightarrow Al(OH)^{+2} + H_2O \tag{4}$$
$$Al(OH)^{+2} + H^+ \leftrightarrow Al^{3+} + H_2O \tag{5}$$
$$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3 + H_2O \tag{6}$$

The nature of these species, as previously commented, will depend on the pH and the metal concentration. In this way, the pH was naturally maintained in values around 8 without any modifications due to the buffering effect typical of the electrocoagulation processes. For this reason, pH changes, due to the production of H^+ ions (water oxidation) are somehow offset by the production of OH^- (water reduction). Thus, at these conditions, the main species formed during the process are aluminium hydroxide precipitates.

Figure 1b shows the evolution of turbidity with the applied electric charge during the photo-electrocoagulation process. As it can be observed, the turbidity decreases with the applied electric charge until reach zero values at higher electric charges (0.116 Ah dm^{-3}). This fact is related to the increase in the concentration of aluminium species in wastewater (maximum Al concentration: 38.964 mg dm^{-3}). In addition, the coagulants produced in the electrochemical cell are mainly hydroxide precipitates, and these species favour a sweep flocculation as main coagulation mechanism for turbidity removal.

Figure 2 shows the evolution of E. coli with the applied electric charge during the photo-electrocoagulation process with aluminium electrodes.
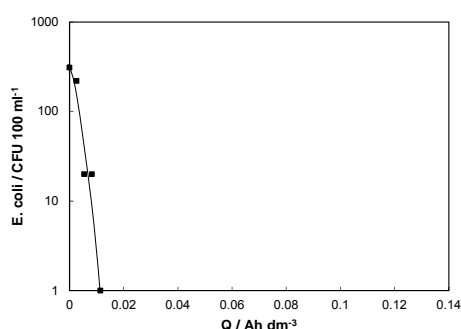

Figure 2: Evolution of E. coli concentration with the applied electric charge during the photo-electrocoagulation of urban wastewater (j: 17.3 A m^{-2}; T: 25°C; anode: aluminium; cathode; stainless steel).

As it can be observed, the E. coli concentration decreases with the applied electric charge following a characteristic trend of first order kinetics. This behaviour can be due to different processes that occur in the electrochemical cell: direct disinfection on the anode surface, mediated disinfection by species formed during the process or direct disinfection by UV light. For this reason, the main disinfectant species formed during the process were measured. Chloride is one of the anions most commonly present in urban wastewater. Its electrooxidation leads to the generation of chlorine (Eq. (7)) but it disproportionates to hypochlorous acid and chloride (Eq. (8)). Next, hypochlorous acid partially deprotonates to hypochlorite anion, depending on the pH (Eq. (9)). Accordingly, there may be a mixture of three oxidants electrochemically produced with different oxidation capabilities in the bulk wastewater: chlorine, hypochlorous acid and hypochlorite.

$$2Cl^- + 2e^- \rightarrow Cl_2 \tag{7}$$
$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \tag{8}$$
$$HClO \leftrightarrow ClO^- + H^+ \tag{9}$$

Figure 3a shows the evolution of free chlorine compounds with the applied electric charge during the photo-electrocoagulation of urban wastewater. As it can be observed, hypochlorite increases with the electric charge until reach a maximum value (2.069 mg dm^{-3}) from which, the concentration starts to decrease. This decrease can be related to different processes that occur in the electrochemical cell: the attack of hypochlorite to E. coli (causing their death), the electrooxidation of hypochlorite to other compounds in high oxidation state (Eqs. (10)-(11)) or the reaction of this compound with other species present in wastewater such as ammonium.

$$2HClO + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \tag{10}$$
$$ClO_3^- + \cdot OH \rightarrow ClO_4^- + H^+ + e^- \tag{11}$$

The production of chlorates and perchlorates has been discarded by ion chromatography and therefore, the second hypothesis is discarded too. On the other hand, the concentration of chloramines was monitored due to the potential reaction between hypochlorite and ammonium (Eqs. (12)-(14)).
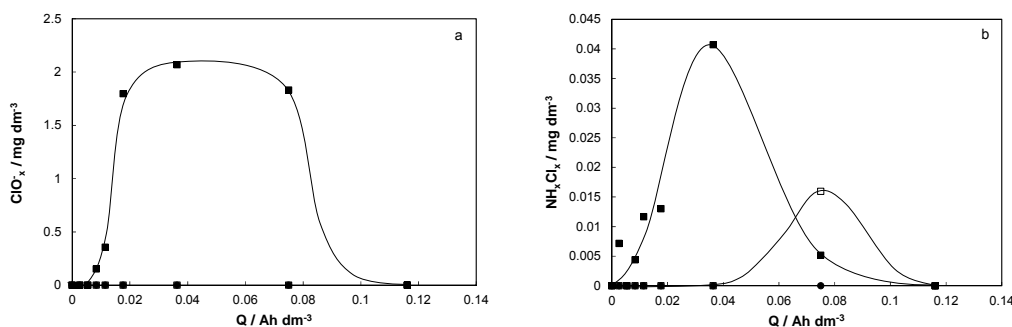

Figure 3: Evolution of chlorine species with the applied electric charge during the photo-electrocoagulation process of urban wastewater. a. Free chlorine. (■) Hypochlorite (□) Chlorate (●) Perchlorate. b. Combined chlorine. (■) Monochloramine (□) Dichloramine (●) Trichloramine. (j: 17.3 A m^{-2}; T: 25°C; anode: aluminium; cathode; stainless steel).

$$NH_3 + HClO \leftrightarrow NH_2Cl + H_2O \tag{12}$$
$$NH_2Cl + HClO \leftrightarrow NHCl_2 + H_2O \tag{13}$$
$$NHCl_2 + HClO \leftrightarrow NCl_3 + H_2O \tag{14}$$

Figure 3b shows the concentration of chloramines with the applied electric charge during the electrochemical treatment of urban wastewater. As it can be observed, there is an initial increase in monochloramine concentration that corresponds with the rapid reaction between hypochlorite and ammonium. The decrease observed in this compound is related to its attack to *E. coli* or the continuous reaction with hypochlorite, favouring the formation of di- and tri-chloramine (Eqs. (13)-(14)). The presence of trichloramine has not been detected during the experiment but the concentration of dichloramine follows a similar trend than monochloramine. There is an initial increase due to the reaction between monochloramine and hypochlorite followed by a decrease. In this case, the decrease is mainly caused by the attack to *E. coli* because its promotion to trichloramine has not been registered.

The formation of chloramines during the electrochemical treatment and the subsequent disinfection of urban wastewaters presents advantages over the disinfection by hypochlorite. Chloramines are less reactive than hypochlorite and therefore, its presence can avoid the formation of undesirable organochlorinated compounds such as trihalomethanes. These compounds are harmful to human health and its presence should be avoided. In this context, the concentration of trihalomethanes was measured during the experiment, finding that the generation of these does not occur during the photo-electrocoagulation.

On the other hand, it is important to note that light irradiation not only ensures the elimination of *E. coli* by the attack of the cell membrane, but also can promote the production of hydroxyl and chlorine radicals by means of hypochlorite decomposition as it is shown in Eqs. (15)-(16) (Chan et al., 2012; Oliver and Carey, 1977).

$$ClO^- + h\upsilon \rightarrow O^{\bullet-} + Cl^\bullet \tag{15}$$
$$O^{\bullet-} + H_2O \rightarrow OH^- + \bullet OH \tag{16}$$

The generation of these radicals explains the higher effect of the combined electrocoagulation with UV irradiation technology on the removal of *E. coli* and the lower detection of disinfectant species. In addition, the production of chlorine radicals contributes to the chemical dissolution of the aluminium electrode, helping to remove passive layers which can be formed when working at low current densities. Finally, regarding the results obtained during the electrocoagulation-UV irradiation process, the data presented in this work improve favorably with respect to single electrocoagulation (Zaleschi et al., 2013) and other electrochemical techniques such as CDEO (Cano et al., 2012).

4. Conclusions

From this work, the following conclusions can be drawn:

- The photo-electrocoagulation process with aluminium electrodes allows to simultaneously remove the microbiological content and turbidity present in urban wastewater. However, the applied electric charge to achieve the completely removal of turbidity is higher than that necessary to eliminate the *E. coli* concentration.

- Hypochlorite and chloramines are the main responsible of the elimination of microorganisms in wastewater. In addition, the application of UV irradiation favours the formation of free radicals that significantly contribute to the disinfection process.

- The formation of undesirable chlorine compounds was not detected during the process and therefore, photo-electrocoagulation is an efficient technology to obtain reclaimed water without disinfection-by-products.

- The pH was maintained constant around 8 due to the buffering effect during the photo-electrocoagulation process. This value favours the formation of aluminium hydroxide precipitates and therefore, a sweep flocculation as coagulation mechanism for turbidity removal. In addition, the generation of free radicals due to the UV irradiation improves the chemical dissolution of the anode, favouring turbidity removal.

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