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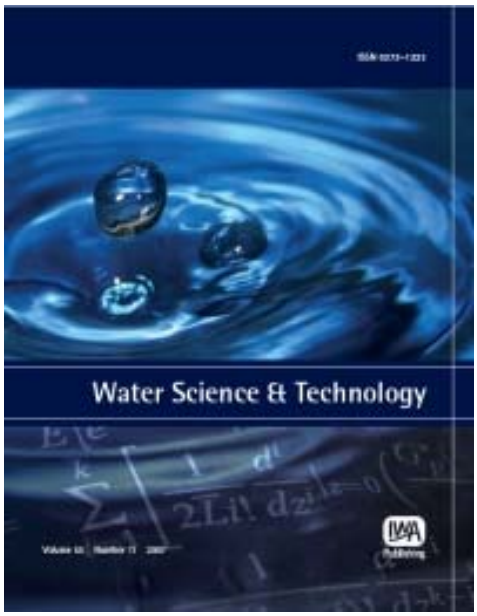

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Electrochemical oxidation of wastewater – opportunities and drawbacks

D. Woisetschläger, B. Humpl, M. Koncar and M. Siebenhofer

ABSTRACT

Electrochemical oxidation by means of boron-doped diamond (BDD) anodes generates a very efficient oxidizing environment by forming hydroxyl radicals, providing effective water purification for elimination of persistent pollutants. In this project the degradation rates of organic and inorganic substances are investigated. Experiments were performed in laboratory and pilot scale with synthetic and industrial wastewaters. Performance parameters were evaluated in terms of total organic carbon/chemical oxygen demand (COD) removal, specific energy consumption and current efficiency. The integration of this advanced oxidation technology combined with conventional technology was then applied in a wastewater treatment concept of landfill leachate. The raw leachate with a low biochemical oxygen demand/COD ratio was electrochemically oxidized to prepare the purified leachate for discharge into a sewage system or a receiving water body. The cost estimation regarding operation and capital costs addresses the economics for the treatment of heavily polluted effluents.

Key words | anodic oxidation, boron-doped diamond (BDD), industrial wastewater, landfill leachate, pilot plant

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INTRODUCTION

Industrial effluents may have toxic properties, difficult to characterize because of a complex water matrix, including organic and inorganic constituents. Conventional technologies, such as biological oxidation, filtration, adsorption, incineration or chemical oxidation may fail because of infeasible economics, poor reliability or efficiency (Panizza *et al.* 2008). In recent years the interest has been focussed on advanced oxidation processes, which offer effective water purification performance and can eliminate persistent pollutants. This field of research includes photochemical oxidation, wet oxidation, ozonation, Fenton oxidation and electrochemical oxidation. In particular, anodic oxidation by means of boron-doped diamond anodes (BDD) has demonstrated its high potential for the degradation of persistent organic pollutants. This electrode material has great advantages such as high chemical inertness, low adsorption properties and high oxygen evolution overpotential. Applied as anodes in electrochemical reactors, BDD anodes generate hydroxyl radicals due to the decomposition of water molecules. These electrochemically produced radicals have a high oxidation potential and are non-selective oxidizers. Based on this very efficient oxidizing environment, complete mineralization of organics in wastewater of very different nature can be achieved. Due to the short lifetime and the high reactivity of hydroxyl radicals it is difficult to detect the amount of the produced hydroxyl radicals. A direct detection and identification of free radicals by electron spin resonance (ESR) is theoretically possible. Indirect measurements, which are the mainly used methods, use spin trapping (Marselli *et al.* 2003; Kapalka *et al.* 2009).

The oxidation of synthetic wastewaters with appropriate test substances as well as industrial wastewater has been extensively investigated. A mathematical model for the prediction of chemical oxygen demand (COD) depletion and the instantaneous current efficiency (ICE) has been developed for electrochemical batch reactor operation under galvanostatic conditions. The model, which approximates charge and mass transport limitations, shows satisfactory agreement with the experimental data during oxidation of organic substances (Gherardini *et al.* 2001; Panizza *et al.* 2001). The ICE can be defined as the part of the current directly used for the oxidation reaction as shown in Equation (1):

$$\mathrm{ICE} = \frac{z * F * V * \Delta\mathrm{COD}}{I * \Delta t} \quad (1)$$

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where z (–) is the number of electrons, F (As/mol) is the Faraday constant, V the volume of the solution (m^3), ΔCOD ($molO_2/m^3$) the decrease of COD during Δt (s) and I (A) the current.

Most of these studies were performed in laboratory scale. Only a few research groups have done scale-up into pilot plant scale. Pilot plant scale operation does need an anode area of 0.35–1.05 m^2 (Urtiaga *et al.* 2009; Anglada *et al.* 2010; Alvarez-Guerra *et al.* 2011).

The main drawbacks of electrochemical oxidation are currently the high cost of BDD-electrodes, the energy demand and the risk of formation of chlorinated by-products (Canizares *et al.* 2009; Anglada *et al.* 2011). The aim of this work is the characterization of limiting factors in laboratory and pilot scale, steady state operation of electrochemical oxidation in pilot plant scale and a reliable estimation for investment costs as well as operation costs.

METHODS

Processes and procedure

The selected effluents for investigation were synthetic mixtures of wastewater, industrial wastewaters from dye industry, pharmaceutical industry, chemical industry and landfill leachate. The synthetic solutions contained the test substances glucose, humic acid, 1,4-dioxane and phenol. Sodium sulfate was added to provide sufficient electrical conductivity. The industrial wastewaters and the raw landfill leachate were obtained from original sources. These wastewater samples were not pretreated. In Table 1 the investigated synthetic effluents are listed and in Table 2 the treated industrial wastewaters are shown.

Laboratory scale setup

Two different types of electrochemical flow cells were used in the laboratory-scale experiments, the Electro MP cell® manufactured by Electrocell with an active anode surface of 200 cm^2, and a laboratory electrolysis cell, constructed by Diaccon with an active anode area of 750 cm^2. The anodes are based on conductive thin-films of BDD on niobium substrate. The cathodes used in the electrolysis process were stainless steel electrodes. Both electrolysis cells had an interelectrode gap of 2 mm. The setup consisted of an electrolysis cell, a batch reactor, a heat exchanger, a power supply and a pump. The flowsheet of the laboratory setup is shown in Figure 1. All experiments were carried out in batch mode at a temperature of 25 °C. The reactor was stirred and flow rate through the interelectrode gap of the cell was 80 L/h. Electrical power was supplied under galvanostatic conditions with a laboratory-size power supply EA-PS3016–40B and a Munk E230G20/75 rectifier.

Table 1 | Investigated constituents in synthetic wastewater

Synthetic wastewater	
Glucose	Easily accessible substance
Humic acid	High-molecular, persistent pollutant
1,4-Dioxane	Toxic pollutant with high aqueous solubility
Phenol	Toxic organic pollutant

Table 2 | Treated industrial wastewater and specific contaminants

Industrial wastewater	
Dye industry	Colour, COD
Pharmaceutical industry	Active pharmaceutical ingredients
Chemical industry	Phenol, 1,4-dioxane
Landfill leachate	COD, colour

Pilot scale setup

The pilot plant was equipped with two electrolysis cells, each with 1.05 m^2 active anode area. The cells, consisting of seven BDD anodes and eight stainless steel cathodes, were designed and assembled by VTU company and Graz University of Technology. The interelectrode gap was 2 mm. Experiments were performed in batch mode at a temperature of 30 °C. Both cells can be operated in serial or parallel mode. The flow rate through one electrolysis cell was 2,800 L/h. As power supply a Flexkraft rectifier with a maximum output of 4,200 A/12 V was installed. The test runs were performed under galvanostatic conditions.

Analytical procedure

The COD, adsorbable organic halogens (AOX) and inorganic components (ammonium, calcium, chloride, magnesium, nitrate, sulfate) were measured during electrolysis with a Macherey-Nagel Photometer NANOCOLOR. Total organic carbon (TOC) was monitored with an Elementar liquiTOC II analyser. When sediments were formed in the reactor during electrolysis, the samples were filtered with a 0.45 μm syringe filter. A Thermo Scientific Orion

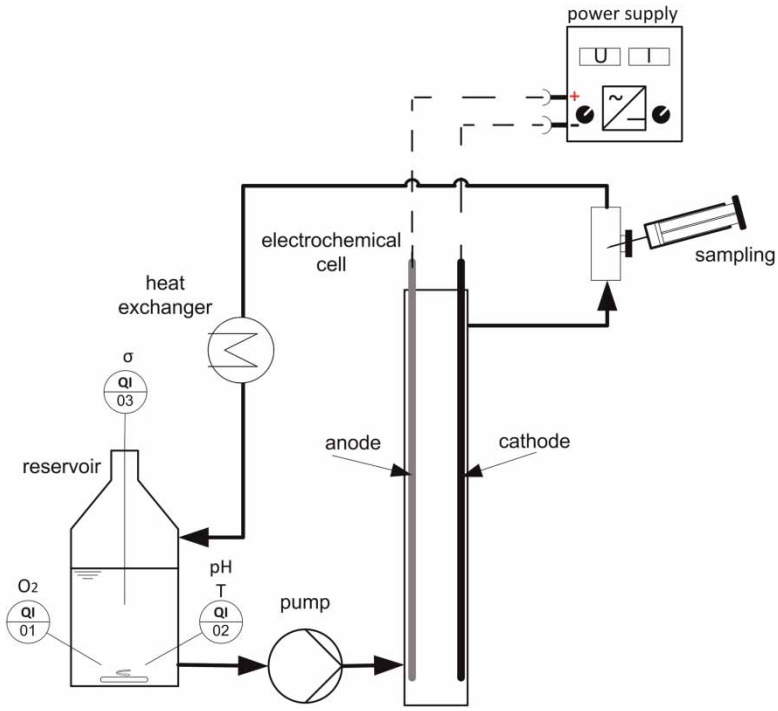

Figure 1 | Laboratory setup.

five star unit was used to measure pH, conductivity and dissolved oxygen.

RESULTS AND DISSCUSSION

Mineralization of organic compounds

Table 3 shows the process parameters of the set of experiments and the characteristics of the treated effluents. Different types of constituents were electrochemically oxidized in laboratory and pilot scale. The current density influences the electrolysis time, the energy consumption and the current efficiency. Depending on the water matrix, the limiting current density and the installed electrode area, a current density of 500–1,500 A/m² was applied.

In Figure 2 the oxidation trends of different types of constituents are shown. As expected, degradation of all substances is possible due to non-selectivity of hydroxyl radical attack. Regarding the chemical structure, substances such as glucose, phenol or 1,4-dioxane are easily oxidizable organic compounds. Humic acid is a high-molecular weight molecule with a complex structure. Because of the thin hydroxyl radical layer thickness at the surface of the electrodes and the chemical structure, degradation of humic acid is poor.

Qualitatively, Figure 2 already indicates areas of mass transfer control and charge transfer control for oxidation of selected target substances. In the charge transfer controlled region a linear decrease of the concentration of the corresponding organic constituents is measured, until the limiting current density is reached. At this concentration level the mechanism of oxidation changes from charge transfer control into the mass transfer control, following an exponential decrease. The limiting current density $i_{\lim}$ is calculated according to Equation (2):

$$i_{\lim} = z * F * k_{\mathrm{m}} * c_i \tag{2}$$

with the number of exchanged electrons z (–), the Faraday constant F (As/mol), the mass transport coefficient k_{m} (m/s) and the concentration of organics c_i (mol/m³).

Concerning the poor accessibility of humic acid in the treated effluents, mixtures of glucose and humic acid were electrochemically oxidized. In Figure 3 the degradation trends of these synthetic wastewater mixtures are presented. With an increase of the amount of humic acid, degradation gets increasingly inhibited. Inhibition of treatment and limitation of process efficiency is best indicated by the dissolved oxygen content. The inset of Figure 3 shows the measured

Table 3 | Effluents and process parameters

Experiment code	Effluent	Scale/anode area (m^2)	i (A/m_2)	Target compound (measured as)	c_0 target compound (mg/L)	c_0 total COD (mg/L)	Treated volume (L)
L-1	Industrial wastewater	Lab/0.075	500	Phenol (phenol index)	70	7,000	5.5
L-2	Synthetic wastewater	Lab/0.02	500	1,4-Dioxane (1,4-dioxane)	14,000	33,000	0.75
L-3	Industrial wastewater	Lab/0.075	1000	Organics (COD)	10,000	10,000	3.5
L-4	Synthetic wastewater	Lab/0.02	500	Glucose (COD)	10,000	10,000	1.0
L-5	Industrial wastewater	Lab/0.02	500	Humic acid (COD)	5,600	5,600	1.0
L-6	Synthetic wastewater	Lab/0.02	500	Glucose (COD)	10,000 Glucose	10,000	1.0
L-7	Industrial wastewater	Lab/0.02	500	Glucose/Humic acid (COD)	7,500 Glucose 2,500 Humic acid	10,000	1.0
L-8	Synthetic wastewater	Lab/0.02	500	Glucose/Humic acid (COD)	5,000 Glucose, 5,000 Humic acid	10,000	1.0
L-9	Industrial wastewater	Lab/0.075	500	Organics (COD)	6,500	6,500	7.0
P-1	Synthetic wastewater	Pilot/1.05	500	Organics (COD)	6,700	6,700	400
P-2	Industrial wastewater	Pilot/1.05	1000	Organics (COD)	6,700	6,700	400
P-3	Synthetic wastewater	Pilot/1.05	1500	Organics (COD)	6,700	6,700	400
P-4	Industrial wastewater	Pilot/1.05	500	Organics (COD)	5,400	5,400	410

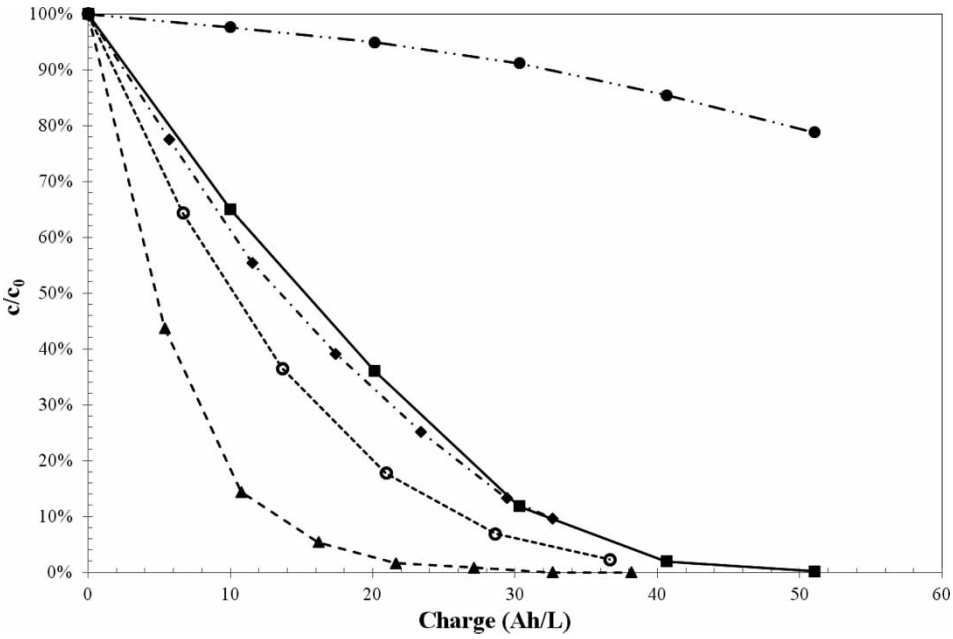

Figure 2 | Degradation trends of target compounds vs. charge. (▲) L-1, phenol; (○) L-2, 1,4-Dioxane; (◆) L-3, COD; (■) L-4, glucose; (●) L-5, humic acid according to the operation specification in Table 3.

values of dissolved oxygen during electrolysis. A low oxygen value indicates high current efficiency and linear depletion of the COD. During electrochemical oxidation, hydroxyl radicals will primarily react with organic substances to form partially oxidized intermediate products and carbon dioxide. Retardation and inhibition of these reactions due to mass transport limitation or because of low reactivity of constituents will preferably lead to decomposition of hydroxyl radicals to oxygen. As a consequence, the dissolved oxygen content increases. The comparison of the degradation trend of

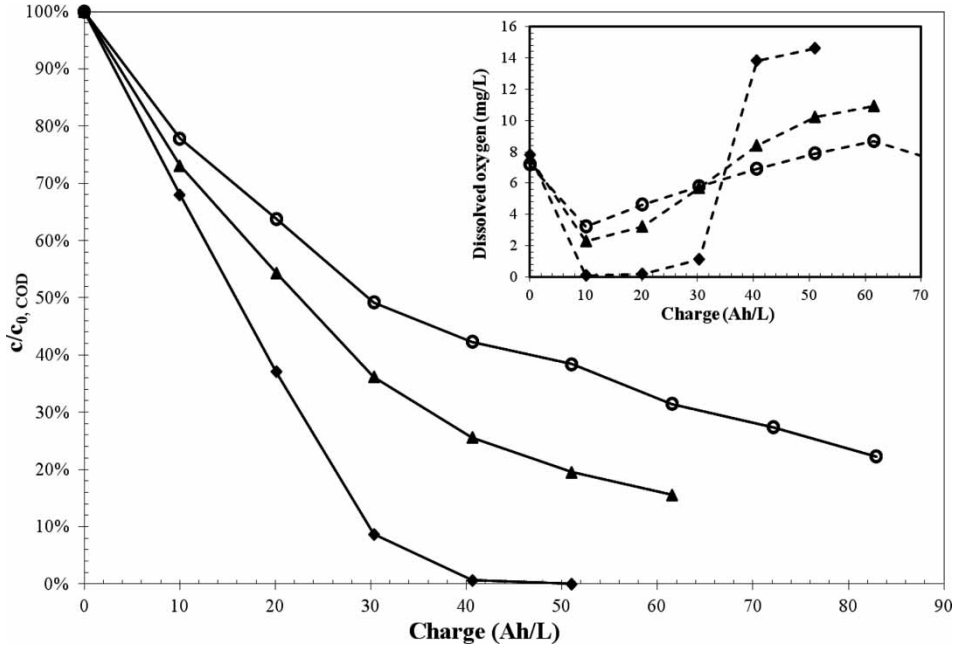

Figure 3 | Oxidation of glucose and humic acid. (♦) L-6, 100% glucose; (▲) L-7, 75% glucose and 25% humic acid; (○) L-8, 50% glucose and 50% humic acid; Inset: Dissolved oxygen vs. charge. (♦) L-6; (▲) L-7; (○) L-8. Process specification according to Table 3.

mixtures of the easily accessible test constituent glucose and the hardly accessible test constituent humic acid, by means of dissolved oxygen, confirms these effects. Indirect oxidation of organic compounds and oxygen evolution at BDD-electrodes validate these reaction mechanisms (Marselli *et al.* 2003).

Scale-up based on COD depletion

In order to validate scale-up of processes, industrial wastewater was treated in laboratory and pilot scale. In Figure 4 COD depletion trends for selected process conditions are shown. Regarding COD the trends between laboratory and pilot plant are similar. Both trends show linear depletion close to theoretical current limited electro-oxidation with charge transfer control, until finally the shape of the oxidation process trend shifts into an exponential trend at low COD values. In the inset of Figure 4 the variation of the current density for pilot scale operation is presented. It does not show any difference of current efficiency between treatment at 500 and 1,000 A/m² except the higher cell voltage. At current density of 1,500 A/m², retardation of COD depletion is monitored and extended formation of gas bubbles in the cell is observed, indicating operation beyond the limiting current density for oxidation of constituents even at high load. As a consequence a maximum current density of 1,000 A/m² for pilot plant electrolysis was applied.

Theoretical current controlled electro-oxidation for the mineralization of organics can be defined with Faraday's law, according to Equation (3):

$$Q_{\text{theo}} = n * z * F \tag{3}$$

with the charge for organics mineralization Q_{theo} (As), the molar amount of the corresponding organic compound n (mol), the number of electrons z (–) and the Faraday constant F (As/mol). The theoretical $\text{dCOD}/\text{d}Q_{\text{theo}}$ ratio is calculated with Equation (4):

$$\frac{\text{dCOD}}{\text{d}Q_{\text{theo}}} = 298.49 \left[\frac{\text{mg}}{\text{Ah}}\right] \tag{4}$$

This value is the slope of the theoretical current controlled electro-oxidation trend, which represents the maximum possible electrochemical oxidation.

Electrochemical treatment of raw landfill leachate in pilot scale

The degradation trends of organic and inorganic substances in raw landfill leachate in pilot scale are shown in Figure 5. Electrochemical oxidation of the organics in the leachate is possible. The gap between the theoretical current controlled electro-oxidation and the measured COD values during

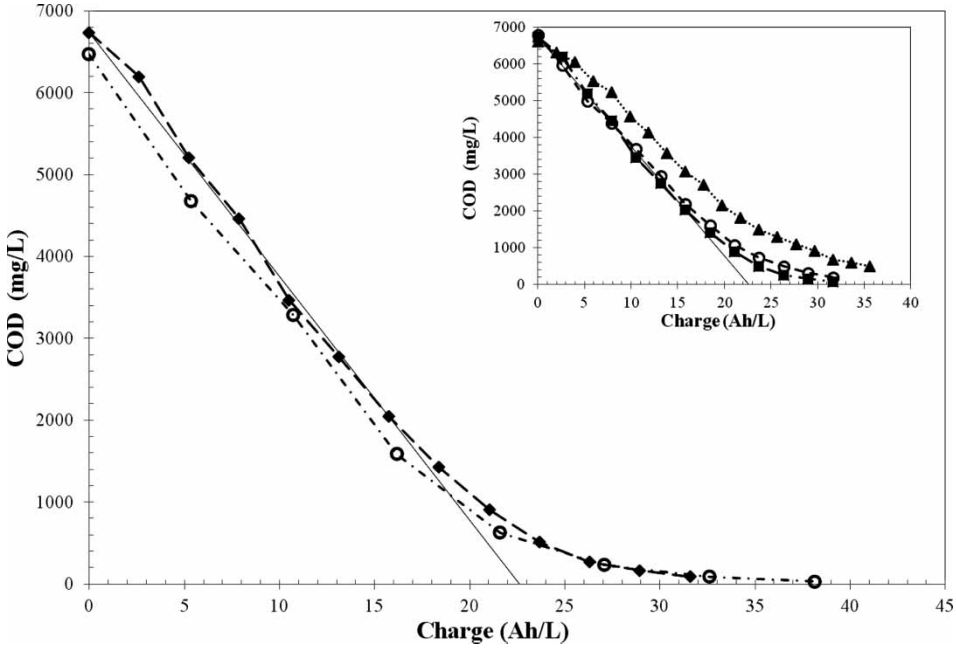

Figure 4 | Comparison of COD depletion in laboratory scale (○) L-9 and pilot-plant scale (♦) P-1; Inset: Effect of the current density, COD depletion pilot plant (■) P-1, 500 A/m²; (○) P-2, 1,000 A/m²; (▲) P-3, 1,500 A/m². Solid line: calculated current controlled electro-oxidation; process parameters according to Table 3.

electrolysis indicates limited efficiency. This inhibition can be explained with the amount of humic acid in the leachate.

Because of significant chloride load of the effluent, formation of chlorinated by-products has to be considered. During electrolysis, an increase of AOX at low COD and high chloride level is monitored. After complete oxidation of chloride to chlorine, degradation of AOX was determined. Based on these results, a combination of wastewater treatment technologies is needed to improve efficiency of raw landfill leachate purification.

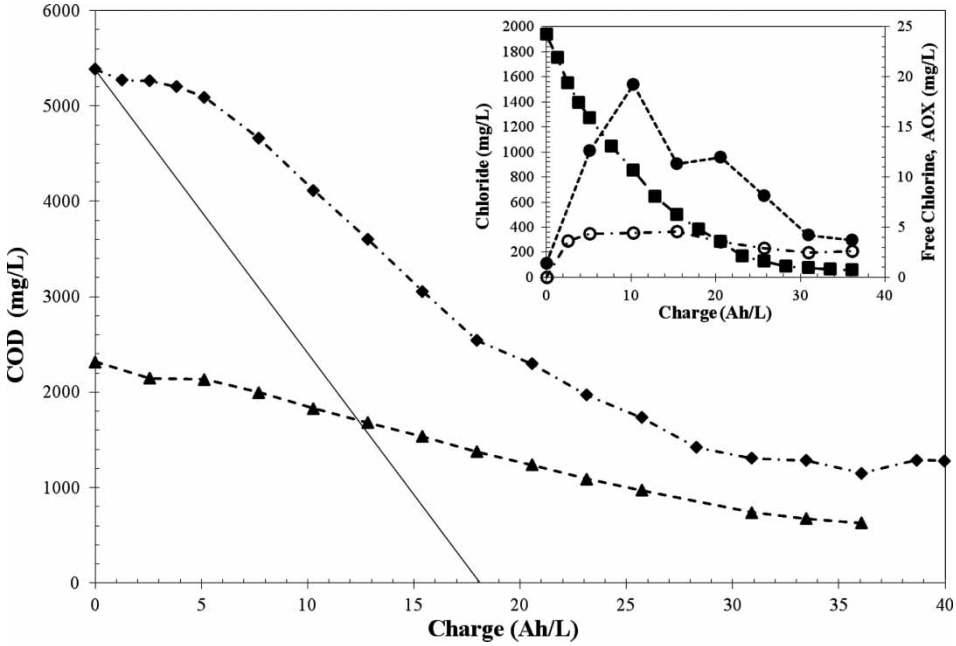

Figure 5 | Degradation trends for treatment of organic and inorganic substances in landfill leachate (P-4) according to the specification in Table 1. (♦) COD; (▲) TOC; (■) choride; (○) free chlorine; (●) AOX. Solid line: calculated current controlled electro-oxidation; process parameters according to Table 3.

Wastewater treatment concepts must consider the combination of coagulation, electrochemical treatment and activated carbon adsorption. By means of this treatment concept it is possible to purify raw landfill leachate according to the needs for discharge into a sewage system.

Cost estimation

Based on the results of laboratory and pilot plant electrolysis experiments a reliable cost estimation for full scale operation capacity is possible. The operation and investment costs depend on the COD value, the current efficiency, the conductivity and the current density. The operation costs show a span from 22 kWh/kg_{COD} at high current efficiency in charge transfer controlled range to a maximum economic value of 95 kWh/kg_{COD} for low current efficiency in the mass transfer controlled region. Investment costs, including electrolysis cells, rectifier and equipment can be estimated for a 2 m^2 electrolysis plant with €95,000 and for a 10 m^2 electrolysis plant with €380,000.

CONCLUSION

The results confirm the high potential of electrochemical oxidation in a wide range of different applications under varying conditions. Complete degradation of several persistent pollutants was validated. Scale-up from 0.02 m^2 laboratory size to 2 m^2 pilot plant size was successfully carried out. Experiments with industrial wastewater and landfill leachate in laboratory and pilot scale validated the comparability of results for operation in laboratory scale and pilot plant scale. A minimum specific energy consumption of 22 kWh/kg_{COD} was determined for COD depletion at high current efficiency. Depending on the water matrix and discharge limits it is recommended to combine electrochemical treatment with conventional wastewater treatment technologies. Currently limiting drawbacks are the cost of electrodes and AOX formation. Improvements are expected in BDD electrode cost, energy demand, cell construction and operation mode. These steps will intensify the role of EAOPs in the treatment of heavily polluted wastewater effluents.

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