DEVELOPMENT OF ELECTROCHEMICAL TECHNOLOGIES FOR THE TREATMENT OF LIQUID AND GASEOUS EFFLUENTS POLLUTED WITH CHLORINATED HYDROCARBONS

UNIVERSITY OF CASTILLA-LA MANCHA

Chemical Engineering Department

Martín Muñoz Morales

Summary

The removal of chlorinated hydrocarbons (CHCs) from soil has become an environmental priority during last decades, in order to avoid further magnification of the environmental problem, associated with a later spreading and pollution of water reservoirs. The occurrence of these compounds is related to industrial or agricultural activities and because of its anthropogenic nature and properties, such as high volatility and strong recalcitrance to degradation, the potentiality of damage that they can cause in the environment and humans is extremely high.

In this context, electrochemical technologies related to the remediation of polluted soils seem to be very promising for the removal of organic pollution. Previous studies about the in-situ electrochemically assisted soil remediation technologies (EASRTs) pointed out an outstanding performance but, unfortunately, some disadvantages were found, such as extremely large treatment times and a potential transport of pollution from soil or liquids to the atmosphere. Because of that, it was required the development of new technologies which can face fastly the remediation of accidental discharges avoiding the spreading of pollutants. Among them, soil washing technologies (SWTs), although known to be more invasive than in-situ EASRTs, can help to solve this problem rapidly and efficiently.

This PhD thesis is framed within this line of research of the Environmental and Electrochemical Engineering Laboratory (E3L) of the TEQUIMA group of the University of Castilla-La Mancha, trying to combine soil washing with electrochemical technologies to treat the wastes produced during this separation stage. Thus, in this work, it was considered not only the treatment of polluted soils, but also the treatment of liquid and gaseous effluents produced in those soil remediation treatments.

Considering this background, this thesis proposes the development of combined technologies to remove CHCs from soil and water, based on the combination of SWTs with the electrochemical treatment of soil washing effluents (SWE) and to retain and/or remove gaseous pollutants than can be generated in those processes.

To reach this goal, in Chapter 5, it was carried out an extense characterization of the soil washing (SoWa) process, trying to determine the requeriments of solubilizing reagents capable to transfer efficiently pollution from soil to the soil washing fluid (SWF), minimizing the impact of products dosed to improve this transport. As model compounds, three chemicals were chosen, with different properties in order to evaluate the feasibility of the technology for a wide range of potential pollutants: clopyralid (highly soluble in water and non-volatile), perchloroethylene (non-polar compound, highly volatile) and lindane (non-polar and non-volatile), in a concentration about 100 mg of pollutant per kg of soil. Then, a further anodic oxidation with diamond electrodes (BDD-AO) of the produced SWEs was analyzed in each case. In the case of spiked soils with clopyralid, it was not necessary the addition of any surfactant in the SoWa to extract it and high recovery was obtained in all ratios SWE/soil studied. Then, it was confirmed that low current densities applied during the treatment of SWE using BDD-AO increase the process performance and large ammount of pure electrolytes does not improve the degradation efficiencies. Regarding to spiked soils polluted with lindane and perchloroethylene, they require the addition of high quantities of sodium dodecyl sulphate (SDS), an anionic surfactant that helps to solubilize the pollutant in the SWF. However, SoWa results in a very complex matrix with a clarified phase, an interphase and a solid phase. During the BDD-AO of the liquid phases, it was confirmed the faster removal of pollutants respect to SDS, which promoted the partial regeneration of the SWE for a further re-use. Additionally, it was compared the performance of the AO process of SWE with BDD, as a model of non-active electrode, and platinum, as a model of active electrode, confirming the higher efficiency of BDD anodes, although it seems that platinum anodes attain higher oxidation rate on their surface. Nervertheless, no significant differences were obtained in each anode according to the intermediates detected and it was stated that the same removal mechanisms developed in both types of electrolysis, involving stages of dechlorination and ring-opening.

Subsequently, the aim of Chapter 6 was to go further in the efficient treatment of soil polluted with CHCs previously evaluated, by improving the treatment of SWEs generated in the SoWa process, proposing some alternatives to the BDD-AO treatment. Among these alternatives, the use of another advanced oxidation process (AOP), the photolysis, demonstrated that not only AO but also other AOPs could degrade pollutants to stable intermediates and they could have a great potential for combination with biological technologies. Also, the use of another anode material that promote softer oxidation conditions, the mixed metal oxide (MMO) anodes, could be a feasible alternative for a further coupling of AO with biological processes.

Regarding to the improvement of the SoWa treatments, the dehalogenation with zero valent iron (ZVI) has been extensively applied to transform CHCs into other less halogenated molecules, with the release of chloride and ferrous ions and the consumption of the acidity. In this context, it was designed sequential and integrated AO with ZVI dehalogenation processes, using clopyralid-SWE to test them, because of the simplicity of the SWE produced with this pollutant. These studies allow to confirm that the production of non-chlorinated species did not favor the mineralization of the waste by AO, although it influenced very positively on the improvement of their biodegradability. Also, it was observed that the size of ZVI particles had a very important impact on the treatability of intermediates detected.

Then, the coupling of photolysis and MMO-AO with dehalogenation technologies, either previously or simultaneously to the treatment, indicated low changes in the mineralization degree, although biological characteristics of the effluents were rather significantly modified. Some tests, such as respirometry, toxicity and biodegradability tests, pointed out that photolysis and MMO-AO process demonstrated good changes as a pretreatment for a further biological degradation, although the coupling with BDD-AO showed the highest ratio of biodegradability. So, in the last part of this Chapter, an identification of main transformation products of the most important coupled technologies was carried out using LC-MS, in order to clarify the mechanisms of oxidation and to propose tentative pathways for preferential clopyralid degradation.

Next, although good results were obtained in the AO processes, there was still slot for improvement. So, considering the mass transfer limitations that appear during the AO of low concentrated SWE, in the Chapter 7, it was developed an alternative to improve the performance of the AO by the pre-concentration of pollutants, coupling an adsorption-desorption process using granular active carbon (GAC) particles to BDD-AO. In this process, firstly, pollutant in aqueous solution would be adsorbed into GAC particles and then methanol, which has different retention capacity, was used to extract the pollutant into a more concentrated stream. Afterwise, a more efficient AO is applied.

The most influent parameters determined in the novel treatment technology proposed were the concentration degree and the total recovery obtained. Clopyralid and perchloroethylene, which are more polar than lindane, were concentrated up to 8 times, while lindane, which is extremenly non-polar, up to 2 times due to the restriction of desorption stage. However, just clopyralid appeared as a good alternative for the treatment of diluted wastes, because of its high recovery (88%), which constrasted with the values obtained for the other non-polar compounds (under 25%).

Regarding to the BDD-AO processes, all the compounds were depleted in both solvents, without promoting a significant concentration of intermediates. The wide electrochemicall windows of the voltammetric response pointed out the importance of transformations that occur directly on the BDD surface.

Finally, GAC particles were also applied to treat gaseous effluents throught the adsorption/desorption processes. It was used perchloroethylene as a model compound due to its higher vapour pressure. After recovery with methanol, the BDD-AO was demonstrated to be able to remove the pollutant and deplete all the intermediates detected.

The last part of this Thesis was devoted to developing novel electrochemical technologies applied to the treatment of gaseous pollution, topic which has received residual attention in last decades. In this context, this study was focused on the very important fraction of pollution that it has been emitted to the atmosphere during the application of conventional treatment of soil and liquid effluents. For the treatment, it has been combined the absorption and BDD-AO processes to obtain novel electro-absorption technologies.

Then, in the Chapter 8, two electro-absorption set-ups were evaluated, and in both cases, it was observed low mineralization and the transformation of perchloroethylene into refractory products that sometimes could be more dangerous than the parent compound. Transformations in wet gas phase were claimed as the responsible of this bad result.

The first was a jet electro-absorber, which was based on the Venturi effect to transfer the gaseous streams into a liquid stream, with the absence of a compressor. It worked well, but the efficiency depended on the solubility of perchloroethylene and the removal pathway was highly influenced by the size of bubbles and the gas-liquid contact surface. The second was a packed electro-absorption column that used a compressor pump and a wide liquid-gas contact surface using glass spheres packing. This system promoted more liquid intermediates than the jet electro-absorber and, although it was coupled with UV irradiation, it did not improve the results of the treatments as compared with single AO.

Finally, the use of a stack cell of five electrodes to test the scale-up of packed column electro-absorbers confirmed that the increasing in the electrode’s surface by staking was not very relevant to improve the efficiency in the electrochemical treatment proposed.

Hence, as a consecuence of the research carried out in this PhD thesis, not only relevant conclusions and a progress in the knowledgement state has been reached but it has been opened a line to scale-up definitely the SoWa processes for real applications and to start with the design of more efficient electrochemical cells for the treatment of gaseous pollutants.