Improvement of electrochemical oxidation efficiency through combination with adsorption processes.

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Abstract

In this work, a three-step process (adsorption-desorption-electrolysis) is evaluated as an interesting approach for the removal of organochlorinated compounds (clopyralid, lindane and perchloroethylene) with different physical properties (solubility and vapor pressure) from low concentrated wastewater. First steps are based on the adsorptive capacity of granular active carbon (GAC) particles to retain organics and on the solvent capacity of methanol to extract them to concentrated solution and regenerate GAC. In the last step of electrolysis with conductive diamond electrodes, the degradation of pesticide is projected, as well as the recovery of methanol. Results show that clopyralid, lindane and PCE are efficiently retained in GAC, although adsorption efficiency depend on pollutant/GAC ratio and physicochemical properties of pollutant. Pretreatment allows the concentration of clopyralid and PCE solutions up to 8 times, but worse results are obtained in case of lindane solutions. Electrolysis of concentrated methanol solution seems to be more efficient than electrolysis of diluted aqueous wastes, mainly in the case of clopyralid. In all cases, electrochemical degradation fits a first order kinetics confirming mixed oxidation mechanisms with diffusion control of the direct processes and mediated oxidation. Results obtained in terms of current efficiency and energy consumption of electrolysis step point out the lower operation cost of concentrated liquid wastes and encourage further works on the development of cost-effective combined

processes for the treatment of diluted solutions polluted with polar compounds (such as clopyralid).

Keywords

Adsorption-desorption process, GAC particles, organochlorinated, electrolysis, methanol

Highlights

- Efficiency of electrolysis of organochlorinated compounds in methanol depends on pollutant properties.
- Desorption of lindane in methanol solution is less efficient than those of clopyralid and perchloroethylene.
- Overall removal efficiency of combined process is higher in the case of polar compounds.
- Electrolysis of preconcentrated wastewater is 10-20 times more efficient than electrolysis of diluted wastewater.

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1. Introduction

During last decades electrochemical oxidation has attracted considerable attention as an efficient technology for the treatment of industrial wastewater and the removal of emerging and persistent pollutants from aqueous matrices (Särkkä et al., 2015). In general, efficiency of electrochemical oxidation strongly depends on anodic material and current density, which are key parameters to promote the formation of hydroxyl radicals and other oxidants during electrolysis of aqueous solutions. Besides direct oxidation on electrode surface, all these electrogenerated oxidants are involved on the overall oxidation process (Panizza and Cerisola, 2009; Scialdone et al., 2009) by the so-called mediated oxidation processes. The contribution of both oxidation mechanism is the responsible of the typical high efficiencies of electrochemical oxidation.

Additionally, other factors such as pollutant concentration and supporting electrolyte can also hardly affect to the overall efficiency. In fact, it is highly reported the appearance of diffusional problems during the electrochemical treatment of low concentrated wastewater because of the necessity of transporting pollutants to the nearness of the anodic surface, where direct and hydroxyl-radical mediated oxidation take place. This is even most relevant in the case of working at high applied electric charges, due to the high amount of supplied electrons that are not only used in the main reaction but in side and parasitic reactions (such as water decomposition) (Martínez-Huitle and Panizza, 2018; Panizza et al., 2001; Scialdone, 2009).

For these reasons, recent studies have focused on increasing the efficiency of electrochemical technologies to treat low concentrated wastewater. To do this, different strategies have been evaluated such as coupling UV light irradiation (Cotillas et al., 2020; Rubí-Juárez et al., 2016) or ultrasounds waves (Cotillas et al., 2016; Dionisio et al., 2019; Martín de Vidales et al., 2019; Martín de Vidales et al., 2013; Sáez et al., 2011; Vidales

et al., 2014)–with electrochemical system to promote the formation and activation of oxidants and free radical in the bulk and, thus, to improve the mass transfer of pollutants to the electrode surface, respectively. Additionally, the search of synergisms of anodic and cathodic reactions has been also studied (Llanos et al., 2014; Llanos et al., 2018). Another option consists on coupling–electrochemical process with pre-concentration technologies, not only to concentrate target wastewater but also to reduce volume to be treated, and thus, to reduce operating cost. In literature, the use of membrane technologies(Llanos et al., 2014; Llanos et al., 2018; Miralles-Cuevas et al., 2016) and/or electrocoagulation (EC) (Muñoz et al., 2017) have been proposed although they have shown important drawbacks related to the fouling of the membrane or the appearance of polymeric compounds related with the iron complex generated in the EC process. In the search of new strategies, this work evaluates the use of sequential adsorption-desorption processes to concentrate organics and as pretreatment of electrochemical oxidation technique. This pretreatment is based on the well-known good adsorptive capacity of granular active carbon (GAC) or other adsorbent. In fact, recently different materials such as Akaganeite-activated carbon and Rhizopus oryzae biomass have been tested for the removal of perchloroethylene (Zeng et al., 2015) and lindane in water (Ghosh et al., 2009), respectively. Also Hsu et al. (2014) produced activated carbon using Jatropha seeds which were tested for the removal of different organochlorinated compounds. This work is not based on the search of novel adsorbent material but on the use of GAC adsorption (Areerachakul et al., 2007; Bouwer and McCarty, 1982) to retain, in a first stage, organic contained in diluted wastewater. Then, based on the high solubility of organics in given solvents (Michael et al., 2013), pollutants will be concentrated during a second stage of desorption. This allows obtaining highly-load liquid phase as well as recovery of GAC bed.

In the search of a holistic and cost-effective process, the selection of solvent is critical, because pollutants must be highly soluble in the solvent and this should be easily recovered after electrochemical treatment. According to previous works (Muñoz-Morales et al., 2019b; MuñozMorales et al., 2018), methanol could be a good candidate not only for its high solvent capacity for many organics but also it remains almost unmodified during electrolysis (Martín de Vidales et al., 2012) (Martín de Vidales et al., 2013) (Muñoz-Morales et al., 2019a) and, therefore, it could be recovered and reused in successive cycles.

Based on this background, the present work describes the evaluation of the combined adsorption-desorption-electrolysis process with GAC bed and methanol as solvent to treat low-concentrated wastewater polluted with organochlorinated compounds with different physical properties (in terms of polarity and volatility): lindane (non-polar and non-volatile pesticide included in 2009 in the list of Stockholm Convention on persistent organic pollutants (POPs) ~~((POPs)) ((POPs)))~~, perchloroethylene (PCE) (non-polar and volatile compound widely used as solvent and degreaser in many industries areas) and clopyralid (CP) (polar and non-volatile compound that is a selective herbicide for control of weeds in crops). These compounds are found in the environment in estimated concentrations ranged from 300-500 ng dm⁻³ to 10-20 mg dm⁻³ (Donald et al., 2007; Huang et al., 2014). Results will be compared with electrooxidation of diluted streams in terms of energy consumption.

2. Materials and Methods

2.1. Chemical products

Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid) were provided from Cymit Quimica S.L. (Barcelona-Spain). Perchloroethylene (C₂Cl₄ > 99%), lindane (97%) and

Sodium Dodecyl Sulphate (SDS), (Sigma Aldrich, Spain) were analytical grade and used as received. Granular Active Carbon (GAC), (Chemviron, Feluy, Belgium) was used as received. Hexane HPLC grade were obtained from VWR International Eurolab S.L. (Barcelona, Spain) and used for GC-ECD. Methanol HPLC grade and formic acid (Merck, Spain) were used as solvent and as mobile phase in HPLC. Double deionized water (Millipore Milli-Q system, resistivity: $8.2\text{M}\Omega\text{ cm}^{-1}$ at 25°C) was used to prepare aqueous solutions.

2.2. Analytical techniques

The concentration of clopyralid during electrooxidation process was followed by reversed-phase chromatography as described elsewhere (MuñozMorales et al., 2018) with a quantification limit of 0.5 mg dm^{-3} . The analysis of lindane and PCE were developed after using L-L extraction with hexane from both aqueous and methanol solutions. To do this, samples (2.0 mL) were mixed with hexane (2.0 mL) and stirred for 2 min in a vortex stirrer and for 10 min with a centrifugal pump at 4000 rpm. Then, hexane phase was filtered ($0.22\text{ }\mu\text{m}$ nylon filters) and analysed by Gas Chromatography Electron Capture Detector (GC-ECD) using a TG-5MS capillary column ($30\text{ m} \times 0.25\text{ mm}$ $0.25\text{ }\mu\text{m}$), 63 Ni micro-electron capture detector, a split/splitless injector and ChromCard Software. At these conditions, the quantification limit of the GC-ECD was 0.02 mg dm^{-3} for lindane and 0.1 mg dm^{-3} for PCE.

2.3. Adsorption and desorption tests

Adsorption tests were carried out in closed bottles placed in an incubating orbital shaker (VWR) with a stirring speed of 180 rpm for 24 hours to guarantee thermodynamic and kinetics equilibria. Ratio $\text{mg pollutant (g GAC)}^{-1}$ used in each case was similar: 50 mg g^{-1}

¹ in the case of clopyralid (4L of 500 mg dm^{-3} of clopyralid solution and 40 g of GAC) and 25 mg g^{-1} in the case of lindane and PCE (5L of 25 mg dm^{-3} of lindane or perchloroethylene solutions and 5 g of GAC). In all adsorption experiments temperature was kept at 25°C.

Afterwards, GAC particles were separated using a filter of 0.1 mm of diameter from aqueous solutions and mixed with fresh methanol (0.15 L in the case of clopyralid and 0.03 L in the case of lindane and PCE) to carry out desorption process. To promote it, desorption systems were stirred at 250 rpm in closed bottles placed in an incubating orbital shaker again at 25°C. Liquid phase was sampled periodically (intervals of 3 hours until reaching kinetics equilibrium in a limited time of 9 hours) to measure clopyralid, lindane and PCE concentration. Once attained this point, liquid and solid phase are separated again by filtration. Then, liquid phase is storage while solid phase is subjected to desorption several times using the same volume of fresh methanol (0.15 or 0.03 L) each time (three or four serial stage desorption, depending on the pollutant).

2.4. Electrooxidation set-up

In a first approach, the electrooxidation of synthetic methanol and aqueous solutions containing 100 mg dm^{-3} of clopyralid, lindane or PCE and 50 mmol of NaCl as electrolyte was carried out. Additionally, 10 g dm^{-3} of SDS (as solubilizing agent) was added to lindane aqueous solutions to attain target concentration. Secondly, the electrooxidation of methanol phases obtained from adsorption-desorption pre-treatment was carried out. All these electrolyses were carried out in a cylindrical, undivided, water-jacket glass cell as described elsewhere (MuñozMorales et al., 2018). Finally, the electrolysis of the target diluted wastewater was also carried out using a filter press electrochemical reactor in which electrodes are packed in a closed structure of polyvinyl chloride (PVC) and

separated by a thin (250 μm) insulating layer of polytetrafluoroethylene (PTFE). Reservoir tank (10 L) was closed to minimize losses of volatile organic compounds (VOCs) to the gas phase.

A thin-film boron doped diamond (BDD) electrode supported on a niobium mesh (supplied by Condias GmbH (Germany)) was used as anode with a total size of 8×9.5 cm. On the other hand, a stainless-steel perforated plate (thickness 3mm) with holes ($\varnothing$ 2mm) uniformly distributed throughout the surface was used as cathode. The electric current was provided by a Delta Electronika ES030-10 power supply (0-30V, 0-10A). Current density applied was in the range of 200- 300 mA cm^{-2} according with typical values previously reported (Muñoz-Morales et al., 2019b; MuñozMorales et al., 2018). Reaction solution was stirred vigorously with a magnetic bar (300 rpm) to ensure good mixing and reproducible mass transport conditions.

3. Results and Discussion

Figure 1 shows the electrolysis of clopyralid, lindane and PCE solutions (100 mg dm^{-3}) in aqueous and methanol media at 250 A m^{-2} of current density. As can be observed, clopyralid and PCE can be completely removed in both aqueous and methanol media after passing around 40 Ah dm^{-3} , while higher electric current seems to be required to remove lindane. In fact, electrolysis of clopyralid and PCE behave similar and, in both cases, 10 Ah dm^{-3} of electric charge are required to remove around 85% and 60% of pollutants in aqueous and methanol media, respectively. As mentioned, degradation in water is more efficient than in methanol but differences are not excessively large. On the other hand, the evolution of lindane behaves clearly different, electrochemical degradation is faster and more efficient in methanol solution. As stated before, lindane is a very non-polar compound with a maximum water solubility of 7.3 mg dm^{-3} at 25°C (POPs); (National Center for Biotechnology Information); and therefore, the addition of a solubilizing agent

was required to attain target concentration (100 mg dm^{-3}) in aqueous solution. In this case, 10 g dm^{-3} of SDS was added. According to results, SDS-lindane micelles do not seem to be so accessible as lindane in methanol solution (Muñoz-Morales et al., 2017). Likewise, SDS may compete with target pollutant to be oxidized, consuming a fraction of the electrons supplied and justifying the slower degradation of lindane in aqueous solutions. The higher efficiency observed during aqueous electrolysis of clopyralid and PCE solutions can be explained in terms of the contribution of both direct and hydroxyl radical-mediated oxidation (Sáez et al., 2010; Volpe et al., 2007). In methanol, hydroxyl radicals are not generated but methanoate radicals, which do not seem to be so efficient as hydroxyl radicals (Muñoz-Morales et al., 2019a; Vidales et al., 2014).

Figure 1. Removal of concentrated wastes of clopyralid (●), PCE (■) and lindane* (▲) in water (empty points) and methanol (full points) with the applied electric charge. $j = 250 \text{ A m}^{-2}$, 50 mmol of NaCl . Anode: DDB, Cathode: Stainless Steel. $C_0 = 100 \text{ mg dm}^{-3}$. *lindane is solved with 10 g dm^{-3} of SDS to be solubilized in water.

In general, and according to literature (Caro et al., 2007; Sáez et al., 2009), reaction intermediates are detected only in trace concentration in aqueous media, which is

typically observed in the treatment of low concentrated wastes and it is related to typical harsh oxidation conditions generated during electrolysis with diamond electrodes. In methanol media, intermediates are not detected but once pollutant molecule starts its oxidation it seems to proceed up to its complete removal.

Figure 2 shows average mineralization current efficiency (estimated for 80% of total organic carbon removal) of electrolysis of the three tested compounds in both media. As can be observed, in terms of mineralization electrolysis of aqueous solutions is also more efficient, mainly in the case of PCE. Apart from this, results confirm an important hypothesis: methanol does not suffer significant changes during electrochemical oxidation with conductive diamond electrodes and all the species formed from the adsorbate are depleted. This opens up the possibility of using methanol as inert solvent easily recovered by electrolysis. Nevertheless, it is important to take in mind that in the electrolysis of methanol solutions the direct oxidation seems to be the main oxidation mechanism (in absence of water, hydroxyl radicals are not massively generated) and thus, **kinetics** may be controlled by transfer of pollutant to the nearness of the electrode surface (mass-transfer controlled). This means that pollutant concentration will influence significantly on the process efficiency.

Figure 2. Mineralization current efficiency (MCU) of electrolysis of organochlorinated compounds in aqueous (■) and methanol (□) solutions. $j = 250 \text{ A m}^{-2}$. Anode: BDD, Cathode: Stainless Steel.

Once confirmed these important outcomes, this work evaluates the implementation of combined process of pre-concentration (by successive stages of GAC-adsorption and methanol-desorption) and electrolysis as alternative to the treatment of diluted aqueous wastes polluted with organochlorinated compounds. Initially, GAC-adsorption capacity was evaluated. The experimental conditions had to be adapted to each case due to the different nature of the three compounds tested. In the case of clopyralid, 5 L of an aqueous solution with 500 mg dm^{-3} were mixed with 40 g of GAC particles to attain a ratio of 50 mg pollutant $(\text{g GAC})^{-1}$. In the case of PCE and lindane, 5 L of an aqueous solution with 25 mg dm^{-3} were mixed with 5 g of GAC particles to attain a ratio of 25 mg pollutant $(\text{g GAC})^{-1}$.

GAC)⁻¹. Figure 3 shows the variation of the concentration of three pollutants in the aqueous solutions and in the GAC bed during adsorption tests.

Figure 3: a) Evolution of the pollutant concentration in water solution during the adsorption into GAC particles. b) Evolution of the adsorptive capacity of GAC particles (mg g⁻¹) with time. Clopyralid (●); Lindane (▲), PCE (■).

As can be observed, relevant differences are observed in the three cases studied. Clopyralid is rapidly adsorbed (less than 2 h) into GAC particles as reported previously (MuñozMorales et al., 2018), but adsorption is slightly slower in the case of lindane and PCE (around 5 h). Anyway, adsorption was ranged during 24 h to guarantee complete retention of pollutants. In this point, it is important to consider that adsorption process of organic species from liquid phase onto the adsorbent surface involves mass transfer of the adsorbate molecules across the external boundary layer, intra-particle diffusion migration of the organic species within the pores of the adsorbent and adsorption at internal surface sites. Thus, adsorption kinetics may be influenced 3D structure of pollutants. This could help to explain differences observed in each case.

Additionally, GAC adsorbent was used in successive steps with similar aqueous solutions, due to the rather removal observed of all compounds in the first cycle (figure

3a) with the aim to determine the number of cycles in which the same adsorbent can be reused to adsorb more pollutant. Results shown that in the case of clopyralid and lindane, GAC was almost saturated in the first step while in the case of PCE it can be successfully used in a second step although adsorbed amount of PCE decreases by half. Anyway, for this study only one adsorption step, using the ratios pollutant/GAC previously mentioned, was carried out.

After that, liquid and solid phase was separated, and the desorption of pollutant was evaluated. In this point, selection of solvent is also extremely important not only to extract target pollutant but also to recover the adsorbent and to ascertain the potential of the adsorbent to be reused. On base of previous results, methanol was selected as solvent in the desorption process. Previously, also it was discarded the use of mixtures methanol/H₂O due to their lower extraction efficiency from GAC particles in comparison with pure methanol. Additionally, three (in the case of clopyralid) or four (in the case of PCE and lindane) sequential desorption stages were carried out using the same volume of fresh methanol (0.15 mL in the case of clopyralid and 0.03 mL in the case of lindane and PCE) and stirring conditions (300 rpm and 5 h) in each stage. Figure 4 shows the percentage of pollutants extracted to liquid phase in serial desorption stages with methanol.

Figure 4: Percentage of pollutant released from GAC particles saturated with clopyralid, lindane and PCE in serial desorption stages with fresh methanol each one. Lindane (●), PCE (■) and Clopyralid (▲). Full points, first desorption stage; grey points, second and third desorption stage; empty points, fourth desorption stage.

As can be observed, after three stages, 88 % (1755.4 mg) of clopyralid has been recovered in 0.45 L of methanol with a final average concentration of 3900.8 mg dm^{-3} . In the case of PCE, finally 21.2 % (26.2 mg) was recovered in 0.12 L of methanol solution (average concentration of 218.5 mg dm^{-3}). On contrary, in the case of lindane, the amount release was very low (5 %) in comparison with total amount retained in GAC bed. This result was not initially expected because of the higher solubility of lindane in methanol. However, it is important to take in mind that adsorption process involves complex mechanisms of interactions of GAC particles with pollutants and, in this case, lindane does not seem to be easily accessible to methanol and this may limit desorption stage. Figures 5 shows concentration of lindane of methanol phases in four sequential desorption

stages. Data obtained in desorption process of PCE has been also included for comparison purpose.

Figure 5. Desorption of (a) lindane and (b) PCE contained in 5 g of GAC using four serial steps with 0.03 L of methanol each one: ● first desorption test; ■ second desorption test; ▲ third desorption test; ◆ fourth desorption test.

As can be observed, concentration of lindane extracted in each stage trends to slightly decrease, but nothing in comparison with **tends** observed in the **PCE desorption**. In this later case, around 15% of PCE is extracted in the first stage and 4.5 % in the second one. In this point, it is important to take in mind the high vapor pressure of PCE, that leads to a complex equilibrium between PCE in liquid and gaseous phase and that can affect obtained results (Nijhuis N, 2010). On contrary, the amount of lindane remained in GAC does not limit the desorption process, and similar amounts of lindane are obtained in the four stages (**ranged** from 1.2 to 1.95 mg lindane per desorption step). Indeed, total amount of lindane extracted was low (around 5% of lindane previously adsorbed) and further desorption steps should be carried to recover adsorbed lindane. These results support the idea previously mentioned based on the role of pollutant characteristics (3D structure, polarity and vapor pressure, among other) in adsorption-desorption processes because they affect the accessibility of those compounds to be retained in the porous-structure of

GAC particles and/or to be extracted. This seems to be relevant in the case of non-polar compounds tested (mainly in the case of lindane).

At this point, the final step of combined treatment is the electrooxidation of overall methanol phase obtained in desorption stages (0.45 L with an average concentration of 3900.90 mg dm^{-3} of clopyralid, and 0.12 L with an average concentration of 50.73, 218.5 mg dm^{-3} of lindane and PCE, respectively), and its comparison with electrooxidation of initial low concentrated aqueous solution (4 L with 500 mg dm^{-3} of clopyralid or 5 L with 25 mg dm^{-3} of lindane or PCE) to verify the relevance of the combined treatment proposed and to compare both strategies in terms of technical and economic feasibility. Concerning lindane solution, preconcentration step of lindane did not work as it was expected and, for this reason, initial concentration in methanol solution is only slightly higher than in aqueous media, while PCE and clopyralid are around 8 times more concentrated in methanol media.

Figure 6 shows semi-logarithmic variation of pollutant concentration during electrolysis of concentrated methanol solution and diluted aqueous wastes and onset of Figure 6 shows percentage removal. In no case, additional electrolyte was added.

Figure 6. Removal of lindane (●), clopyralid (▲) and PCE (■) during the electrolysis of diluted aqueous solutions (empty points) and concentrated methanol solutions obtained after adsorption-desorption pretreatment (full points).

The first important remark is that in all cases, independently on the nature of the pollutant, target organics can be removed not only in aqueous but also in methanol media and all the more so the oxidation of the three compounds in methanol media is more efficient than in aqueous solution. In the case of lindane these differences are less marked. In fact, higher removal percentages are observed (see onset of Figure 6) in organic phase, even in the case of lindane in which initial concentrations are similar (but not volume treated). Results obtained with PCE and clopyralid are promising. The decay fits well to first order kinetics (Table 1), not only in aqueous but also in methanol media. However, the depletion of PCE in methanol solutions seems to be more complex with a slow removal at the beginning and then a faster depletion. This may be associated to the promotion of evaporation of PCE during the electrolytic treatment that may contribute in a synergetic way to remove rapidly this pollutant from liquid wastes. In aqueous media, this is an expected behavior for the electrolysis of diluted solutions of organics, which is explained in terms of a mixed oxidation mechanism that include diffusional control of the direct processes and mediated oxidation. However, in this case, electrolyte was not added, and mediated oxidation may be mainly related to hydroxyl radicals and chloride oxidants formed from chlorine ions released from target molecule during its degradation. Opposite, in methanol media the contribution of hydroxyl radicals is not expected, but results suggests that both direct and mediated mechanisms can contribute to the decay of the pollutants. Previous works have demonstrated the formation of oxidants during methanol electrolysis (Muñoz-Morales et al., 2019a, b). As observed, higher removal was obtained during the electrolysis of PCE-concentrated wastes, but higher electrical charges are

required to attain its complete mineralization (Lugaresi et al., 2014; Sáez et al., 2009). In this case, it is important to highlight that the high vapor pressure of PCE and its derivatives promotes their transference to gas phase, and this can limit electrochemical treatment.

Table 1. First order kinetics constants of electrolysis of aqueous and methanol solutions.

Pollutant	Electrolysis in aqueous solution		Electrolysis in methanol solution	
	k (s ⁻¹)	R ²	k (s ⁻¹)	R ²
Lindane	0.0033	0.971	0.0017	0.972
PCE	0.0017	0.965	0.0068	0.981
Clopyralid	0.0014	0.983	0.0025	0.950

Regarding clopyralid, electrolysis of methanol concentrated solutions seems to be more efficient. This supports the relevance of mass transport control in diluted aqueous wastes. Differences seem to be most relevant during the initial stages of the electrolysis when direct oxidation or hydroxyl-radical mediated oxidation in the nearness of electrode surface are the main degradation mechanisms. After that, chloride ions released from clopyralid during its degradation can be further oxidized promoting the formation of hypochlorite, which can extend the oxidation reaction to bulk and then, weakening the effect of pollutant concentration.

Table 2 summarizes concentration factor and average removal efficiencies of electrochemical process of both treatment strategies (with and without preconcentration) estimated after passing 0.56 Ah dm⁻³ of electric current. Results show that, except in the case of lindane, the novel treatment evaluated in this work is 10-20 times more efficient than the sole electrolysis of low concentrated wastewater. This improvement is even higher than those expected considering the concentration factor of pretreatment step

(around 8). Regarding to lindane, preconcentration attained during ~~obtained with~~ adsorption-desorption pretreatment advices against the use of a combined treatment.

Table 2. Removal efficiency of organochlorinated compounds in terms of mass removed by the electric charge applied and concentration reached after passing 0.56 Ah dm^{-3} .

Pollutant	Concentration factor	Electrolysis of diluted wastewater (mg (Ah)^{-1})	Electrolysis of concentrated wastewater (mg (Ah)^{-1})
Lindane	2.0	27.2	11.6
PCE	8.7	31.3	647.2
Clopyralid	7.8	182.8	2034.0

Nevertheless, these results open the possibility of using this approach as an alternative to remove similar compounds from the environment (Muñoz-Morales et al., 2019b), although, especially in the case of polar compounds, it cannot be generalized and there are factors that should not be ignored. Additionally, the efficiency of reused-methanol in further desorption cycles and the possible addition of fresh methanol should be considered.

A final point is the estimation of the energy requirements of electrolysis in both scenarios due to the ohmic losses associated to the low ionic conductivity of organic solvents could be an important limitation. Figure 7 shows the removal of clopyralid and PCE as function of the energy consumption (W). As expected, in terms of energy consumption marked differences are obtained in the case of clopyralid. Less than 5 Wh are required to remove 350 mg of clopyralid in concentrated-methanol media versus 150 mg of clopyralid removed in diluted-aqueous media for the same energy consumed. From this point, the process is less efficient and extra 25 Wh are required to remove 30 mg of clopyralid. This is the typical behavior of diluted wastes. Regarding to PCE, combined process does not seem to be cost-effective and higher energy is required during electrolysis stage to attain a given removal percentage due to the higher cell voltage recorded during the electrolysis

in methanol media in comparison with aqueous media. Nevertheless, in this case it is important to warn about the rapid volatilization of PCE and its transference into gas phase.

Figure 7. Evolution of the mass removal of clopyralid (▲) and PCE (●) vs. energy consumption (W) during the electrolysis of diluted aqueous solutions (empty points) and concentrated methanol wastes (full points).

4. Conclusions

From this work, the following conclusions are drawn:

- Lindane, clopyralid and perchloroethylene can be removed from aqueous and organic solutions by electrochemical oxidation with conductive diamond electrodes but efficiency depends on their physicochemical properties. For the same initial concentration, lindane electrolysis is faster in methanol solution while electrolysis of clopyralid and PCE is favored in aqueous media.

- Efficiency of adsorption-desorption pretreatment depends on pollutant. Clopyralid and PCE are concentrated up to 8 times, while lindane up to 2 times due to restriction of desorption stage.
- Combined treatment is up to 10-20 times more efficient than single electrolysis of diluted wastewater polluted with clopyralid or PCE.
- Three step process of adsorption-desorption-electrolysis appears as a good alternative for the treatment of diluted wastewater polluted with clopyralid but side processes limit the efficiency of PCE and lindane solutions.

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