Turkish J. Eng. Env. Sci.
28 (2004) , 377 – 380.

Ultrasound Assisted Electrochemical Degradation of Cyanides: Influence of Electrode Type

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Received 10.05.2004

Abstract

The sonoelectrochemical degradation of cyanide ions (CN^-) in the presence of 6 types of electrodes (aluminium, titanium, nickel, copper, stainless steel (inox), and graphite) were investigated in order to emphasise the influence of the electrode type on the efficiency of the degradation process.

Key words: Cyanide degradation, Electro-oxidation, Sonoelectro-oxidation, Sonoelectrochlorination.

Introduction

Cyanide (CN^-) is a species with high toxicity found mainly in industrial effluents. Inorganic cyanide salts are regularly used in metallurgical industry activities such as metal surface treatment but also in the mining industry, for example in gold extraction. All these activities consume large amounts of water and the water effluents always contain cyanide that must be treated before disposal in water environments.

A large number of procedures exist for treating cyanides: physical (dilution, membranes, hydrolysis/distillation), physico-chemical (adsorption – on minerals, activated carbon and resins, acidification/volatilisation, metal addition, flotation, solvent extraction), chemical (oxidative methods) and/or biochemical (bio-oxidation) (Young and Jordan, 1995). There are several methods (catalytic, electrolytic or photolytic) in which chemical oxidants (oxygen, ozone, hydrogen peroxide, chlorine, sodium hypochlorite and sulphur dioxide) are used, with each technique having its own advantages and disadvantages (Nechita *et al.*, 2003).

The electrochemical oxidation is already a classical method for cyanide degradation. Two major techniques for the electrochemical treatment of aqueous cyanide solutions are commonly used: direct and indirect electrochemical oxidation. In direct electrochemical oxidation (electrooxidation) the cyanide ions are directly oxidised at the anode to cyanate (Eq. 1-1′), while in the indirect electrochemical process (electrochlorination), chloride ions act as an oxygen carrier (forming ClO^-) in the oxidation of cyanide to cyanate (Eq. 2-2‴) (Young and Jordan, 1995).

$$CN^- + 2OH^- \leftrightarrow OCN^- + H_2O + 2e^- \quad (1)$$

$$2OCN^- + 4OH^- \leftrightarrow N_2 + 2CO_2 + 2H_2O + 6e^- \quad (1')$$

$$Cl^- + H_2O \leftrightarrow OCl^- + 2H^+ + 2e^- or, \quad (2)$$

$$Cl_2(g) + 2OH^- \leftrightarrow OCl^- + Cl^- + H_2O \quad (2')$$

$$CN^- + OCl^- \leftrightarrow CNO^- + Cl^- \quad (2'')$$

$$2OCN^- + 3OCl^- + H_2O \rightarrow N_2 + 2CO_2 + 3Cl^- + 2OH^- \quad (2''')$$

Iordache *et al.* (2003) have proved the capacity of ultrasound to enhance the electrochemical degradation of cyanide; the sonoelectrochemical method was found to be more efficient than the electrochemical method for cyanide treatment.

The most important effects of ultrasound upon an electrochemical system are well presented in the literature (Compton *et al.*, 1997; McMurray *et al.*, 1998; Hardcastle *et al.*, 2000; Walton, 2002): general improvement in the hydrodynamics and movement of species; mass transport enhancement owing to turbulence and microstreaming; alteration of concentration gradients at various points in the reaction profile, and consequent switching of kinetic regimes with effects on the mechanism and reaction products; continuous activation of the electrode surface, a cleaning and abrading effect upon an electrode surface and product desorption; sonochemical formation of species that react electrochemically in conditions where the silent system is electroinactive; and formation of ions, radicals and other high energy intermediates. Moreover, sonoelectrochemistry has been successfully applied for removing organic pollutants (especially dyes residues) from wastewater and effluents (Foord *et al.*, 2001; Lorimer *et al.*, 2001; Abramov *et al.*, 2002).

Therefore, the aim of this work was to investigate the influence of the electrode type (Al, Ti, Ni, Cu, stainless steel (inox), and graphite) on the electro-oxidation, sonoelectro-oxidation and sonoelectrochlorination of cyanides.

Materials and Methods

The experiments were run with 200 ml of bidistilled water (0.5 mS conductivity) samples with initial concentrations of 0.1 mg CN^-/ml and 1 mg NaCl/ml respectively for the electrochlorination measurements. The sodium chloride (99.99%) (used as a source of chlorine) and potassium cyanide (99.99%) were purchased from Merck. The cyanide concentration was measured following the international standard ISO 6703 recommendation.

The experiments were performed with a CFT:IUS-30 apparatus produced by the Romanian National Institute of Technical Physics, with 37 kHz working frequency and working temperatures between 30 °C and 35 °C, using 6 types of electrode: Al, Ti, Ni, Cu, inox, and graphite, each with a 0.5 dm^2 surface. The distance between the anode and the cathode (inox) was 20 mm, and the experiments were run at constant current density (0.03A/dm^2) during 1 h contact.

In order to highlight the influence of the electrode type on the sonoelectrochemical remediation of cyanide, 3 types of experiments were performed for each electrode: electro-oxidation, sonoelectro-oxidation and sonoelectrochlorination.

Results and discussion

An evaluation of the electro-oxidation efficiency for cyanide degradation (at 0.03 A/dm^2 current density) using different types of electrodes indicates Ti < inox < Ni < Cu = Al < graphite. The highest efficiency was obtained with the graphite electrode – 22% (Figure 1) and the lowest with the Ti electrode – 10%.

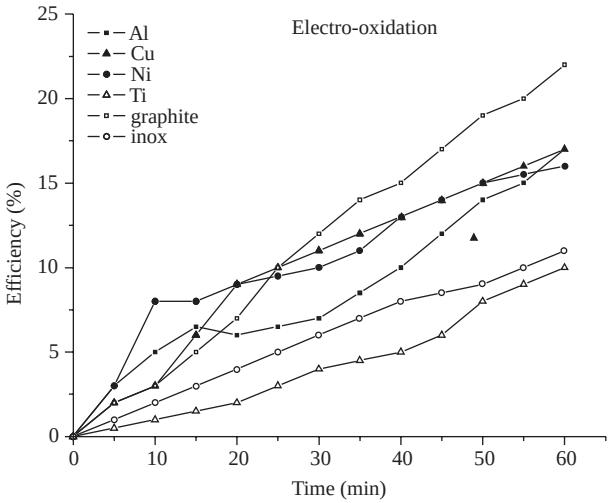

Figure 1. Cyanide degradation by electro-oxidation.

The efficiency of water decontamination (E%) was calculated with the formula presented in Eq. (3).

$$E\% = [(C^i - C^t)/C^i] \times 100 \quad (3)$$

where C^i = initial cyanide concentration and C^t = cyanide concentration after a certain time of treatment.

In the presence of ultrasound (Figure 2) the most efficient electrode was the aluminium one, while graphite showed the lowest efficiency among the 6

electrodes used: graphite < Ti < inox < Ni < Cu < Al. The efficiency of aluminium was increased almost 4-fold by ultrasound irradiation: from 17% in the first case to 60% in the second.

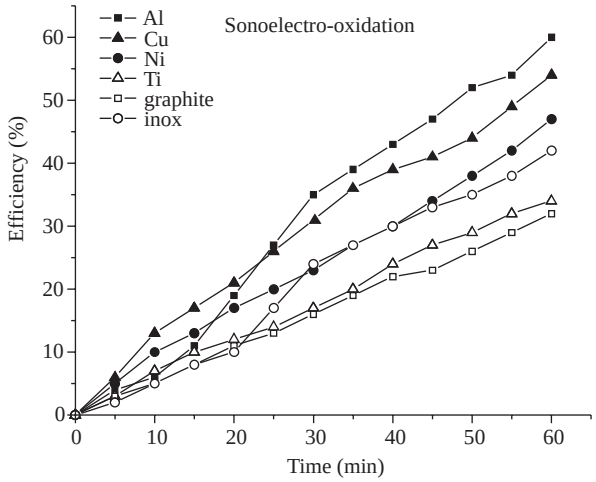

Figure 2. Cyanide degradation by sonoelectro-oxidation.

This surprising enhancement of aluminium efficiency might be the result of continuous activation of the electrode surface by a cleaning and abrading effect upon the passivating aluminium oxide coating on the electrode surface induced by the ultrasound irradiation. All metallic electrodes have shown similar behaviour, their efficiency being increased 2 or 3 - fold by sonication. Even the graphite electrode, the last one in the activity scale, which cannot form passivating coatings, had increased efficiency (from 22% in electroxidation to 32% in sonoelectro-oxidation) most likely due to the general improvement in the hydrodynamics and movement of species.

In the case of sonoelectrochlorination (ultrasound assisted electrochlorination), aluminium was the most efficient electrode (78%), while the other electrodes showed similar performances: 58% for copper and nickel, 59% for titanium and 56% for graphite (Figure 3). All electrodes performed better in sonoelectrochlorination than in sono-oxidation, in concordance with silent systems, where electrochlorination is more efficient than sono-oxidation (Perret *et al.*, 1999).

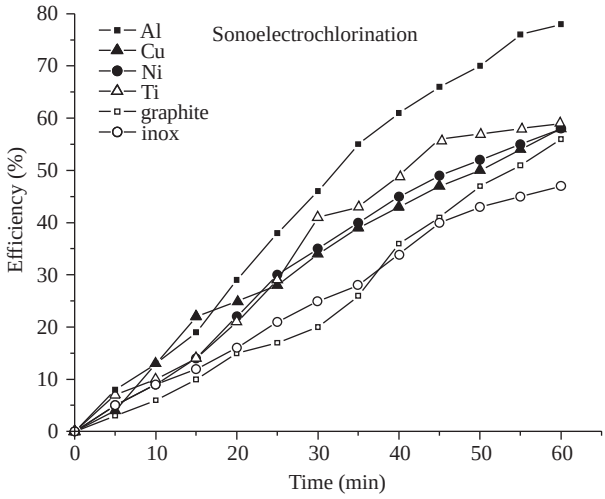

Figure 3. Cyanide degradation by sonoelectrochlorination.

Conclusion

The efficiency of cyanide oxidation at constant values of ultrasound frequency (37 KHz) depends upon the electrode type. The best electrode for both sonochemical methods (sonoelectro-oxidation and sonoelectrochlorination) was the aluminium one, as a result of continuous activation of the electrode surface induced by the ultrasound irradiation. The best method for cyanide degradation among those presented was proved to be sonoelectrochlorination. Generally, for all types of electrodes used, the efficiency of cyanide treatment methods follows the following order:

Electro-oxidation < sonoelectro-oxidation < sonoelectrochlorination.

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