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Complete oxidation of organic substances in wastewater using an Advanced Oxidation Process with synthetic diamond electrodes

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1. Introduction

The method introduced in this article is an Advanced Oxidation Process (AOP) where synthetic diamond electrodes are used for water electrolysis. In the course of water electrolysis extremely effective OH radicals are formed instead of oxygen. These OH radicals are able to oxidise and remove all dissolved organic substances present in the waste water. Results are presented by the parameters COD, hydrocarbons and AOX as well as by the colour as e.g. when wastewaters from textile industries are decolourised. Examples from three different industries are presented to describe the removal characteristics of pollutants and colour with AOP.

2. Setup and functionality of diamond electrodes

At a temperature of 2500 ℃ the gases methane and h ydrogen are used to coat a conductive substrate material with a thin, only a few thousandths of a millimetre thick crystalline diamond layer. The diamond´s conductivity is generated by doping the diamond with the element boron. The electrochemical behaviour of these electrodes is mainly defined by the polycrystalline diamond layer. Diamond electrodes show an extremely high stability to aggressive substances in water.

The outstanding property of diamond electrodes is a unique form of water decomposition. During electrolysis water is normally directly split into hydrogen and oxygen whereas when using diamond electrodes a working area is created whereby ozone or hydroxyl radicals are formed instead of oxygen. Figure 1 schematically shows this property for different electrode materials. It is obvious that diamond has the highest over potential for the generation of oxygen. For water treatment diamond offers, at a potential of a few volts, the possibility to form hydroxyl radicals simply in the course of water decomposition.

Figure 1: working potential windows of different electrode materials up to the generation of hydrogen (left edge of bar) and oxygen (right edge of bar). Blue: the potential required to produce hydroxyl radicals.

Due to their high oxidation potential (Fraser & Sims, 1984) hydroxyl radicals can completely oxidise organic substances such as oil-water emulsions, phenols, endocrine disruptors, hormones, EDTA, organic dyes to CO_2.

If a wastewater tends to form strong deposits diamond electrodes are used as cathodes and anodes which can be kept free of deposits by continuous reversal of polarity. If a wastewater only shows a slight tendency to form deposits the reversal of polarity is not necessary. In this case a cathode made of stainless steel is used instead of a diamond cathode. Contrary to the anode the cathode receives a cathode protection. This electrochemical protection method for corrosion protection is known from earth-laid and water-laid pipelines as well as from tanks and ships.

3. Tests and results

To show the efficiency of this method the elimination of pollutants in three different companies of different industries is described in the following:

Chemical industry

The first industrial company uses renewable primary materials to produce basic and auxiliary products for the chemical industry. The first tests were carried out here. Among others things vegetable-based fatty acids are changed at high pressures and high temperatures by e.g. additive reactions. Due to the use of sulphuric acid the generated wastewater does not only have extremely high salt concentrations and a low pH-value but also shows a high degree of organic pollutants in the form of fats (2300 mg COD/l). The wastewater's temperature ranges between 70℃ und 90℃. Neither the high salt concen trations nor the high temperature are suitable for a biological treatment.

The wastewater treatment aims at reducing the COD concentration to a value of less than 100 mg/l and thus allowing for a direct discharge into the environment (North Sea).

The pilot plant was installed in the production facilities so that the tests provided realistic results. Figure 2 shows the electrolytic cell through which the wastewater to be treated is pumped. The diamond electrodes are rectangular plates which are fitted into the electrolytic cell if required.

Figure 2: Electrolytic cell with diamond electrodes for batch and continuous operation to remove non-biodegradable wastewater substances

The tests were carried out in batch mode. At first a defined amount of wastewater is pumped from the storage container into the batch container. After having determined its initial values the wastewater is continuously pumped in a cycle through the electrolytic cell for a definite period of time. A stirrer in the container makes sure that the wastewater is constantly stirred. The current density and thus the number of hydroxyl radicals formed can be adjusted at the transformer. At the end of the treatment period the container is automatically emptied and the whole process starts again. The samples were taken along a timeline out of the fully stirred batch container.

The test objective was to prove the efficiency of the treatment method for this specific wastewater and to determine the optimum settings such as treatment time and current or current density (A/m2).

When examining the applied amount of charge it shows that the high current density of 100 mA/cm^2 does not make sense economically because in this case the efficiency compared to 70 and 30 mA/cm^2 decreases. The lower the concentration of organic load the lower can also be the number of OH radicals because otherwise too many of them react unused. The tests and results of Michaud, P.-A. (2002) give a model description of this behaviour. Michaud has developed an adjusted calculation model where initial and final COD value, volume and electrode area are used as parameters for the calculation. This model helps to calculate the optimum current density for each particular concentration and thus to achieve a high current efficiency.

The lowest operating costs result from a current density of 30 mA/cm^2. The operating costs for the treatment and rates for direct discharge are considerably lower than those for indirect discharge (municipal sewage system). An indirect discharge is prohibited because of the high sulphate concentration (limit value 400mg/l as a protection against concrete corrosion). But also for ecological reasons it makes sense to aim at a direct discharge (North Sea). There is an even bigger incentive if COD polluters have to pay a surcharge when discharging into the municipal sewage system.

Figure 3: COD decomposition of a wastewater from a chemical plant for direct discharge

Decolourisation of wastewater from textile industry

In a textile-producing plant children's clothes are manufactured. Due to the use of reactive dye the wastewater strongly differs in colour depending on the current fashion.

The working processes in textile finishing can be roughly divided into the following steps:

- ⇒ pre-treatment,
- ⇒ dyeing,
- ⇒ printing,
- ⇒ finishing.

For the dyeing process the spectral absorption coefficient in the yellow, red and blue range has to be met.

Figure 4: Simultaneous decolourisation of a textile wastewater

Visually the colourisation disappears nearly fully after 5 minutes. It can be determined photometrical that the extinction was reduced by 90% in all wavelength ranges.

Cleaning of tank vehicles

When cleaning tank vehicles partly heavily loaded wastewaters with a COD of 90,000 mg/l and more are generated which contain lightly volatile and low volatile chlorinated hydrocarbons. As a sum parameter AOX specifies the total concentration of 200 mg Chlorine/l for all halogenated compounds.

Figure 5: COD and AOX elimination of heavily loaded wastewaters from cleaning of tank vehicles

The organic wastewater substances are completely removed by electrolysis with diamond electrodes. This complete conversion to carbon dioxide is normally only achieved by thermal processes at high temperatures. However, since the organic portion of 9% in the wastewater is relatively low for combustion the heating value is low and the burning costs high. Catalyst-supported oxidations which take place at high pressures and temperatures of up to 400 ℃ also only have a limited conversion of organic load as well as of AOX. In this respect it is simple to approve of electrolysis with diamond electrodes because neither is a pressure tank necessary nor are exhaust emissions and waste materials produced.

4. Summary

The chemical oxidation using diamond electrodes in the form of an AOP (Advanced Oxidation Process) is an effective way for the purification of wastewaters which are difficult to treat biologically or non-biodegradable at all. Due to the substantial formation of OH radicals the technology presents a high potential for converting organic substances into inorganic compounds such as H_2O, CO_2 and Chloride without producing any residues.

Using this method the limit values such as COD concentration for direct discharge as well as the sum parameters such as colouring, AOX and hydrocarbons for direct or indirect discharge in the environment are lower than the values usually required.

Chemical oxidation using diamond electrodes offers a cost-efficient alternative to conventional disposal methods. In the described examples the costs for direct discharge including operating costs are lower than the rates for indirect discharge.

This innovative method is particularly impressive because of its enormous simplicity. Besides current no other resources are necessary. In the first application diamond electrodes have been operated faultlessly for 2 years so that a lifetime of 3 to 4 years can be expected.

Literature:

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Michaud, P.-A. (2002), Comportement anodique du diamant synthetique dopé au bore, Thèse Nº 2595, Ecole Polytechnique Fédérale de Lausanne

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Figure 1

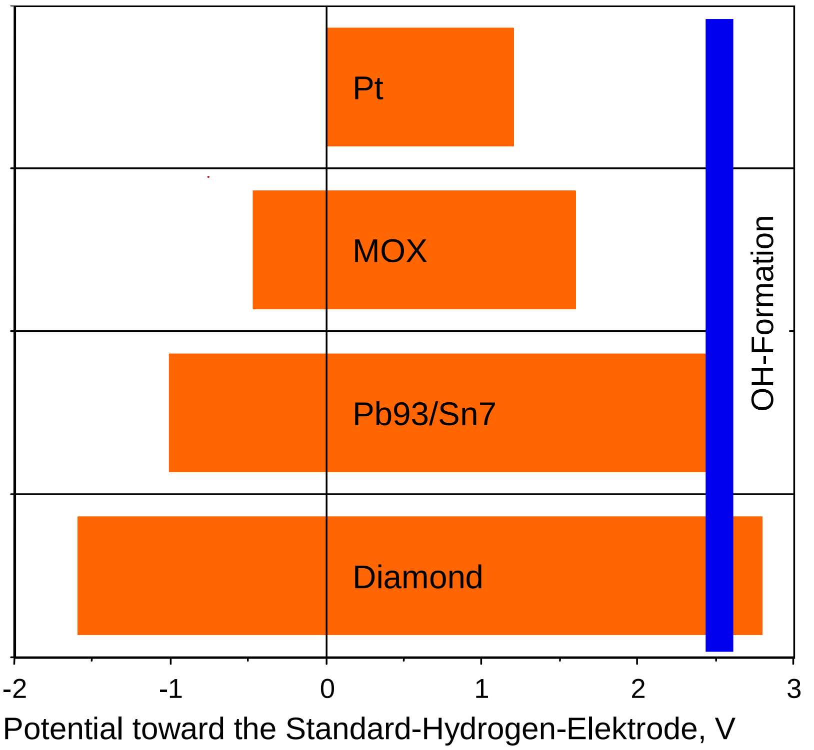


Figure 2

Figure 3

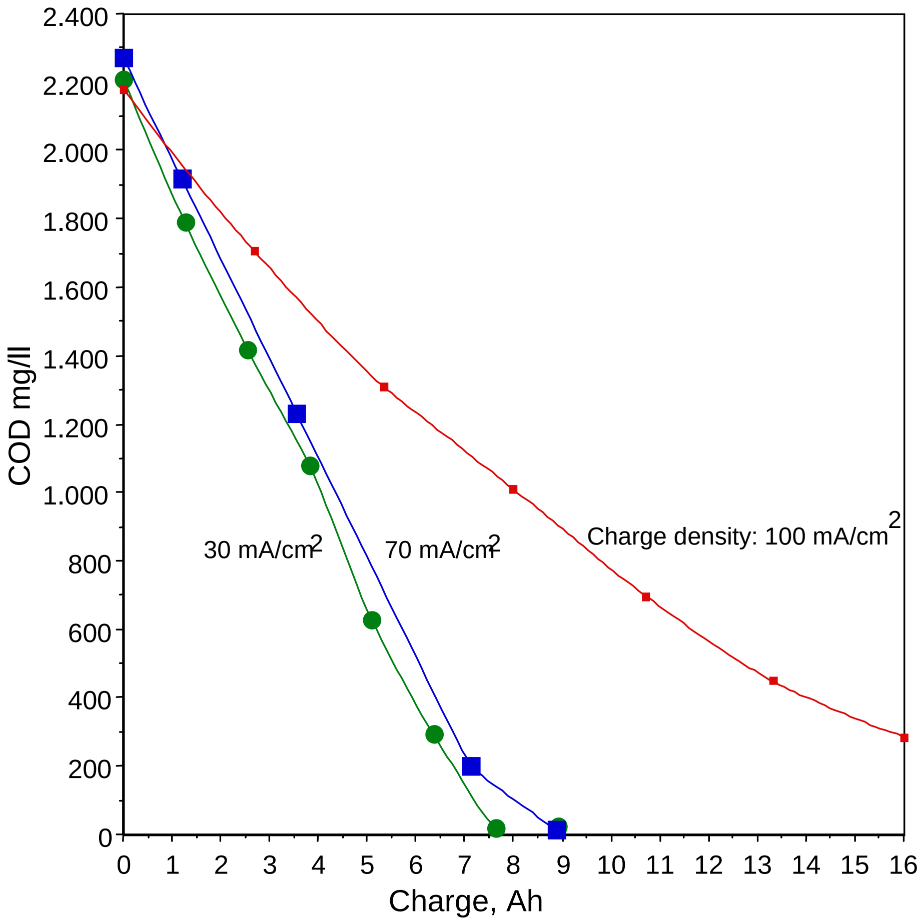
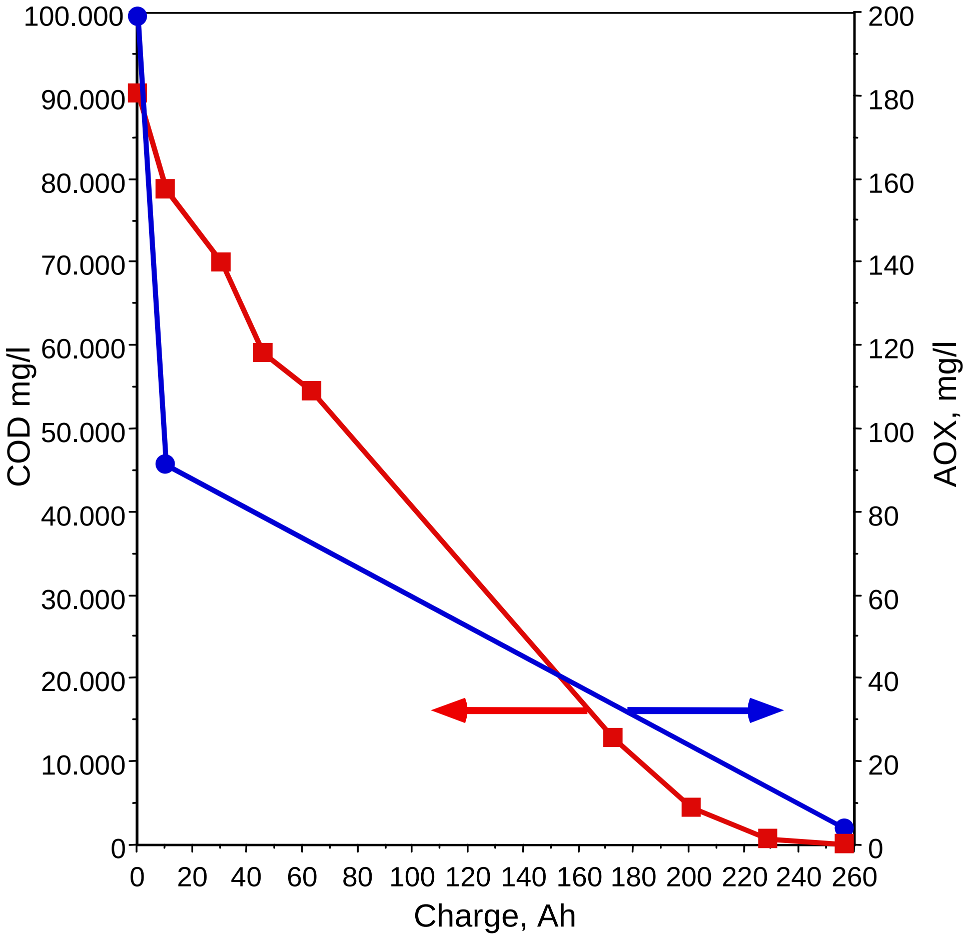


Figure 4

Figure 5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AOX, mg/l
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Charge, Ah