The electrochemical elimination of coliforms from water using BBD/Ti or graphite anodes: a comparative study

Edison GilPavas, Paula Arbeláez, José David Medina, Izabela Dobrosz-Gómez and Miguel Ángel Gómez-García

ABSTRACT

The elimination of total and fecal coliforms, from raw surface water, was carried out by electrochemical oxidation using either boron doped diamond (BDD/Ti) or graphite (GP) anodes, in a chloride-free medium. The optimal values of the operation parameters, maximizing the coliform elimination percentage, were determined using statistical experimental design. The current density (j: 2–20 mA/cm^2), the conductivity (σ: 500–900 μS/cm) and the anode materials (An) were considered as variables to perform the Box-Behnken experimental design together with the response surface methodology analysis for optimization. The statistical analysis indicated that, in the evaluated range, the disinfection efficiency increased with an increase in j and decreased with an increase in σ. The following optimal conditions for the elimination of total and fecal coliforms were found: j: 10 mA/cm^2, σ: 500 μS/cm and BDD/Ti used as anode material. The BDD/Ti electrode let to achieve complete coliform elimination after *ca.* 20 min of reaction while the GP one needed *ca.* 27 min. In water treated with both BDD/Ti and GP anode, after 7 days, any coliforms growth was observed. As a result of the oxidation process, the total organic carbon and nitrite concentration decreased while nitrate concentration increased.

Key words | BDD, disinfection, electrochemical, graphite, optimization, water treatment

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INTRODUCTION

The purpose of disinfection processes is to eliminate pathogens as bacteria and viruses responsible for waterborne diseases. Nevertheless, according to statistics of the Water Project Foundation, 783 million people do not have access to clean and safe water and almost 2.5 billion do not have access to adequate sanitation, being exposed to a permanent health risk. Children are especially vulnerable to untreated water and it is estimated that one out of every five deaths in the population under 5 years old is due to a water related disease. The situation is even more complex in developing countries where around 80% of illnesses are linked to both poor quality of water and sanitation conditions. Consequently, it is of high priority to develop and evaluate new low cost disinfection systems accessible for rural communities (Hunter *et al.* 2009; GilPavas *et al.* 2014; Kostyla *et al.* 2015).

Different technologies have been used to eliminate pathogens from water. Chlorination is the most common and effective way to remove a wide range of microbial pathogens (Barashkov *et al.* 2009). However, the addition of chlorine induces the formation of potentially harmful disinfection by-products (DBPs). Over 600 DBPs can be formed as a result of the contact of chemical oxidants with organic matter present in water (Castro-Hermida *et al.* 2008; Park *et al.* 2016). Moreover, in some rural areas, where continuous transportation of chemical oxidants is

doi: 10.2166/ws.2017.147

unviable, it is necessary to develop and implement processes using *in-situ* formation of disinfection agents. Searching for alternative treatment processes that can overcome these drawbacks, electrochemical disinfection of water has emerged as a promising option. It has shown to be cost efficient, environmentally friendly and competent in the elimination of microorganism from water (Bergmann & Rollin 2007; Ndounla *et al.* 2014). This technique implies *in-situ* formation of oxidizing species (for instance, $^{\bullet}OH$, H_2O_2, O_3, peroxodisulfate, peroxodicarbonate and peroxodiphosphate) by the pass of electric current through a suitable electrode, avoiding transportation and storage of hazardous chemicals (Hussain *et al.* 2014).

The effectiveness of electrochemical disinfection depends on different parameters including: electrolyte-cell configuration, electrode material, electrolyte type, solution composition, type of microorganisms, mass transfer conditions and current density/electrode potential ratio (Kerwick *et al.* 2005). In relation to the electrode material, the usefulness of different anodes (such as Pt, graphite (GP), activated carbon fibers, IrO_2, RuO_2, PbO_2, SnO_2, TiO_2, boron doped diamond (BDD), etc.) has been reported in open literature (Kerwick *et al.* 2005; Polcaro *et al.* 2007; Jeong *et al.* 2009; Akhavan & Ghaderi 2010; Bruguera-Casamada *et al.* 2016). However, some of them (for instance, Pt and RuO_2) require the presence of chloride ions or/and chlorine containing species (for instance, Cl_2, HClO and/or ClO^-). Consequently, the formation of harmful disinfection by-products (named DBPs) can be expected. In contrast, the application of BDD anode let to produce the $^{\bullet}OH$ radical, which is very reactive and highly appropriated for environmental applications. Moreover, it is very effective in the absence of Cl^- ion, preventing the accumulation of active chlorine and the possible formation of DBPs (Bruguera-Casamada *et al.* 2016). However, the cost of this type of electrodes is significantly higher than the other materials (for example, GP) (Martínez-Huitle 2007). The GP has also been reported to present an inherent antibacterial activity, attributed to membrane stress induced by sharp edges. It can result in physical damages of cell membranes, leading to the loss of bacterial membrane integrity and the leakage of its RNA (Akhavan & Ghaderi 2010). Liu *et al.* (2011) have reported that GP dispersion exhibits a moderate cytotoxicity with the *Escherichia coli* cell (inactivation percentage of $26.1 \pm 4.8\%$). On the other hand, Qi *et al.* (2015) have detected that any inactivation of BDD anode was observed when used without current density. Therefore, the disinfection occurs mainly due to the formation of oxidizing species on the anode material.

Thus, the aim of this work is: (1) to define a simple, low cost system for the electrochemical treatment of water available in rural areas of developing countries, able to eliminate pathogenic microorganisms; and (2) to assess its disinfection efficiency on both total and fecal coliform bacteria. Two different anodes materials (GP and BDD/Ti) were tested separately under different operational conditions (in the absence of chloride ions). The Box-Behnken experimental design (BBD) and the response surface methodology (RSM) were used to optimize the electrooxidation process.

MATERIALS AND METHODS

Reagents and water samples

Water samples were taken directly from a creek passing through EAFIT University, in Medellín-Colombia, and processed right after being collected to avoid bacterial death during storage. The commercial medium Petrifilm (EC Petrifilm™, 3 M Microbiology, St Paul, MN, USA) was used to detect and count *E. coli* (blue colonies) and total coliform (violet colonies) bacterias. Macherey-Nagel Nano-Color reagent kits (references: 0–26, 0–94, 0–68, 0–65) were used to quantify chemical oxygen demand (COD), total organic carbon (TOC), nitrites (NO_2^-) and nitrates (NO_3^-). Additionally, sodium thiosulfate ($Na_2S_2O_3$, 99.5% pure, Aldrich Co.) was used as support electrolyte. Table 1 presents the characterization of the raw water used in this study.

Analytical methods

For each sample of water, the number of microorganisms was stated as colony forming units (CFU). The concentration of viable cells was evaluated using the plate count method. The growth medium contained Violet Red Bile, a gelling agent soluble in cold water, and an indicator of beta-glucuronidase activity that facilitates colony

Table 1 | Physicochemical and bacteriological properties of studied water samples

Parameter	Value
pH	6.6
Conductivity, μS/cm	500
Turbidity, NTU	8
COD, mg/L	46.5
TOC, mg/L	18
NO_3^-, mg/L	0.870
NO_2^-, mg/L	0.183
Total coliforms (TC), CFU/mL	6,750
Fecal coliforms (FC), CFU/mL	5,600

quantification. Plates were incubated at 30 °C for 24 h. Next, the number of colonies on the plates was counted. For all counts, at least three replicate plates were used and the results were reproducible within an average relative error of ±10%. During the experiments, at each sampling time, 1 mL of suspension was withdrawn and immediately quenched with excess of $Na_2S_2O_3$ (10 mM) to eliminate the residual disinfectants in the sample. Then, each sample was kept in a sterile container, in darkness, at room temperature (25 ± 1 °C). The COD analyses were performed following the closed reflux method with colorimetric measurements (method 5220D). The TOC measurements were carried out following the method 5310D. The NO_3^- and NO_2^- concentrations where determined according to the Standard methods 4500B and 4500D, respectively. For NO_2^-, NO_3^-, COD and TOC measurements, a Nano-Color thermo-reactor and spectrophotometer were used. Turbidity was determined following the 2130B standard method. Additionally, conductivity and pH were determined with a Thermo Scientific Orion 5 start multiparameter analyzer. In all cases, the average value of the measurements is reported. Error bars (indicating the error or uncertainty in a reported measurement) present the variability of data graphically.

Disinfection process and electrolytic system

The electro-oxidation experiments were carried out in a Plexiglas, continuously stirred, batch jacketed reactor (80 mL). Two vertically-placed plates, with 1 cm separation between them, were used as electrodes. Two different anode materials were evaluated: (i) a graphite rectangular plate (GP) (with dimensions of 34.1 × 24 × 6 mm, and a total surface area of 21.9 cm^2) and (ii) BDD film deposited on a titanium substrate (BDD/Ti) (BDD coating: p-doped, polycrystalline, ≈3 micrometer thick; doping level: 700–800 ppm boron, with dimensions 15 × 50 × 5 mm. Supplier: Fraunhofer, USA). The cathode consisted of a titanium electrode (Ti (99. 4%) with dimensions of 3.6 × 0.11 × 2.7 cm) or a BDD/Si electrode with the same dimensions of BDD/Ti one. The voltage was regulated with a BK-Precision source (0–30 V, 0–5 A). Test's temperature was maintained at 25 °C using a Polyscience 712 thermostat connected to the reactor jacket. For disinfection experiments, the total reaction time was fixed at 12 min, the stirring intensity at 350 RPM and the anode available area was equal to 4 cm^2. At each sampling time, in order to avoid any contamination, the coliform measurements were performed immediately inside a sterile chamber. The possible bacterial growth was monitored with coliform measurements after 24 h, 94 h and 7 days.

Experimental design and statistical analysis

According to the literature (Brillas & Martínez-Huitle 2015), several operational factors can affect the efficiency of electrochemical disinfection process. The following ones were taken into consideration in this study: current density (j), conductivity (σ), electrode surface area, type of anode material and stirring velocity. The other variables, such as pH and bacterial population, corresponded to the natural conditions of the raw water. In order to evaluate the effect of process variables on the efficiency of coliform elimination and to establish their optimal values, two statistical experimental designs were randomly programmed, to avoid any systematic error, using Statgraphics Centurion XVI. They were performed as follows:

- The first group of experiments, corresponding to a fractional factorial design, 2^{5-1} with three central points, consisted of 19 experimental runs with two replicas (not shown here). It determined that j and σ present, statistically, the most significant effect on the disinfection process. Similar results were reported previously (Mascia *et al.* 2012; Mascia *et al.* 2013; Long *et al.* 2015; Qi *et al.* 2015). Notice that an increase in j enhanced the

process efficiency and increased the energy cost. Therefore, j, σ and anode material were chosen as operational variables to be optimized in the next experimental design.

- In the second group of experiments, the BBD coupled with the RSM was applied to evaluate the individual and synergetic effects of the most significant operation variables. It consisted of 15 tests with two replicas. It let to: (i) reduce the number of experimental trials, comparing to a complete factorial design, (ii) adjust a second order polynomial model and predict the response variable from the experimental factors, (iii) establish limitations of the fitted model with regression coefficient determination, and (iv) determine the optimal conditions of the process. It is important to remark that RSM was not used to understand the mechanism of coliforms inactivation, but to determine the optimal operating conditions at certain operating specifications. Thus, the following independent variables (factors) and their operational ranges were selected, considering also the results of the first experimental design: (i) current density (j: 2–20 mA/cm^2); (ii) conductivity (σ: 500–900 μS/cm); and (iii) anode material (An: GP or BDD/Ti). Since An is a discrete variable, the following three levels were defined to understand the influence of the anode and cathode material on the electrochemical disinfection process: level 1: corresponding to BDD/Ti anode and Ti cathode; level 2: BDD/Ti used as anode and BDD/Si as cathode; and level 3: corresponding to GP/Ti anode and Ti cathode. When required, the initial conductivity was adjusted adding the corresponding volume of Na_2SO_4 (1 mM). The upper conductivity value in the studied range was fixed according to Colombian regulation for drinking water (1,000 μS/cm).

The efficiency of the electrochemical process was defined based on total coliform (%ETC) and fecal coliform (%EFC) elimination percentages. They were calculated according to Equation (1), where Zi and Z account for the initial and final values of FC and TC measured concentrations.

$$\%EFC\ (or\ \%ETC) = \frac{Z_i - Z^*}{Z_i}\ 100 \tag{1}$$

For the experimental design, the independent variables and their levels, summarized in Table 2, were coded according to Equation (2). The experimental results were adjusted to a second-order multi-variable polynomial model (Equation (3)):

$$X_i = \frac{(x_i - X_{pc})}{\Delta X} \tag{2}$$

$$Y_i = \beta_0 + \sum_1^3 \beta_i x_i + \sum_1^3 \beta_{ii} X_{ii}^2 + \sum_1^3 \sum_1^3 \beta_{ij} X_i X_J \tag{3}$$

where Yi is the predicted response variable, β_0, β_i, β_{ii}, β_{ij} are the regression coefficients for: the intercept, lineal, square, and interaction terms, respectively; and X_i and X_J are independent variables. The quality of the fitted model and its prediction capacity were judged from the variation coefficient, R^2. Determination of the significant main and interaction effects of factors, influencing the %EFC and %ETC, were followed by analysis of variance (ANOVA), Pareto diagram, response surface plot and variation coefficients. More details on the applied methodology have been reported elsewhere (GilPavas *et al.* 2014).

The energy consumption (EC) during the EO process (expressed in kWh/m^3) was calculated using Equation (4):

$$EC\left(\frac{kWh}{m^3}\right) = \frac{IVt}{V_R} \tag{4}$$

where I = average applied current (A); V = average cell potential (V); t = electrolysis time (h); V_R = solution volume (m^3).

Table 2 | Variables (factors) and their levels for experimental design

	Coded factors, X		
Variable	−1 Level 1	0 Level 2	1 Level 3
A: Current density (j) mA/cm^2	2	11	20
B: Conductivity (σ), μS/cm	500	700	900
C: Electrodes' material (anode–cathode)[a]	1	2	3

[a]1: BDD/Ti-Ti, 2: BDD/Ti-BDD/Si, 3:GP-Ti.

The operational costs (OC, USD/m^3) were calculated as follows:

$$OC\left(\frac{USD}{m^3}\right) = aEC + bC_{electrolyte} \quad (5)$$

where $C_{electrolyte}$ is the amount of electrolyte consumed (kg/m^3), a and b correspond to the cost of electrical energy (0.18 USD/kWh) and $NaSO_4$ electrolyte (1.23 USD/kg), respectively, matching to the Colombian market prices in October 2016.

RESULTS AND DISCUSSION

To examine the combined effect of the three independent process variables (j, σ and electrode material) on %ETC and %EFC, 15 experiments with two replicas were performed. Independent variables, their experimental ranges and the corresponding experimental data (their average values) are given in Table 3. The %ETC and %EFC values ranged from 68% to 100% and from 74% to 100%, respectively. The following changes in the OC, varying j in the range of 2–20 mA/cm^2, were determined: 0.014–1.17 USD/m^3 and 0.022–1.176 USD/m^3 for BDD/Ti and GP electrodes, respectively. The operational conditions that maximized both the %ETC and %EFC correspond to the run 7 (Table 3). However, in this case, the OC are one of the highest (*ca.* 1.17 USD/m^3). Notice that using j as low as 2 mA/cm^2, it is still possible to achieve *ca.* 90% of ETC with the OC of 0.025 USD/m^3 (run 6, Table 3). These results imply the possibility of total coliform elimination from water without the necessity to induce high electric current, indicating lower operational costs and higher reaction time. The use of GP-Ti electrodes also obtained very high %ETC (*ca.* 96%) for intermediate values of j (11 mA/cm^2) and σ (500 μS/cm) (see run 5 in Table 3), representing intermediate OC (0.054 USD/m^3). Considering the difference in price between BDD (25 USD/cm^2, Fraunhofer USA) and GP ($0.84 USD/cm^2 available at Medellin's local market) electrodes, the GP one becomes an interesting alternative for bacteria elimination.

In order to determine the main and double-interaction effects of factors influencing the disinfection process, an ANOVA was performed. It consists of classifying and cross-classifying statistical results, decomposing the contribution

Table 3 | The experimental and predicted results for the three factors (j, σ and An) and their corresponding values

				%ETC		%EFC		OC (USD/m^3)	
Run	j (mA/cm^2)	σ (μS/cm)	An	Y_{Exp}	Y_{Pred}	Y_{Exp}	Y_{Pred}	Y_{Exp}	Y_{Pred}
1	11	900	3	88	87.7	81	83.47	0.357	0.38
2	2	900	2	75	73.8	77	73.44	0.014	0.018
3	11	700	2	84	82.3	82	80.67	0.462	0.450
4	11	900	1	89	89.0	82	83.35	0.340	0.370
5	11	500	3	96	93.0	94	92.65	0.540	0.510
6	2	500	2	89	87.20	87	87.76	0.025	0.030
7	20	500	2	100	100	100	100	1.172	1.220
8	11	700	2	83	82.30	81	80.67	0.455	0.450
9	20	900	2	100	100	100	99.04	1.040	1.010
10	20	700	1	95	93.21	99	98.41	1.170	1.150
11	11	500	1	96	96.57	96	93.02	0.540	0.510
12	2	700	3	68	69.79	77	77.59	0.022	0.026
13	11	700	2	80	82.33	79	80.67	0.045	0.045
14	2	700	1	75	76.21	74	76.21	0.021	0.025
15	20	700	3	96	94.79	99	96.79	1.176	1.15

of each variable (factors) and double-interactions in the variance of each response variable. Table 4 presents the ANOVA for %ETC and %EFC and the p statistical parameter. The p-values were used to identify experimental parameters that present statistical influence on the particular response. The value of $p \leq 0.05$ means that the studied variable is statistically significant with the 95% confidence level. As shown in Table 4, the j and σ present p-values ≤ 0.05 for the three response variables, suggesting that they influence directly the disinfection efficiency and the operational costs. Moreover, the following double-interactions of different factors also fulfil the statistical constraint: for %ETC: $\sigma - \sigma$ and j-σ; for %EFC: $\sigma - \sigma$; and for OC: j-j. In numerical terms, it implies that their corresponding coefficients in the regression model present significant weight in the polynomial equation. Thus, three second order polynomial equations (Equations (6)–(8)) were fitted to the experimental data, as functions of the three independent process variables (j, An and σ).

$$\%\text{ETC} = 213.523 - 0.7192^{*}j - 0.3362^{*}\sigma - 9.1528^{*}\text{An} + 3.6523\text{E}^{-3*}j^2 + 1.9444\text{E}^{-3*}j^{*}\sigma + 0.2222^{*}j^{*}\text{An} + 2.0927\text{E}^{-4*}\sigma^2 + 2.875\text{E}^{-3*}\sigma^{*}\text{An} + 0.870833^{*}\text{An}^2 \quad (6)$$

$$\%\text{EFC} = 177.046 - 0.9138^{*}j - 0.2351^{*}\sigma - 7.1^{*}\text{An} + 0.0581^{*}j^2 + 1.3611\text{E}^{-3*}j^{*}\sigma - 0.0833^{*}j^{*}\text{An} + 1.3948\text{E}^{-4*}\sigma^2 + 6.2501\text{E}^{-4*}\sigma^{*}\text{An} + 1.8792^{*}\text{An}^2 \quad (7)$$

$$\text{OC} = -0.1646 + 0.0415^{*}j + 6.901\text{E}^{-4*}\sigma - 0.0732^{*}\text{An} + 1.5610\text{E}^{-3*}j^2 - 2\ \text{E}^{-*}j^{*}\sigma - 2\text{E}^{-5*}j^{*}\text{An} - 6.01\text{E}^{-7*}\sigma^2 + 1.625\text{E}^{-5*}\sigma^{*}\text{An} + 0.016^{*}\text{An}^2 \quad (8)$$

The adjustment of developed models was evaluated based on the variation coefficients (R^2 and R^2_{adj}). The R^2_{adj} is a more suitable parameter, because it takes into account the size of the data set. Both coefficients were very close to unity, indicating that RSM was very suitable to describe the electro-disinfection process using BDD anode

Table 4 | ANOVA results for the %ETC and %EFC as a function of j, An and σ

	Sum of squares	Degrees of freedom	Mean square	F-ratio	p-value
Factor (%ETC)					
A:*j*	882	1	882	145.84	**0.0001**
B:σ	102.961	1	102.961	17.02	**0.0091**
C:An	5.61125	1	5.61125	0.93	0.3797
AA	0.023141	1	0.023141	0	0.9531
AB	49	1	49	8.1	**0.036**
AC	16	1	16	2.65	0.1648
BB	282.423	1	282.423	46.7	**0.001**
BC	0.1225	1	0.1225	0.02	0.8924
CC	5.73083	1	5.73083	0.95	0.375
Error total	30.2392	5	6.04783		
Total (corr.)	1371.92	14			
$R^2 = 97.8\%$ $R^2_{adj} = 93.8\%$					
Factor (%EFC)					
A:*j*	856.98	1	856.98	67.97	**0.0004**
B:σ	177.661	1	177.661	14.09	**0.0132**
C:An	0.03125	1	0.03125	0	0.9622
AA	81.7078	1	81.7078	6.48	0.0515
AB	24.01	1	24.01	1.9	0.2261
AC	2.25	1	2.25	0.18	0.6903
BB	114.931	1	114.931	9.12	**0.0294**
BC	0.0625	1	0.0625	0	0.9466
CC	13.0385	1	13.0385	1.03	0.3558
Error total	63.0392	5	12.6078		
Total (corr.)	1311.74	14			
$R^2 = 95.19\%$ $R^2_{adj} = 86.54\%$					
Factor (OC)					
A:*j*	2.46642	1	2.4664	1435.52	**0.0000**
B:σ	0.03726	1	0.0373	21.69	**0.0055**
C:An	0.00002	1	0.0000	0.01	0.9096
AA	0.05905	1	0.0590	34.37	**0.002**
AB	0.00526	1	0.0053	3.06	0.1407
BB	0.00213	1	0.00213	1.24	0.3157
BC	0.00004	1	0.00004	0.02	0.8815
CC	0.00094	1	0.00094	0.55	0.4927
Error total	0.00859	5	0.00172		
Total (corr.)	2.58116	14			
$R^2 = 99.75\%$ $R^2_{adj} = 98.90\%$					

containing system. According to Table 4, the following values of R^2_{adj} were found: 93.8, 86.54% and 98.90% for %ETC, %EFC and OC, respectively. Indeed, good agreements between the experimental and predicted values were observed (see Table 3). Next, the response surface plots were drafted with the regression models (Equations (4) and (5)) to see the simultaneous effects of two factors on a response variable (Figure 1). Thus, it was possible to determine the optimal operating conditions as follows.

Interactive effect of current density (j) and conductivity (σ) on %ETC and %EFC

The obtained surfaces indicate that, for both BDD (An: 1) and GP (An: 3), an increase in j resulted in an increase in the disinfection efficiency. It is in agreement with the results previously reported by Qi *et al.* (2015) for disinfection of solution containing 10^7 UFC/mL of *E. coli* (using a BDD anode and 0.05 M of Na_2SO_4). They found that the increase in current density from 15 to 20 mA/cm achieved almost complete microbial elimination, reducing the reaction time from *ca.* 30 min to 20 min. It occurs due to the more intensive production of oxidizing species, mainly the $^{\bullet}OH$, responsible for coliform membrane disruption. Figure 1 shows that j presents similar influence on disinfection efficiency independent of types of anode material. Jeong *et al.* (2006) and Gómez-López *et al.* (2013) also have found that, in the disinfection of water containing *E. coli*, high j values are beneficial for fast microbial inactivation. Nevertheless, it is less efficient from the point of view of EC. Moreover, σ presents the highest positive effect on the process efficiency at its minimal value (500 μS/cm). According to the literature (Flox *et al.* 2006), it

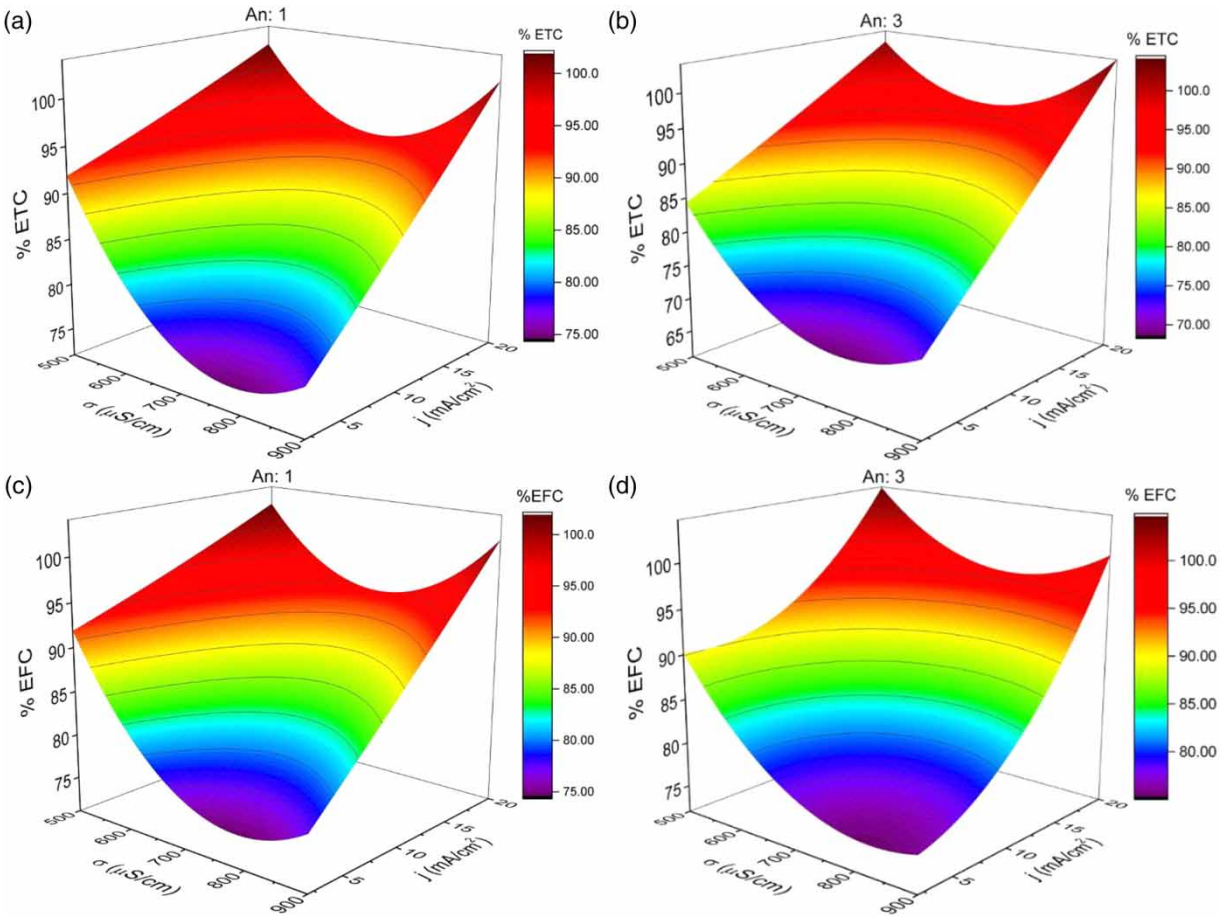

Figure 1 | Response surface plots for the interactive effect of j and σ on %EFC and %ETC. Reaction time = 12 min, T = 25 °C. (a) %ETC with BDD/Ti; (b) %ETC with GP; (c) %EFC with BDD/Ti; (d) %EFC with GP.

can be caused by an increase in Na_2SO_4 concentration promoting the formation of $S_2O_8^{2-}$. However, it has any significant effect on the electrochemical oxidation process due to its lower oxidation potential, comparing to that of $^{\bullet}OH$ radical. Additionally, if Na_2SO_4 is used at high concentrations, it can act as culture media for bacterial growth (Muralitharan *et al.* 1991), being even self-defeating for the elimination process. The other studies have also reported a decrease in the disinfection efficiency under increasing Na_2SO_4 concentration (Qi *et al.* 2015). It implies that electro-generated $S_2O_8^{2-}$ plays a role in combination with the $^{\bullet}OH$ radical decreasing the disinfection efficiency.

Effect of electrode material (An) on %ETC and %EFC

As it can be seen, for the elimination of total coliforms, BDD/Ti anode gives better results than GP one (for the reaction time of 12 min, Figure 1). For σ value of 500 μS/cm, it was possible to achieve near 100%ETC and %EFC, with 20 mA/cm^2, using both BDD/Ti and GP anode. However, high current combined with low conductivity implies the usage of high voltage and consequently higher energy cost. When $j = 10$ mA/cm^2, the %ETC reaches 96 and 92% using BDD/Ti and GP, respectively. Similar behavior was observed for $j = 2$ mA/cm^2, with efficiencies of 92 and 84%ETC using BDD/Ti and GP anodes. These results imply that BDD/Ti anode produces larger amount of the $^{\bullet}OH$ radical than GP one. The inherent cytotoxicity of GP would compensate the lower $^{\bullet}OH$ production comparing to that of BDD/Ti anode. Therefore similar efficiencies are obtained with both materials, as it was shown by the ANOVA results.

Interactive effect of current density (j) and conductivity (σ) on OC

Figure 2 presents the response surface plots for OC, using: (a) BDD/Ti and (b) GP electrodes. The σ seems to present slightly 'positive' effect on the OC, since there is a small decrease in the cost at higher conductivities values. This is due to the lower electricity resistance involved in the use of lower voltages. However, high conductivity may significantly reduce the process efficiency. From this reason, 500 mS/cm was selected as the optimal condition to carry out the process. On the other hand, the OC rapidly increased with an increase in j from 2 to 20 mA/cm^2 (Figure 2). For example, when $j = 10$ mA/cm^2, the operational cost accounts for *ca.* 0.45 USD/m^3, which is a reasonable value for this type of processes. Additionally, at these conditions (Figure 1), coliform elimination efficiencies reaches *ca.* 90% after 12 min of treatment. Therefore, $\sigma = 500$ μS/cm and $j = 10$ mA/cm^2 were selected as the most appropriate conditions for water treatment.

Evolution of the %ETC and %EFC of the wastewater at selected conditions

At selected conditions, the evolution of the electrochemical disinfection process was monitored as function of time

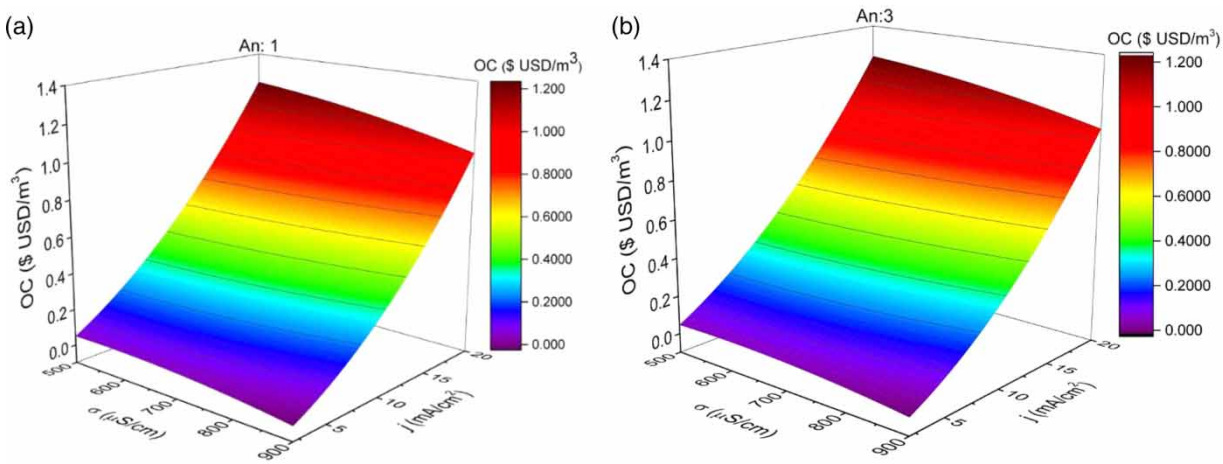

Figure 2 | Response surface plots for the interactive effect of j and σ on OC. Reaction time = 12 min, temperature = 25 °C. (a) OC with BDD/Ti; (b) OC with GP.

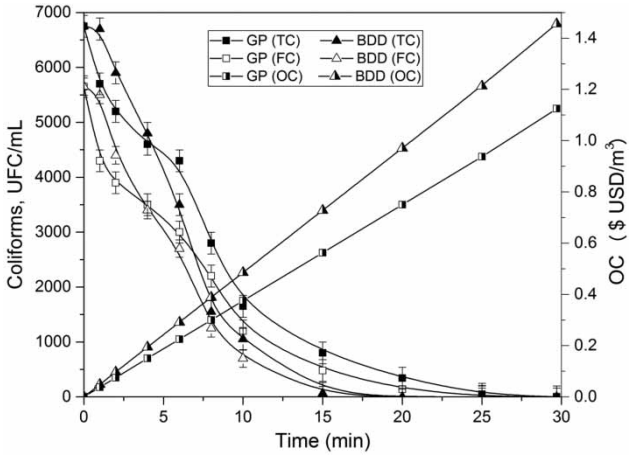

Figure 3 | Evolution of FC, TC and OC with GP and BDD electrodes at $j = 10$ mA/cm^2, $\sigma = 500$ μS/cm, temperature = 25 °C.

(Figure 3). As it can be seen, in the elimination of both FC and TC, BDD/Ti electrode presents slightly better performance than GP one. Using GP electrode, it is possible to achieve complete elimination of coliforms after *ca.* 27 min of reaction. The application of BDD/Ti one requires *ca.* 20 min. Notice that at the beginning of the disinfection process, GP based treatment is faster than the BDD/Ti one. However, after the reaction have progressed a few minutes (*ca.* 5 minutes), BDD/Ti reaches higher degree of coliform elimination. It can be related to a two-step mechanism of coliform elimination using GP electrode as follows: (i) the first one caused by the cytotoxicity of GP, which have been reported to inactivate *ca.* 26% of *E. coli* (Liu *et al.* 2011) and (ii) the second one caused by the formation of oxidizing species (Polcaro *et al.* 2007). On the other hand, BDD/Ti has not been reported to present inherent cytotoxicity, even if it is more efficient in the production of $^{\bullet}$OH radicals than GP (Brillas & Martínez-Huitle 2015).

Once reaction was finished, the microorganism evolution was monitored analyzing samples after 24 h, 94 h and 7 days. Any coliforms growth was observed for water treated using both BDD/Ti and GP electrode, indicating that the cell damage was enough to the complete elimination of coliforms. Thus, from the experimental results presented in Figure 3, the following observations can be stated for GP and BDD/Ti electrodes, respectively: (i) the 13% and 25% of reduction in TOC; (ii) the decrease in nitrites concentration from 0.183 mg/L to 0.096 and to 0.038 mg/L; (iii) the increase in nitrates concentration from 0.87 mg/L to 1.23 and to 1.44 mg/L; (iv) the increase in OC with an increase in electrolysis time, for both electrodes. Notice that lower OC, using GP electrode, can be related to its higher electrical conductivity compared with that of the BDD film; (v) the required time for total removal of TC and FC was of *ca.* 30 min for GP electrode and 20 min for BDD/Ti one.

CONCLUSIONS

Electro-oxidation using BDD/Ti or GP anodes and $Na_2S_2O_3$ as supporting electrolyte let to achieved complete elimination of total and fecal coliform of raw surface water (without any additional chemical substances). This method can be considered as a suitable chlorine-free disinfection treatment. The statistical analysis of the experimental data indicated that the operational factors presenting the highest influence on coliform elimination efficiency are conductivity and current density. From the RSM, the following optimal operational conditions were established: $j = 10$ mA/cm^2, 500 μS/cm and temperature = 25 °C. The variation of FC and TC with time indicated that BDD/Ti electrode presents slightly higher efficiencies that GP one. However, the GP electrode cost is only a fraction of the BDD/Ti one. Thus, GP electrode become a very promising material for the electrochemical disinfection of raw surface water. The preliminary operational cost analysis for water disinfection treatment using an electro-oxidation system led to a total unitary cost, aiming to achieve complete disinfection, of 1.1 USD/m^3 for GP anode and 1 USD/m^3 for BDD anode.

ACKNOWLEDGEMENTS

The authors acknowledge 'Dirección de Investigación de la Universidad EAFIT, Medellín, Colombia' for financial support of this research. The staff of the 'Laboratorio de Ingeniería de Procesos' is also recognized for their participation.

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First received 31 January 2017; accepted in revised form 26 June 2017. Available online 21 July 2017