Electrochemical disinfection of swimming pool water by electro-oxidation process: Operating parameters effect and by-product formation

Touriya Naji 1, Ahmad Dirany 2, Anne Carabin 3, Patrick Drogui 4*

1 Graduated Master Student, Institut national de la recherche scientifique (INRS-Eau Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-2550, Fax: (418) 654-2600, email: touriya.naji@ete.inrs.ca

2 Research associate, Institut national de la recherche scientifique (INRS-Eau Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-4483, Fax: (418) 654-2600, email: ahmad.dirany@ete.inrs.ca

3 Research assistant, Institut national de la recherche scientifique (INRS-Eau Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-3805, Fax: (418) 654-2600, email: anne.carabin@ete.inrs.ca

4*Professor, Institut national de la recherche scientifique (INRS-Eau Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-3119, Fax: (418) 654-2600, email: patrick.drogui@ete.inrs.ca

*Corresponding author:
E-mail: patrick.drogui@ete.inrs.ca
Tel: (418) 654-3119; Fax: (418) 654-2600

November, 2017
Abstract

Swimming pool users are a source of various contaminants and microorganisms. Conventional chlorine-based reagents treatment is commonly used to disinfect water. However, this disinfection treatment can present various inconveniences such as formation of carcinogenic by-products (i.e. trihalomethanes THMs). In order to prevent this problem, an electrochemical disinfection process was carried out using synthetic and real swimming pool waters. The performance of the electrochemical system was evaluated by studying the effect of current intensity (0.5-3.0A), treatment time, type of anode (Nb/BDD and Ti/Pt) and the initial concentration of pathogens (Escherichia coli and P. aeruginosa). Real swimming pool water (initially containing $10^6$ CFU/100mL of pathogens) was significantly disinfected at current intensities of 1.5 and 3.0A using respectively Nb/BDD and Ti/Pt as anode materials. Finally, this work is one of the few showing the up-scale of electrochemical disinfection of real swimming pool water (V=100L) for which perchlorate evolution was recorded at 3.0 A without addition of any chemicals.

Keywords

Swimming water; electrochemical disinfection; Nb/BDD; oxidizing species; Ti/Pt.
1. Introduction

Microbiological and physico-chemical characteristics of swimming pool water are constantly altered by bathers. In fact, users of swimming pool water are a source of various contaminants and microorganisms coming from the skin, genitals, feet, armpits or fecal accidents. Thus, chlorine-based reagents are commonly used to disinfect water due to their proven efficacy against germs, remnant effect, and advantageous economic cost. However, these conventional techniques of recreational water disinfection can present various inconveniences. For example, the formation of chlorinated by-products to likely be hazardous and carcinogenic (Bull, 1982). Further, various emerging contaminants detected in swimming pool water remain none degraded via chlorination. Other techniques such as ozonation, ultraviolet treatment, filtration, etc., are expensive or less effective. Nevertheless, potentially greener and more efficient new water treatment technologies known as Advanced Oxidation Processes (AOPs) have been recently proposed as alternatives to conventional methods.

Electrochemical disinfection (ECD) is among various AOPs based upon in-situ generation of powerful reactive oxygen species (ROS). These ROS have higher oxidation potential compared to chlorine and derivatives. In fact, free radicals alone are 105 times more potential as compared to chlorine compounds (Cho et al., 2004). Moreover, these species are highly reactive and non-selective towards pollutants.

During electrochemical disinfection (ECD), the disinfection can occur by the means of (1) direct oxidation of microbes on the anode’s surface caused by electron exchange and hydroxyl radicals producing \( E^\circ(\text{HO}^\cdot/\text{H}_2\text{O})= 2.80 \ \text{V-vs.SHE} \) from the anodic oxidation of water (2) indirect oxidation by in situ generation of various oxidants (HClO, O₃, H₂S₂O₈, H₂O₂, etc.) in the bulk are capable of destroying organic pollutants and disinfect swimming water.
Consequently, this process may minimize addition, manipulation, and storage of chemical reagents as well as the formation of disinfection by-products. This work evaluates the performance of electrochemical disinfection while monitoring and minimizing energy cost and by-products. Different operating parameters including current intensity, treatment time and anode material have been tested in order to determine the optimal conditions for the electrochemical disinfection.

2. Materials and methods

2.1. Swimming water

2.1.1. Synthetic swimming pool water

Synthetic swimming pool water was prepared from artificial sweat mixture liquor (ASML) (Borgmann-Strahsen, 2003; Schwake et al., 1998). One liter of ASML was comprised of 20 g sodium chloride (NaCl), 17.5 g ammonium chloride (NH₄ Cl), 1.0 g urea ((NH₂)₂CO), 15 g lactic acid (C₃H₆O₃) and 5.0 g acetic acid (CH₃ COOH). The synthetic swimming pool water was prepared in a 2.0 L PVC tank containing 1.0 L of distilled water in which 3mL of ASML was added. The pH was adjusted to 7.4 by adding a few drops of 10N sodium hydroxide solution.

2.1.2. Real swimming pool water

Real swimming pool water was obtained from a public swimming pool in Québec City. The samples were collected in sterile polypropylene tank of 20 L and stored at 4 °C until use. Free chlorine was neutralized by adding sodium thiosulfate (Na₂S₂O₃).

2.2. Electrolytic reactor set up

2.2.1. Parallelepipedic electrolytic cell (Unit C1)
The first set of tests was carried out at room temperature using a batch electrolytic cell (C1) made of acrylic material with a dimension of 17 cm (depth) \(\times\) 5cm (width) \(\times\) 11.5 cm (length) with a capacity of 500 mL. Two electrodes were placed vertically in the cell with a 0.5 cm inter-electrode gap. Niobium boron-doped diamond (Nb/BDD) and titanium coated with platinum (Ti/Pt) were used. The two anodes had an active surface area of 68 cm\(^2\) and a void surface area of 45 cm\(^2\). On the other hand, carbon felt was used as cathode with a total area of 127 cm\(^2\). Water was recirculated in a 2.0 L tank using a peristaltic pump (Master Flex L/s. Model 77200-50) operating at 170 mL/min flow rate. Current intensity was supplied using DC power generator Xantrex XFR 40V-70A.

2.2.2. Cylindrical electrolysis cell (Unit C2)

The cylindrical electrolysis cell (C2) having 2.0 L of capacity, were used. The cell was made of PVC material with a dimension of 15 cm height and 13 cm diameter. The cylindrical electrolytic cell was comprised of two horizontal circular mesh anodes of boron doped diamond (Nb/BDD) (12 cm diameter \(\times\) 0.1 cm thick) and two carbon felt cathodes (12 cm diameter \(\times\) 0.3 cm thick) separated by a 1.0 cm inter-electrodes gap. The carbon felt had a high surface area associated with high porosity (10-20 \(\mu\)m diameter fibers) giving a low flow resistance. The experimental unit C2 included a recirculation tank of 100 L in a closed loop using a recycling pump of 2L/min.

2.3. Bacterial cultures

Pure cultures of \textit{E. coli} and \textit{P. aeruginosa} were used as bacterial indicators. A pure strain of \textit{E. coli}. purchased from Sigma-Aldrich was stored at \(-29^\circ\)C before being revived. \textit{P. aeruginosa} strain HSJ2 was isolated in the laboratory at INRS-Armand-Frappier. Lennox L Broth (LB broth base) provided by Invitrogen\(^\text{TM}\) was used to revive both cultures at 37 \(\pm\) 1 \(^\circ\)C. Enumeration of cells was established using 0.45 \(\mu\)m nitrocellulose grid membrane filter method (9222D Center of
expertise in environmental analysis of Quebec). Two selective culture media m-CF-BCIG provided by Oxoid and m-PA-C provided by BD were used for growth of *E. coli* and *P. aeruginosa* respectively. Plates were incubated at 37 ± 1 °C for 24 hours for *E. coli* and 41.5 ± 1 °C for 72 hours for *P. aeruginosa*.

### 2.4. Analytical details

During this study, hydrogen peroxide (H$_2$O$_2$) concentration was determined by the cerium sulfate (Ce(SO$_4$)$_2$. 2(NH$_4$)$_2$SO$_4$.2H$_2$O) method (Drogui et al., 2001).

Total oxidants generated during the electro-oxidation were determined by iodide method using thiosulfate solution (Na$_2$SO$_3$).

Chlorine was determined using a handheld colorimeter (Pocket Colorimeter™ II) provided by HACH. Perchlorates were analyzed using a Dionex IonPac AG 16 column. 50 mm × 2 mm. The detection limit of perchlorate was 0.5 mg/L.

### 3. Results and discussions

#### 3.1. H$_2$O$_2$ production

Hydrogen peroxide can be generated in situ via electrolysis of water according (Da Pozzo et al., 2005). Breakdown of water (into oxygen molecule and proton ions) takes place on the surface of the anode. Simultaneously, oxygen is reduced on the surface of the cathode to form hydrogen peroxide (Drogui et al., 2001). Various cathode materials such as carbon felt and vitreous carbon can be used (Özcan et al., 2008).

Four cathodes were tested in order to identify the material that produces maximum of H$_2$O$_2$: carbon felt, vitreous carbon, graphite and titanium. In all experiments, Ti/Pt was used as anode. Current intensity was set to 0.5 A during 2 hours of electrolysis time in the presence of NaCl.
(0.06 g/L) and NH₄Cl (0.0525 g/L). The results are presented in Figure 1a. The concentration of H₂O₂ increased with time for the four electrodes but most notably for carbon felt. Hydrogen peroxide concentration increased from 0.06 to 0.23 mmol/L after 20 and 100 min respectively. Similar results were reported by (Drogui et al., 2001). The spongy and porous texture of the carbon felt leads to a better contact with oxygen and consequently a better production of H₂O₂ (Özcan et al., 2008).

In order to determine the applied current intensity effect on the hydrogen peroxide generation using carbon felt cathode, current intensities ranging between 0.1 and 2.0 A were applied. The results are shown in Figure 1b. The concentration of hydrogen peroxide was proportional to current intensity (Kraft et al., 1999). Thus, H₂O₂ concentration increased with increasing current intensity from 0.0 to 0.8A. Peroxide maximal concentration of 0.53 mmol/L was recorded at 0.8A after 80 min of electrolysis time. However, a significant drop was observed at current higher than 0.8 A. Same results have been reported by Ozcan et al. (Özcan et al., 2008). This decrease can be attributed to the fact that at potentials higher than 9.7 V, reduction of O₂ to water takes over its reduction to hydrogen peroxide (Badellino et al., 2006).

### 3.2. Electrolytic disinfection efficiency using cell C1

#### 3.2.1. Synthetic medium

Synthetic swimming pool water was contaminated with an initial concentration of 10² colony-forming unit (CFU)/100 ml of *E.coli* and *P. aeruginosa*. Table 1a summarizes results comparing disinfection performances of Ti/Pt and Nb/BDD at current intensity of 0.8A using carbon felt cathode. Both anodes were able to total disinfection of *E.coli* and *P.aeruginosa* in synthetic swimming pool water after two hours of electrolysis. Therefore, this electrolytic process proved to be efficient for synthetic pool water treatment by dint of electro-generated oxidants action.
3.2.2. Real swimming pool water

3.2.2.1. Effect of bacterial concentration

Real swimming pool water samples were used to evaluate disinfection efficiency of proposed electrolytic system. Free chlorine contained in the sample was neutralized by sodium thiosulfate (0.1 M). Afterwards, samples were initially contaminated with $10^2$, $10^4$ and $10^6$ CFU/100 ml of *E. coli* and *P. aeruginosa*. The results are given in Table 1b. Expectedly, current intensity of 0.8 A (using Nb/BDD) was inefficient against bacterial concentrations greater than $10^2$ CFU/100 mL and specifically for *P. aeruginosa*. Thus, thereabout $136 \pm 22$ CFU/100 ml of *P. aeruginosa* persisted in the treated water (initial concentration was $58.5 \times 10^4 \pm 27$ CFU/100 ml).

The increase in current intensity to 1.5 A in the presence of Nb/BDD, led to a nearly total elimination of germs for all concentrations $10^2$, $10^4$, and $10^6$ CFU/100 mL. On the other hand, Ti/Pt failed to remove a residual of $66 \pm 2$ CFU/100 mL of *P. aeruginosa*. The resistance of *P. aeruginosa* to electrolysis, compared to *E. coli*, is mainly due to its protective layers of exopolysaccharides which causes a mass transfer barrier (Wei and Ma, 2013). Complete disinfection was achieved when current intensity of 3.0A was applied to Ti / Pt. (Schmalz et al., 2009) have reported an improvement in the efficiency of electro-oxidation disinfection of biologically treated wastewater on Nb/BDD. They noted that the increase in current density results in acceleration of *in-situ* electrogeneration of oxidants species.

3.2.2.2. Effect of treatment time

Figures 2a and 2b show a comparison of time effect on disinfection using conventional chlorination (2.20 mg/L of chlorine) and the ECD. The difference between chlorination and ECD is most accentuated when it comes to eliminating *P. aeruginosa* as the first one took more than 90 min (Fig. 2b). This difference can be attributed to the simultaneous generation of several electro-oxidants
(EORs and chlorine) that target germs altogether compared to chlorination where chlorine is the only active disinfectant in the solution. Removal of *E.coli* (Fig. 2a) and *P.aeruginosa* (Fig. 2b) was achieved in less than 30 min in the presence of Nb/BDD at 1.5 A. However it took about 60 min in the presence of Ti/Pt at 3.0 A. To understand the reasons behind this difference in behavior between the two anodes, dosage of total oxidants was carried out as shown in Figure 2c. During the first 40 minutes, the concentration of total generated oxidants (g/L) at Nb/BDD’s surface was much greater than that produced at Ti/Pt (0.07 versus 0.002 g/L in 40 min for Nb/BDD and Ti/Pt respectively). Due to its high oxygen overpotential, Nb/BDD is able to generate, in large quantities, several oxidants *in-situ* (Martínez-Huitle and Brillas, 2009). These oxidants can be in radical form such as hydroxyl radicals or stable compounds form such as chlorine, ozone, and hydrogen peroxide. A significant drop in total oxidants concentration generated on Nb/BDD’s surface occurred after 40 min of electrolysis. However, production of oxidants continued to increase slightly using Ti/Pt (0.01 g/L after 120min). Residual concentration of total oxidants after two hours of electrolysis is about 8 mg /L for Ti/Pt and 20 mg /L for the Nb/BDD. These residual concentrations will ensure residual effect against probable bacterial proliferation. The observed decline of total oxidants speculated formation of an electro-chlorination by-product since chlorine is to be likely the most dominant oxidant. Indeed, several authors have linked electrochemically generated free chlorine decrease to perchlorate occurrence during electrolysis of water containing chloride ions using Nb/BDD (Bergmann et al., 2009; Kapalka et al., 2010). Perchlorate (ClO$_4^-$) is a stable and persistent emerging contaminant which is related to various health problems such as altering thyroid gland function (Greer et al., 2002). This proposal has been confirmed by perchlorate and active chlorine analysis using LC-MS-MS (Fig. 2d). During first 40 minutes of electrolysis, the two compounds simultaneously increased linearly however, active chlorine concentration started dropping significantly with time while perchlorate continued to increase gradually to reach 0.35 g/L. These
results confirm results reported by (Hubler et al., 2014; Palmas et al., 2007). However, no drop of active chlorine concentrations was observed in the presence of Ti/Pt anode. Results demonstrated that perchlorate is formed on Ti/Pt but in lower concentrations (0.02g/L after 2 hours) compared to Nb/BDD. These results are in agreement with other reported other studies (Bergmann et al., 2009; Jung et al., 2010; Oh et al., 2010).

3.3. **Real swimming pool water using cylindrical unit C2**

Larger real swimming pool water volume of 100 L disinfection was investigated. Only Nb/BDD was used as the anode in this experiment. The scale-up from 1.0 liter to 100 L required to keep fixed current density and amount of electricity “Q”.

\[ Q = \frac{It}{V} \]

Where, I= maximal current in (A); t = treatment time (min) and V= volume of water to be treated (L). An average concentration of \(10^4\) CFU/100 mL of \(E. coli\) was used to contaminate this real pool water. Thus, the required amount of applied current was 3.0A for two cylindrical mesh Nb/BDD anodes.

Surprisingly, only one single hour was sufficient to eliminate almost all bacterial cells in 100 L as shown in Figure 3a. These results were intriguing since a larger electrolysis time was expected for the 100 L disinfection. Free chlorine and pH fluctuations during electrolysis time suggested that one parameter or both are likely influencing the disinfection results. As a matter of fact, free chlorine evolution was significant in 100 L (1.01mg/L after 60 min) (Fig. 3b), which led to a fast disinfection. Moreover, pH was visibly stable in 100 L as it ranged between 7.3 and 7.7 (Fig. 3c). It has been demonstrated that dominance of hypochlorous acid (HClO) or hypochlorite ion (ClO\(^-\)) depends on pH (Nakagawara et al., 1998). For pH lower than 8.0, free chlorine is in the form of
HClO which has greatest disinfecting ability compared to ClO\(^{-}\). Finally, perchlorate production was to be likely influenced by pH variation as shown in Figure 3b. A noticeable decrease in \(\text{ClO}_4^-\) concentration during electrolysis of 100L has been noticed compared to 1L.

4. Conclusion

This work investigated the disinfection of synthetic and real swimming pool water respectively using an electrochemical process. Several parameters including current intensity, duration of treatment, type of working anode, and pathogen concentration were studied in order to evaluate the process. The scale up of the process that allowed the disinfection of 100L of real swimming pool water using Nb/BDD at 3.0A showed that the diffusion of generated oxidants in larger amounts led to a faster disinfection. pH influenced the distribution of chlorine but also of perchlorate concentration that has remarkably dropped in 100L compared to 1L. The proposed electrochemical process for the disinfection of real swimming pool water is very promising and can easily replace chlorination.
Acknowledgements

Sincere thanks are extended to the National Sciences and Engineering Research Council of Canada and Terralpha company for their financial support for this study.


Figures Captions

**Fig. 1.** (a) Effect of type of cathode on the production of H₂O₂; Cathode: Vitreous carbon, Carbon felt, Graphite, Titanium; Anode: Ti/Pt; I=0.5A; cell C1, best H₂O₂ production was obtained with carbon felt; (b) Effect of current intensity on the production of H₂O₂; Cathode: FC; Anode: Ti/Pt; I=0.2, 0.4, 0.8 1.0 and 2.0A and cell C1, best H₂O₂ production was obtained at 0.8 A. Synthetic medium of NaCl (0.06 g/L) and NH₄Cl (0.0525 g/L).

**Fig. 2.** Influence of treatment time on the removal of (a) *E.coli* and (b) *P. aeruginosa*; Anode: Ti/Pt at 3.0A and Nb/BDD at I=1.5A, best disinfection rate was obtained using BDD anode, (c) Comparison of generated total oxidants concentrations using Nb/BDD at 1.5A and Ti/Pt at 3.0A in real swimming pool water, (d) Formation of perchlorate (ClO₄⁻) during ECD using Nb/BDD anode at I=1.5A. Cell C1, real swimming pool water and carbon felt cathode.

**Fig. 3.** (a) Influence of treatment time on the removal of *E.coli*, only one hour was needed for complete disinfection, (b) Evolution of free chlorine and perchlorates concentrations (c) pH variation during ECD treatment. Real swimming pool water containing 10⁴ UFC/100mL, anode: Nb/BDD; cathode: carbon felt; I=3.0 A; volume =100 L; cell C2.
Fig. 1

(a) Concentration of $\text{H}_2\text{O}_2$ (mmol/L) over time (min) for different materials:
- Carbon Felt
- Titanium
- Vitreous Carbon
- Graphite

(b) Concentration of $\text{H}_2\text{O}_2$ (mmol/L) over time (min) for different current densities (A):
- 0.1 A
- 0.2 A
- 0.4 A
- 0.8 A
- 1.0 A
- 2.0 A
Fig. 2

(a) Residual E. Coli (%) over time for different treatments with Ti/Pt and Nb/BDD, showing chlorination control with [Chlorine] = 2.2 mg/L.

(b) Residual P. Aeruginosa (%) over time for different treatments with Ti/Pt and Nb/BDD, showing chlorination control with [Chlorine] = 2.2 mg/L.

(c) Total oxidants (g/L) over time for Ti/Pt and Nb/BDD treatments, with concentrations of 3.0A and 1.5A, respectively.

(d) Perchlorate concentration (g/L) over time, showing active chlorine and perchlorate concentrations.
Fig. 3

(a) Residual E. Coli (%)

(b) Free chlorine (g/L) and Perchlorate (g/L)

(c) pH

Time (h)

Time (min)
Table. 1. (a) Electrochemical disinfection results of synthetic swimming pool water containing 10^2 UFC/100mL of *E. coli* and *P. aeruginosa*, at 0.8 A; (b) Comparison of disinfection efficiency of real swimming pool water at 1.5 and 3.0 A respectively. Anode: Nb/BDD and Ti/Pt, cathode: CF, treatment time =120 min, cell C1, volume 1 liter, C₀=initial concentration, Cᵢ=final concentration

### (a) Electrochemical disinfection results of synthetic swimming pool water

<table>
<thead>
<tr>
<th></th>
<th>C₀ [UFC/100 mL]</th>
<th>Cᵢ [UFC/100 mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nb/BDD</td>
<td>Ti/Pt</td>
</tr>
<tr>
<td><em>E. coli</em></td>
<td>(59.5± 5) × 10²</td>
<td>(0 ± 1) × 10²</td>
</tr>
<tr>
<td><em>P. aeruginosa</em></td>
<td>(32.0 ± 1) × 10²</td>
<td>(0 ± 1) × 10²</td>
</tr>
</tbody>
</table>

### (b) Comparison of disinfection efficiency of real swimming pool water

<table>
<thead>
<tr>
<th></th>
<th>C₀</th>
<th>Cᵢ</th>
<th>C₀</th>
<th>Cᵢ</th>
<th>C₀</th>
<th>Cᵢ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UFC/100 ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₀</td>
<td>Cᵢ</td>
<td>C₀</td>
<td>Cᵢ</td>
<td>C₀</td>
<td>Cᵢ</td>
</tr>
<tr>
<td></td>
<td>Anode: Nb/BDD. I = 1.5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>E. coli</em></td>
<td>(46.5±3) × 10²</td>
<td>0</td>
<td>(3.8 ± 1)×10⁴</td>
<td>0</td>
<td>(1.4± 0.2)×10⁶</td>
<td>0</td>
</tr>
<tr>
<td><em>P. aeruginosa</em></td>
<td>(35± 2) × 10²</td>
<td>0</td>
<td>(2.8±1)×10⁴</td>
<td>0</td>
<td>(0.2±0,1)×10⁶</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Anode: Ti/Pt. I = 1.5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>E. coli</em></td>
<td>(3.0 ± 3)×10²</td>
<td>0</td>
<td>(12.6±2)×10⁴</td>
<td>0</td>
<td>(1.18±30)×10⁶</td>
<td>0</td>
</tr>
<tr>
<td><em>P. aeruginosa</em></td>
<td>(21.4± 6)×10²</td>
<td>0</td>
<td>(1.07±1)×10⁴</td>
<td>66 ± 2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Anode: Ti/Pt. I = 3.0A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>E. coli</em></td>
<td>-</td>
<td>(3.8 ±0.4)×10⁴</td>
<td>0</td>
<td>(1.4± 0.2)×10⁶</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><em>P. aeruginosa</em></td>
<td>(2.8±1)×10⁴</td>
<td>0</td>
<td>(0.26±0.1)×10⁶</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>