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# Elektrokimyasal Su Dezenfeksiyonunda Elektrot Tipinin Bakteri Arıtımı ile Klor ve Radikal Üretimine Etkisi

## Effect of Electrode Type on Bacteria Removal with Chlorine and Radical Production in Electrochemical Water Disinfection

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**Öz**

Su kaynaklarında tehlikeli bakteri ve virüs üremesi önemli bir problem olmaya devam etmektedir. Bu kirlenmenin başlıca nedeni, su kaynaklarından önemli bir kısmını oluşturan yeraltı suyunun şehir ve endüstri atıklarından bulaşmaya açık olmasıdır. Bu çalışmada bu tarz suların dezenfeksiyonu için elektrokimyasal arıtım ele alınmaktadır. Literatürde tek tek ele alınmış pek çok elektrokimyasal arıtım çalışması mevcuttur. Bu çalışmada bor kaplı elmas elektrot, iridyum metal-oksit elektrot ve grafit plaka elektrotları ele alınmaktadır. Pek çok elektrokimyasal parametre seviyesinde bakteri ölümleri izlenirken bir yandan da klor ve diğer toksik radikal oluşumları izlenmiştir. Deneyler, gerçek yeraltı suyuna kontrollü şekilde eklenmiş *E.coli* kültürü ile yapılmıştır. Reaksiyon sırasında mikroorganizmalar hem doğrudan elektriksel ve fiziksel nedenlerle, hem de oluşan radikaller nedeniyle ölmektedir. Dolayısıyla arıtım esnasında bakterilerin eliminasyonu ile zehirli çıktı oluşturma arasında hassas bir denge mevcuttur. Bu süreçte mikroorganizmaların biyolojik yapısı ya da yer altı suyunun kimyasal kompozisyonu kontrol edilemeyeceğine göre araştırma parametresi olarak elektrot tipinin değiştirilmesi ve elektrik seviyesinin ayarlanması mantıklı bir yaklaşımdır. Deneysel olarak görülmektedir ki hem sürekli akış, hem de kesikli arıtım sistemlerinde bor kaplamalı elektrotlar, denenenler arasında en ideal seçim olmaktadır, zira dezenfeksiyon seviyelerini iridyum metal-oksit elektrot seçimi kadar yüksek seviyede yapabilirken bir yandan da grafit plaka elektrotlar kadar az miktarda radikal üretmektedir.

***Anahtar Kelimeler:*** *elektrokimyasal dezenfeksiyon, elektrot türleri, bakteri arıtımı, radikal ve oksitlendirici üretimi*

**Abstract**

Formation and contamination of malicious microorganisms and viruses remain to be major problem of water resources. This is mostly due to the fact that, groundwater, which constitutes a large share of available fresh water content, is prone to contamination from urban and industrial wastes. In this work, electrochemical treatment is considered as a disinfection mechanism. The literature presents

several cases of individual of electrochemical disinfection experiments. In this particular work, we aim to focus on the comparative disinfection efficiency of Boron-doped diamond electrodes, Iridium metal-oxide electrodes and Graphite plate electrodes at various electrochemical settings, whilst monitoring formation of toxic bi-products, such as chlorine and other radicals. Experiments of electrochemical water disinfection were carried out on real groundwater samples deliberately contaminated with *E. coli* culture. During the reaction, microorganisms die due to both direct physical damage and due to the electrochemically generated radicals. Therefore, there is a gentle balance of bacteria elimination versus avoiding excessive radical production in the treated water. Since the biological behaviour of the microorganisms and the chemical properties of the available groundwater cannot be changed, the research parameters boil down to experimenting through various popular electrode types and electrical current settings. In both continuous-flow and recursive systems, the Boron-doped diamond electrodes are observed to provide desirable level of disinfection (as good as Iridium metal-oxide), while yielding lower radicals (as low as those of Graphite-plate), making an ideal compromise for the process.

***Keywords:*** *electrochemical disinfection, electrode types, bacteria removal, radical and oxidant formation*

## 1. Introduction

Water pollution is among the most important environmental problems on earth. The source of life for humans, as well as all other living beings is water. Unfortunately, the total amount of usable water in the world is very limited. A large portion (97.5%) of the water stock is in the oceans and in the sea as salty water and only 2.5% of the whole water content is in rivers and lakes in the form of fresh water. Furthermore, 90% of *already* scarce freshwater resources are trapped in the north and south poles, or too deep underground, leaving a significantly small fraction for practical use.

Groundwater can be found in flowing or still forms on saturated soil or in between geological formations. Particularly, underground waters are resisting more to surface contamination and have a relatively stable temperature throughout the year, making it an efficient resource, when available [1]. Such waters are good drinking waters, thanks to the dissolved minerals from geological rocks [2]. Unfortunately, urban and industrial wastes are threatening even the most protected underground water reserves. Among several chemical disposals, pesticides, fertilizers and animal/human wastes are contributing activities for the deterioration of groundwater quality [3]. The resulting contaminated groundwater must be disinfected from pathogenic microorganisms. Due to the described necessity, this research is focused to the popular case of groundwater disinfection.

Disinfection of water is a relatively old concept, where various physical and chemical processes can be applied. Common practices include addition of chemicals, use of physical agents, mechanical tools and radiation. A long-known cheap and effective germ-killing chemical class contains chlorine and its derivatives [4]. Unfortunately, chlorine reacts with organic contaminants in the water and forms carcinogenic substances such as trihalomethanes [5].

Water disinfection can also be performed by electrochemical disinfection systems, as they are more effective than conventional disinfection devices [6–10]. An important advantage of electrochemical disinfection is that disinfecting chemicals can be produced in situ with minimal application area [11, 12]. Therefore, the hazards that may occur during storage and transport of chlorine or other chemicals can be avoided. Electrochemical disinfection is environmentally more friendly, space-saving, low cost and easy to apply; it cleans bacteria, viruses, algae and many other microorganisms from the environment and is suitable for automation [13–17].

Factors such as the type and concentration of the organism, the type, concentration, application time and usage of the disinfectant, physical and chemical properties of the water (temperature, suspended solids, organic material's concentration, pH, etc.) are all influential in the electrochemical disinfection process [16, 18–20]. For a fixed disinfectant concentration, the amount of killed bacteria is expected to be

directly related to the contact time during electrolysis [21].

Studies concerning electrochemical way of disinfection present various parametric alternatives throughout the process. The applied electrical current may be put in DC or AC form, with DC electricity being the effective selection. An obvious parameter to research is the type and structure of the electrode in the reactor. The literature is full of research papers proposing variants of carbon-based, metal-based, or hybrid electrodes. The carbon-based electrode choice includes variations such as low-cost graphite, diamond, or doping of such electrodes with doping from the same group (e.g. Boron-doped diamond) [12, 20, 22–29]. Clasical metals have also been utilized as electrodes [10, 19, 30–34].

Another variation of the electrochemical reaction process is the hybrid use of elecrodes [7, 8, 18, 28, 35–37], or combining electrolysis with other techniques such as nanofiltration [38], membrane technology [23], sunlight [39, 40], Ozone [41], etc. The above-mentioned works present comparably successful results, but do not generally attribute the reason to a particular aspect of the overall mechanism. Consequently, it is difficult to assess the contribution from a specific item, such as the electrode type, only.

In electrochemical water disinfection, various electrode materials can be used, including graphite, granular activated carbon, activated carbon fiber, or metals, such as silver electrodes. In some cases (where the electrical conductivity of the wastewater may be poor), the efficiency of the process may be increased by adding salt ions, such as NaCl or NaBr to the water. The active mechanism of electrochemical water disinfection basically depends on the direct oxidation of the bacteria at the anode or the indirect oxidation of the bacteria in the electrochemical reactor by electrochemically producing an oxidant [7, 42].The radical or non-radical behavior of the electrolysis needs to be investigated for a selected electrochemical disinfection mechanism [24, 25]. In case of disinfection with direct oxidation, electrochemical reactive voltage is applied to induce electron exchange (hence current) and decrease the respiratory activity of bacterial cells and ultimately cause them die [31]. This method is based on the electrochemical oxidation of intracellular coenzyme A [8, 36, 43, 44].

The principle of electrochemical disinfection by indirect oxidation is based on the production of an oxidant in an electrochemical cell [11, 17, 19]. The generated oxidizer is usually chloride [9, 45]. Chloride, which is usually found in water, can be used for the disinfection of pollutants by indirect production of chlorine or hypochlorite via electrochemical oxidation (with or without sodium chloride addition) of water [12, 41, 46]. Another oxidant that is effectively formed during electrochemical disinfection of living organisms in groundwater is persulfate [16, 20, 24, 30]

Tens of different species of microorganisms, ranging in size from viruses to gram-positive or gram-negative bacteria or algae, can be successfully removed from water by electrochemical water treatment [16, 18, 20, 27, 33, 42, 44, 47, 48]. In electrochemical disinfection, the mixture of produced disinfectant and the disinfection by-products can vary according to the composition of the aquatic medium. The components of the mixture, which are oxidants such as reactive oxygen compounds, active chlorine and its compounds, and hydrogen peroxide, all intertwine one another. So, the precise measurement of these components is a challenge.

The information regarding different radicals that form in electrodes at high electrical potentials is well researched, but rather limited [7, 32, 49]. Reactive Oxygen Species (ROS) include not only radicals and ozone, but also $O_2$ - $H_2O_2$ and other species. OH and $O_2$ are known to damage the cell membrane [39, 41]. Loss of membrane permeability will cause the cells to lose their shape and cause sagging and leakage. It has been reported that the elimination of *E. coli* results from cell detachment by ROS followed by peroxidation of the non-saturating phospholipid component in the cell lipid membrane [21, 36, 44, 50].

Use of additive chemicals or materials is also a common practice in electrochemical disinfection [18]. Regarding the conductivity of the water medium, Kerwick et al investigated the effectiveness of electrochemical disinfection against the *E. coli* and bacteriophage MS2 in the model drinking water solution and found that the electrochemical disinfection in both model drinking waters containing NaCl and not

containing NaCl ($Na_2SO_4$) was successful [13]. In another study, Hsu investigated the effect of salt concentration, water flow rate and working temperature on electrolytic production of water for disinfection purposes [51]. Active chlorine production was targeted in the working solution prepared by adding sodium chloride (NaCl) as a salt to the bi-distilled water [9, 12]. Other studies include combined use of chlorine, ozone and electrolytic reactions [41, 52]. Clearly, wastewaters contain complex mixtures of chemical and biological content. Therefore, electrochemical reactions with or without additive materials cause very nonlinear effects. For example, Bergmann and Koparal investigated the formation of chlorodioxide in electrochemical disinfection of drinking water in their study [53]. Such bi-products are difficult to foresee and their formation may impose potential health risks. Hence, assessment of electrochemical process items in terms of effectiveness as well as unintentional bi-products remains to be an important research issue.

The above studies are among the landmarks of electrochemical disinfection. They consider various aspects of the electrochemical process, ranging from novel proposals of electrodes to combination of the process with different tools, such as sunlight or membranes. However, the studies mostly propose one particular method and tries to locate it well in the related literature. There are also comparative studies, but the comparisons are either among different works from literature (where the water compositions may not be equated) or with respect to a homogeneous group of electrodes, such as metals. Although radical generation is always mentioned, a unified and comparative assessment for excess radical generation together with disinfection efficiency was not encountered in the literature. In this study, the effect of electrode type selection on groundwater disinfection is considered from a perspective of joint disinfection efficiency and radical formation in parallel plate reactors. Since disinfection efficiency is positively affected by all types of oxidants and radicals, overall disinfection should not be considered as a unitary success parameter. Therefore, in this work, radical bi-products are simultaneously monitored. In the experimental studies, electrochemical disinfection of additive *E. coli* culture was carried out in real groundwater samples using three different electrodes in recursive and continuous flow systems at different flow rates and different current densities in a parallel plate reactor. The electrodes were selected from a different range of materials, but only among the ones with scientifically proven reputations. Boron-doped diamond electrodes are praised for their successful overall results and graphite plates are low cost for production and maintenance. The third electrode was also chosen to be a successful one; Iridium metal-oxide plates [10]. Although the popularity of these types of electrodes are lower due to their manufacturing difficulties, their oxidizing capability are known to be among the highest. The effect of these electrodes in both bacteria removal and chlorine and radical formation was investigated. A compromise between the two aspects are expected in all electrode cases. However, at the same working conditions, it is also expected that electrode type should significantly affect the useful point of minimal radical formation with maximum disinfection efficiency.

## 2. Material and Method

### 2.1. Water Samples

Actual samples of groundwater from Eskişehir (Muttalip suburb) area was used during the study. Average chemical composition and microbiological status of groundwater were analysed and given in Table 1.

**Table 1.** Properties of the used underground water

| *Parameters* | **(mg/l)** |
|---|---|
| Chloride ($Cl^-$) | 50 |
| Nitrite nitrogen ($NO_2$-N) | - |
| Nitrate nitrogen ($NO_3$-N) | 4,5 |
| Sulfate ($SO_4^{-2}$) | 108 |
| Total Organic Carbon (TOC) | 19 |
| Carbonate ($CO_3^{-2}$) | 185 |
| pH | 7,8 |
| **Conductivity** | 700-900 µs/cm |

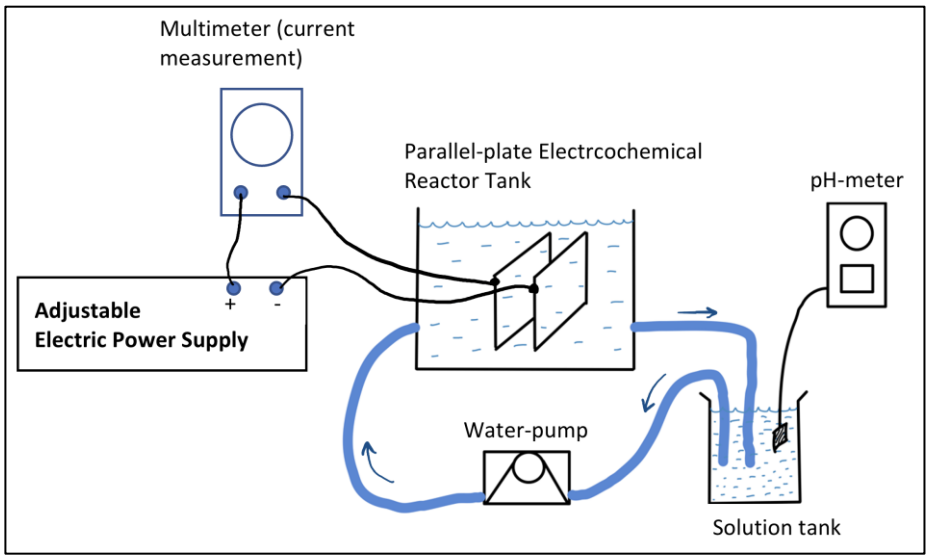



**Figure 1.** Electrochemical reactor setup.

The presented values are nominal and depending on the time the sample water was acquired, the ion concentrations were observed to vary around 10%. The actual groundwater samples were, then, deliberately contaminated with *E. coli* culture (ATCC 25922). *E. coli* was incubated in 500 ml sterile broth for 24 hours at 37°C. The microorganism was centrifuged at 9000 rpm for 10 minutes in a centrifuge tube and the cell suspension with about $10^5$ cfu of *E. coli* bacteria was seeded in the sample groundwater to mimic contamination of approximately $10^5$ cfu/ml for the experiments. Seeding was performed together with shaking to improve homogeneous suspension of the bacteria. Furthermore, the flow due to the reactor process pump (Figure 1) also helps the bacteria to sustain a homogeneous suspension throughout the process.

### 2.2. Electrochemical Experiments

Electrochemical water disinfection was applied in parallel plate reactors with

- Boron-doped diamond,
- Iridium metal-oxide, and
- graphite plate

electrodes. These electrode types were deliberately chosen to comprise well proven disinfection tools in the literature, due to various strengths such as successful disinfection efficiency or low operational costs. The bacteria-wise contaminated real water samples were passed through a parallel plate reactor with recursive and continuous flow systems. According to the lab instrument limits, the electrical current densities of 10, 20, and 30 mA/cm$^2$ and water flow rates of 50, 100 and 150 ml/min were applied and tested. Water was pumped through the reactor via a peristaltic pump and the resulting solution was either fed back (recursive) or collected (continuous flow) according to the adopted system. For both systems, all pairs of Boron-doped diamond electrodes, Iridium metal-oxide electrodes and graphite plate electrodes were tested. In order to make a fair assessment, both the anode and the cathode electrodes were set to have the same electrode type, each with a plate size of 4,5cm × 3,1cm, completely submerged. An illustration of the applied electrochemical process setup is illustrated in Figure 1.

A standard plaque counting method was used to determine the bacterial concentration in output solutions. At the beginning and at every 2-minute intervals, samples were collected from the reactor outlet with 0.1 ml 0.1 N thiosulfate tubes and were sown on Petri dishes with Nutrient agar. The number of living cells was

determined by counting the colonies formed after 24 hours of incubation at 37°C. At the end of the electrochemical processes, pH values were observed to remain between 7,2 and 7,4 for all experiments.

The process of oxidizer and chlorine production normally depends on the utilized electrodes in the electrochemical process. However, the general electrochemical reactions for the oxidizer generation can be expressed as the following reactions:

$$M + H_2O \rightarrow M(HO^{\cdot}) + H^+ + e^-$$

$$HO^{\cdot} \rightarrow O^{\cdot} + H^+ + e^-$$

$$O^{\cdot} + O_2 \rightarrow O_3 ,$$

where *M* can be due to any active electrode. Apart from these reactive oxygen species, the liquid mixtures may also yield chlorine, which is a measurement parameter of this particular research:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \rightarrow Cl^- + HClO + H^+$$

$$HClO \rightarrow ClO^- + H^+ .$$

In this paper, chlorine measurement and total oxidizer measurements were carried out as explained in Sections 2.3 and 2.4.

### 2.3. Chlorine Determination

Chlorine determination was carried out using analysis kits supplied by Lange-Hach company. The working mechanism of the kit is based on spectrophotometric measurement of red color produced by the reaction of chlorine with Diethyl-p-phenylenediamine (DPD) [54].

### 2.4. Radical (Total Oxidizer) Determination

Determination of radicals was carried out by the spectrophotometric method. A 1.5 ml sample taken from the outlet of the reactor was treated with 0.75 ml of 0.1 M potassium biphthalate and 0.75 ml of iodine separator (0.4 M KI, 0.06 M NaOH, ~ $10^{-4}$ M ammonium molybdate) in a 1 $cm^3$ quartz tube. The absorbance of the processed solution at 352 nm wavelength was measured by UV-VIS Spectrophotometer. Outputs are presented as the total value of oxidants that can be measured as hydrogen peroxide and are expressed as hydrogen peroxide equivalent [55].

### 2.5. Tools and Chemical Materials

Nutrient broth (MERCK) was used to prepare overnight bacterial cultures and their dilutions, and Plate Count Agar was prepared to determine the number of viable bacteria in the samples taken throughout the treatment process. For free radical determination, the solutions were prepared using sodium thiosulfate ($Na_2SO_4$, MERCK), potassium biphthalate ($KHC_8H_8O_4$, MERCK), potassium iodide (KI, MERCK), sodium hydroxide (NaOH, MERCK), and ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$, MERCK).

Significant chemical parameters for water electrochemical disinfection were measured by HACH and Dr-Lange DR 2800 spectrophotometer. Groundwater conductivity measurements were made by a Pioneer 30 portable conductivity meter and pH measurements were made by the WTW pH 740 model pH-meter. Other laboratory tools that were necessary for the experiments include Tektronix PS282 DC power supply, Masterflex model 755-375 peristaltic pump, and OHAUS Explorer Pro model analytical balance for weighing. All materials used in bacteriological studies were sterilized in NUVE OT 4060 autoclave (121°C, 20 minutes). Electromag M420 BP model incubator was used for bacterial incubation. Bacterial cultivation was carried out in Heraus KSP 18 Class II sterile cabin. Pioneer 30 water bed was used for fixing temperatures.

## 3. Results and Discussion

### 3.1. Recursive system studies

#### 3.1.1. Disinfection studies

This set of treatment experiments were carried out at electrical current densities of 10, 20 and 30 $mA/cm^2$ and liquid flow rates of 50, 100 and 150 ml/min for all electrode types on a recursive reactor flow.

The disinfection success results at 150 ml/min flow rate and varying electrical current densities for the tested electrodes are given in Fig. 2. The disinfection efficiency order from most to least successful electrode type can be listed as Iridium metal-oxide (Fig. 2(b) with its fastest microorganism killing), then Boron-doped diamond, and lastly graphite plate electrodes. However, it can be seen that Boron-doped diamond electrodes also kill the microorganisms at a reasonable time, quite close to Iridium

metal-oxide plates. Unfortunately, despite their low cost for manufacturing and maintenance, the graphite plate electrodes (Fig. 2(c)) suffer in disinfection, particularly at low electrical current rates. These results are in accordance with the observations of Martinez-Huitle and Brillas, although the considered water output was aimed to be drinking water [46]. For drinking water, different electrode types (such as DiaCell) with Boron-doped electrodes were also observed to perform well at 150 mA/cm$^2$ in [46], however that high current rate was neither available in our parallel-plate reactors with the available groundwater samples, nor was it necessary. It can be seen that higher current densities are not a requirement, as the $10^5$ cfu/ml bacterial concentration was observed to vanish within the experiment durations at 30 mA/cm$^2$ current density for most of the cases. Lower flow rates (i.e. 50 and 100 ml/min) are not presented in this paper, as they gave lower disinfection rates. This interesting observation can be attributed to the fact that the chemicals formed at the electrode surfaces may be more quickly and efficiently dispersed into the liquid volume by creating a more turbulent regime at high flow rates.

### 3.1.2. Chlorine Produced in Electrochemical Reactors

In order to provide a more useful assessment, chlorine production (as well as total oxidizer production) must also be monitored, where less of their excess production would correspond to a more useful disinfection output. Consequently, using the same set of electrode materials, chlorine production was studied. Among the utilized electrode materials, it was observed that the highest production of total chlorine was obtained with Iridium metal-oxide electrodes (Fig. 4), followed by Boron-doped diamond electrodes (Fig. 3) and graphite plate electrodes being the least chlorine-producing electrode (Fig. 5). Clearly, this observation is on par with the disinfection efficiency ordering provided in 3.1.1, as well as the general observations of Li and Ni [57], where disinfection byproducts and their time variations were investigated for Boron-doped diamond electrodes. Similarly, the observation of chlorine generation curves are similar to those in [53] using iridium metal-oxide electrodes.

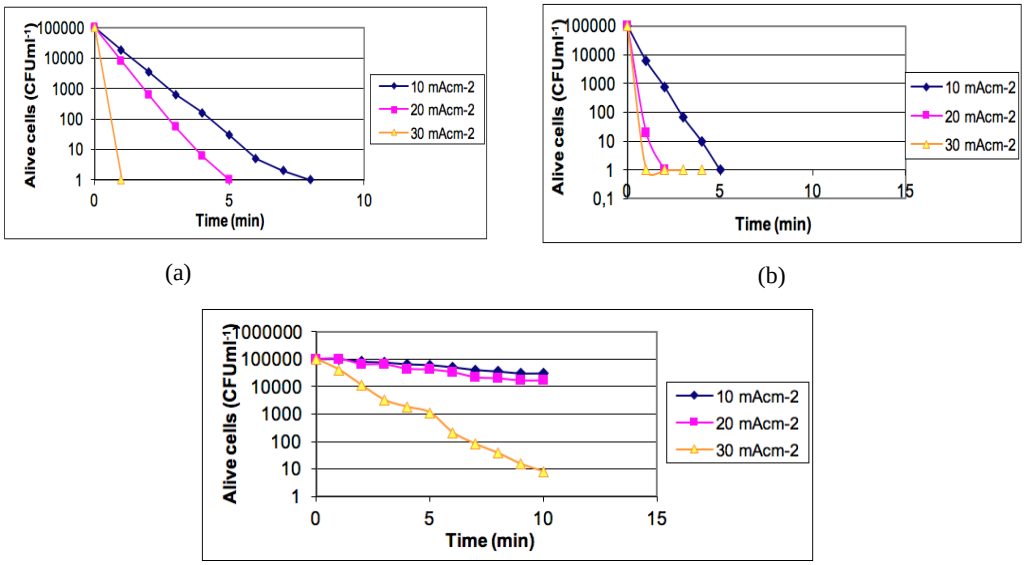
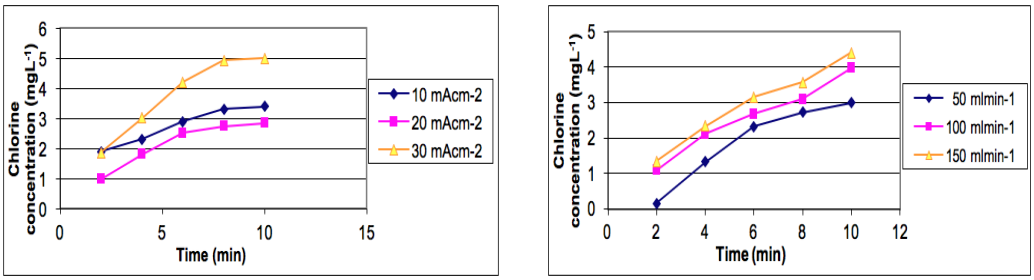
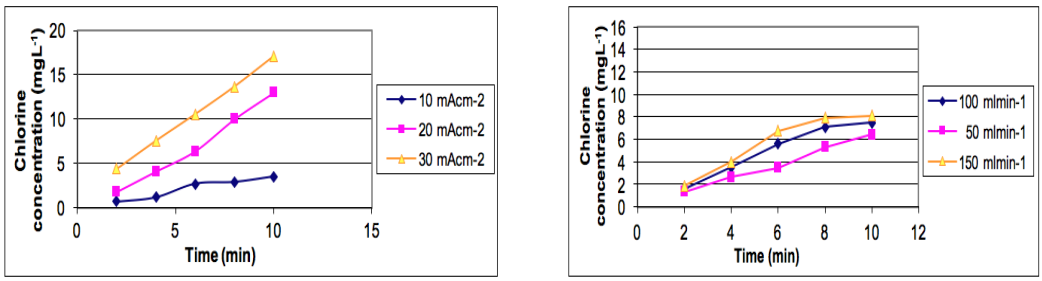



**Figure 2.** Effect of current density on cell survival rate with (a) Boron-doped diamond electrodes, (b) Iridium metal-oxide electrodes, (c) graphite plate electrodes, all in parallel plate reactor.



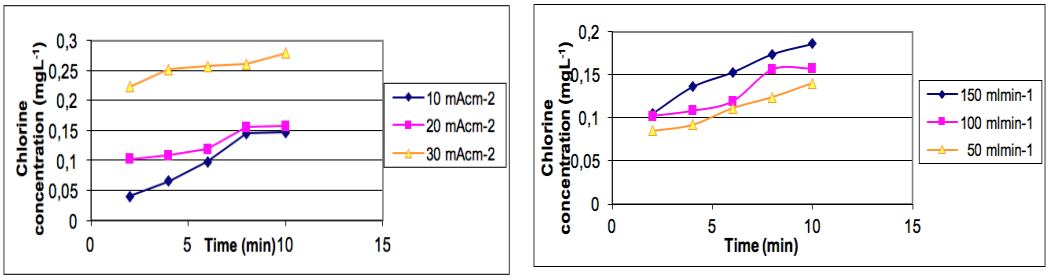

(a) (b)

**Figure 3.** Effect of Boron-doped diamond electrodes on the amount of chlorine production according to (a) current density in parallel plate reactor with flow rate 150 ml/min; (b) flow rate in parallel plate reactor, current density 30 mA/cm$^2$.




(a) (b)

**Figure 4.** Effect of Iridium metal-oxide electrodes on the amount of chlorine production according to (a) current density in parallel plate reactor with flow rate 150 ml/min; (b) flow rate in parallel plate reactor, current density 30 mA/cm$^2$.




(a) (b)

**Figure 5.** Effect of Graphite plate electrodes on the amount of chlorine production according to (a) current density in parallel plate reactor with flow rate 150 ml/min; (b) flow rate in parallel plate reactor, current density 30 mA/cm$^2$.

An immediate observation of our experiments is that, despite a relatively close disinfection performance of Boron-doped diamond and Iridium metal-oxide electrodes, Iridium metal-oxide electrodes cause significantly more excess chlorine, which may be considered relatively undesirable.

Again, three different current densities (10 mA/cm$^2$, 20 mA/cm$^2$, 30 mA/cm$^2$) were used for electrochemical disinfection and electrochemical chlorine production. The number of surviving bacteria drops rapidly with increasing current density, as more total chlorine is produced electrochemically at higher current densities (Fig.s 3-4-5 (a)).

With the available flow rates of 50 ml/min, 100 ml/min and 150 ml/min for all electrode materials, it was observed that higher chlorine production was obtained at high flow rates (Fig.s 3-4-5 (b)). Similar to the argument in 3.1.1, it is argued that the higher flow rates increase mass transfer (of disinfection-active chemicals, including chlorine) rate from the electrode surfaces to the other water portions, yielding a more efficient contact of chlorine with the microorganisms. Besides, faster transfer of these chemicals away from the plates also helps faster re-generations on the electrode surfaces.

### 3.1.3. Radicals (Total Oxidizers) Produced in Electrochemical Reactors

In this part of the studies, the production of radicals (i.e. total oxidizers) were investigated at the same settings as given above. The total value of the oxidants is measured and expressed as the hydrogen peroxide equivalent. Again, current densities of 10 mA/cm$^2$, 20 mA/cm$^2$ and 30 mA/cm$^2$ were applied to monitor electrochemical oxidant production. As expected, due to the electrochemical production of total oxidizing material at high current densities, the number of surviving bacteria rapidly drops with increasing current density (Fig.s 6-7-8 (a)). This observation is in accordance with the disinfection results in 3.1.1 [17, 53, 57].

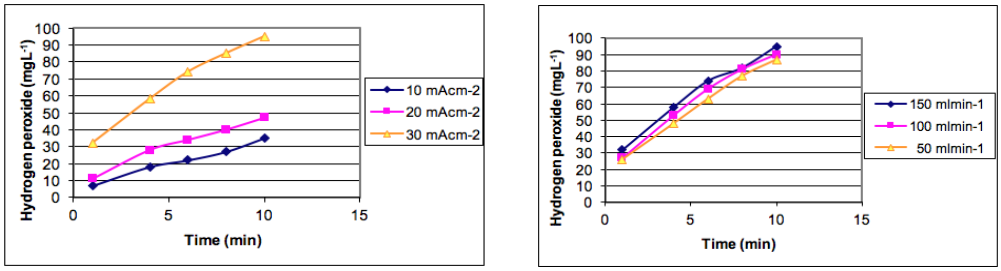
Using the flow rates of 50 ml/min, 100 ml/min and 150 ml/min, it was observed that the oxidative production is higher at higher flow rates (Fig.s 6-7-8 (b)). As in the case of chlorine production, it is argued that the mass transfer from the electrode surface increases at high flow rates and contribute to the transition of the chemicals and radicals towards other liquid parts. Eventually, the contact probability of radicals and microorganisms increase, and re-production of the radicals becomes easier on the electrode surface with reduced radical density along the surfaces.

Using the corresponding measurements, the total oxidant production was found highest with the Iridium metal-oxide electrode material among the three electrode materials used (Fig.s 6-7 (b)). The second total oxidant-producing electrode was, again, Boron-doped diamond electrodes, and least efficient one was graphite plate electrodes, similar to the disinfection (Sec. 3.1.1) and chlorine production (Sec. 3.1.2) cases (Fig.s 6, 8).

As a critical observation, the total oxidizer production of Iridium metal-oxide electrode case is found to be quite more than that of Boron-doped diamond electrodes, although their disinfection results are more or less similar. From this perspective, it is not an immediate conclusion that Iridium metal-oxide electrodes are more useful for disinfection. If the disinfection output waters are to be used for drinking or discharged to places where aquatic animals live (i.e. lakes with fish), excess radicals may be undesirable, and utilization of Iridium metal-oxide electrodes may not be favoured. Therefore, a decisive choice of Iridium metal-oxide electrodes used at a current density of 30 mA/cm$^2$ and a flow rate of 150 ml/min must be well questioned.

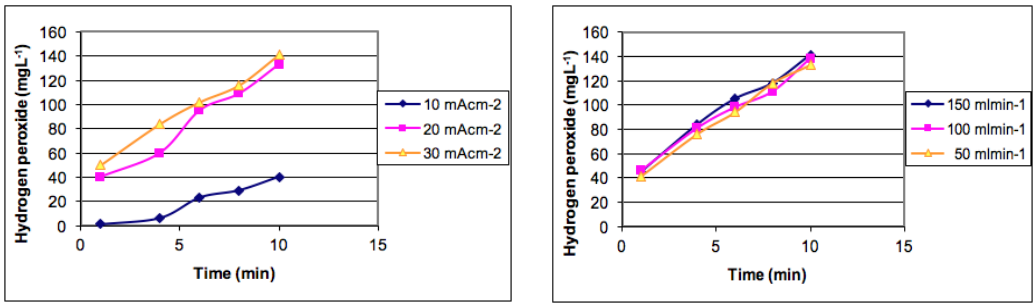
### 3.2. Disinfection studies by continuous flow method

In order to make a fair comparison of the efficiencies of electrodes and electrical current density, continuous flow experiments were also conducted with the same reactors. Similar to the recursive treatment experiments, a constant amount of $10^5$ cfu/ml bacteria-enriched water was used with three different electrode materials. The results were found to be quite parallel to the results from recursive processes (3.1). These results indicate that the observation of Rahmani et al regarding electrolyisis exposition is the foremost critical issue in both oxidant generation and disinfection [7].



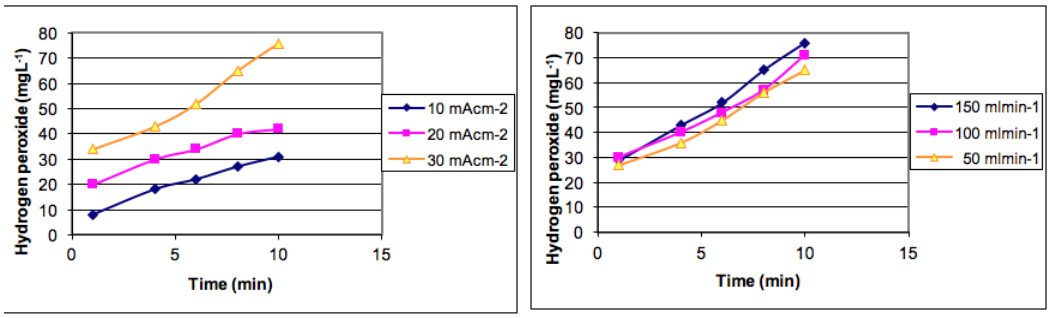

(a) (b)

**Figure 6.** Using Boron-doped diamond electrodes in parallel plate reactor; effect of (a) current density at flow rate of 150 ml/min, (b) flow rate at current density of 30 mA/cm$^2$.




(a) (b)

**Figure 7.** Using Iridium metal-oxide electrodes in parallel plate reactor; effect of (a) current density at flow rate of 150 ml/min, (b) flow rate at current density of 30 mA/cm$^2$.




(a) (b)

**Figure 8.** Using Graphite plate electrodes in parallel plate reactor; effect of (a) current density at flow rate of 150 ml/min, (b) flow rate at current density of 30 mA/cm$^2$.

Similar to the recursive studies, at 30 mA/cm$^2$ electrical current density, it was observed that all of the $10^5$ cfu/ml bacteria died with Iridium metal-oxide and Boron-doped diamond electrodes, and the number of surviving bacteria was only decreased in graphite electrodes. The performance was observed to marginally decrease at lower electrical current densities. The results in this section are presented in a compact form in Table 2.

The relation between chlorine and hydrogen peroxide was also found to be positively correlated to the disinfection success, and the observations share the same ordering as in case of recursive processes. It is clearly evident that the used electrochemical disinfection systems are suitable for continuous disinfection. However, the compromise between excess oxidizers and fast disinfection remains to be a critical issue for continuous process, similar to the observation in 3.1.3. Again, despite its aggressive disinfection strength, the excess chlorine and total oxidizer production with the Iridium metal-oxide electrode may render its use for certain applications obsolete.

**Table 2.** Test results in continuous flow method at parallel plate reactor

| | Boron-doped diamond electrode | Graphite plate electrode | Iridium metal-oxide electrode |
|---|---|---|---|
| Chlorine concentration (mg/L) | 0,833 | 0,173 | 4,2 |
| Hydrogen peroxide concentration (mg/L) | 30 | 130 | 90 |
| **Bacterial concentration after disinfection (CFU/mL)** | 5 | 10 | 1 |

## 4. Conclusion and Recommendations

This study provides comparative results to the electrochemical disinfection methods applied on real-life groundwater samples contaminated with *E. coli* bacteria. Electrochemical generation of oxidizers and direct termination of bacteria in water is a known mechanism for disinfection. In that aspect, the results herein constitute experimental verifications to the effectiveness electrochemical methods. On the other hand, real-life groundwater is a chemically complex medium and application of electrochemical methods produce varying effects of chlorine or other radical generation as well as different success rates of bacteria termination. Therefore, a direct comparison of the obtained results the ones available in the literature is technically not possible. For instance, the works by Diao et al, Bergman et al and Scialdone et al show the existence of oxidizer production and indicates/explains the disinfection process, but do not provide *any* quantitative results for the oxidizers or the disinfection rates [52, 53, 56]. The work by Martinez-Huitle and Brillas provide a detailed analysis of electrochemical methods for disinfection, however the scope was limited to drinking water case, unlike the groundwater application herein [46]. In another comprehensive work by Rahmani et al, disinfection rates of various electrode materials were compared [7]. However, the Boron-doped diamond electrode was not among the tested; furthermore, excess oxidant production was neither considered nor monitored. While Isidaro et al consider Boron-doped diamond electrodes and emphasize on the avoidance necessity of excess chlorates, a comparison with other electrode types were missing [23].

In order to constitute a novel comparison axis of "good disinfection with low excess oxidant

generation" versus "different electrodes at different electrochemical settings", a months-long set of experiments were conducted. A wide set of parametric settings were applied to observe which electrode performs how in the disinfection process. Two highly efficient electrode types (Iridium metal-oxide and Boron-doped diamond) and a low-cost electrode type (graphite plates) were tested to cover a range of possible outcomes. With no surprise, graphite plate electrodes were below the performance of Iridium metal-oxide or Boron-doped diamond electrodes, at any electrical current density or water flow rate. This observation was in parallel with the results of Battisti et al, despite that work being for different reactor structures with different electrical current settings [17].

Due to a more efficient mass transfer from the electrode surface at high flow rates, the flow rate of 150ml/min (as opposed to slower rates of 50 and 100 ml/min) causes faster transition of the chemicals and radicals towards other liquid parts. Eventually, the contact probability of radicals and microorganisms increase, re-production of the radicals becomes easier on the electrode surface with reduced radical density along the surfaces, and overall disinfection efficiency increases.

Both Iridium metal-oxide and Boron-doped diamond electrode cases were capable of eliminating $10^5$ cfu/ml of bacteria within few minutes at electrical current densities of 10, 20 and 30 mA/cm$^2$, with Iridium metal-oxide electrodes having a slight edge over Boron-doped diamond electrodes in terms of microorganism-killing efficiency. Therefore, if killing of bacteria is the sole motivation, Iridium metal-oxide electrodes must be chosen among these electrode types at any electrical current density setting, including drinking water disinfection applications [46]. Unfortunately, it was also observed that the disinfection success goes side-by-side with higher production of chlorine and radicals. Therefore, according to the application reasoning of the disinfection system, special care must be taken regarding the production of excess radicals. At this point, the overly high efficiency of Iridium metal-oxide electrodes in radical generation may be considered "unworthy" despite its slightly higher disinfection efficiency as compared to the Boron-doped diamond electrodes, at the expense of significantly higher excess chlorine and oxidants. Time-wise, both electrodes eliminate microorganisms at a reasonable amount of time (10 minutes) with analogous settings. Therefore, due to its lower chlorine and oxidant generation, Boron-doped diamond electrodes may be favoured if the disinfection output water is destined to drinking medium or aquatic environments with living animals. The observations are very similar in both recursive and continuous flow electrochemical disinfection systems.

It remains to be an interesting study to further investigate various other electrode types, or even their combinations as anode – cathode pairs, as long as the experiments could be carried out on the similar groundwater conditions. Unfortunately, the physical and duration-wise experimental capabilities are limited for any scientific team, therefore further experiments must be left as possible future studies. Nonetheless, consideration of multiple aspects is proposed as a necessity for any such future work. Together with the generated radicals and debris of killed bacteria at high current density conditions, there is a chance that the result may be toxic. Therefore, another noteworthy continuation of this study would be regarding a toxicity analysis of the disinfection output.

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