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Optimization of electro fenton process for effective degradation of organochlorine pesticide lindane

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ABSTRACT

Lindane is an organochlorine pesticide broadly used in the last decades. It is persistent and recalcitrant in aquatic environments and difficult to biodegrade. This study is focused on the complete degradation of lindane by an electrochemical advanced oxidation process, the electro-Fenton (EF) process, using a BDD anode and carbon felt (CF) cathode. The influence of the main operating parameters, *i.e.,* applied current intensity (50–1000 mA), catalyst concentration (0.0–0.5 mM) and initial pollutant concentration (5.0–10.0 mg L^{-1}) has been investigated and optimized. The applied current plays a determinant role both in oxidation of lindane and mineralization of its aqueous solution. Taking into account the mineralization current efficiency (MCE) and the specific energy consumption (EC), the applied current of 400 mA was found to be the most convenient value. Catalyst (Fe^{2+}) concentration as low as 0.05 mM, promotes efficiently H_2O_2 decomposition into hydroxyl radicals improving the efficiency of the process and minimizing the involvement of parasitic reactions. The initial pollutant concentration does not affect the performance of the process. At the optimum operating conditions, the complete degradation of 10 mg L^{-1} lindane solution and 80% of TOC removal were achieved at 15 min and 4 h, respectively.

1. Introduction

The extensive use of synthetic organochlorine pesticides (OCPs) in the agricultural sector during the last decades has led to their occurrence in aquatic, soil and air environment throughout the world. OCPs are toxic and bioaccumulative persistent organic pollutants and represent a great environmental concern nowadays [1,2]. Among them, lindane (γ-hexachlorocyclohexane) has been widely used on fruit, grain and vegetable crops and in warehouses for insect-borne disease control [3] since the Second World War until the 1990s [4,5], making this compound one of the most frequently detected chlorinated contaminants in the environment [6]. Lindane can be detected in water in a quite broad range depending on the use of this pesticide in a given area: from ng L^{-1} in natural water [7] to near its water solubility (10 mg L^{-1}) when polluted water comes directly from the washing of the solid product (HCH residues were often stockpiled in open piles) or by the dissolution of dense non aqueous phase liquid of this compound. Due to its high toxicity lindane brings potential health risks to humans and animals (skin irritation, dizziness, headaches, diarrhea, nausea, vomiting, convulsions, possible changes in the levels of sex hormones in the blood and eventually, even death) [8]. Its low aqueous solubility, relative high stability, lipophilicity and chlorinated nature contribute to its environmental persistence and resistance to degradation. Lindane has been classified as a potential carcinogen to human's beings by the International Agency for Research on Cancer (IARC) [9] and as neurotoxic, carcinogen and teratogen by the Environmental Protection Agency (EPA) and World Health Organization (WHO) [10] resulting in its final inclusion (along to α- and β-HCH) in the list of persistent organic pollutants (POPs) in the Stockholm Convention in 2009 [11]. Therefore, the development of viable treatments for the removal of such a contaminant has become a priority for the scientific community.

The main industrial process for lindane destruction involves thermal oxidation at 1000 °C, an expensive treatment that can lead to the formation of highly toxic by-products such as dioxins and furans [12,13]. This fact, coupled with the refractory nature of lindane, has driven the development of advanced technologies for its destruction.

Due to the high chloride content of the lindane molecule, reduction over zero valent metals was employed as a promising alternative, zero valent iron (ZVI) being the most common metal used [14]. In the presence of ZVI microparticles (ZVIm), lindane is completely dechlorinated obtaining benzene and chloride as final products [15]. ZVIm showed excellent stability and the presence of the most common salts in

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groundwater seems not to affect the process making this technology a potential approach for soil and groundwater lindane remediation. However, if the mineralization of the effluent (and not only its dechlorination) is required, advanced oxidation processes (AOPs) seem to be more suitable. These treatments, which involve the *in situ* production of hydroxyl radicals (·OH), a very powerful oxidant, at near-ambient conditions [16,17], are efficient and promising technologies for water treatment [18]. Among them, the conventional Fenton process [19], based on the catalytic decomposition of hydrogen peroxide (H_2O_2) by ferrous iron (Eq. 1), stands out due to its high efficiency in the degradation of organic matter, operational-simplicity and low cost [18,20,21].

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+} \quad (1)$$

An important disadvantage of this process is the high and fast consumption of both H_2O_2 (which represents the main cost of the process) and iron, giving finally partial mineralization of organic pollutants with sludge formation [17,22,23]. This limitation can be solved by an emerging advanced electrooxidation process (EAOP) such as electro-Fenton (EF), where H_2O_2 is directly electrogenerated at the cathode from reduction of dissolved O_2 (Eq. (2)) and ferrous iron is added as catalyst in low concentrations [24]. Under these conditions, EF does not lead to the formation of process sludge and accumulation of oxidation-refractory organics [25,26]. H_2O_2 formed through Eq. (2) is then quickly decomposed to ·OH by Fenton's reaction (Eq. (1)). The Fe^{3+} formed is reduced at the cathode (Eq. (3)) to regenerated Fe^{2+} leading to higher degradation rate of organic pollutants than the traditional Fenton process [25,27].

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

Moreover, in addition to OH homogeneously generated in the bulk (Eq. (1)), heterogeneous OH are formed from water oxidation at the surface of a high O_2-overvoltage anode (M) according to Eq. (4) [28]:

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \quad (4)$$

being M(·OH) the ·OH adsorbed on the anode surface.

The ·OH and M(·OH) thus formed are powerful oxidants able to oxidize recalcitrant pollutants until their mineralization following Eq. (5) [17,24,29].

$$\text{Organic pollutants} + \cdot OH/M(\cdot OH) \rightarrow [\ldots \text{intermediates} \ldots] \quad (5a)$$

$$\text{Intermediates} + \cdot OH/M(\cdot OH) \rightarrow \rightarrow \rightarrow CO_2 + H_2O + \text{inorganic ions} \quad (5b)$$

The EF process is considered as the most popular, effective and eco-friendly process among Fenton's based treatments [17,24,25,27]. Moreover, in the last decades, this treatment has been successfully applied to the treatment of different pesticides families such as mixture of pesticides (chlortoluron, carbofuran and bentazon) [30], organophosphorus insecticides [31], chlorobenzene [32], fluometuron [33], etc. The efficiency of this process strongly depends on the nature of the electrode materials. High surface 3D carbon felt (CF) is one of the best cathode materials because it favors the H_2O_2 formation and catalyst regeneration [34]. The use of a large O_2-overpotential anode such as BDD promotes the generation of physisorbed M(·OH) which are more reactive in mineralization of carboxylic acids [24,27].

Several items must be considered in order to estimate the cost of a wastewater treatment process, the most important of which are equipment amortization cost, raw materials cost, energy cost and labor cost [35]. The main items of equipment needed to carry out the EF process are the electrochemical cell, the electrodes and the power supply. When boron-doped diamonds electrodes are used, the investment required is greatly influenced by its high price. The price of this material is around 12 000–18 000 € m^{-2}, although this is expected to decrease in the near future to values in the range 6000–10 000 € m^{-2} [35]. Nevertheless, in spite its high price, and thanks to its high efficiency in the degradation of organic matter, BDD is the most promising and widely studied electrode for EAOPs [36].

The elimination of lindane has been studied by different AOPs such as ozonation [37], activated oxone [38], activated persulfate [2], Fenton process [1], photolysis [39], photocatalytic processes [40] and combinations of different oxidants with UV [2] but the results obtained were not fairly conclusive (a wide range of lindane oxidation and mineralization degree, as well as very different reaction times have been published) and the effect of important variables like pollutant concentration has not been studied. Moreover, to the best of our knowledge, there were no works dealing with the removal of this harmful pollutant from water by EAOPs. In this study, we describe an effective removal of this organochlorine pesticide by EF process using a BDD anode and a CF cathode. The effect of the applied current intensity, catalyst dosage and initial pollutant concentration on oxidative degradation and mineralization of lindane was investigated and optimized.

2. Materials and methods

2.1. Chemicals

Synthetic wastewater was prepared by dissolving lindane (Fluka) in milli-Q water (10 mg L^{-1}) and shaking until its complete dissolution. Working standard solutions of lindane, potassium hydrogen phthalate (Nacalai Tesque), NaCl and $NaClO_3$ (Sigma Aldrich) were used for gas chromatography-mass spectrometry (CG-MS), TOC and ionic chromatography (IC) calibration, respectively.

Other reagents used (all of them of analytical grade) were: $FeSO_4{\cdot}7H_2O$ (Sigma Aldrich), acetone (Sigma Aldrich), Na_2SO_4 (Sigma-Aldrich), Na_2CO_3 (Riedel-de Häen), $NaHCO_3$ (Fluka) and 4-methylcyclohexanone (Sigma-Aldrich). Solutions were prepared with high-purity water obtained from a Millipore Direct-Q system (resistivity > 18 MΩ cm at 25 °C).

2.2. Electrochemical system

The electrochemical trials were carried out in an undivided and cylindrical glass electrolytic cell (V = 230 mL) at room temperature (25 °C). The cell was capped to avoid water evaporation and organics volatilization during reaction time. A 3D carbon felt (CF, 18.0 cm × 5.0 cm × 0.5 cm, from Mersen, France) was used as cathode. It was placed on the inner wall of the cell, covering almost the total internal perimeter. The anode was a 24-cm^2 boron diamond doped (BDD) thin film on niobium support (CONDIAS GmbH, Germany), centered in the electrolytic cell and surrounded by the cathode. Prior to electrolysis (15 min), compressed air was bubbled through the solution (1 mL min^{-1}) to maintain a saturated O_2 content for H_2O_2 electrogeneration in the cathode (Eq. (2)). Sodium sulfate (50 mM) was added to the cell as background electrolyte to ensure the conductivity of the reaction medium. Iron salt ($FeSO_4{\cdot}7H_2O$) was used as catalyst (Fe^{2+}) and the pH of the solution was initially adjusted to 3 (sulfuric acid, 1 M), optimal pH value for EF process [21]. The solution was stirred (250 rpm) to enhance the mass transport of reactants toward/from the electrodes. The applied current and the potential difference of the electrochemical cell were measured by a DC power supply (HAMEG Instruments, HM 8040-3).

The EF runs were performed at different current densities (50–1000 mA), catalyst loadings (0-0.5 mM) and initial lindane concentrations (5–10 mg L^{-1}). All the experiments were performed by duplicate being the standard deviation lower than 5%.