Emerging Boron-Doped Diamond Electrode Technology in Wastewater Treatment

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In advanced oxidation processes (AOPs), the removal of organic pollutants from wastewater and disinfection of water can be achieved by the use of hydroxyl radicals. The use of these processes remains limited as every AOP process has its own restrictions. There has not been a competitive electrochemical process for water treatment because the stability and electrochemical properties of conventional electrode materials are not suitable. The diamond electrode has decisively altered this situation, because diamond offers the simple possibility of forming hydroxyl radicals in the course of water decomposition. This presentation will review this emerging technology.

1) Introduction:

Global pollution of the environment, including the contamination , over-use and mismanagement, is threatening the worldwide population. In consequence, the major issue in technological development focuses on protection of the environment and the preservation of resources, particularly for wastewater discharge to the aquatic environment, waste emission limits are determined to prevent pollution.

Currently applied water treatment techniques consist of a combination of different treatment methods to obtain the required purification of wastewater (1). In particular, biological treatment for the removal of organic load from slightly polluted wastewater is well established and relatively cheap. Nevertheless, biological treatment techniques are slow and not suitable for all pollutants. For highly polluted water, which is difficult to deal with, different additional treatment methods have been developed. Chemical treatment, especially for the oxidation of pollutants, aims at mineralization of the contaminants, or at least their decomposition into harmless or biodegradable products. A special class of oxidation techniques defined as advanced oxidation processes (AOP) is characterized by the capability of exploiting the high reactivity of hydroxyl radicals, which are generated from chemical precursors by e.g light irradiation (2). Diamond electrodes, incidentally, produce high amounts of hydroxyl radicals directly in water (3) due to their high overvoltage before water decomposition (4). The high current efficiency for electrochemical hydroxyl generation with diamond electrode expands the range of commonly applied AOP methods, thus defining the electrochemical advanced oxidation process (EAOP), which can only be fulfilled using sophisticated conductive diamond as the electrode material.

2) Electrochemical Advanced Oxidation Process (EAOP)

The acceptation of Advanced Oxidation Processes (AOP) for water treatment has continuously increased over the past few years. Nevertheless the use of these processes has its own restrictions. There has not been a competitive electrochemical process for water treatment up to date because the stability and the electrochemical properties of the conventional electrode materials are not suitable. The development of diamond electrodes has decisively altered this situation.

The outstanding property exhibited by diamond electrodes is a unique form of water decomposition. Normally, water is directly split into hydrogen and oxygen, however when using diamond, a much wider working potential window exists whereby ozone or hydroxyl radicals may be formed instead of oxygen (Figure 1). Diamond has the highest overpotential for the generation of oxygen. In acidic solution, the overpotential ranges from 2.8 V for oxygen evolution to approximately –1.3 V for hydrogen generation (Figure 2). For water treatment diamond offers the possibility to form hydroxyl radicals simply in the course of water decomposition. It is know that in AOPs the removal of organic pollutants from wastewater and the disinfection of water can be achieved by the use of hydroxyl radicals. This is also true for an Electrochemical Advanced Oxidation Process (EAOP) based on diamond electrodes.

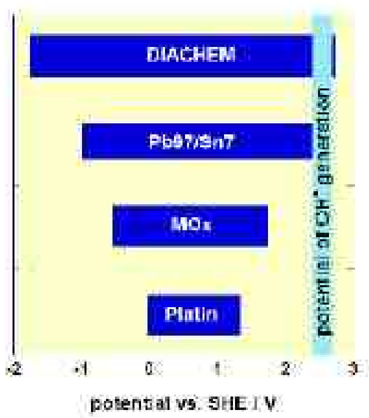

Figure 1

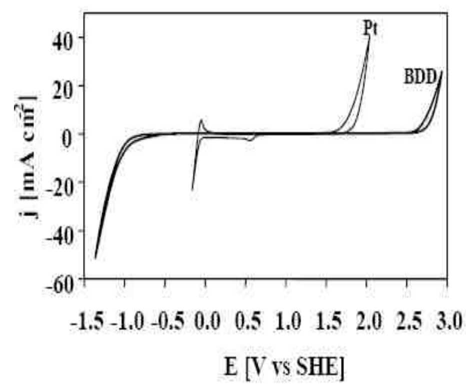

Figure 2

Figure 1: Working potential windows of different electrode materials upto the generation of hydrogen (left edge of bar) and oxygen (right edge of bar). The potential required for producing hydroxyl radicals is marked in light blue.

Figure 2 Typical cyclic voltammogram for diamond electrodes in 0.5 M H_2SO_4

The most important electrochemical properties are the very high corrosion stability and the extremely high overvoltage fro water electrolysis. The large working potential window in aqueous electrolytes provides the possibility of producing strong oxidizing solutions with extremely high efficiency. As reported by Comninellis (3) compared to other electrode materials. , Hydroxyl radicals are produced with higher current efficiency on the diamond surface. These hydroxyl radicals completely mineralize organic impurities in water, such as oils, cooling fluid, toxic compounds (5,6).

. **Key Diamond Properties:**

- Exhibit outstanding physical and chemical properties.
- Chemically, mechanically, thermally enormously stable in fluoride media
- At high current densities do not exhibit any corrosion, extended life time (e.g. 7500 hours at 10 A/cm2, 1 M sulfuric acid).
- Highest known cathodic (-1.2 V vs. SCE) and anodic (+2.6 V vs. SCE) overpotentials.
- Through the use of diamond electrodes, it is possible to reverse polarities in order to prevent calcium build-up on the electrode surface.
- Through the use of diamond electrodes, it is possible to obtain an electrochemical process

which, without addition of further chemicals, results in environmentally friendly and relatively maintenance-free method for the treatment of waste water

Applications:

- Wastewater treatment and water recycling by the electrochemical advanced oxidation process (EAOP).
- Use as anodes in electroplating baths with complexing agents and abrasive particles and high current densities.
- New electrochemical synthesis of both organic and inorganic products (e.g. periodate, persulfate, chlorine, hypochlorite, H_2O_2, ozone, and organic synthesis.
- Highly efficient galvanic procedures (e.g. oxidation of cyanide or chrome co
- Microanalytical sensors

Until now, diamond has not been introduced in electrochemical applications because of the limited availability of industrial size electrodes. TO meet the upcoming diamond for this outstanding electrode material, DIACHEM electrodes with reproducible electrochemical and physical properties are fabricated on metals (e.g Nb, Ta, Ti, Mo, W, Zr), Silicon, ceramic and graphite base materials. The deposition area was enlarged for electrodes sizes upto 500X1000 mm^2.

Benefits of EAOP using DIACHEM® electrodes

- EAOP can be operated with current efficiency up to nearly 100%.
- It is not necessary to add chemicals for the oxidation because hydroxyl radicals are directly formed from water.
- EAOP can be used for decontaminating charged ground waters and for contamination ranges from 0,1 – 100 g O_2 l^{-1} .
- EAOP has a modular design and can therefore be easily expanded.
- Compared to other AOPs the maintenance costs for EAOPs are considerably lower.
- EAOP can be combined with other treatment processes in order to increase the efficiency of the whole process.
- Since EAOP can be effectively used for disinfection as well as for wastewater treatment it is predestined for recycling and downcycling of service and industrial water.

Wastewater Treatment

The following figure 3 shows the analysis of the deep well sample. The EAOP treatment reduced all organic loads by approx. 99% although the initial concentrations were partly already very low. During the whole treatment period of 2h the COD decomposition rate is 10 g O2 (kWh) -1, while for a pure COD reduction, which was completed after approx. 2 Ah a rate of 40 g O2 (kWh) -1 was obtained.

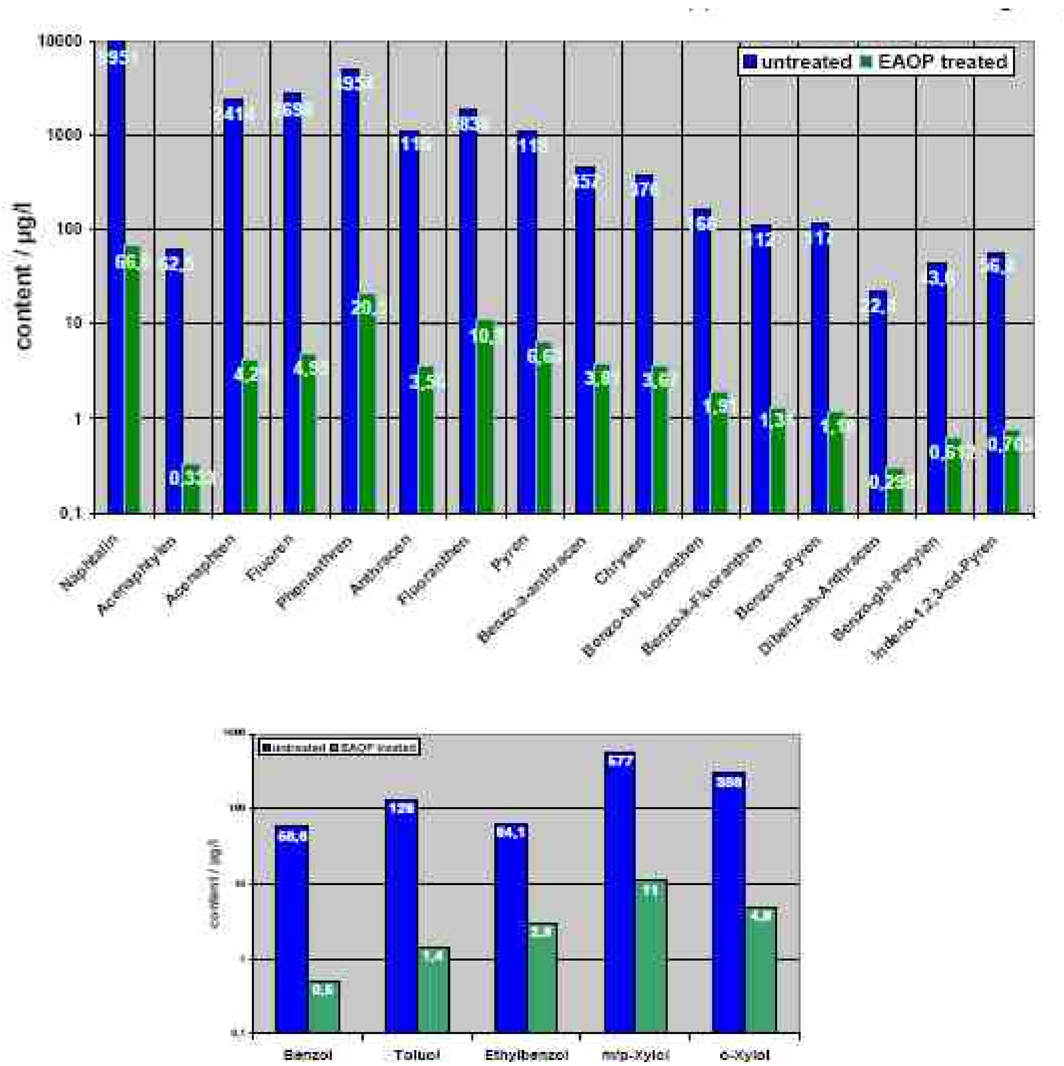

Figure 3: Analysis results of ground water sample from a deep well. The initial values of the untreated sample are displayed in blue and the values after the EAOP treatment in µg/l in green. The displayed values show the different concentrations.

Complete Mineralization of organic compounds:

Complete mineralization of several types of organic compounds i.e., their oxidation to CO_2 has been noted in the literature. For example: Phenol (7,8,9), Benzoic acid (10). Carboxylic acids –acetic, formic and oxalic (11), 2-Naphtol (12), 4-chlorphnoxyacetic acid (13), and Textile auxiliaries (14), e.g. Cl Acid orange 7 (a dye) and its metabolites.

Other Special applications:
Ozone-water

K. Arihara et.al. outlines their application of diamond to direct ozone-water generator in Ref. (15). Ozone water will find applications in 1) sterilization e.g. medical center, sanitary facility, food processing factory, kitchen; 2) decomposition of organic compounds, e.g. water treatment plane and 3) Particle removal e.g. semiconductor industry and electronic parts factory.

Application of self-standing perforated diamond electrodes is a much promising method for direct ozone-water generation. Production of ozone is about 12-15 times more for a particular current, compared to platinum electrodes.

Diamond Electrode with solid polymer electrolyte (SPE):
Kraft et.al. (16) outlines the use of diamond electrode with solid polymer electrolytes and show the combination of diamond electrode and solid polymer electrolytes has been applied successfully. Limitations of current electrochemical devises include 1) a minimum conductivity of the water is necessary, 2) in the case of water disinfection chloride ions are needed, 3) therefore water from different, economically interesting sources cannot be treated by electrochemical means, e.g. semiconductor or pharmaceutical industry, rain water, laboratories, rinsing water in many diverse industries. With this technology the advantages of diamond electrodes can now also be used to treat water with very low conductivity. COD removal and water disinfection are both possible. More work is needed in this area.

Economic Consideration:
Yves Pellet of Electrochemical services (17) discuss cost efficient application of diamond electrodes. Diamond electrodes works well for COD removal while precious metal oxide electrodes works poorly, and diamond electrodes are more expensive than precious metal oxide electrodes. For some of lighter organic molecules diamond electrode is not necessary. A combination of diamond and precious metal oxide electrodes seem to provide better efficiency to over process and better economic viability.

Summary:

Diamond electrodes are entering various industrial applications. The EAOP for wastewater treatment with diamond electrodes has been proven successful for the reduction of even hazardous or persistent water pollutants (e.g. organimetallics, olymers, complex forming agents, etc.) with high current efficienty. Neverthless, there are also results, that have to be reconsidered concerning the utilization of diamond electrodes

a) Before the treatment of new classes of pollutants, the EAOP has be examind concering unfavorable intermediate and products, e.g. increase of AOZ and production of toxic compounds;
b) The utilization of diamond electrodes requires new electrochemical cell systems with parameters fitted to their optimum operation conditions such as current densities, flow rates etc., thus preventing mass transport limitations and the above mentioned side reactions.

However, EAOP systems with diamond electrodes were tested for the treatment of higher amounts of wastewater(1 m^3 per day) at customer sites, and showed an up-scaling without loss of current efficiency. These results are highly promsing for further efforts to establishing EAOP systems with optimized electrochemical cells as a supplement for commonly applied watewater treatment methods.

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