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Electrochemical treatment of diluted cyanide aqueous wastes

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Abstract: The electrochemical oxidation of diluted cyanide aqueous wastes has been studied in a single compartment electrochemical flow cell. It has been determined that the anode material influences greatly the process's performance. Boron doped diamond and PbO_2 anodes can oxidize these wastes in the presence of both sulfate or chloride anions. On the contrary, dimensional stable anodes cannot oxidize cyanide in sulfate-containing wastewaters, and require the presence of chloride ions. The oxidation of cyanides leads to the formation of cyanate in a first step, and later to the formation of carbon dioxide and nitrogen. There is a net consumption of hydroxyl ions during the process. Energy consumptions in the range 20–70 kWh m^{-3} are required to decrease the initial pollutant load by 70–80%. Global current efficiencies in the range 3–8% are obtained. These low current efficiencies are justified by the low cyanide concentrations that the wastes used in this work contain.

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Keywords: cyanide; electrochemical oxidation; boron doped diamond (BDD) electrodes; PbO_2 electrodes; dimensional stable anode (DSA) electrodes

INTRODUCTION

Cyanide-containing wastewaters are characterized by their high toxicity and very low degradability by conventional treatments. Classified as both hazardous and toxic, cyanide is an EPA designated priority pollutant. Cyanide is an important chemical in the electroplating and galvanic industry, in metallurgical processes, as a case hardening agent (leaching of gold and silver ores), in oil refineries, in chemical manufacturing plants and in thermoelectric power stations.[1]

Various procedures exist for treating wastewaters containing cyanide. Alkaline chlorination has been the most commonly applied technique for the destruction of cyanide species.[2–4] Ozonization is a promising technology to treat cyanide effluents. Ozone is a strong oxidant and produces non-toxic products.[5] Advanced oxidation processes, which involve the *in-situ* generation of powerful chemical oxidants such as the hydroxyl radical ($^\bullet$OH), are more reactive and much faster compared with the ozone molecular process and have recently emerged as an important class of technologies for accelerating the oxidation and destruction of a wide range of contaminants in polluted water.[1,6–8] Electrochemical oxidation may offer an attractive alternative for treating cyanide by oxidation, via an indirect electrochemical method based on *in-situ* liberation of hypochlorite by electrolysis of a cyanide waste to which sodium chloride has been added (especially suitable for treating wastewaters with a cyanide concentration less than 500 ppm) and via direct oxidation at the anode surface for higher concentrations.[9]

The key for an efficient electrolytic treatment is the selection of the anode material. In addition to more traditional materials (dimensional stable anodes (DSA), SnO_2, PbO_2, graphite, nickel, stainless steel, etc),[10–15] recent years have seen anodes based on diamond layers, boron doped diamond (BDD) electrodes, the advantages of which include good chemical resistance and high efficiency in the treatment of different kinds of wastewaters.[16–19]

The work described here concerns a study of the electrochemical oxidation process for destruction of cyanide for wastewater treatment. The goal was to elucidate mechanistic aspects of the oxidation process, comparing the results obtained in the electrochemical oxidation of cyanide aqueous wastes carried out with three different anode materials at different operating conditions.

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EXPERIMENTAL

Analytical procedures

Cyanide concentration was measured with a cyanide ion selective electrode (Metrohm, Switzerland) following a standard procedure.[20] Cyanate ions were measured using an HPLC with a Metrosep Anion 2 column with an IC detector. Chemical Oxygen Demand (COD) was determined using a HACH DR200 analyser. Conductivity and pH were determined by using commercial probes (Metrohm, Switzerland). To measure electrogenerated oxidants, I^-/I_2 assays were performed. This technique can quantify by titration with thiosulfate in the presence of starch all the oxidants capable of oxidizing I^- to I_2.

Electrochemical cell

The oxidation of cyanide was carried out in a single-compartment electrochemical flow cell (Fig 1). Dimensional Stable Anodes (DSA), lead dioxide (Pb/PbO_2) and Boron Doped Diamond (p-Si-BDD) were used as anodes and stainless steel (AISI 304) as the cathode. Both electrodes were circular (100 mm diam) with a geometric area of $78.54\,\mathrm{cm}^2$ each and an electrode gap of 9 mm. The electrolyte was stored in a glass tank ($0.5\,\mathrm{dm}^{-3}$) and circulated through the electrolytic cell by means of a centrifugal pump. A heat exchanger was used to maintain the temperature at the desired set point. The experimental set-up also contained a cyclone for gas desorption, and a gas absorber to collect the carbon dioxide contained in the gases evolved from the reactor into sodium hydroxide.

Electrodes

Boron doped diamond films were provided by CSEM (Switzerland) and were synthesized by the hot filament chemical vapour deposition technique (HF CVD) on single crystal p-type Si $\langle 100 \rangle$ wafers ($0.1\,\Omega\,\mathrm{cm}$, Siltronix). Lead dioxide was synthesized in our laboratory by electrochemical oxidation of lead plates at a current density (j) of $10\,\mathrm{mA\,cm}^{-2}$ in a 10% sulfuric acid solution at 25 °C for 90 min. Commercial DSA-O_2 electrodes were supplied by ElectroCell AB (Sweden). Prior to use in galvanostatic electrolysis essays, all electrodes were anodically polarized for 0.5 h in 1 M H_2SO_4 and 0.5 h in 1 M NaOH at $70\,\mathrm{mA\,cm}^{-2}$ to remove any kind of impurity from their surfaces.

Galvanostatic electrolysis

The average composition of the wastewater used in the experiments was $7.7\,\mathrm{mmol\,dm}^{-3}$ of the cyanide, $0.05\,\mathrm{mol\,Na_2SO_4\,dm}^{-3}$, and NaOH in suitable amounts to give a pH of 11. The pH was kept constant by the continuous introduction of sodium hydroxide or sulfuric acid to the electrolyte reservoir. The cell potentials were constant during each electrolysis, indicating that appreciable deterioration of the electrode or passivation phenomena did not take place. The electrolyte's flow rate through the cell was $1250\,\mathrm{cm}^3\,\mathrm{min}^{-1}$.

Determination of the current efficiency

Instantaneous current efficiency was calculated using eqn (1):

$$\mathrm{ICE} = \frac{[\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t}]FV}{8I\Delta t} \qquad (1)$$

where COD_t and $\mathrm{COD}_{t+\Delta t}$ are the chemical oxygen demand (in $\mathrm{g\,O_2\,dm}^{-3}$) at times t and $t+\Delta t$ (in s), respectively, I is the current intensity (A), F is the Faraday constant ($96\,487\,\mathrm{C\,mol}^{-1}$), V is the volume of the electrolyte (dm^3) and 8 is a dimensional factor for unit consistency $(32\,\mathrm{gO_2\,mol^{-1}\,O_2})/(4\,\mathrm{mol\,e^-\,mol^{-1}\,O_2})$.

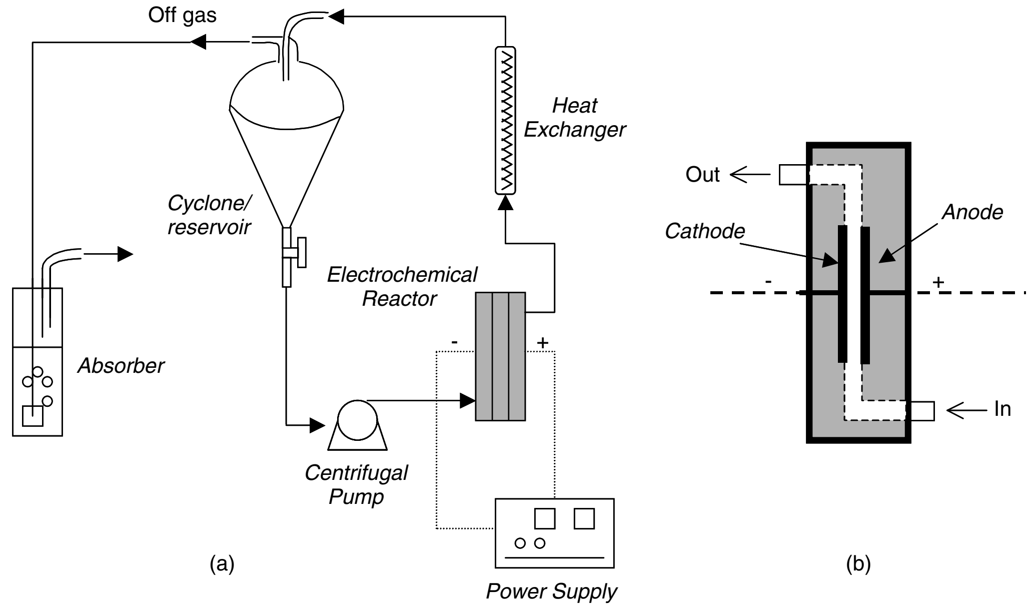

Figure 1. (a) Experimental set-up. (b) Detail of the electrochemical cell.

To calculate an average efficiency the electrochemical oxidation index (EOI) is used where τ is the time at which the average efficiency is calculated.

$$\mathrm{EOI} = \frac{\int_0^{\tau} \mathrm{ICE}(t)\,\mathrm{d}t}{\tau} \tag{2}$$

The EOI value quantifies the average efficiency of the process and it depends on the time of electrolysis. In this work, to obtain self-comparable data, the values of this parameter were calculated for the same length of the treatment in each essay (a conversion of cyanide to carbon dioxide of 0.70 was selected arbitrarily).

RESULTS AND DISCUSSION

Electrolysis in sulfate media

Figures 2, 3, 4 and 5 show the variation with the electrical charge passed (*It*/*V*) of the cyanide, cyanate and COD concentrations and the amount of hydroxyl ions consumed during the electrolysis of a synthetic wastewater that contains 375 mg dm^{-3} of NaCN (200 mg dm^{-3} of CN$^-$) and 0.05 M Na_2SO_4 at an initial pH of 11.

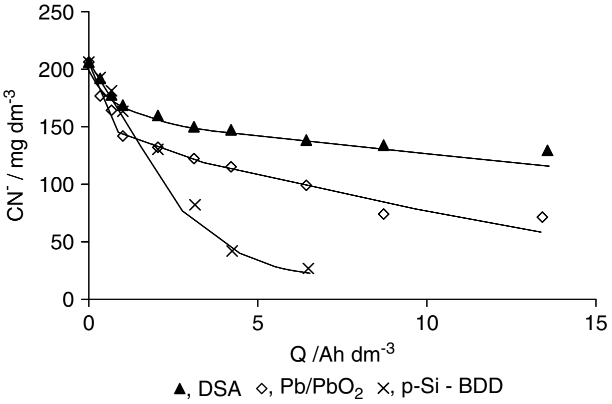

Figure 2. Cyanide concentration variation during the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M Na_2SO_4.

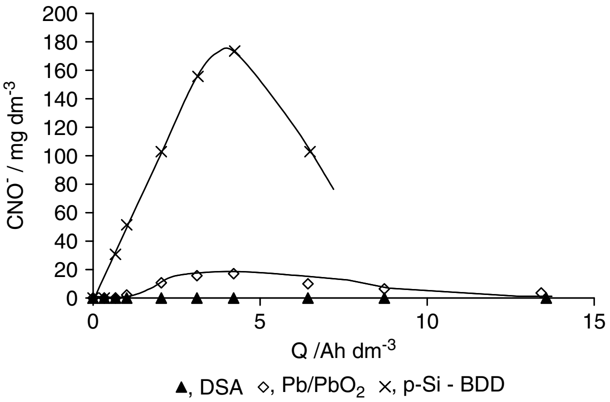

Figure 3. Cyanate concentration variation during the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M Na_2SO_4.

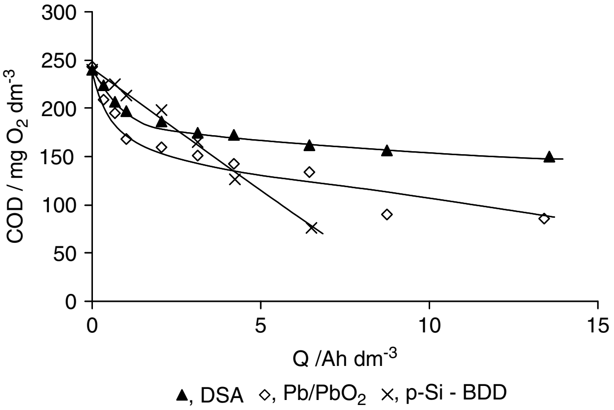

Figure 4. COD concentration variation during the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M Na_2SO_4.

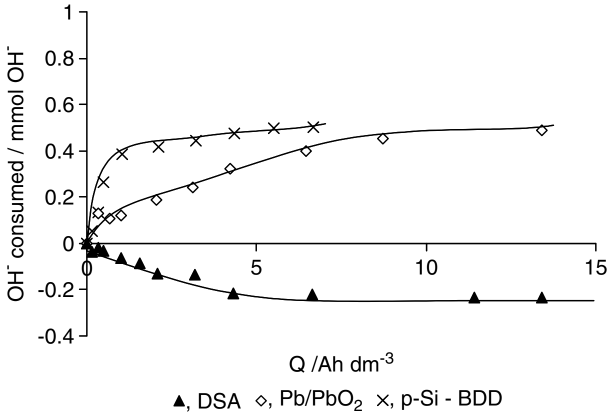

Figure 5. Hydroxyl consumption during the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M Na_2SO_4.

It can be observed that the anode material influences greatly the process's performance. The oxidation of cyanides is carried out via the formation of cyanates on the BDD and on the PbO_2 anodes. Cyanate concentration increases during the cyanide oxidation and later decreases, showing that this compound is a reaction intermediate and not the final product. The decrease of the COD with the time is linear in the oxidation carried out with BDD anodes, exponential with the lead dioxide and complex (initial rapid decrease with a later stabilization) with the DSA. The BDD anode achieves the higher total oxidation rates, although initially the lead dioxide anode reaches a higher value of this rate. The BDD anode also shows the higher concentrations of cyanate, indicating that the surface of BDD favours the oxidation of cyanide over cyanate. The removal of cyanide in the DSA oxidation is very rapid at the initial time but after the first minutes the oxidation rate decreases rapidly and the concentration is maintained almost constant. No cyanates are detected during this process.

Hydroxyl ions are consumed during the oxidation process in the experiments with BDD and lead dioxide anodes. On the contrary, there is a net generation of hydroxyl ions in the treatment with DSA. The consumption of hydroxyl ions observed in the two former cases can be interpreted in terms of the electrochemical reactions that can occur on the anode and on the cathode surfaces of the electrochemical cell[9,21,22] and in terms of the acidity equilibria between carbon dioxide, bicarbonate and carbonate ions. On the anode, the main desired reactions are the cyanide and the cyanate oxidation (eqns (3) and (4)). Oxygen generation by oxidation of hydroxyl ions (eqn (5)) competes with these two reactions and decreases the current efficiency (main anodic side reaction). Hydrogen generation by reduction of water can be considered to be the main reaction which occurs on the cathode surface (eqn (6)).

$$CN^- + 2OH^- \longrightarrow CNO^- + H_2O + 2e^- \quad (3)$$

$$CNO^- + 2OH^- \longrightarrow CO_2 + \tfrac{1}{2}N_2 + H_2O + 3e^- \quad (4)$$

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \quad (5)$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad (6)$$

Carbon dioxide is absorbed into the solution (eqn (7)) and transformed into bicarbonates (eqn (8)) and carbonates (eqn (9)), the concentration of each ion depending on the pH of the solution.

$$CO_2(g) \longrightarrow H_2CO_3(aq) \quad (7)$$

$$H_2CO_3(aq) + OH^- \longrightarrow HCO_3^- + H_2O \quad (8)$$

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O \quad (9)$$

Taking into account the acidity constants of reactions (8) and (9) (4.31×10^{-7} and 5.61×10^{-11}, respectively), at pH 11.0 carbonate and bicarbonate ions are the predominant species. Thus, eqn (4) can be rewritten as eqns (10) and (11) considering the final oxidation products:

$$CNO^- + 3OH^- \longrightarrow HCO_3^- + \tfrac{1}{2}N_2 + H_2O + 3e^- \quad (10)$$

$$CNO^- + 4OH^- \longrightarrow CO_3^{2-} + \tfrac{1}{2}N_2 + 2H_2O + 3e^- \quad (11)$$

In the cyanide and in the hydroxyl ions oxidation processes, one hydroxyl ion per electron is consumed. The ratio is also maintained in the oxidation of cyanates to bicarbonate ions. This consumption ratio is equal to the generation rate obtained on the cathode during the water reduction process. Consequently, if only these reactions occur, the pH of the bulk solution should not change. However, the ratio changes in the oxidation of cyanates to carbonate ions and it increases up to 1.33. Hence, in the global oxidation of cyanide to carbonate (eqn (12)), six hydroxyl ions are consumed by each five electrons involved in the oxidation of cyanide (ratio 1.20). On the cathode the main reaction is still water reduction and consequently the hydroxyl generation ratio is 1.00. Thus, there is a net consumption of 0.20 hydroxyl ions for each electron involved in the oxidation of cyanide to carbonate ion and no net consumption if the final product is bicarbonate. At pH 11, both carbonate and bicarbonate species coexist. This can justify the consumption of hydroxyl ions observed experimentally.

$$CN^- + 6OH^- \longrightarrow CO_3^{2-} + \tfrac{1}{2}N_2 + 3H_2O + 5e^- \quad (12)$$

The strange shape of the cyanide concentration evolution in the electrolysis with DSA, with an initial high oxidation rate and a subsequent large decrease in the rate of oxidation, has been reported previously in the literature,[23] although it was not completely explained.

The experiments carried out in this work under these conditions show no generation of cyanates and only a decrease in the concentration in the initial minutes of the experiment. This strange behaviour seems to be caused not by the electrochemical oxidation of cyanides but by the adsorption of cyanide onto the anode surface (or by the possible reactions of this compound with the metals that it contains). This idea is supported by Fig 6, in which the results of electrolysis carried out at 15 and 30 mA cm^{-2} are compared with those obtained in an essay without current supply. As can be observed, the same behaviour occurs in every case, indicating that the initial decrease in the cyanide concentration is not due to the electrochemical treatment but to the adsorption onto the surface or the chemical reaction between cyanide and any of the metals present in the surface of DSA. This could also explain why cyanates were not detected in the bulk solution. Figure 6 also shows that hydroxyl ions are generated during these processes,

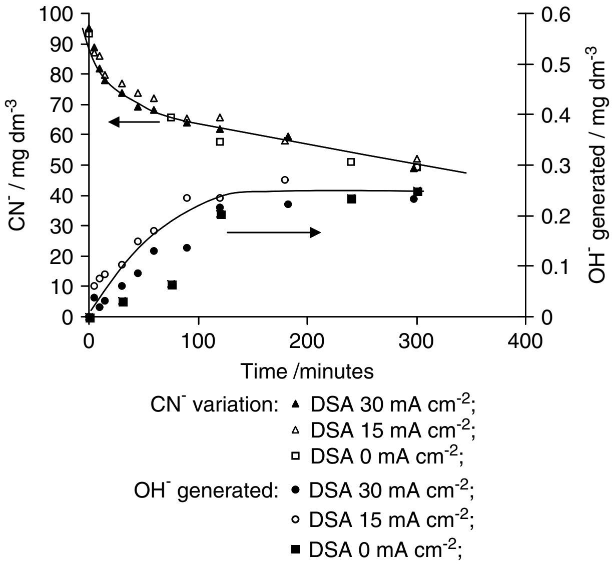

Figure 6. Influence of the current density in the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M Na_2SO_4.

and that their generation rate does not depend on the current, but on the amount of cyanide that disappears.

Figure 7 shows the chemical oxygen demand evolution with time, for electrolysis carried out at 15 and 30 mA cm^{-2} compared with that predicted if the process were purely electrochemical. It can be observed that the oxidation rates are higher that those expected for pure direct electrochemical processes, indicating that mediated oxidation processes are important in the oxidation of cyanides with both the BDD and the PbO_2 anodes. The model used to make the comparison was previously proposed in the literature.[24] This model is based on calculating the limiting current intensity, and it considers two types of behaviour depending on the value of this parameter. The reaction is charge-controlled if the applied current intensity is lower than the limiting current intensity. In this case, the decrease in COD with time depends only on the current and a 100% efficiency is applied in the oxidation calculations. Conversely, if the applied current intensity is higher than the limiting current intensity, the process is mass-transfer controlled. In this case, the decrease in COD with time depends on the transfer of cyanide and cyanate from and to the anode surface. The efficiency decreases linearly with the ratio COD/COD_{lim}, where COD_{lim} is the chemical oxygen demand for which the process becomes mass-transfer controlled. The main advantage of this model is that it does not include any adjustable parameters. Thus, the behaviour of the system can be predicted if the experimental conditions (applied current intensity, solution flow rate and mass transfer coefficient) are known and only the mass transfer coefficient must be calculated. In this work, the mass transfer coefficient of the cell (for the fluid dynamic conditions used) was previously calculated with a typical ferrocyanide/ferricyanide assay, obtaining a value of 1.29×10^{-5} m s^{-1}.

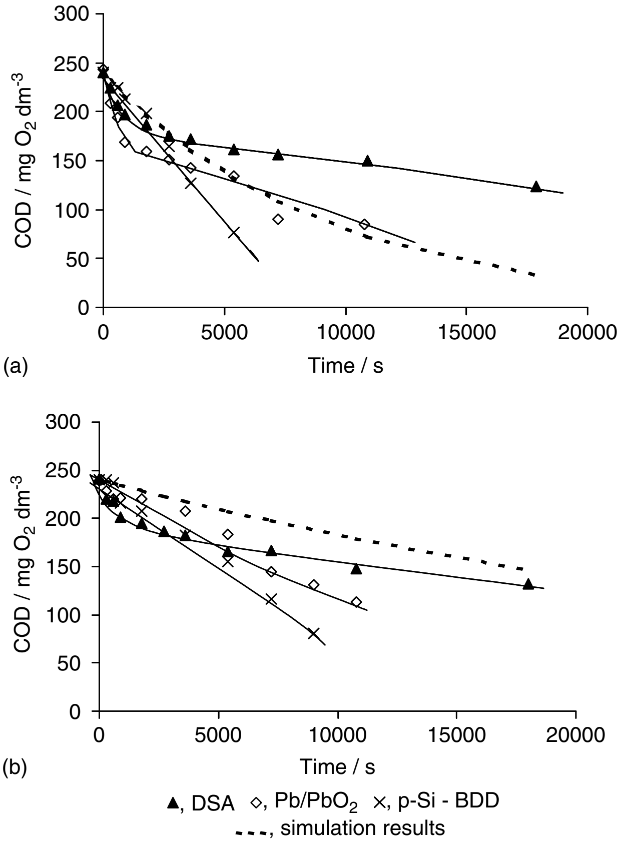

Figure 7. Chemical oxygen demand (COD) variation in the electrochemical oxidation of wastes polluted with cyanide (180 mg NaCN dm^{-3}) at $j = 30$ mA cm^{-2} (a) $j = 15$ mA cm^{-2} (b). Supporting electrolyte: 0.05 M Na_2SO_4. Simulation results were obtained for a pure direct electrochemical process[24] assuming a mass transfer coefficient of 1.29×10^{-5} m s^{-1} (calculated by a ferrocyanide/ferricyanide test).

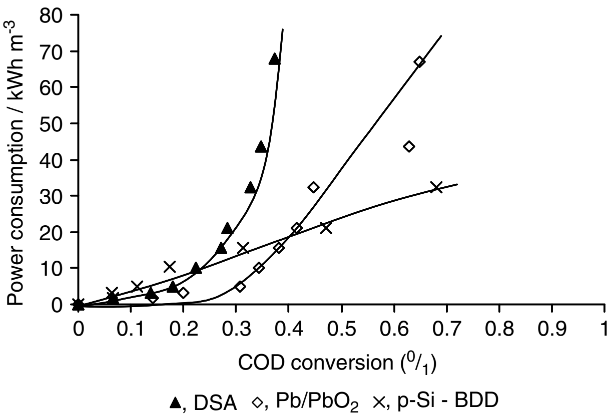

Figure 8. Power consumption in the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M Na_2SO_4.

Figure 8 shows the power consumption necessary to remove a given percentage of the initial contaminant load of the waste. It can be observed that for high COD removal the BDD anode achieves the lowest treatment costs. Removals of 70% of the total contaminant load and more than 90% of the initial cyanide concentration can be obtained with an energy consumption of 40 kWh m^{-3}.

Electrolysis in chloride media

Figures 9, 10, 11 and 12 show the variation with the electrical charge passed of the cyanide, cyanate and COD concentrations and the consumption of hydroxyl ions during the electrolysis of a synthetic wastewater that contains 375 mg dm^{-3} of NaCN, 0.05 M NaCl, at pH 11.

Completely different behaviour is observed with respect to the electrolysis in sulfate media. The PbO_2 electrode achieves a greater cyanide oxidation rate than the BDD. Likewise the shape of the cyanide vs time evolution curve on the DSA is completely different from that obtained in sulfate media, and more similar to those obtained for the other two anode materials used in this work. Nevertheless, the DSA is still the

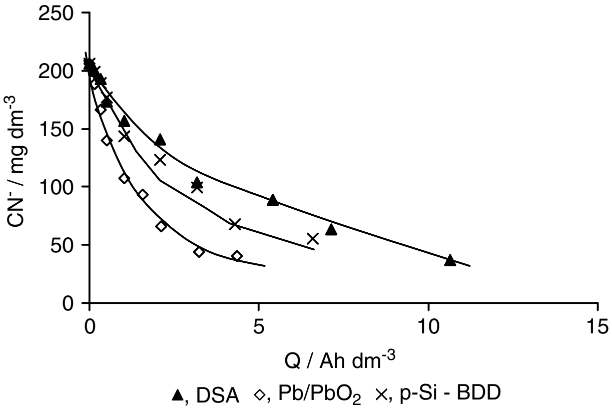

Figure 9. Cyanide concentration variation during the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M NaCl.

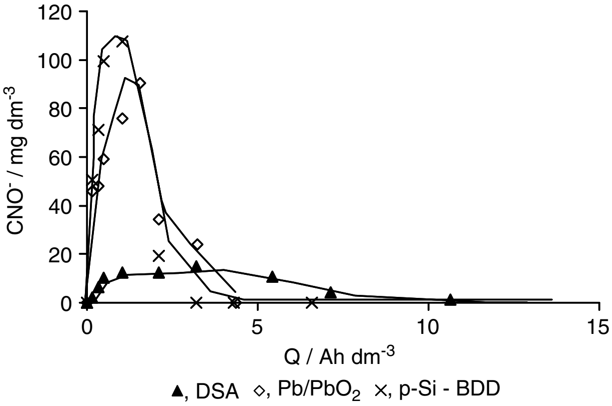

Figure 10. Cyanate concentration variation during the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M NaCl.

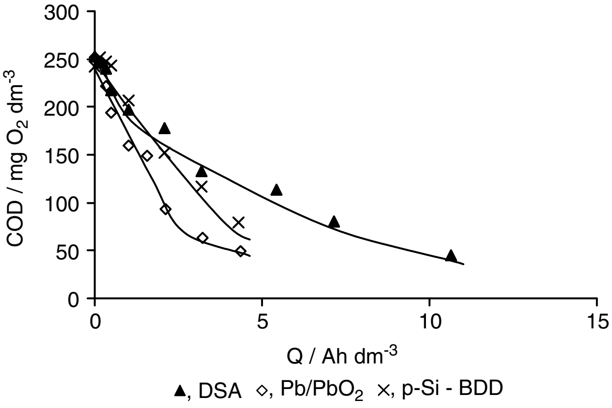

Figure 11. Chemical oxygen demand concentration variation during the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M NaCl.

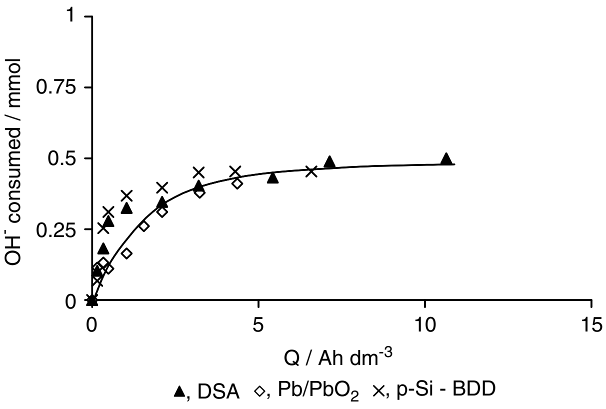

Figure 12. Hydroxyl ions consumption during the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M NaCl.

less efficient anode material. Cyanates are found in the electrolysis carried out with the three anode materials.

According to the literature,[25] the electrochemical oxidation of cyanides in chloride media can be carried out directly by electrochemical processes (eqns (3) and (4)) and indirectly by chemical processes mediated by hypochlorite. In the latter case, it is assumed that chloride is first oxidized to hypochlorite on the anode surface (eqn (13)) and later this hypochlorite reacts with cyanide to yield carbon dioxide. This carbon dioxide is absorbed into the solution and transformed into bicarbonate and carbonate (eqns (14) and (15)):

$$Cl^- + 2OH^- \longrightarrow ClO^- + H_2O + 2e^- \qquad (13)$$

$$2CN^- + 5ClO^- + H_2O \longrightarrow 2HCO_3^- + N_2 + 5Cl^- \qquad (14)$$

$$2CN^- + 5ClO^- + 2OH^- \longrightarrow 2CO_3^{2-} + H_2O + N_2 + 5Cl^- \qquad (15)$$

In the former case (eqn (14)), no hydroxyl ions are consumed but in the latter case (eqn (15)), the ratio between the consumed hydroxyl ions and the electron exchanged in the oxidation process is 1.20, the same value as that obtained in the direct electrochemical process. Hence a net consumption of 0.2 hydroxyl ions per electron involved in the oxidation of cyanide to carbonate can be expected. Thus, independently of the mechanism, the complete oxidation of cyanides to carbonate generates a net consumption of 0.2 hydroxyl ions per electron involved in the oxidation of cyanide to carbonate and no net consumption if the final product is bicarbonate. Figure 12 shows that hydroxyl ions are consumed in the concentration expected during the oxidation of cyanides with the three electrodes. This indicates the formation of carbonate, bicarbonate and nitrogen as final oxidation products of cyanide electrolyses.

To compare the oxidation rates of each electrode in the two media studied (chloride and sulfate), experimental COD data were fitted to the mass balance equation shown in eqn (16), in which it is assumed that the global oxidation process obeys first order kinetics.

$$\ln\left[\frac{COD(t=0)}{COD(t)}\right] = K_{app}t \qquad (16)$$

Table 1. Apparent decay rate for the cyanide electrooxidation as a function of the anode material and of the supporting electrolyte

		DSA	BDD	Pb/PbO2
Sulfate	K_{app} (min^{-1})	0.00276	0.01113	0.00705
	r^2	0.4725	0.9430	0.7441
Chloride	K_{app} (min^{-1})	0.00597	0.00846	0.01440
	r^2	0.9898	0.9545	0.9807

Table 1 shows apparent oxidation rates constants (K_{app}) for the oxidation of cyanide wastes as a function of the anode material and the supporting media (chloride and sulfate). It can be seen that the obtained values are inside the typical range of apparent kinetic constants reported in the literature for cyanide electrooxidation with different anode materials including tin dioxide,[25] stainless steel[26] or DSA electrodes.[27] Likewise, it can be observed that the model fits better the chloride media experiments, suggesting a higher complexity of the mechanism that happens in the experiments using sulfate media. Likewise, it can be seen that the apparent oxidation rate constants are higher in media containing chloride for PbO_2 and for DSA and smaller for BDD anodes.

The former case can be easily justified by the formation of hypochlorite in the reaction media. Hypochlorite is reported to be generated on both surfaces and this reagent can easily oxidize cyanide aqueous wastes with a high efficiency. In contrast, the latter case is more difficult to justify. In the literature, it is proposed[28] that in the electrochemical oxidation of wastes containing sulfates on BDD electrodes, some peroxodisulfates can be formed (eqn (17)). These compounds are known to be very powerful oxidants and consequently they can oxidize cyanide to form carbon dioxide.

$$2\,SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2\,e^- \qquad (17)$$

To confirm the generation of electroreagents in the experiments carried out with the BDD anode in sulfate media, and to compare the amount in which these compounds are formed in comparison with those formed in chloride media, two oxidation trials were carried out. In these trials, two aqueous solutions, which contain chloride or sulfate in the concentration used in the experiments and with the same pH, were electrolysed with a BDD anode in the single electrochemical cell used in this work. Figure 13 shows the oxidants generated in both cases. It can be observed that oxidants are generated during the treatment of sulfate solution with the BDD anode. However, it can also be observed that the concentration of oxidants generated in chloride media is higher that those obtained with sulfate media. This disagrees with the higher oxidation rate obtained in sulfate media and suggests an electrocatalytic effect of the persulfate formed on the oxidation of cyanides.

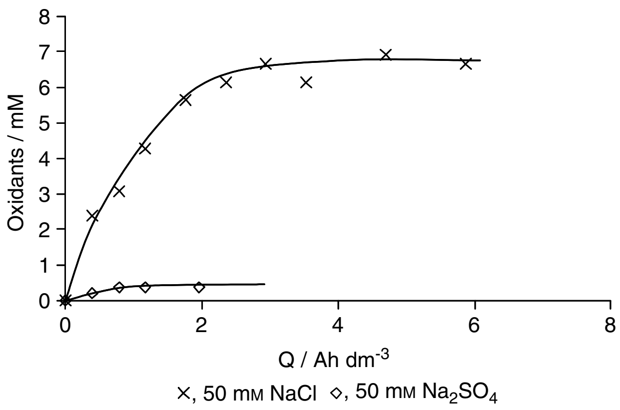

Figure 13. Electrogeneration of inorganic oxidants with BDD anodes at 60 mA cm^{-2} as a function of media.

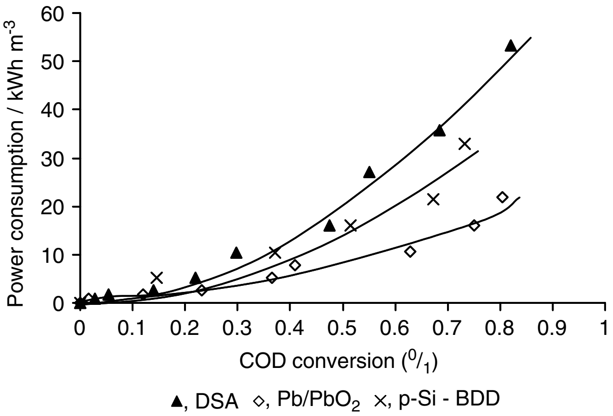

Figure 14. Power consumption in the electrochemical oxidation of wastes polluted with cyanide (375 mg NaCN dm^{-3}). Supporting electrolyte: 0.05 M NaCl.

Figure 14 shows the energy required to oxidize cyanide as a function of the percentage of COD elimination. A typical exponential variation is observed and the lower cost can be obtained when using the PbO_2 anode. An 80% COD removal with an energy consumption of 21 kWh m^{-3} can be achieved. Hence, the energy requirements are lower when the media contains chloride ions, due to the electrogeneration of hypochlorite.

Effect of the operating conditions and waste characteristics on the efficiency of the process

The effect of the different variables on the global current efficiency, quantified as the electrochemical oxidation index (EOI), is shown in Table 2.

It can be observed that the current efficiencies obtained are very low. This seems to be in disagreement with the current efficiencies reported during recent years for the oxidation of organic compounds (aromatics, carboxylic acids) on lead dioxide and boron doped diamond anodes, close to 1 when the process is kinetic-controlled.

To explain these low efficiencies, it must be taken into account that the wastewater used in these experiments is very dilute (average COD value about 250 mg O_2 dm^{-3}) if compared with the concentrations required by the electrochemical

Table 2. Electrochemical oxidation index (calculated for a 70% contaminant removal) for the electrolysis of diluted cyanide aqueous solutions[a]

	Experimental conditions					Anode material		
Expt	*j* (mA cm^{-2})	pH	[Cl$^-$] (mmol dm^{-3})	[SO$_4{}^{2-}$] (mmol dm^{-3})	T (°C)	DSA	p-Si-BDD	Pb/PbO$_2$
1	30	11	0	0.050	25	—	7.0	3.5
2	15	11	0	0.050	25	—	8.0	6.4
3	30	10	0	0.050	25	—	4.5	2.9
4	30	11	0	0.025	25	—	4.6	3.4
5	30	11	0	0.050	50	—	7.2	3.1
6	30	11	0.050	0	25	3.2	5.2	7.8
7	30	11	0.025	0	25	3.0	5.0	7.2

[a] The values corresponding to the oxidation of sulfate-containing solution on DSA anodes are omitted as it is not possible to reach a 70% removal ratio under these experimental conditions.

process to be kinetic-controlled. Thus, the minimum COD at which the process is kinetic-controlled (COD limit) was calculated for this cell and for the operating conditions used by means of a ferrocyanide/ferricyanide test, obtaining a value close to 2000 mg O_2 dm^{-3}. Consequently, the process is under mass transfer control. This means that not enough cyanide ions arrive at the anode surface and, thus, an important fraction of the current is employed in the oxygen generation process, decreasing the current efficiency. In the presence of cyanide or cyanates on the anode surface, the generation of oxygen is not favoured, due to the larger overpotential required for this reaction.

Nevertheless, the results obtained are better than those which can be obtained if only direct processes occur, as stated previously in Fig 7, and this must be explained in terms of the electrogeneration of inorganic reagents, which later react with cyanides and cyanates to form carbon dioxide.

The effect of the current density shown in Table 2 also supports the fact that the electrochemical process is under mass transfer control. The current density does not affect the mass transfer rate and, thus, it does not affect the amount of cyanide ions that arrive at the anode surface. However a decrease in the current density implies a decrease in the current available to oxidize in the anode surface. As the cyanide ions are easier to oxidize that the hydroxyl ions this implies that the oxidation of hydroxyl ions is unfavoured and consequently an increase in the current efficiency of the process is obtained (the ratio between cyanide ions on surface and current increases). This increase is more marked for the lead dioxide anode. This can be easily explained by taking into account that the generation of mediated electroreagents is not favoured for this electrode in sulfate media. Hence, the current efficiency obtained can be considered to be due mainly to direct electrochemical processes or to mediated electrochemical processes carried out by short-lived reagents (such as ozone and hydroxyl radicals). On the contrary, the BDD anode favours the generation of persulfates, which increases strongly the current efficiency. Hence, the differences in the EOI for both electrodes can be justified by the generation of persulfates. This is also confirmed by the results of experimental condition No 4 (Table 2) in which it is shown that a decrease in the concentration of sulfates in the wastewater only affects the results of the electrolysis with BDD. Temperature does not seem to influence the process efficiency. This confirms the strong influence of the direct electrochemical processes in the electrolysis with lead dioxide anodes. For the BDD anode experiments this low influence can be justified in terms of two opposite effects of temperature:

1. The increase in the rate of the chemical oxidation processes caused by an increase in temperature
2. The decrease in the concentration of persulfates, caused by their instability at temperatures close to 55 °C.

The current efficiencies obtained were higher in the treatment of wastewater containing chloride for electrolysis with PbO_2 and DSA anodes and smaller for BDD anodes. This effect was previously justified in the section 'Electrolysis in chloride media' of this work. The decrease in the chloride concentration does not seem to affect significantly the efficiency of the treatment, indicating that concentrations of 0.025 M NaCl are enough to generate the reagents required to carry out the process. The lower efficiency observed for the electrolyses of cyanate in chloride media on BDD anodes with respect to those observed in the electrolyses with lead dioxide anodes can be justified by assuming the formation of chlorate in the former case. This compound has a higher oxidation state than hypochlorite but it can be considered as an inactive species.

CONCLUSIONS

From this work the following conclusions can be drawn:

1. The electrochemical oxidation of diluted cyanide aqueous wastes can be obtained in sulfate or chloride media using both boron doped diamond and lead dioxide anodes. Energy consumptions in the range 20–70 kWh m^{-3} are required to decrease

the initial pollutant load by a 70–80%. Global current efficiencies in the range 3–8% are obtained.

2. The low efficiencies obtained in the electrochemical treatment can be justified by the low initial cyanide concentration (200 mg CN^- dm^{-3}). Under the experimental conditions used in this work, the electrochemical treatment was under mass transport control. Consequently, the efficiency is increased by lowering the current density and by increasing the concentration of compounds that can act as mediated electro-oxidants.
3. The oxidation of cyanide on BDD and PbO_2 anodes leads to the formation of cyanate in a first step, and later to the formation of carbon dioxide and nitrogen. There is a net consumption of hydroxyl ions during the process.
4. The electrochemical oxidation of diluted cyanide aqueous wastes cannot be obtained in sulfate media using DSA anodes. In these conditions the concentration of cyanide decreases initially and later it is maintained constant. No cyanates are formed during the process and a net generation of hydroxyl ions is obtained. All these observations should be interpreted in terms of the adsorption of cyanide onto the anode surface or by the chemical reaction of this ion with any of the components of this surface.
5. Cyanide aqueous wastes can be treated using DSA when chloride ions are present in the waste. This anode material achieves higher energy requirements and lower efficiencies than the BDD and the lead dioxide anodes.

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