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Electrochemical Treatment of Landfill Leachate: Oxidation at Ti/PbO_2 and Ti/SnO_2 Anodes

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Leachate originating in landfills where municipal solid wastes are disposed is a wastewater with a complex composition that could have a high environmental impact. The primary goal of this research was to investigate the feasibility of removing refractory organic pollutants and ammonium nitrogen from landfill leachate by electrochemical oxidation. The effects of current density, pH, and chloride concentration on the removal of both chemical oxygen demand (COD) and ammonium nitrogen were investigated. Titanium coated with lead dioxide (PbO_2) or tin dioxide (SnO_2) was used as the anode. An effective process was achieved in which the leachate was decolorized, COD was removed up to a value of 100 mg L^{-1}, and ammonia was totally eliminated. Average current efficiency of about 30% was measured for a decrease of COD from 1200 to 150 mg L^{-1}, while efficiency of about 10% was measured for a near complete removal of ammonium nitrogen, starting from an initial value of 380 mg L^{-1}. Results indicated that the organic load was removed by both direct and indirect oxidation. Indirect oxidation by chlorine or hypochlorite originating from oxidation of chlorides is believed to be mainly responsible for the nitrogen removal.

Introduction

Leachate from MSW (municipal solid waste) is a wastewater with a complex composition, characterized by high COD (chemical oxygen demand) and high concentration of ammonium and reduced nitrogen compounds, that gives high TKN (total kjeldahl nitrogen) values. In an effort to minimize the environmental impacts resulting from leachate contamination, many treatment processes have been studied. Biological methods are very effective for the treatment of landfill leachate with a high value of BOD (biological oxygen demand) but are ineffective if recalcitrant organic compounds are present, so that they must be supported by a physical−chemical process (*1*). Up to now, great attention has been directed toward either new techniques, based on chemical or physical processes (*2*−*4*), or older techniques, like electrochemical oxidation, never applied for this particular purpose.

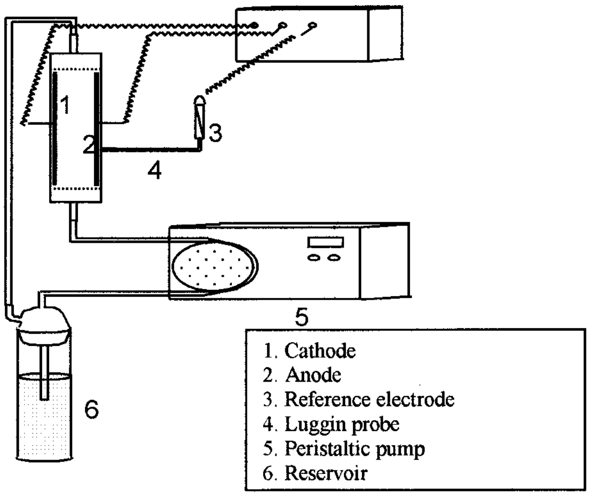

FIGURE 1. Experimental apparatus.

Electrochemical oxidation of organic compounds in aqueous solution is an anodic process occurring in the potential region for discharge of water to produce oxygen. There is consensus among electrochemists that the first step in the oxygen evolution is the anodic discharge of water to produce adsorbed hydroxyl radicals ($OH^{\bullet}$), which are oxidizing agents for the majority of organic pollutants (*5*). Thus, carbon electrodes and titanium sheets coated with active oxides (such as RuO_2, IrO_2, or SnO_2) have been successfully utilized in order to oxidize both synthetic solutions of phenol and chlorophenols (*6*−*9*) and real wastes such as tannery wastewaters (*10*) and landfill leachates (*1*).

However, the anodic oxygen evolution represents an unwanted leakage current, reducing the overall current efficiency that could be maximized through the choice of an anodic material that presented low overpotential for the first step of reaction (production of $OH^{\bullet}$ radicals) and high overpotential for the second step (oxygen evolution) (*11*).

From an economical point of view, it can be observed that, since electrochemical oxidation process is fairly expensive in comparison with biological treatment, the former should not be considered as a single treatment for a real waste but as a finishing stage in a combined process or as an auxiliary unit capable to work in emergency situations.

The present paper deals with the anodic oxidation of a MSW landfill leachate biologically stabilized but still characterized by a high COD value (BOD/COD < 0.2) due to the presence of recalcitrant organic compounds. The leachate was also characterized by a high concentration of chlorides and ammonium nitrogen.

Experimental Section

The apparatus (Figure 1) consisted of a stirred reservoir (300 mL), a peristaltic pump, and the three-electrode electrochemical cell. A sheet of steel was used as the cathode, while the anode (working electrode) was made of a sheet of titanium (4 × 3 cm) coated with SnO_2 or PbO_2. The potential of the working electrode was measured with respect to a saturated calomel reference electrode (SCE), connected to the working

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TABLE 1. Mean Values of Relevant Physical Parameters in Raw Leachate

pH	8.3
BOD	80 mg L^{-1}
COD	1200 mg L^{-1}
TKN	420 mg of N L^{-1}
ammonium-N	380 mg of N L^{-1}
chlorides	1600 mg of Cl^- L^{-1}
conductivity	12 mS cm^{-1}

electrode through a Luggin probe. All potentials quoted in this paper are with reference to the SCE.

Preparation of Electrodes. The pretreatment of the titanium surface was performed following the procedures suggested by Feng (*12*): the sheet of titanium was polished on 320-grit paper strips, using water as lubricant, followed by 1 μm siliceous paste blasting. The sheet was then degreased in 40% NaOH, cleaned in a hot 1:1 mixture of HNO_3 and H_2SO_4, and finally washed in water. The treated surface was immersed in boiling aqueous solution of oxalic acid (15%) until the TiO_2 dissolved. The coating by active metal oxide proceeded immediately to minimize formation of TiO_2.

The electrodeposition of PbO_2 was achieved at constant anodic current (100 mA, 30 min) from 0.1 M HNO_3 solution containing 0.5 M $Pb(NO_3)_2$ and 0.04 M NaF. During electrolyses, the potential ranged from 1.5 to 1.8 V. To achieve a PbO_2 loading of about 14 mg cm^{-2}, it was normal to carry out the electrodeposition for 30 min.

The thermal deposition of SnO_2 on a titanium sheet was achieved following the procedure suggested by Lipp and Pletcher (*13*). The pretreated titanium sheet was immersed for some minutes into a solution of 20 wt % $SnCl_4 \cdot 5H_2O$ and 0.2 wt % $SbCl_3$ in 2-propanol. The excess of alcohol was allowed to evaporate by heating it in air at 363 K for 10 min. This stage was then repeated. After two applications, the oxide layer was formed thermally by heating it at 773 K for 20 min in a muffle furnace with a low and continuous flow of oxygen. These stages were repeated until the SnO_2 coating reached a loading of about 0.8 mg cm^{-2}: it was normal to employ five applications. Finally, the coating was annealed at 773 K for 60 min.

To verify the reproducibility of electrode preparation, experimental runs were repeated with three different electrodes, prepared according to the procedure described above. Results obtained showed a fairly good reproducibility within the experimental error (5%). Electrodes were also stable enough to allow their use also in consecutive runs: the analyses of solutions revealed that no metal dissolution occurred during electrolyses.

Characteristics of the Leachate. Leachate samples were collected from a sanitary landfill of Vado Ligure (Savona, Italy), and they were pretreated by aerobic lagooning, denitrification, and activated sludge processes. Physical–chemical characteristics of the leachate samples are summarized in Table 1. The collected landfill leachate was stored in a 4 °C refrigerator to keep the wastewater characteristics unchanged.

Experimental Runs. The electrochemical experiences were carried out on both kinds of electrodes at constant current density, ranging from 2 to 40 mA cm^{-2}. Flow rate ranged from 0.3 to 1.5 cm^3 s^{-1}, corresponding to a linear velocity of 0.1 and 0.5 cm s^{-1}, respectively. Experiments were performed with the raw leachate or after the addition of sulfuric acid to correct pH to a value of 3. Some runs were also performed in which chloride concentration was increased up to 3600 mg L^{-1}.

Analyses. The progress of the electrochemical oxidation was monitored by measuring COD (closed reflux, titrimetric method), ammonium nitrogen (titrimetric method), chlorides (potentiometric method), hypochlorite (iodometric method), and pH. All the analytical procedures followed the methods stated in the ref *14*.

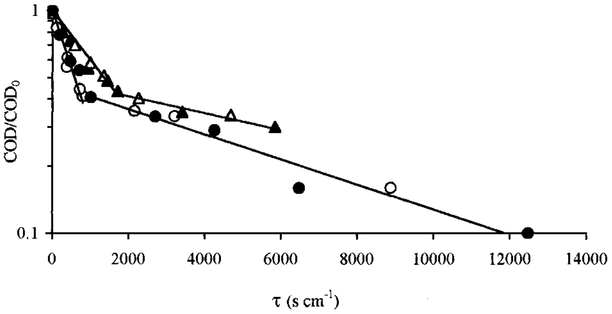

FIGURE 2. Trend of residual normalized COD during electrolyses in different experimental conditions. Ti/PbO_2 anode: 5 mA cm^{-2} (▲) and 15 mA cm^{-2} (●); Ti/SnO_2 anode: 5 mA cm^{-2} (△) and 15 mA cm^{-2} (○).

Results and Discussion

The electrochemical oxidation of landfill leachate was studied under different experimental conditions to investigate the influence of operative parameters on efficiencies of removal of COD and ammonium nitrogen. Preliminary experiments were performed in order to verify the influence of mass transfer on the process kinetics: no variation in the reaction trend was observed at different flow rates, showing that mass transfer of the reactant from the solution bulk to the electrode surface did not constitute a limiting step.

The influence of anodic material and current density on reaction trend was also examined. It was observed that, at both kind of electrodes, a minimum current density of 5 mA cm^{-2} was required in order to achieve an effective process. In fact, regular COD decrease and decolorization of the solution during the reaction occurred only when the anodic potential reached the value of oxygen evolution (between 1.8 and 2.0 V, depending on experimental conditions). At these potential values, a high coverage of the anode with $OH^{\bullet}$ radicals originated from water oxidation can be achieved (*15*), allowing an effective oxidation of several organic compounds present in the leachate. On the other hand, at lower potential values the solution became darker, and a brown precipitate was found at the anode surface. The formation of polymeric compounds could be suggested as already observed in previous work during oxidation of organics under weak oxidative conditions (*7*, *16*).

When a current density greater than 5 mA cm^{-2} was imposed, a faster decrease of COD was achieved, as can be seen from Figure 2, where experimental results from electrolyses performed at 5 and 15 mA cm^{-2} are shown. A pseudo-first-order kinetics might describe the behavior of the system, at least until the COD is reduced by 50% of the initial value. In fact, a linear trend of logarithm of COD, normalized with respect of initial COD, as a function of the parameter τ was verified according to

$$\ln\frac{COD}{COD_0} = -k_{app}\tau$$

where k_{app} is the pseudo-first-order rate constant, and $\tau = tA_eV_s^{-1}$. t, A_e, and V_s represent the electrolysis time, the electrode geometric area, and the solution volume, respectively.

Values for k_{app} of $5 \pm 1.7 \times 10^{-4}$ and $12 \pm 1.3 \times 10^{-4}$ cm s^{-1} were evaluated when the current density was 5 and 15 mA cm^{-2}, respectively. Within experimental errors, these values can be considered proportional to current density,

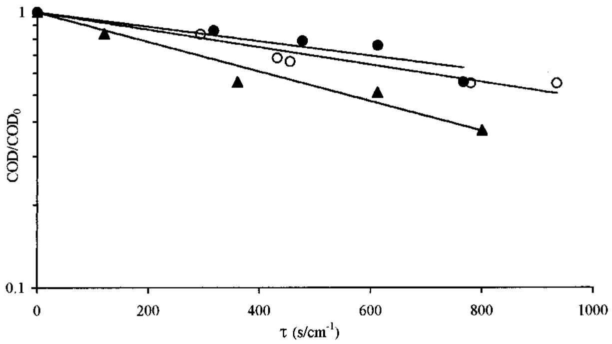

FIGURE 3. Effect of pH and chloride concentration on COD removal at Ti/PbO$_2$ anode with $i = 5$ mA cm^{-2}. [Cl$^-$] = 1600 ppm: pH = 8.3 (●) and pH = 3 (▲); [Cl$^-$] = 3600 ppm: pH = 8.3 (○).

but only a little increase of k_{app} was observed when a current density higher than 15 mA cm^{-2} was applied. Therefore, in the range from 5 to 15 mA cm^{-2}, a current efficiency independent of the current density was obtained, and the amount of removed COD only depended on the charge supplied for unit solution volume.

The figure also shows that the reaction rate decreased when COD was under 50% of the initial value. A pseudo-first-order kinetics might be adopted also for this final stage, but k_{app} is 1 order of magnitude lower than in the first part of the reaction. This behavior might be due to the presence in the leachate of compounds that are more easily oxidized than others. In fact, the composition of old landfill leachates is very complex; nevertheless, species in solution may be grouped in two main classes, characterized by a different attitude toward oxidation: compounds with a high molecular weight such as humic and fulvic acids and recalcitrant substances with a low molecular weight such as halogenated compounds (*17*).

A similar behavior of the rate of TOC removal was observed by Ribordy during the electrochemical oxidation of an industrial wastewater. The author suggested that either the formation of more stable compounds might occur or initially the wastewater might contain oxidized substances that were little affected by electrochemical oxidation (*18*). As far as the anodic material influence is concerned, Figure 2 shows that substantial differences did not arise when the anodic material was Ti/PbO$_2$ or Ti/SnO$_2$.

To investigate the influence of pH, experimental runs were carried out at pH = 8.3 (raw leachate) and pH = 3. When electrolysis of acid solutions was performed, a slight increase in k_{app} was observed (Figure 3). This behavior could be due to a lowering of concentration of CO_3^{2-} and HCO_3^- ions always present in the leachate. These ions can react with OH$^\bullet$ more rapidly than organic compounds, so that a removal of carbonate from the leachate can be advantageous (*19*).

The effect of an increase in chloride concentration was also investigated by adding NaCl to the raw leachate. Figure 3 provides the COD/COD$_0$ profiles as a function of τ, obtained at chloride concentration of 1600 and 3600 ppm, from which values for k_{app} equal to $(6 \pm 1.5) \times 10^{-4}$ and $(7 \pm 1.4) \times 10^{-4}$ cm s^{-1} were respectively calculated. These values can be considered equal within the experimental errors, showing that, under conditions adopted in this work, a variation of chloride concentration did not affect the oxidation rate.

On the contrary, an increase in the rate of COD removal after the addition of chlorides was observed in previous work dealing with electrochemical oxidation of landfill leachate (*1*), but these results were obtained at current density higher than that used in this work.

During the electrochemical treatment, the competitive removal of ammonium was observed. Figure 4 shows that the specific rate of ammonium nitrogen removal was lower than that of COD, at least in the first part of the reaction, but it increased remarkably at longer electrolysis time: ammonium was almost completely removed when an electric charge of 30 Ah dm^{-3} was supplied.

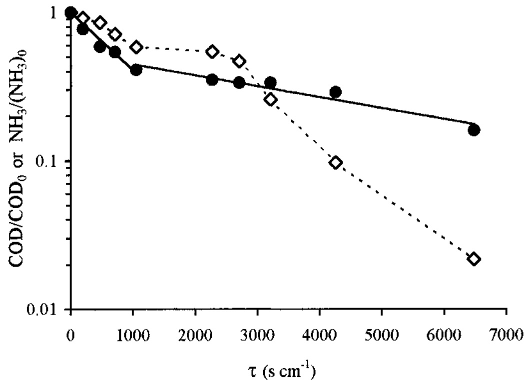

FIGURE 4. Trend of normalized COD (●) or ammoniacal nitrogen concentration (◇) during electrolyses at Ti/PbO$_2$ anode with $i = 15$ mA cm^{-2}.

This behavior could be related to the increase of ClO$^-$ concentration in solution that occurs during the electrolysis. In fact, in the first part of the process, the anodic reaction of chloride ions to form chlorine and hypochlorite ions seemed to occur in a minor extent, while it became an important secondary reaction when 50% of COD was removed. In this final part of the process, the anodic potential slightly increased up to values ranging from 2.2 to 2.5 V, chloride concentration decreased, and increasing amounts of ClO$^-$ were detected in the solution. It is well-known that the anodic direct oxidation of ammonia is fairly slow, unless catalytic anodes such as Pt are used, while the oxidation by means of ClO$^-$ is likely, in particular at pH values near to 8.3, which is the pH value of the leachate used in this work.

The formation of hypochlorite ions in the final part of the electrolysis might also promote the removal of residual organic compounds, such as humic acids and their reaction intermediate products, that are little affected by the electrochemical oxidation. As clearly shown in the literature, the product of the reaction between humic acids and chlorine is chloroform (*19*). In experimental apparatus adopted in the present work, chloroform could leave the system with the anodic gas together with oxygen and CO$_2$.

During the whole process, chlorinated organic compounds could be generated. However, analyses performed on samples withdrawn when residual COD was about 100 ppm showed that the concentration of adsorbable halogenated compounds (AOX) was really low. Also in a previous work dealing with the electrochemical oxidation of phenol from solution containing chlorides (*20*), although organochlorinated compounds were detected during electrolysis, they completely disappeared at the end of the process.

Faradic efficiency was calculated both for COD and ammonia removal according to (*21*):

$$\eta_F = \frac{V_{sol}}{wI}\frac{F(\Delta X)}{\Delta t}$$

in which V_{sol} is the volume of treated solution, I is the current intensity, F is the Faraday constant (96 487 C mol^{-1}), ΔX represents the variation (expressed in g L^{-1}) of COD or ammonia concentration in the interval of time Δt, and w is the equivalent weight (8 for oxygen and 17/3 for ammonia). Average current efficiency of 30% was measured for a decrease of COD from 1200 to 150, while a value of 10% was measured for a near complete removal of ammonium nitrogen, starting from an initial value of 380 mg L^{-1}.

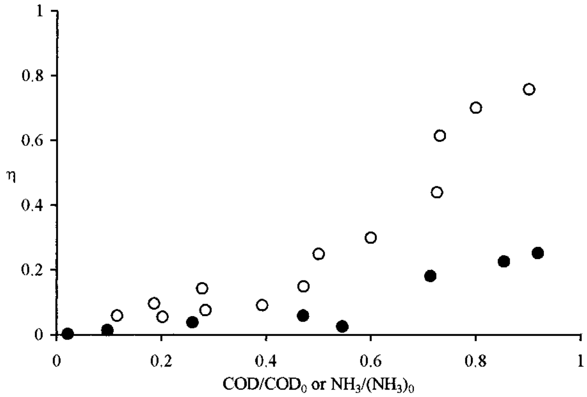

FIGURE 5. Faradic efficiency for COD (○) and ammoniacal nitrogen (●) during electrolyses at Ti/PbO_2 anode with $i = 10$ mA cm^{-2}.

As it could be expected, both efficiencies decreased with the residual concentration of COD and ammonia. Figure 5 shows that the efficiency for COD removal initially ranged from 80 to 60%, but it collapsed when the COD concentration was about 400 ppm.

Further studies are still going on in order to optimize the operating parameters and to extend experimental results to a pilot plant scale. In particular, attention will be paid to verify the economic feasibility of the process and its flexibility to different aged leachates and to leachates coming from different landfills or different pretreatments.

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