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Anodic oxidation with doped diamond electrodes: a new advanced oxidation process $\stackrel{\text{th}}{\sim}$

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Abstract

Boron-doped diamond anodes allow to directly produce OH• radicals from water electrolysis with very high current efficiencies. This has been explained by the very high overvoltage for oxygen production and many other anodic electrode processes on diamond anodes. Additionally, the boron-doped diamond electrodes exhibit a high mechanical and chemical stability. Anodic oxidation with diamond anodes is a new advanced oxidation process (AOP) with many advantages compared to other known chemical and photochemical AOPs. The present work reports on the use of diamond anodes for the chemical oxygen demand (COD) removal from several industrial wastewaters and from two synthetic wastewaters with malic acid and ethylenediaminetetraacetic (EDTA) acid. Current efficiencies for the COD removal between 85 and 100% have been found. The formation and subsequent removal of by-products of the COD oxidation has been investigated for the first time. Economical considerations of this new AOP are included. © 2003 Elsevier B.V. All rights reserved.

Keywords: Diamond electrodes; Anodic oxidation; Advanced oxidation process; Mineralization; Water treatment

1. Introduction

By far the most important method for removal of the biodegradable fraction of the chemical oxygen demand (COD) of wastewaters is biological treatment, well-established and relatively cheap. But unfortunately not all substances which are responsible for COD

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are easily biodegradable. Toxic substances can inactivate the microorganisms and biological processes are relatively slow: other methods for COD removal are hence required.

The most suitable alternative method is chemical oxidation, aiming at the total mineralization or the production of harmless or biodegradable compounds by use of oxidants. Commonly used chemicals for this purpose are oxygen, hydrogen peroxide, ozone, permanganate or persulfate. The higher the oxidation potential of the reagent used, the more efficient is the chemical oxidation process. The most powerful oxidant in water is the hydroxyl radical with a redox potential of about 2.8 V_{NHE}. Advanced oxidation processes (AOP) are characterized by the production and use of these hydroxyl radicals for the oxidation of chemical substances [1–3]. The hydroxyl radical reacts strongly with all organic substances usually by hydrogen abstraction.

The most common AOPs for the production of OH^{\bullet} radicals are the Fenton process (addition of hydrogen peroxide to Fe²⁺ salts) [4], the photoassisted Fenton process, photocatalysis using TiO₂ and UV radiation [5], the combination of ozone and hydrogen peroxide and the hydrogen peroxide photolysis using UV light. Disadvantages of the conventional AOPs are: the relatively high costs, the necessity of adding chemicals and complications by using UV light such as high absorption coefficients of the water to be treated or the relatively short lifetime of UV light sources.

A new process which can avoid the drawbacks of the conventional AOPs is the electrochemical advanced oxidation process (EAOP) [6]. In this process, OH[•] radicals are produced electrochemically in an anodic reaction directly from water which has to be treated [7] according to Eq. (1):

$$H_2O \to OH^{\bullet} + e^- + H^+ \tag{1}$$

By using the electrochemical production of hydroxyl radicals, no addition of chemical substances is necessary and the process can be performed at affordable costs, determined mainly by the power required for driving the electrochemical process and without the common AOP drawbacks.

This new electrochemical AOP became possible due to the recent development of large area doped diamond electrodes [8,9]. This process represents not only a new promising AOP but also a great progress in the development of electrochemical water treatment processes.

Recent overviews on modern electrochemical methods of water treatment have been published by Jüttner et al. [10] and Janssen and Koene [11]. These methods include heavy metal removal by cathodic electrodeposition, anodic destruction of organic pollutants by redox mediators (Ag^{2+} , OCl^- , $S_2O_8^{2-}$ among others) and electromembrane processes (membrane electrolysis, electrodialysis). Electrochemical water disinfection by producing disinfecting agents (mainly active chlorine produced from the naturally dissolved chloride ions) during electrolysis of water is another attractive water treatment process [12].

Electrochemical methods which can be used to reduce COD values of wastewaters due to the direct mineralization (cold electrochemical oxidation) of organic substances are long sought for. However, with the electrode material available until recently this could not be accomplished or only with low current efficiencies and electrode lifetimes due to the fact that for the electrochemical production of OH[•] radicals, electrode materials with a very high oxygen overvoltage are necessary [7]. Mainly molecular oxygen is produced during water electrolysis if the oxygen overvoltage is not high enough. Additionally, the electrode material has to be stable in the presence of large amounts of hydroxyl radicals. The use of graphite or other carbon-based electrodes with relatively high overvoltages for oxygen production leads to the formation of carbon dioxide as a by-product and consequently to a continuous degradation of the electrode material. Conventional more stable anode materials with high overvoltage for oxygen production are PbO_2 [13,14] and SnO_2 [15,16]. However, if using lead dioxide or tin dioxide as anode materials, there is still a much too low current efficiency for OH[•] production. These electrode materials are moreover not stable during polarity reversal. In the practical application of electrochemical water treatment this current reversal is often necessary to remove calcareous deposits from cathode surfaces [12]. SnO₂ or PbO_2 are reduced when working as cathode. Other drawbacks of these conventional materials are their low chemical and mechanical stability. Even platinum electrodes were investigated for the degradation of organic compounds [17,18]. Although these electrodes are much more stable than tin dioxide or lead dioxide electrodes, the current efficiency for OH• production is extremely low.

Electrodes made of boron-doped diamond thin films deposited on self-passivating metals such as niobium show the largest overvoltage for oxygen production from water ever found for an electrode material [6–9,19]. They also exhibit high chemical and mechanical stability. Because of their unique properties boron-doped diamond electrodes are much more suited for electrochemical advanced oxidation than the conventional electrode materials. It has been shown that COD removal with diamond anodes can proceed with current efficiencies higher than 90% (100% current efficiency = 298.5 mg O_2/Ah).

Another quasi-electrochemical method for OH[•] production is the so-called electro-Fenton or photoelectro-Fenton process [20] where hydrogen peroxide is produced on a gas diffusion cathode by reduction of molecular oxygen according to Eq. (2).

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$
⁽²⁾

This hydrogen peroxide subsequently reacts with Fe^{2+} to give OH^{\bullet} (Fenton process). Allthough this process has been called advanced electrochemical oxidation process (AEOP) [20], the OH^{\bullet} radicals themselves are not produced by the electrochemical step but rather by the well-known Fenton or photo-Fenton process. Using diamond anodes to produce hydroxyl radicals by the anodic oxidation of water represents a real electrochemical advanced oxidation process.

Recently, there were several reports on the mineralization of certain organic target compounds dissolved in water by use of diamond electrodes with very high current efficiencies. These reports concerned isopropanol and acetic acid [21], phenol and isopropanol [8], different carboxylic acids [22], 4-chlorophenol [23,24], phenol [25], 3-methylpyridine [26], benzoic acid [27], polyacrylates [28], 4-chlorophenoxyacetic acid [29] and an amaranth dyestuff [30]. All these investigations could confirm very high current efficiencies for COD removal, usually higher than 90%.

The present work reports on the use of diamond anodes for the COD removal from several industrial wastewaters. Additionally, the COD removal of some interesting compounds such as ethylenediaminetetraacetic (EDTA) acid or malic acid has been studied.

The formation and subsequent reduction of unwanted by-products of the COD removal has been investigated for the first time.

2. Experimental

Laboratory scale experiments were performed in a glass beaker of 500 ml sample volume, vigorously stirred during electrolysis at room temperature. An electrode stack consisted of two diamond sheet anodes and three titanium sheet cathodes with an electrode distance of 4 mm. The thickness of the niobium substrate (area = $10 \text{ cm} \times 2.5 \text{ cm}$) and the titanium sheet was 1 mm. The overall diamond electrode surface used in the experiments was 100 cm^2 . Boron-doped diamond electrodes with two different levels of boron doping were used. The first material had a boron concentration below 1000 ppm, whereas the second material possessed a boron concentration higher than 1000 ppm. The boron-doped diamond electrodes were produced at the Fraunhofer-Institut für Schicht- und Oberflächentechnik FhG IST (Braunschweig, Germany).

Iridium oxide coated titanium sheet electrodes (active coating: $IrO_2-Ta_2O_5$ with 8 g Ir/m² in a molar ratio of Ir to Ta: 70 to 30) used for comparison were supplied from Metakem GmbH (Usingen, Germany). In these experiments, electrode stacks similar to the diamond electrode tests were realised.

Experiments were conducted with variations in current and current density, boron-doping of diamond anodes, electrolyte temperature, initial COD of electrolysed solutions and with a variety of different organic substances (malic acid, EDTA, triethanolamine, wastewaters from the paper industry, the motor industry and the pigment industry).

The synthetic test solutions of malic acid, EDTA and triethanolamine were prepared by dissolving the respective substance in deionized water in the concentration given below. In the case of malic acid and EDTA, no additional chemicals were used to adjust the pH or conductivity. The pH of the triethanolamine solution was adjusted to 11.1 by addition of NaOH. Malic acid (extra pure) and triethanolamine (p.a.) and ethylenediaminetetraacetic acid, disodium salt (EDTA, purum) were purchased from Riedel-deHaen and used without further purification. The real wastewaters were used as received from industry.

The COD was determined by common photometric tests using COD test tubes and a Nanocolor[®] 100D (Macherey-Nagel, Düren, Germany) photometer. Chloride, nitrite, nitrate and ammonium were also determined by Macherey-Nagel tube tests. The determination of adsorbable organic halogens (AOX) was performed using Dr. Lange (Düsseldorf, Germany) test tubes and photometer. The EDTA concentration was determined by complexometric titration with Mg²⁺ [31].

The current efficiency for COD removal was calculated using Eq. (3) for the electrolytic production of oxygen.

$$2H_2O \to O_2 + 4H^+ + 4e^-$$
(3)

According to Faraday's law, 298.5 mg O_2 /Ah are produced. At 100% current efficiency, all oxygen is consumed by the oxidation of substances which is responsible for the COD of the solution. Therefore, a maximum COD reduction of 298.5 mg O_2 /Ah is possible.



Fig. 1. COD removal of an aqueous solution of malic acid. Comparison of different boron dopings; A: boron concentration <1000 ppm, B: boron concentration >1000 ppm (initial concentration of malic acid: 2 g/l, current density: 4 mA/cm²).

3. Results and discussion

3.1. COD removal

3.1.1. Malic acid

Malic acid is a dicarboxylic acid sometimes used as complexing agent, e.g. in electroless nickel plating baths. High COD values pose a substantial problem when such platings baths have to be discarded. The biological degradation of malic acid is very inefficient especially in the presence of nickel ions. We therefore used malic acid as test substance for our first experiments on the COD removal using anodic oxidation with diamond anodes. In these experiments, we tested boron-doped diamond electrodes at different levels of boron doping.

Fig. 1 shows the dependence of the COD on the charge per volume during electrolysis of an aqueous solution of malic acid with diamond anodes with different doping level. The initial concentration of malic acid was 2 g/l (pH 2.7) and the current density was 4 mA/cm^2 . In the higher concentration range which is displayed exclusively in this figure, a linear decrease of the COD can be seen. The COD removal rate was about 267 mg O₂/Ah, which corresponds to a current efficiency of about 90%. The decomposition of this complexing agent is therefore very efficient by using diamond anodes. The nearly identical curves of Fig. 1 show that the boron doping level has no or only a minor influence on the current efficiency and the COD removal at least in the range of doping levels investigated in the present paper. All further investigations gave the same result, i.e. no dependence of the COD removal rate on boron doping of the diamond electrodes. In all experiments presented in the following part of the paper, no mention on boron doping level were used.

The influence of the current density on the reduction of the COD was also investigated using malic acid. Fig. 2 depicts the dependence of the COD reduction on the charge per volume for two different current densities. Again, both curves are nearly identical with a current efficiency for COD removal of about 90%: no dependence of the COD removal rate on current density exists at least for three current densities (4, 16 and 36 mA/cm²) if the COD concentration exceeds 500 mg/l.



Fig. 2. COD removal of an aqueous solution of malic acid (initial concentration: 2 g/l). Comparison of different current densities: 16 and 36 mA/cm².

A reduction of the current efficiency can be expected only due to mass transfer limitations of the organic substances to the vicinity of the anode surface. This can happen at low COD values and under unfavourable hydrodynamic conditions. In this case, side reactions of the hydroxyl radicals will become important.

3.1.2. EDTA

EDTA (ethylenediaminetetraacetic acid) is a strong complexing agent still widely used in many industrial applications. EDTA is poorly biodegradable [32] and the destruction of this chemical substance due to the anodic oxidation by use of diamond anodes would provide a powerful means for remediation of polluted waters. We therefore investigated the possibility of EDTA destruction by the new EAOP. The starting values of the electrolysed EDTA solution are following: EDTA concentration 0.05 mol/l, pH 9.05, conductivity: 9.86 mS/cm and COD 13.4 g O_2/l .

Fig. 3 shows the COD removal in function of the charge per volume. The current efficiency of this process is again about 90%. The complexometric effect of EDTA can be eliminated



Fig. 3. COD removal and dependence of EDTA concentration on charge per volume during electrolysis of an EDTA solution using diamond anodes.



Fig. 4. COD removal of a wastewater from the paper industry: comparison of diamond electrodes (current density 7.5 and 13.3 mA/cm^2) and iridium oxide (IrO₂) coated electrodes (current density: 7.5 mA/cm²).

much faster. This is also shown in Fig. 3. After about 15 Ah/l, the EDTA concentration has dropped to a very low value although the COD of the solution is still relatively high. This result shows, that if the destruction of an organic compound is the aim of the process rather than the total mineralization, this can be achieved much faster with substantially lower charges per volume.

3.1.3. Wastewater from the paper and pulp industry

The chemical analysis of the starting solution gave the following values: pH 6.6, conductivity 2.9 mS/cm, chloride concentration 528 mg/l and COD 4023 mg O_2/l .

In this experiment, we compared the performance of diamond anodes for COD removal with the performance of conventional iridium oxide coated titanium electrodes at a current density of 7.5 mA/cm^2 . The results of our experiments are displayed in Fig. 4. The diamond anodes are much more effective in COD removal than the iridium oxide electrodes as expected. Again, there is no significant difference for diamond electrodes using different current densities ($7.5 \text{ and } 13.3 \text{ mA/cm}^2$). The current efficiency for COD removal between the start of the experiment and a charge per volume of 11.5 Ah/l was about 100% with diamond electrodes, and only 14.8% with iridium oxide electrodes.

With a current density of 7 mA/cm², the COD removal using diamond anodes was also investigated at two different temperatures of the solution: 19 and 41°C. Again, no significant differences in the COD removal rate were found.

3.1.4. Wastewater from the motor industry

Two different samples from a major German motor company were received. The initial characteristics are given in Table 1.

Sample 1 was a mixture of oil-containing wastewater from different processes and sample 2 was a condensate. The current density in the trials was 13.3 mA/cm^2 .

Fig. 5 shows the dependence of COD of samples 1 and 2 with charge per volume during EAOP treatment of the wastewaters. In both samples, the electrochemical reduction of the COD was nearly constant with a current efficiency of about 85% until a COD of about 500 mg/l was reached. Below this COD concentration, the current efficiency was reduced eventually down to approximately 50%. The COD could be lowered to about 20 mg O_2/l in

	Sample 1	Sample 2
pH	5.19	6.62
Conductivity (mS/cm)	3.74	5.63
$COD (mg O_2/l)$	3200	1496
Hardness (dH)	5.2	<1
Chloride (mg/l)	135	43

Table 1			
Initial values	s of the samples	s from the m	otor industry

sample 1 and 26 mg O_2/l in sample 2. During the experiments, the pH was slightly rising for both samples. In sample 1, it increased from 5.19 to 7.73 and in sample 2 from 6.62 to 8.83.

The reduction of the current efficiency in the lower concentration range of COD can be explained by side reactions of the OH[•] radicals. Due to mass transport limitations at low COD concentrations, insufficient COD compounds are available in the vicinity of the electrode surface to react with the OH[•] radicals produced according to Eq. (1). Thus, the highly reactive hydroxyl radical undergoes other reactions such as the formation of hydrogen peroxide by the combination of two OH[•] radicals according to Eq. (4) [7] or the reaction with scavenger substances (e.g. hydrogen carbonate [1]).

$$2OH^{\bullet} \to H_2O_2 \tag{4}$$

Hydrogen peroxide will be further oxidized to oxygen [7]:

$$H_2O_2 \to O_2 + 2H^+ + 2e^-$$
 (5)

Different possibilities exist to enhance the performance in the lower COD concentration range. The mass transfer has to be improved by optimizing reactor geometry and hydrody-namic conditions providing high through flow velocities with turbulent flow characteristics. Moreover, it is possible to perform efficient COD degradation at lower COD concentration levels by applying lower current densities. To efficiently treat waters with very low COD values (below about 100 mg/l) with diamond anodes, the use of three dimensional diamond



Fig. 5. COD removal of a wastewater from the motor industry (current density: 13.3 mA/cm²).

	Sample 1	Sample 2	
рН	12.46	12.34	
Conductivity (mS/cm)	34.1	14.9	
Chloride (mg/l)	4200	200	
$COD (g O_2/l)$	7.9	8.4	
AOX (mg/l)	>30	6.84	

Characteristics of the two different samples from the pigment industry

Table 2

anodes is inevitable. For this purpose small diamond coated electrode spheres or the like have to be developed.

3.2. Wastewater from the pigment industry

A wastewater from the copper phthalocyanine production in a factory from the pigment industry was investigated next. We received two strongly coloured samples from this plant with characteristics of Table 2.

Fig. 6 shows the dependence of COD of both samples with the charge per volume during electrolysis at a current density of 36 mA/cm^2 . In both cases, the COD could be reduced below 25 mg O₂/l with a current efficiency of about 90%. Also, a decoloration of the initially strongly coloured wastewaters could be achieved.

Besides the COD reduction and the decoloration of the solution, a decrease of the AOX could also be measured. After a charge per volume of 43 Ah/l, the AOX was reduced from 30 mg/l to 7.2 mg/l in sample 1 and from 6.84 mg/l to 0.75 mg/l in sample 2.

All our experiments on COD removal showed a current efficiency from about 85-100% independent of boron doping of the diamond electrode, of the current density in the range between 4 and 36 mA/cm^2 , of the temperature and of the wastewater used be it of synthetic or industrial nature. These results were recently confirmed by the successful electrochemical oxidation of radioactive contaminated lubricants [33].



Fig. 6. COD removal in phthalocyanine containing wastewaters from the pigment industry (current density 36 mA/cm^2).



Fig. 7. AOX formation and decomposition during COD removal in a wastewater from the motor industry.

3.3. Side reactions

In dealing with advanced oxidation processes, the consideration of possible side reactions is very important. A multitude of side reactions is possible due to the extremely high reactivity of OH[•] radicals. Some of them can produce unwanted highly toxic compounds. The most relevant side reactions are the production of chlorinated organic compounds, the oxidation of amines to nitrate and the oxidation of chloride to chlorate and perchlorate. All three possibilities were investigated in the present study.

3.3.1. AOX formation and decomposition

Fig. 7 depicts the COD reduction of a wastewater from motor industry together with the evolution of the concentration of chloride ions and AOX (chlorinated organic compounds). Again, the COD removal is achieved with high current efficiency. But with chloride ions present in the electrolyzed solution, AOX is formed during the initial stages of COD removal. This can be seen in the decrease of chloride concentration and the rise in the AOX level. The chlorinated organic compounds are, however, also eventually destroyed by OH[•] radicals, thus finally reducing the AOX value. The chloride concentration decreased during the whole electrolysis process until very low end concentration. This can only be explained by the formation of chlorine–oxygen compounds such as chlorate and perchlorate, which concentrations were not determined in the present study.

3.3.2. Formation of nitrate

The oxidation of amines by OH^{\bullet} radicals can probably result in the formation of nitrite and nitrate. To test this possibility we investigated the anodic oxidation of a 10 mmol/l solution of triethanolamine (1.49 g/l) in water at a current density of 27.9 mA/cm². The initial pH of the solution was adjusted to 11.1 by addition NaOH. As can be seen from Fig. 8, the linear COD removal was as expected with a current efficiency of about 90%.

Fig. 9 depicts the simultaneous development of the concentration of ammonium ions, nitrite and nitrate. The concentration of ammonium and nitrite are initially increasing during COD removal. The concentration of ammonium and nitrite are decreasing whereas the nitrate concentration increases in the later part of the oxidation process. This is probably



Fig. 8. COD removal in an aqueous triethanolamine solution (initial concentration: 10 mmol/l, current density: 27.9 mA/cm²).

due to the fact that first the carbon atoms of triethanolamine are oxidized by hydroxyl radicals leaving behind ammonium ions. Subsequently they are oxidized to form nitrite and later the end product nitrate.

3.4. Cathodic reduction of by-procucts by use of diamond cathodes

The formation of unwanted by-products such as chlorate and nitrate can constitute a major disadvantage of the EAOP. However, it is well known that diamond electrodes also posess a high overvoltage for the cathodic hydrogen production, thus enabling cathodic reactions which are impossible by use of other electrode materials [19,34]. We therefore tested the possibility of destroying nitrate and nitrite by the use of diamond cathodes. For this purpose, a similar electrode stack as was used for the anodic oxidation was employed but with reversed polarity and using iridium oxide coated titanium counter electrodes rather than uncoated titanium ones.

The elimination of nitrate and nitrite by electrochemical reduction using diamond cathodes was tested with a solution obtained in the experiments on COD removal of a triethanolamine solution. The results are shown in Fig. 10. A decrease of the concentration of



Fig. 9. Formation of nitrate via ammonium and nitrite ions (current density: 27.9 mA/cm²).



Fig. 10. Cathodic reduction of by-procucts by use of diamond cathodes.

both species can clearly be seen. However, the current efficiency for this process is very low, due to the low concentration range in which the experiments were performed consequently leading to mass transport limitations to the cathode surface.

The results of this experiment show that it is indeed possible to eliminate unwanted oxidised substances from polluted waters by the use diamond cathodes. It will hence be advantageous in future applications of the EAOP to use both diamond anodes and cathodes if undesired by-products can be formed in the anodic half-reaction.

3.5. Economic considerations

The treatment costs have to be evaluated for the future application of the new EAOP. The overall costs are represented by the sum of the capital costs, operating costs and the maintenance. In an electrochemical process, it is relatively simple to calculate the operating costs which are determined mainly by the energy consumption.

The energy consumption $C_{\rm E}$ for the removal of COD in aqueous solutions can be calculated using the following formula:

$$C_E = \frac{(P_{\text{COD}} \times U)}{(298.5 \,\text{mg}\,\text{O}_2/\text{Ah}) \times \eta \times \text{EC}}$$
(6)

with P_{COD} : the eliminated COD (g O₂), which can be calculated from the COD of the solution which should be eliminated (mg O₂/l) and the volume which is to be treated (l), U: the cell voltage (V), η : the current efficiency for COD removal, EC: the electricity cost (ϵ /kWh).

In general, current efficiency and voltage have to be determined by laboratory experiments.

The cell voltage U is the sum of the voltage which is thermodynamically and kinetically necessary for performing the electrochemical reaction U_{ec} (about 3 V) and the voltage drop ΔU due to the resistance of the electrolyte. For parallel plate electrodes this voltage drop is given by

$$\Delta U = \frac{j \times d}{\Lambda} \tag{7}$$

with d: electrode distance (cm), Λ : conductivity (mS/cm), j: current density (mA/cm²).

Thus Eq. (6) becomes

$$C_E = \frac{P_{\text{COD}} \times (U_{\text{ec}} + (j \times d)/\Lambda)}{(298.5 \,\text{mg}\,\text{O}_2/\text{Ah}) \times \eta \times \text{EC}}$$
(8)

For the removal of 1 kg COD about 16.8 kWh are necessary, assuming a current efficiency of 90%, a conductivity of 2 mS/cm, a current density of 30 mA/cm² and an electrode distance of 1 mm. With electricity costs of $0.1 \notin$ /kWh this results in operating costs of $1.7 \notin$ /kg COD.

The capital costs are extremely dependent on the anode area since the price of the diamond electrodes is currently very high. For the calculation of the electrode area necessary for solving a given problem, the following equation can be used:

$$A = \frac{C_{\text{COD}} \times v}{((298.5 \,\text{mg}\,\text{O}_2/\text{Ah}) \times \eta)/j}$$
(9)

with A: diamond anode area (cm²), C_{COD} : the COD concentration which should be reduced (g O₂/l), *v*: flow through velocity of the water to be treated (l/h).

Also very important for the capital costs is the overall current because of the price of the rectifier (the second largest component in the capital cost next to the diamond electrodes). The current I (A) necessary in a monopolar device can be calculated according to:

$$I = \frac{C_{\text{COD}} \times v}{(298.5 \,\text{mg}\,\text{O}_2/\text{Ah}) \times \eta} \tag{10}$$

4. Conclusions

Diamond anodes can very efficiently produce OH[•] radicals. Consequently, the COD removal of wastewater contaminated with organic compounds proceeds with very high current efficiency independent of the class of organic compound as long as the mass transport of organic compounds to the anode is not a limiting factor. Experiments were successfully performed for industrial and synthetic wastewaters.

However, the unspecific oxidation of all substances by the hydroxyl radicals leads to side reactions. Unwanted substances such as nitrite, nitrate, chlorate and other oxidation products can be formed. This has to be considered when designing electrochemical water treatment devices with diamond anodes. In the near future, anodic oxidation with diamond anodes (EAOP) can become one of the most interesting advanced oxidation processes.

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