Applied Catalysis B: Environmental 162 (2015) 252–259

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Use of carbon felt cathodes for the electrochemical reclamation of urban treated wastewaters

Salvador Cotillas, Javier Llanos*, Manuel A. Rodrigo, Pablo Cañizares

Chemical Engineering Department, University of Castilla-La Mancha, Edificio Enrique Costa Novella, Campus Universitario s/n, 13005 Ciudad Real, Spain

ARTICLE INFO

Article history:
Received 12 May 2014
Received in revised form 27 June 2014
Accepted 1 July 2014
Available online 8 July 2014

Keywords:
Anode materials
Electrodisinfection
Electrochemical oxidation
Electro-Fenton
Carbon felt

ABSTRACT

This work focuses on the application of electrolysis with carbon felt cathodes for the reclamation of actual effluents from municipal wastewater treatment facilities (WWTFs) in combination with different anode materials (dimensionally stable anodes-DSA, conductive diamond anodes-CDA and iron–Fe). First of all, the efficiency of electrodisinfection with CDA and DSA was assessed, finding that total elimination of *Escherichia coli* (*E. coli*) can be attained at applied electric charges below 0.03 Ah dm^{-3}, and that the disinfection process is more efficient when using CDA. Furthermore, it was observed that the formation of hydrogen peroxide on carbon felt cathodes limits the concurrence of disinfection by-products (chlorates, perchlorates and organic chlorinated by-products), an interesting result that broadens the potential of CDA for the regeneration of urban wastewater. Results with Fe anodes show that it is possible to attain the complete removal of microorganisms with comparable efficiency to that of CDA (due to the contribution of Fenton's reaction) and that it was possible to totally remove the turbidity of the effluent when working at current densities from 12.50 A m^{-2}. Finally, it was found that Fe is the most efficient anode material (lowest power consumption) at low current densities and CDA is the most appropriate one at current densities higher than 5 A m^{-2}. According to these results, the pairs anode-cathode CDA-carbon felt and Fe–carbon felt behave as the most promising electrode materials to be applied in wastewater reclamation processes.

1. Introduction

Wastewater reuse has attracted great interest due to the potential uses of reclaimed wastewaters in agriculture or industry sectors and to the scarcity of fresh water sources [1–4]. In the reclamation of municipal wastewater, a disinfection stage is always required to obtain a high quality effluent as established by the Spanish legislation [5]. For this reason, many water disinfection technologies have been developed within the last years [6–8]. In this sense, several authors have reported the elimination of microorganisms, mainly *Escherichia coli*, by the addition of chemical reagents such as ozone, hydrogen peroxide or chlorine derivate products [9–12].

In this context, electrochemical technologies emerge as a good alternative to carry out the on-site generation of disinfectant agents from the species naturally contained in wastewater [13–17]. This production of disinfectants can be classified into anodic processes (i.e. the electrooxidation of chlorides to produce hypochlorite [Eqs. (1) and (2)]) and cathodic processes (i.e. the electrochemical reduction of oxygen to produce hydrogen peroxide [Eq. (3)]).

$$Cl^- + H_2O \rightarrow HClO + H^+ + 2e^- \quad (1)$$

$$HClO \leftrightarrow ClO^- + H^+ \quad (2)$$

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3)$$

The electrosynthesis of chloride oxoanions can be efficiently carried out by using anode materials such as dimensionally stable anodes (DSA) or conductive diamond anodes (CDA) [4]. These materials have exhibited great performance on the production of chlorine derivates during the electrochemical treatment of wastewaters [18]. Regarding the electrochemical production of hydrogen peroxide, the search of new electrode materials to obtain higher production rates of hydrogen peroxide has become matter of interest for several authors [19,20]. Thus, carbon felt emerges as a promising cathode material to produce hydrogen peroxide in high concentrations [21–25] as this material presents higher specific area than other electrodes made of carbon such as carbon cloth or graphite.

When hydrogen peroxide is electrochemically produced on the cathode of an electrochemical cell, the use of iron as anode

* Corresponding author. Tel.: +34 926 29 53 00x3508; fax: +34 926 29 52 56.
E-mail address: javier.llanos@uclm.es (J. Llanos).

http://dx.doi.org/10.1016/j.apcatb.2014.07.004
0926-3373/

material can promote the well-known Fenton's reaction [26], producing hydroxyl radicals (•OH) a powerful oxidant [Eq. (4)].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (4)$$

In addition, the use of iron anodes combined with the production of hydrogen peroxide, not only favors the Fenton's reaction, but also promotes coagulation processes from the generation of soluble and insoluble iron species. In this context, an interesting approach was carried out by Daghrir and Drogui [27], who described a combined electrocoagulation–electrofenton treatment for domestic wastewater using Ti–IrO_2 or iron as anode and graphite or vitreous carbon as cathode. With this system, it was possible to decrease efficiently the chemical oxygen demand (COD), turbidity and total suspended solids (TSS) in wastewater.

With this background, the main aim of the present work is to evaluate the efficiency of an electrochemical cell equipped with a carbon felt cathode and different anode materials (DSA, CDA and Fe) for the reclamation of actual effluents from municipal WWTFs, specifically, the elimination of *E. coli* and the removal of turbidity. In a first approach, the performance of the cell with commercial DSA and CDA was evaluated. Next, the anode was substituted by Fe, looking for the simultaneous removal of turbidity and microorganisms. For all anodes (DSA, CDA, iron), the effect of the current density on the process performance was studied and a first preliminary approach to the calculation of the energy consumption of the treatment process was also confronted.

2. Material and methods

2.1. Experimental setup

The electrodisinfection process was carried out in a batch electrochemical reactor. DSA (DSA-O_2, DeNora, Italy), CDA (Adamant Technologies, Switzerland) and Iron (Fe) (Mervilab, Spain) were used as anodes and carbon felt (CF) (SGL Carbon, Spain) as cathode. DSA and Fe were rectangular with a geometric area of 80 cm^2 and CDA was circular with a geometric area of 68 cm^2. CF was rectangular with dimensions of 14×25 cm^2 and a thickness of 1 cm. The electrode gap between anode and cathode was 75 mm. A power supply (0–30 V, 0–10 A) was used to apply current in electrodisinfection experiments (Delta Electronika ES030-10). To enhance the production of hydrogen peroxide, the wastewater was saturated by bubbling air into the reactor, maintaining a constant oxygen concentration of around 8 mg dm^{-3} during the electrodisinfection process. Wastewater was stored in a glass tank (5 dm^3), stirred by a magnetic stirrer (100 rpm).

2.2. Experimental procedure

Wastewater was collected daily at the secondary clarifiers of the WWTF of Ciudad Real (small town at the centre of Spain with 80,000 inhabitants). The influent of this municipal WWTF is domestic wastewater without a significant industrial contribution. Composition of the effluent sampled in terms of chemical parameters was very uniform. However, in terms of coliforms it varies significantly from day to day, as a consequence of the realistic conditions used. In spite of this, and after a SWOT (strengths, weaknesses, opportunities, and threats) analysis the use of any preservation method was discarded in order to assess purely the efficiency of the technologies studied. The average chemical and microbiological composition characteristics of the samples used in this work are shown in Table 1.

All experiments (3 dm^3) were carried out under galvanostatic conditions and discontinuous mode. At this mode of operation, the production of oxidant and disinfectant species is cumulative and it is related to the total Q (Ah dm^{-3}) applied at a given moment.

Table 1
Average composition of target wastewater.

Parameter	Value
Chloride (mg dm^{-3})	204.8
Nitrate (mg dm^{-3})	23.7
Sulphate (mg dm^{-3})	334.5
Ammonium (mg dm^{-3})	43.4
Iron (mg dm^{-3})	n.d.
Turbidity (NTU)	10–11
TOC (mg dm^{-3})	10.0
E. coli (CFU/0.1 dm^3)	2400–24,000

n.d.—Non detectable; TOC—total organic carbon.

The samples were collected in the glass tank and the sample volume was 0.1 dm^3. The *E. coli* and disinfectant compounds (free and combined chlorine and hydrogen peroxide) were measured immediately. In this way, it is not necessary the addition of reagents (e.g. $Na_2S_2O_3$) to stop the reaction between microorganisms and disinfectants.

The current density applied ranged from 1.25 to 25 A m^{-2}. Prior to use in galvanostatic electrolysis assays, the electrode was cleaned for 10 min in a 5000 mg dm^{-3} Na_2SO_4 solution at pH 2 and 300 A m^{-2} to remove any kind of impurity from its surface.

2.3. Analytical techniques

The *E. coli* from wastewaters were estimated using the most probable number (MPN) technique [28] (confidence level: 95%). Microorganism counts were carried out by the multiple-tube-fermentation technique (24 h of incubation at 44 °C) using five tubes at each dilution (1:10, 1:100, and 1:1000). After incubation time, the tubes with yellow color were considered positive (presence of *E. coli*) and the tubes in where the color remained red, were considered negative (absence of *E. coli*). The media culture used was E.C. MEDIUM ISO 7251 (the composition of the medium per liter of distilled water was 20 g dm^{-3} tryptose, 5 g dm^{-3} lactose, 1.9 g dm^{-3} bile salts no. 3, 4 g dm^{-3} K_2HPO_4, 1.5 g dm^{-3} KH_2PO_4 and 5 g dm^{-3} NaCl) provided by Laboratorios Conda (Spain). For the determination of *E. coli*, 37.4 g of this reactive was dissolved in ultapure water and were sterilized at 121 °C during 10 min.

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, 1×10^{-3} dm^3 min^{-1} (concentration accuracy: ±0.5%). The peak corresponding to hypochlorite interferes with that of chloride; therefore, the determination of hypochlorite was carried out by titration with 0.001 M As_2O_3 in 2.0 M NaOH [29,30]. This method consists of a redox determination to selectively quantify the hypochlorite concentration, specifically, it is based on the redox reaction between the hypochlorite and arsenite. Hypochlorite is reduced to chloride by the continuous addition of arsenite whereas this last one is oxidized to arsenate. The pretreatment of the samples consists of the addition of 2×10^{-3} dm^3 of 2.0 M NaOH in order to increase the pH.

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, 1×10^{-3} dm^3 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 [28].

The presence of trihalomethanes (THMs) was evaluated by gas chromatography (detection limit <0.2 ppb) using a SPB 10 column (30 m × 0.25 mm; macroporous particles with 0.25 μm diameter). Injection volume was set to 1×10^{-6} dm^3.