A patent review of technologies for wastewater treatment by electrochemical oxidation with boron doped diamond electrodes

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5. A patent review of technologies for wastewater treatment by electrochemical oxidation with boron doped diamond electrodes

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Abstract. This chapter reviews the developments of the boron doped diamond electrodes through patent applications in the most import patent offices of the world. A special focus was given to the treatment of wastewater considering four topics: synthesis of novel materials, industrial applications, disinfection processes and commercial non-industrial applications. A total of 74 patents and patent applications were analyzed, finding that despite of being a novel technology, electrochemical wastewater treatments with boron-doped diamond electrodes present an interesting dynamic of innovation, with a growing interest by researchers and industry on the development of new methods of production, reactors and applications.

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Introduction

Wastewater treatment for residential or industrial processes has had a special interest in the last 50 years, due to the strengthening of environmental regulations. As a result, a large number of technologies has been studied, such as physicochemical, chemical, microbiological and electrochemical treatments.

In this latter category, the electrochemical oxidation processes, particularly the ones involving boron doped diamond (BDD) electrodes are one of the most promising techniques because of its high current efficiency, electrochemical stability, corrosion stability even in very aggressive media, inert surface with low adsorption properties and a wide potential window that promotes the discharge of water and the subsequent formation of reactive physisorbed ●OH radical that allow the complete degradation of organic compounds [16]; as it has been reported in multiple studies in the laboratory and pilot scale for the treatment of different types of pollutants [1-6], synthetic wastewaters [2, 7-9], actual industrial wastewaters [2, 10-15] and water and wastewater disinfection [16].

The BDD electrochemical treatment, consist in the oxidation of pollutants in an electrolytic cell, mediated by hydroxyl radicals (●OH). The mechanism begins when H2O is oxidized at the anode to produce slightly adsorbed hydroxyl radicals in the electrode surface (Eq. 1), causing the combustion of any organic molecule that reaches this zone, producing CO_2 and H_2O, as shown in Equation 2 [16].

$$H_2O + BDD \rightarrow BDD(\bullet OH) + H^+ + e^- \qquad \text{(Eq.1)}$$

$$BDD(\bullet OH) + R \rightarrow BDD + CO_2 + H_2O + H^+ + e^- \qquad \text{(Eq.2)}$$

Furthermore, depending on the concentration of certain precursors on the wastewater or the electrolyte, several electrochemical generated species like ozone, chlorine ion, hypochlorite, hypochlorous acid, persulfate and sulfate ion, among others, can be produced, which enhance the oxidation process and more easily degrade the strong pollutants [16]. There are even some electrochemical processes with BDD, in which the final product are these generated species at high concentration, which are afterward sold for use in disinfection, cleaning and bleaching procedures.

The aim of this chapter is to review major advances in wastewater treatments by electrochemical oxidation with boron doped diamond electrodes, specifically patent applications and patents granted in major patent offices in the world: United States, Europe and Japan, as well as via the Patent Cooperation Treaty PCT published by the World Intellectual Property Organization(WIPO).

1. Methodology

Initially, several patent search engines were used including: Espacenet, USTPO, WIPO, Google Patents and Acclaim, IP; for the initial query: "boron doped diamond". Without fixing the date range, due to the novelty of this technology.

The results of the initial query were compared and the search engines with more results were preselected (Google Patents and AcclaimIP). However, AcclaimIP was selected over Google Patents, because it allows the execution of complex queries, data export and advanced analysis of the documents.

The consulted databases of patents and patent applications are listed below:

- USPT: Patents for the U.S. Patent and Trademark Office (PTO)
- USAPP: Patent Applications to the U.S. Patent and Trademark Office (PTO)
- EP: Patents and applications of the European Patent Office (EPO)
- JP: Patents and applications of the Japan Patent Office
- WIPO: Database Applications PCT via the World Intellectual Property Organization (WIPO)

A preliminary study was performed in order to limit the results to those related exactly to wastewater treatment with electrochemical oxidation with BDD electrode by sorting the search results through its four-digit international patent classification, as reported in figure 1.

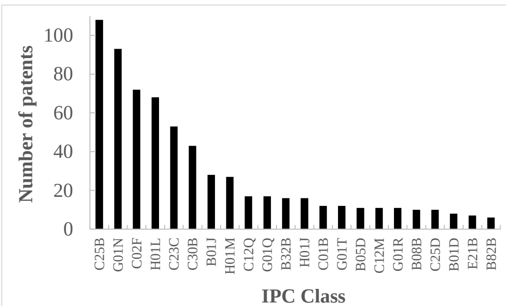

Figure 1. Number of patents by IPC classification to 4 digits.

The keywords chosen were "boron doped diamond", "diamond anode "and "diamond electrode", and the search was restricted to the results that contained those keywords in their claims (ACLM) . Therefore the search equation at this stage was:

(ACLM:("Boron doped diamond" or "diamond anode" or "diamond electrode"))

The results in Figure 1 show that the highest number of patents related to the subject of BDD electrodes are classified into electrolytic production of inorganic compounds or non-metals (C25B), equipment and methods for analysis of chemical and physical properties of materials (G01N) and treatment of water, wastewater and sludge (C02F). The “C02F” classification (72 results) was the most import category for this research. This category includes the following subcategories that are directly related to the fundamentals of this investigation:

- C02F1/46 wastewater treatment by electrochemical methods.
- C02F1/467 wastewater treatment by electrochemical disinfection.
- C02F1/461 wastewater treatment by electrolysis.

Therefore, the query was constricted to include only patents classified as “C02F”. As a result, the search equation used for this research was:

((ACLM : (" Boron doped diamond" or "diamond anode " or "diamond electrode")) AND IPCR : C02F)

Furthermore, an additional sub-category was investigated for the disinfection processes (A61L). These results were included in the investigation in section 5.

On the other hand, Journal Articles and Reviews data, were collected from the document database Scopus ®, using the following search equation:

TITLE-ABS-KEY(" Boron doped diamond" OR "diamond anode" OR "diamond electrode" AND wastewater) AND (LIMIT-TO(DOCTYPE, "ar") OR LIMIT-TO(DOCTYPE, "re"))

The patent and article searches were conducted between June 2013 and March 2014.

2. Overview

The examination of 74 patents and patent applications on technologies for treating wastewater by electrochemical oxidation with BDD electrodes shows the novelty of the technology, since the first application appeared in 1998, presenting a subsequently exponential growth during the first four years of XXI century. The production of new technology related to the topic seems to stagnate between 2004 and 2007, and then present an explosive growth in 2008. Between 2011 and 2012 there is again a large number of patents published (twelve), as shown in figure 2.

The historical trend of the published patents is almost identical to the one displayed by the 229 published articles of the topic. In fact the first journal publication was done one year after the first published patent (1998 and 1999, respectively) and the peaks and valleys on both graphs occurs in the same years. The other studied variable was the number of citations presented by these documents, which exhibits and exponential growth, reaching 1302 citations in the 2012 out of 6836 from 2000 to 2012; it is important to note that these citation came from over 3000 papers.

In the geographical field, the main patent applicants come from the United States of America and Japan (Table 1). In fact, Japanese scientists at the Institute of Physical and Chemical Research (RIKEN) reported the first application of diamond electrochemistry in science literature [17]. Another interesting issue in the applicant list (Table 1) is that almost 90% of all the applicants for intellectual property rights on this topic come from multinational corporations such as Permelec, Fuji or Dow, while universities or individuals represents a small proportion of the total.

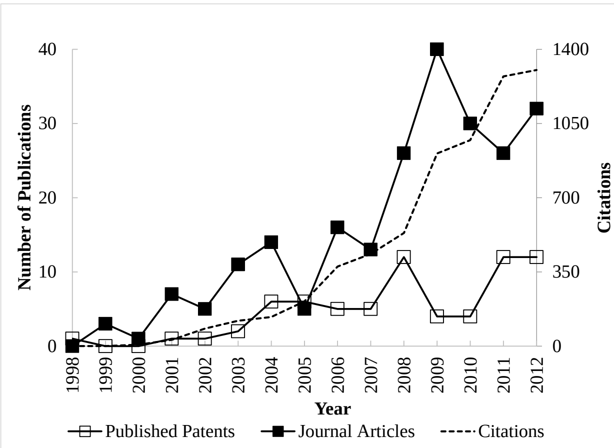

Figure 2. Number of published patents including patent applications (left Y-Axis), journal articles (left Y-Axis) and journal articles citations (right Y-Axis) of wastewater treatment by electro-oxidation with BDD in the period of 1998-2012.

Table 1. Applicant list of patents related to wastewater treatments by electro-oxidation with BDD.

Applicant	Number of granted patents or applications *	Country of origin
Permelec Electrode LTD	4	Japan
Pro Aqua Diamantelektroden Produktion	4	Austria
Sumitomo Electric Hardmetal COR.	3	Japan
Watkins Manufacturing Corporation	3	EE.UU
Element Six LTD	3	Luxemburg
Industrie De Nora S.p.A.	2	Italy
Michigan State University & USA Energy Depart.	2	EE.UU
Kurita Water Industries LTD	2	Japan
Schwartzel, David, T.; Fraim, Michael, L.	2	EE.UU
A-Zone Technologies LTD	1	U.K
Battelle Energy Alliance, LLC	1	EE.UU
Deshmukh, Prasanna	1	India
Dow Global Technologies INC	1	EE.UU
Fuji Photo Film Co LTD	1	Japan
Kabushiki Kaisha Kobe Seiko Sho	1	Japan
Linxross INC	1	Japan
Lynntech INC	1	EE.UU
Proterrgo INC	1	Canada
RWO GmbH	1	Germany
Apollo Diamond INC	1	EE.UU
Siemens AG	1	Germany

Table 1. Continued

Applicant	Number of granted patents or applications *	Country of origin
The Secretary of the Navy of EE.UU	1	EE.UU
Unilever	1	UK/Netherlands
Vws (UK) LTD	1	UK
Windsor Scientific LTD	1	UK
Xh2o Solutions Private LTD	1	India
Hydac Filtertechnik GmbH	1	Germany

* one for each patent family.

The following sections are a compilation of the main inventions on the field. For practical reasons the inventions were further divided into four sections: (3) the synthesis of new materials and their use in wastewater treatment, (4) the industrial wastewater applications, (5) the disinfection processes, and (6) the commercial applications for non-industrial water treatment.

3. Synthesis of novel materials and their use in wastewater treatment

The first patent on the subject was published in 1998 and was presented by the Japanese companies Kobe and Seiko [18]. It shows a method of manufacturing diamond electrodes with high electrical efficiency, long life, high capacity to be reusable and specially a wide potential of application in wastewater treatment. In 2001, the United States Navy introduced a new breakthrough in the field with the development of a BDD electrode supported on a metal mesh [19] that can be used into electrochemical reactions for organic pollutants removal, either as anode or as cathode, which dramatically increase the active electrode area influencing favorably the process efficiency.

In 2004 a novel diamond electrode material was presented [20] having a long life and an strong oxidation power, by combining a conventional diamond electrode supported on a catalyst layer like titanium oxide powder

(Fig. 3A), which improved the conductivity without forming a stable oxide layer on the substrate surface.

An interesting invention in the field was the improvements made to prevent hydrogen evolution at the cathode of the electrochemical cells used with BDD anodes; in 2004 a patent application 2004 [21], which was granted in 2007, uses gas diffusion electrodes as cathodes that reduces atmospheric oxygen to hydroxyl ions or hydrogen peroxide. This development intended to solve the problem of bubbling and loss of efficiency by the foam generated in the electro-oxidation process, and allows the production of hydrogen peroxide at the cathode, that may act as an oxidant for the pollutants.

In 2006, the company Element Six [22] enhance the deposition of the diamond layers by applying new conditions in the method of chemical vapor deposition (CVD) which improve the chemical stability of the material and allow the production of an inert electrode. In 2008, the company also patented the first method for the production and use of bipolar boron doped diamond electrodes [23] as shown in figure 3B.

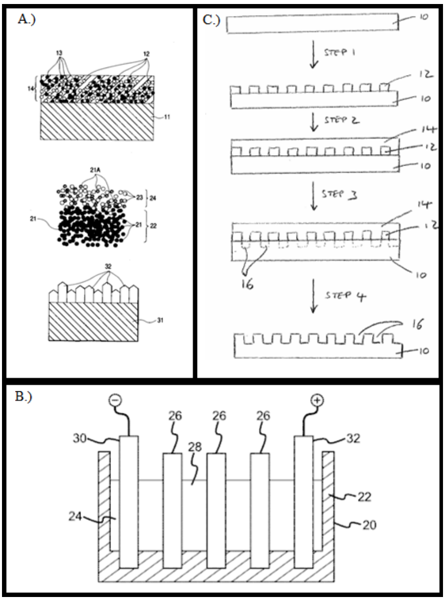

Figure 3. A.) BDD electrode with titanium dioxide, (ref [20]). B.) Bipolar BDD electrodes array (ref. [23]). C.) Slotted BDD electrode (ref. [25]).

In the recent years, there has been progress in the adhesion of the diamond film on the substrate [24], making possible the formation of a nonporous surface diamond and avoiding the deterioration of the electrodes caused by the separation of the film, which enables the use of these electrodes in severe electrolysis conditions, such as working on solution containing highly oxidizing substances and at high current densities.

Furthermore, in 2012 was published a patent for the production and use of three-dimensional BDD electrodes, with canals for improving the efficiency of fluid transport at the anode surface [25] (Fig. 3.C). The electrode, in this case is oriented within the electrochemical device so that the canals are aligned in a direction parallel to the flow of the electrolyte, enhancing the mass transfer of organics to the electrode surface, where oxidation mediated via hydroxyl radicals occurs.

4. Industrial wastewater applications

The first reference on applications of industrial wastewater treatment with BDD electrodes is the patent issued in 2002, which discloses a method for the production of ozone [26] (Fig. 4). The method claimed to achieve high concentrations of ozone in water (15-20 w/w%). Curiously, the first patented application with BDD electrodes was issued for the oxidation of pollutants mediated by ozone, instead of OH radicals that have a higher oxidation potential.

A year later, in 2003, the Japanese company Permelec Electrode published in Europe and United States applications of a batch recirculation electrochemical oxidation process [27], where the electrolyte was recirculated through an undivided flow cell, as shown in figure 5. This is the first of a series of patents granted to the company, which according to Table 1, can be considered the main holder of intellectual property in the field.

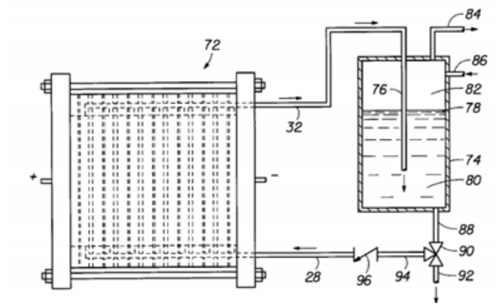

Figure 4. Cross-sectional side view of the ozone electrolysis cell (ref. [26]).

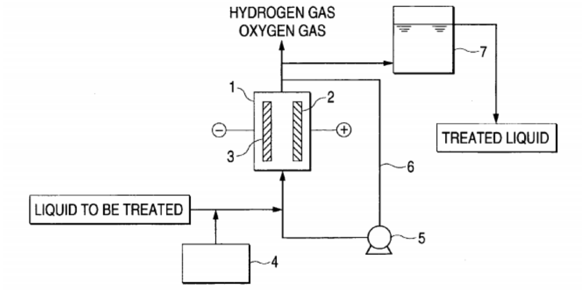

Figure 5. Recirculating batch process (ref. [27]).

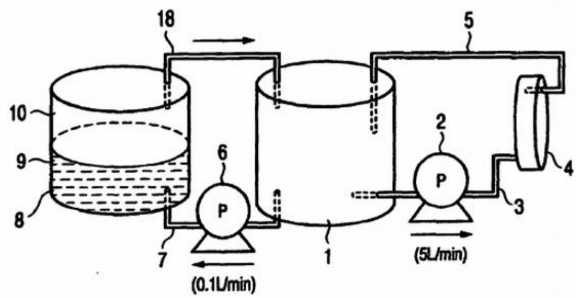

Figure 6. Recirculating batch process described (ref. [28]).

In 2004, the renowned Japanese company Fuji Photo Films patented the first treatment process for a real residue, in this case, liquid wastes from the photographic industry [28] by an electrolytic oxidation treatment with BDD electrodes as shown in figure 6. A year later, another patent with a similar method was published, in this case for the treatment of wastewater from metal coating industry [29].

In 2006, the Italian company Industry SPA Nora, also presents an important advance in the subject [30], with the contribution of a combined use of two different types of anodes for wastewater electrochemical oxidation. The method claimed the use of diamond and novel metal oxides electrodes in order to improve the electrochemical process in at least two cells in series. In the first cell hydroxyl radicals mediate the oxidation while in the second cell electro-generated oxidants are produced in the novel metal oxide surface, enhancing the oxidation of pollutants in the bulk solution.

An alternative use for the BDD electrodes was patented in 2008 by Windsor Scientific Ltd [31], in this work the authors claimed the usage of this type of electrodes for decomposing organic insoluble liquid by emulsifying the liquid within an aqueous medium in an electrochemical cell and oscillating the surface of an electrode at a frequency of at least 5 KHz, thus occurring micro cavitation bubbles within the solution, causing the oxidation of organic insoluble pollutants.

In 2009 and 2010 two major global companies patented processes for wastewater treatment with diamond electrodes, the first one was Dow Chemical Company that patented an application for the reduction organic content from brine [32]. The other company, Unilever, patented a process that includes transition metal catalysts, hydrogen peroxide and hydroxyl radical production with BDD electrodes. This last method claims to be capable of producing an effluent that can be disposed of directly into the environment [33].

Finally, the process presented by Proterrgo INC in Figure 7, unveils a complete four stage combined treatment [34] consisting in an electro-coagulation unit for the removal of raw contaminants, an electro-floatation equipment that separates the flows produced in the previous stage, an electrochemical oxidation on BDD cell to oxides the remained organic pollutants and finally a unit for the removal of residual oxidants.

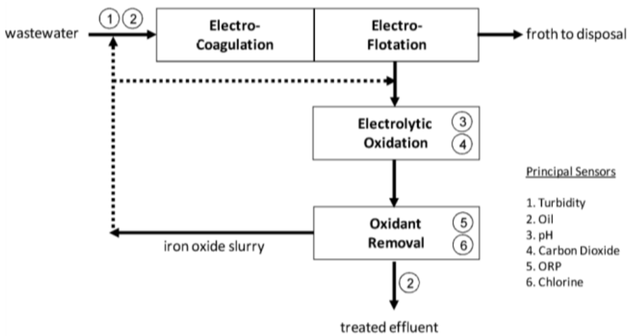

Figure 7. Block diagram of the four-stage electrochemical wastewater treatment (ref. [34]).

5. Disinfection processes

Ten patents related with diamond anodes listed in the IPC category for disinfection and sterilizing methods (A61L) were found, covering processes for the disinfection of water [35], air and different surfaces. The patents in the field have been presented within the last four years of the studied period, the first one was published in 2009 and the last reported is dated 2012, which shows that the developments in the area of materials synthesis and basic research with this type of electrodes (during the first decade of the 21st century) were necessary for the emergence of disinfection applications with diamond electrodes.

The first patent found, was from the German company Condias Gmbh how is one of the main BDD electrodes and reactors providers nowadays. The invention patented claims the removal of harmful components like germs and microorganisms from air via hydroxyl radicals or oxidative byproducts formed in a reaction vessel with BDD electrodes, where the air is mixed with an aqueous electrolyte. This technology is intended to be used in air conditioning systems [35].

Another patent from the same company, involves spraying foodstuff surfaces with enriched water, that is previously subjected to an in-situ-electrochemical treatment for producing an oxidizing agent by a diamond electrode arrangement [36].

Surface disinfection patents are very common within this category, including applications for floors [37], kitchen utensils [38], industrial equipments [39] and contact lenses [40] that claimed to eliminates up to 99.9% of microorganisms such as viruses, gram-positive and gram-negative bacteria, yeasts, fungi, algae and protozoa microorganisms nonselectively and without resistances.

A method for exterminating parasites on pisciculture, was also patented by Perlemec Electrodo, consisting in a electrolytic ozone generator for electrolyzing farm raw water and loading cultured fishes into the electrolytic ozone water tank to exterminate the microorganisms [48].

6. Commercial applications for non-industrial water treatment

In the last decade, there has been an increasing interest in the use of electro oxidation technologies at small scales for non-industrial uses like the in situ pocket size ozone generator for water purification presented in 2008 [41]. This ozone generator, capable to treat water for human consumption comprises a power supply, a super capacitor and a pair of electrodes, where in comprises BDD as electrode material, for generating ozone. Another patent in the field is the one presented in figure 10 [46] that includes an electrolytic BDD cell that contains a float and solar cell, allowing the apparatus to operate exclusively with solar energy but only on a very small scale due to the low power of the actual solar cell technologies.

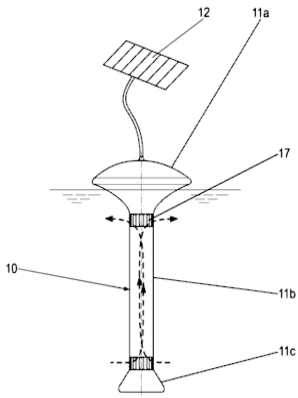

Figure 8. Mobile electrolytic cell for water purification (ref. [46]).

Another ozone generator based on diamond electrodes, is the one published in Korea in 2010 in a hand-disinfecting device that generates ozone by electrolyzing water, having a sterilization function for spraying the oxidizer over the hands of a user [47].

The swimming pools and hot tubs water treatment systems have been another source of significant developments in the field [42-44], since electrochemistry offer an efficient way to supply chloride-produced oxidants in these bodies of water, that are traditionally added in the form of hypochlorous acid powder.

The electrochemically generated chloride oxidants that promote the elimination of organic pollutants in the swimming pools are primarly chlorine, hypochlorite and hypochlorous acid, which are formed following the subsequent reactions:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{(Eq. 3)}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad \text{(Eq. 4)}$$

$$HOCl \rightarrow H^+ + OCl^- \qquad \text{(Eq. 5)}$$

An example of these new developments is the patent application of a drop-in cylindrical chlorinator [42] comprising a three electrodes assembly made of titanium and at least one with a diamond surface. Another example is the comprehensive design of a swimming pool with an incorporated electrochemical treatment with BDD anodes for the water [43] as is shown in Figure 9.

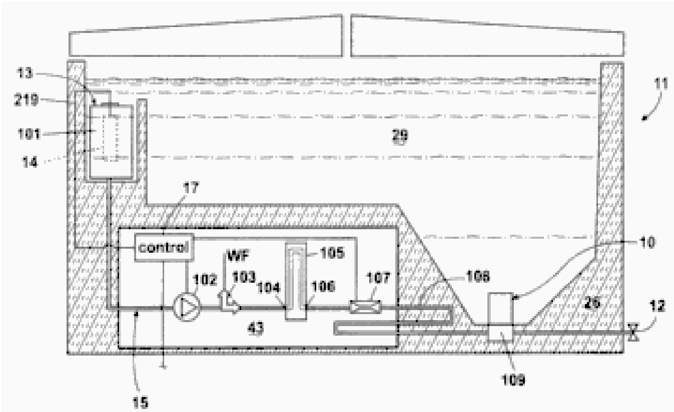

Figure 9. Swimming pool with built in electrochemical treatment (ref. [43]).

Another interesting development, is the invention presented in 2012 by Xh2O Solutions Private Limited [45] that relates to a system and method for washing, cleaning, disinfection and sterilization of laundry using a mixed oxidants solution in situ generated by passing the electrolyte through an electrolytic cell with BDD electrodes.

7. Conclusion

Regardless of being a novel technology with less than 20 years of development, the electrochemical technologies in wastewater treatment using boron-doped electrodes evidence an interesting dynamic of innovation with a growing interest by the industry, academics and independent researches on the development of new methods of fabrication, different reactor configurations and a vast amount of applications that allows the more efficient use of this technology in the abatement of pollutants from water.

Acknowledgements

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