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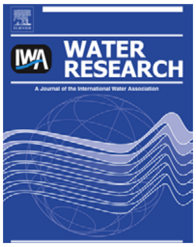

Electrochemical degradation of perchloroethylene in aqueous media: An approach to different strategies

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ABSTRACT

An approaching study to the electrochemical degradation of perchloroethylene (PCE) in water has been carried out using controlled current density degradation electrolyses. The different electrochemical strategies to degrade perchloroethylene in aqueous media (i.e. cathodic, anodic and dual treatments) have been checked using divided and undivided configurations. The influence of the initial concentration, pH and current density on the general behavior of the system has been studied, and special attention was paid to the nature of the byproducts formed and to the analysis of the closed mass balance at the end of the reaction. Results from several analytical techniques have been compared. Undivided configuration provides the best results in these experimental conditions, with degradation percentages higher than 50% and with only 6% of the initial perchloroethylene concentration remaining in the system.

1. Introduction

Electrochemical degradation in wastewater treatment is not being routinely used because cheaper conventional treatments are available. They are usually composed of a physico-chemical step followed by a biological degradation. However, these methods have continuously presented deficiencies, mainly treating some refractory compounds because they are toxic for the microorganisms in the biological plant (Tarr, 2003). One of the most common pollutants are chlorinated compounds. Chlorinated compounds have focused the attention from health authorities due to their emerging presence in any kind of fluvial medium (groundwater, rivers, lakes) (Pecoraino et al., 2008), and their toxicity and persistence in the environment due to their wide range of industrial and commercial applications (metal degreasing, ink and paint components, cleaning of electronic materials and dry cleaning). The degradation of chlorinated compounds is a good example to show the deficiencies of biological treatments and has led to the development of a large number of alternative technologies (Hitchman et al., 1995) for the treatment of these refractory compounds: combined treatments (Kastanek et al., 2007) with alkali metal (Alonso et al., 2002) in organic solvents, catalytic hydrogenation (Song and Carraway, 2008), metal alloys in dilute aqueous alkaline solutions (Lee and Doong, 2008), hydride complex (Yang and Pittman, 1998), and other techniques such photochemistry (Satuf et al., 2008), sonochemistry (Ince et al., 2001) and also

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Nomenclature

CTR	column concentric packed column
DCE	dichloroethylene
E_{aw}	working potential at anode
E_{cw}	working potential at cathode
ECD	electron capture detector
FAAS	flame atomic absorption spectrometry
GC-FID	gas chromatography with flame ionization detector
GC/MS	gas chromatography with mass selective detector
HPLC-UV	high performance liquid chromatography with ultraviolet detector
IC	ion-exchange chromatography
MTBE	methyl-tert-butyl-ether
PCE	perchloroethylene
TCD	thermal conductivity detector
TCE	trichloroethylene
(ϕ_{Cl})	current efficiency calculated from chloride concentration measurements
(ϕ_{org})	current efficiency calculated from organics concentration measurements

electrochemistry (Isse et al., 2008). Electrochemical technology presents some advantages: (i) it is applicable for a wide range of pollutants; (ii) it avoids the addition of chemicals using the electron as unique reactant; (iii) they are easily controlled by a personal computer; (iv) processes run under room temperature and atmospheric pressure; (v) they are easy to scale-up; and (vi) compact facilities (Walsh, 1993).

The electrochemistry of halogenated organic compounds has been routinely focused on studying mechanistic details about the cleavage of the carbon–halogen bond in organic solvents (Torii, 2006; Peters, 2004). However, due to the recent environmental applications of electrochemical technology in the degradation of persistent and pollutant compounds in wastewaters, the aqueous medium is being again subjected to analysis (Brillas et al., 2003). Despite the theoretical advantage in electrochemical technology to use reduction, oxidation and both electrode reactions for other applications such electroplating or electrosynthesis (Amatore and Brown, 1996), the electrooxidation of chlorinated compounds has so far been little explored (Berríos et al., 2008). The chlorinated compounds have been mainly studied by electroreduction with only acceptable results (Rajeshwar and Ibañez, 1997) establishing that the organic compounds decomposition takes place in the potential region close to the water/supporting electrolyte decomposition reaction. This results in a decrease of the current efficiency and the mechanism usually follows a radical pathway, with intermediates that can undergo further reactions. Within this context, electrocatalytic properties of cathodic materials such as silver (Rondinini et al., 2001), new electrode materials (Wiyaratn et al., 2003) or treated electrodes (Simonet et al., 2006) have been recently revised.

These fundamental studies are being carried out in parallel to analyses of the electrochemical degradation for this kind of compounds (Miyoshi et al., 2004). Chloroform has been routinely the most studied molecule by electrochemical methods. Sonoyama et al. (1997) studied Ag, Zn, Cu and Pd as cathodes and they presented current efficiencies close to 100% with methane and dichloromethane as major final products. Other minor products were ethane, ethylene, propane and propylene. Dichloromethane was found as a final product for Pb and Sn electrodes. Criddle and McCarty (1991) used a divided glass cell with a cationic membrane, silver cathode and platinum anode and formate, CO, CH_2Cl_2 and $CHCl_3$ were detected as final products from the electroreduction of carbon tetrachloride.

C_2 chlorinated compounds have been also electrochemically degraded. Li and Farrell (2001) detected chloroform as the main byproduct from carbon tetrachloride, and chloroacetylene, acetylene and finally ethylene were identified in the reduction of trichloroethylene (TCE). They suggested different mechanisms for both electroreductions: direct electron transfer for chloroform, and reaction between adsorbed atomic hydrogen and the TCE. Scherer et al. (1997), using an oxide-free iron electrode, analyzed the kinetics of carbon tetrachloride reduction to chloroform addressing that the process is under charge transfer control rather than mass transport control. Liu et al. (2000) presented a reaction mechanism for TCE and PCE. Chen et al. (2003), using Ebonex as cathodic material, analyzed the electrochemical reduction of TCE and chloroform yielding methane from chloroform, and ethane and ethylene from TCE for lower potentials, and dichloromethane from chloroform and dichloroethylene (DCE)/n-butane from TCE at higher potentials, with a mass balance error of 5–10%. On the other hand, Farrell et al. (2000), using iron aggregates, reported TCE reduction by indirect reduction with atomic hydrogen, and PCE by direct reduction. These results were compared with those obtained by amperometric experiments in a glass cell. Further work done by Wang and Farrel, 2003, using iron as cathode, related these mechanisms with pH and suggested 75% of ethene and 25% of ethane as reduction products for TCE and PCE electroreduction at pH 3 and 7.

In spite of the fact that PCE is a widely used solvent in many areas of the industry and has been reported as a major intermediate in the degradation of other chlorinated compounds, to our knowledge, there is not an extensive study about the electrochemical degradation of this compound. In our laboratory we are analyzing the degradation of this compound by electrochemical methods and spectroelectrochemical studies (Saez et al., 2008a). A preliminary study of any electrochemical system using voltammetric techniques can provide useful information about electrocatalysis of the electrode materials, reversibility of the process and general information about the influence of several variables such as temperature, initial concentration and mass transport conditions. Our study is focused on the degradation of aqueous solutions with low concentrations of PCE (below 75 ppm). Linear sweep voltammetry using a rotating disk electrode was previously carried out in our laboratory (Saez et al., 2008b), in order to analyze the influence of the convection and electrode materials on the process kinetics. In that preliminary study, lead, copper and glassy carbon were analyzed as cathode materials. Increases in the initial