Electrochemically assisted dewatering for the removal of oxyfluorfen from a coagulation/flocculation sludge

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Abstract

This work focuses on the evaluation of the electrochemical dewatering of sludge obtained in the coagulation of wastes polluted with oxyfluorfen. To do this, sludge samples were treated, aiming not only to reduce the sludge volume, but also to facilitate the degradation of oxyfluorfen contained in the cake via electrolysis with a boron-doped diamond anode. Results show that water can be effectively recovered through the three sequential stages: first, a gravity-driven stage that can recover around 60% of initial volume and where no oxyfluorfen is lost; then, a second stage that involves the application of pressure and which accounts for the recuperation of an additional 25 % of total volume of the water removed and in which oxyfluorfen also remained in the cake, and a final electrochemical stage, which involves the application of electricity with increasing electric fields (1, 2, 4, and 16 V cm⁻¹) accounting for the recovery of the rest of water released and where an electrolytic degradation of oxyfluorfen is obtained, whose extension depends on the electrode configuration used in the electro-dewatering cell. This electrode configuration also influences the retention or loss of oxyfluorfen from the cake, being the optimum choice the placement of the cathode downstream, next to the outlet of the dewatering cell.

Graphical abstract

Keywords

Coagulation-flocculation; electrochemical dewatering; highly polluted sludge; organochlorine pesticides.

Highlights

- Electro-dewatering of coagulation sludge allows an improved removal of water.
- Position of the electrodes in the electro-dewatering cell has a significant influence on the dewatering.
- Position of the electrodes also influences the oxidation of the pollutant contained in the sludge.
- A configuration anode-upstream / cathode-downstream yields the best results, removing more water and avoiding the loss of herbicide.
- A configuration cathode-upstream and anode-downstream contributes to the retention of water in the cake and to the draining of the pollutant.

1. Introduction

Due to the health risks associated with many persistent pollutants in water effluents, and considering that, from the total amount of water in the World, only about 0.65% is directly usable by human beings, there is a need for the development of effective and energy-sustainable methods that can help to reduce or completely eliminate pollutants from wastewater (Garcia-Segura et al., 2017; Garcia-Segura et al., 2018; Oturan and Aaron, 2014). Pollution by herbicides is among the most significant environmental problems, due to the increased bad-use of these chemicals in the agriculture, the persistence in the environment and the absence of appropriate remediation technologies for the treatment of soils and wastewater effluents polluted with these compounds (Rodrigo et al., 2014).

Oxyfluorfen is one of the most effective and widely-used herbicides. It is a diphenyl-ether, considered a hazardous non-soluble and non-volatile organochlorinated compound due to its low solubility in water (0.116 mg L^{-1}) and low vapor pressure (0.026 mPa at 25 °C) (Barba et al., 2017). In the commercial formulations, it is very often mixed with different organic substances commonly used as solvents (liquid hydrocarbons, acetonitrile, xylene, N-methyl pyrrolidine) to improve water solubility, product management and ensure safe operating conditions. This chemical compound is known to contaminate surface water through spray drift and runoff, being classified as slightly mobile to immobile in soil, and it is nearly insoluble in water with a tendency to absorb in soils (Food Safety Authority, 2014). According to the World Health Organization (WHO) and the Environmental Protection Agency (EPA), oxyfluorfen is classified as a low acute toxicity compound. Nevertheless, it is considered as very toxic to aquatic organisms and it can affect terrestrial plants and aquatic ecological systems at all levels (Das et al., 2003; Hall et al., 2012; Sondhia, 2010).

There are currently different technologies for the remediation of water effluents polluted with oxyfluorfen, such as: advanced oxidation processes, biological technologies and coagulation or electrocoagulation (Muñoz et al., 2017). Coagulation/flocculation is usually applied to remove colloid pollutants from a liquid phase. In this sense, this technology can concentrate

1 non-ionic chemical compounds, such as oxyfluorfen, into a sludge. Because of its
2 hazardousness, the sludge disposal and management are nowadays facing challenges, that
3 require the development of efficient technologies. Electrochemical technologies are amongst
4 the most promising nowadays, because they have been proven to be clean, flexible and
5 powerful for the treatment of wastes. This type of technologies is generally characterized by
6 the use of very simple equipment, ease of operation, and no need for adding chemicals (Acar
7 et al., 1995). Among the electrochemically assisted processes, electric-field assisted
8 dewatering or electrochemical dewatering (ECD), is a technology that uses an electric field
9 between an anode and a cathode to promote the mobilization of charged ions (electro
10 migration) or particles (electrophoresis), and additionally, to mobilize water from the
11 nearness of the anodes to the proximities of the cathodes by the well-known electro-osmotic
12 process, extensively studied for soil decontamination (Mahmoud et al., 2011; Mahmoud et
13 al., 2010; Silva et al., 2019). This technology has to be combined with a previous
14 conventional dewatering mechanism (gravitational and pressure-driven dewatering) prior to
15 the electrochemically-assisted process (Mahmoud et al., 2011; Mahmoud et al., 2010). Then,
16 the electrochemically assisted technology allows to go further in the remediation of the
17 sludge or soil (Mahmoud, 2010). Thus, as shown in Table 1, in the literature it is found how
18 this technology can enhance the results obtained in the treatment of sludge produced in
19 municipal and industrial wastewater, not only in terms of dewatering but also in the removal
20 of heavy metals and even antibiotics.

1 Table 1. Representative works in recent years using dewatering processes for the elimination
2 of water content and pollutants from sludges.

Reference	Type of dewatering	Treated compound	Main results
(C.Hwang and Min, 2011)	Electro-dewatering process	Different heavy metals	Electro-osmosis coupled to mechanical belt filter press increased the water obtained content by 18%
(Tuan and Sillanpää, 2010)	Electro-dewatering process	Different compounds (Na ⁺ , K ⁺ , Cr ⁶⁺ , Zn ²⁺ , Ca ²⁺)	Concentration of metals was reduced up to 80%, depending on the metal.
(Mahmoud et al., 2010)	Electric field-assisted dewatering	Wastewater sludge	The use of an electric field combined with mechanical compression required less than 10 and 25% of the theoretical thermal drying energy using low and moderate voltages (10-50 V), respectively.
(Tuan and Sillanpää, 2010)	Electro-dewatering process	Extracellular polymeric substance	Electrolysis pretreatment enhanced sludge dewaterability, reaching a sludge with good extracellular polymeric substance contents (15-20 mg/L) and sludge disintegration degrees (1.4-2.0%) .
(Mahmoud et al., 2016)	Electrochemical dewatering process	Activated and digested wastewater sludge	Savings of around 10-12% in the case of voltage electro-dewatering and 30-46% in the case of current electro-dewatering were indicated.
(Li et al., 2019)	Bio-drying after electro.-dewatering pretreatment	Sewage sludge	Electro-dewatering achieved a good dewatering, as compared with other treatments tested, providing the most appropriate conditions for the bio-drying process (water removal rate of 51.13%)
(Qian et al., 2019)	Electro-dewatering process	Sewage sludge	Electrodewatering can improve the final dry solids content (32%) and reduce the heating rate (0.093-0.113 kWh/kg _{water}).
(Silva et al., 2019)	Electrochemical dewatering process	Clopyralid, amoxicilin, ampicilin	Electrochemically-assisted process helped to exhaust the pollutant absorbed onto the sludge and attain a supplemental removal of water content

3
4 Hence, the technology has been applied to improve dewatering of biological sludge,
5 obtaining interesting results. However, to our knowledge, no prior research has been done in
6 the treatment of sludges obtained from coagulation or electro-coagulation essays, which are
7 characterized for enmeshing the pollutant into a matrix of amorphous metal hydroxide, with
8 very different characteristics of those exhibited by biological sludges. For this reason, in this
9 work, it is going to be studied how an iron sludge polluted with oxyfluorfen undergoes
10 electrochemical dewatering to reduce the volume of sludge and simultaneously achieve
11 oxidation of the pollutants enmeshed. Configuration of the electro-dewatering cell (in
12 principal, the relative position of the anode and cathode) is going to be the primary input

evaluated, by determining its influence on the efficiency of the dewatering, on the loss of oxyfluorfen drained from the cake and on the anodic oxidation of the herbicide.

2. Materials and methods

2.1. Chemicals

The commercial herbicide Fluoxil-24 (Barre) containing oxyfluorfen was supplied from Cheminova Agro, S.A. (Spain), containing 24% (wt) of oxyfluorfen as the active substance and presented mixed with other compounds such as xylene (<60%), cyclohexanone (<13%) and calcium dodecylbenzene sulphonate to help the emulsification of oxyfluorfen. Fe_2SO_4 (>75%), sodium sulphate anhydrous (>99%), phosphoric acid (>85%, solvent with TOC-grade), and hydrochloric acid (>37%) were obtained from Panreac. Deionized water (Millipore Mili-Q system) was used to prepare all solutions.

2.2. Preparation of oxyfluorfen polluted flocculation-coagulation sludge

Sludge used in this work to test the electro-dewatering technology was obtained by coagulating a dispersion of 1400 mg L^{-1} oxyfluorfen with 2800 mg L^{-1} iron in the form of Fe_2SO_4 . Once dissolved the iron salt, the solution was taken to a pH of 6.5 ± 0.2 using NaOH 1.0 M and stirred to allow the formation of flocs containing oxyfluorfen with the transformation of the soluble iron (II) salts into iron (III) hydroxide. Final oxyfluorfen concentration and zeta potential from the sludge and the supernatant were measured to confirm the encapsulation of oxyfluorfen in the sludge. The water obtained from the initial filtration of the sludge had a pH of 6.27 with an electric conductivity of 16.8 mS cm^{-1} , turbidity of 1.0 FTU and an oxyfluorfen concentration of 2.27 mg L^{-1} .

2.3. Experimental setup

Figure 1 shows the experimental setup used in this work to evaluate filter press and electrochemically assisted dewatering, as reported previously [14], consisting on a column

made of methacrylate, with an outlet for the filtered liquid at the bottom. A mesh circular cathode (stainless steel or boron doped diamond (BDD, Condias, Itzehoe, Germany) is located at the bottom of the cylinder and fixed to the internal structure of the cylinder, and it is also used as a support plate for the sludge. Below this electrode, a sand filter was placed to ensure a proper filtration of the water from the sludge. The anode (BDD) is located at the top of the sludge and serves as support for the weight (8 kg steel cylinder) used to get the pressure filtration. Diameter of anode and cathode was 10 cm. The liquid was collected into a flask placed on the top of a scale, which quantified gravimetrically the amount of water removed from the sludge. These flasks were periodically replaced, and the samples were characterized in terms of pollutant concentration. Due to the diameter of the setup (10 cm), the application of the steel cylinder produced an external pressure of 0.102 kg cm^{-2} (0.1 bar). During electrochemical tests, the cell voltage was maintained constant at the desired set point (related to the electric field applied and the distance between the anode and the cathode).

Figure 1. Schematic representation of the experimental setup used for the electrochemically-assisted dewatering of a coagulation/flocculation sludge polluted with oxyfluorfen.

2.4. Experimental procedure

3.0 L of solution containing the coagulation-flocculation sludge were introduced in the column and underwent a first phase of gravity filtration until no more water was obtained from the filtrate. Then, the sludge underwent a second phase dewatering by pressure filtration (using a steel cylinder of 8 kg was sited at the top of the sludge) until no more water was recovered at the bottom of the experimental device. Finally, a third stage of dewatering (in this case assisted by an electrochemical process) was attained by connecting the electrodes to a power source (Delta Elektronika ES 030-5; 0-30 V and 0-5 A), which applied increasing electric fields (1.0, 2.0, 4.0, 8.0 and 16.0 V cm⁻¹), until no more water was recovered from the sludge, as schematically depicted in Figure 2.

Figure 2. Schematic representation of the experimental procedure using the electrochemically-assisted dewatering device.

For a better understanding of the results, the measured variables for this set of experiments are depicted in Table 2.

Table 2. Assessed variables in both analyzed electrode schemes.

Variables	
pH	
Electric conductivity	mS/cm
Zeta potential	mV
Recovered water	Weight (%)
Released water	mL
Oxyfluorfen concentration	mg/L
Solid concentration	(mg ox/g soil)

2.5. Analysis of dewatered final sample (post-mortem analysis).

Once the dewatering concluded and no more water was obtained from the experimental device, the cylindrical steel cylinder and the anode were withdrawn from the device and the final solid sample was collected integrally to determine the amount of oxyfluorfen present in different parts of the sample following the scheme depicted in Figure 3. These samples were separated with the help of a scalpel and they were subdivided into zone close to the anode (AN), middle zone (MD) and zone close to the cathode (CA). These samples were dissolved in water (0.1 g of solid sample in 1 mL of distilled water), shaken vigorously for 10 minutes and from this mixture, a sample of 1 mL was taken and mixed in 1 mL acetonitrile (v/v) to extract oxyfluorfen.

Figure 3. Schematic representation of *post-mortem* analysis of the final cake.

2.6. Analytical techniques

To determine the efficiency of the electro-dewatering device, both oxyfluorfen concentration and total organic carbon were monitored. The oxyfluorfen concentration was determined by high performance liquid chromatography (HPLC) after a liquid–liquid (L–L) extraction process using analytical column Phenomenex Gemini 5 μm C18 with a mixture of acetonitrile/water (70:30 (v/v)) as mobile phase at 0.3 mL min^{-1} . Aliquots of $20\text{ }\mu\text{L}$ were injected at a detection wavelength of 220 nm , and the temperature of the oven was maintained at 25°C . The L –L extraction process was carried out in separator flasks of 100 mL using acetonitrile as extraction solvent (ratio oxyfluorfen solution/solvent = 1:1 v/v). Total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytic Jena analyzer. Prior to each analysis, all samples were filtered with $0.22\text{ }\mu\text{m}$ nylon filters provided by Scharlab.

Total iron concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian) with a detection limit $< 1.5\text{ ppb}$. To determine the total metal concentration, samples were diluted to 50:50 (v/v) using 4 N HNO_3 to ensure the total solubility of the metal. The pHs and conductivities of the samples were measured using a CRISON pH25+ and CRISON CM35+, respectively and the zeta potentials were determined using a Zetasizer Nano ZS (Malvern, UK).

3. Results and discussions

The sludge, obtained according to the procedure previously described, was placed in the dewatering cells, where two different configurations were evaluated: scheme 1 (anode upstream and cathode downstream) and scheme 2 (anode downstream and cathode upstream). The percentage of recovered water in each of these schemes is depicted in Figure 4, where it can be noticed that to obtain the maximum dewatering, Scheme 2 (anode downstream and cathode upstream) requires only the application of an electric field of 1.0 V cm^{-1} and after that, no more water could be obtained from the iron cake when applying higher electric fields (values up to 16.0 V cm^{-1} were tested). Conversely, to reach the maximum dewatering from

the cake in Scheme 1, it was needed the increasing application of electric fields from 1.0 up to 16.0 V cm⁻¹. It is important to take into account that the maximum dewatering was different in both schemes, being higher in the case of Scheme 1, as it will be shown later. Differences observed may be explained because of the effect of the pH on the the Z-potential of the sludge, which is known to affect the charged layer of water surrounding the flocs in the sludge(Chon et al., 2014; Gronchi et al., 2017; Ma et al., 2016; Tang et al., 2017; Yu et al., 2017). Initially the sludge placed in the cells had a z-potential of -13.4 mV (pH 6.8) which was modified importantly with the application of the electric fields because of the extreme changes in the pHs observed in the nearness of the electrodes. Therefore, z-potential decreases in the nearness of the anode (-10.6 mV at pH 1.0) and increases in the nearness of the cathode (-18.6 mV at pH 10). Although z-potentials were always negative, these changes are influencing the electro-osmotic mobility, the strength of the electrostatic interactions between flocs and the layer of water that surround them, and they can also affect to the mobility of other species (either by electromigration or electrophoresis)(Gronchi et al., 2017; Ma et al., 2016; Rodrigo et al., 2014; Trellu et al., 2016). This means that, the higher the z-potential, the higher is the expected EOF (electro-osmotic flux), which, in addition, in the two schemes tested, can be in the same or in opposite direction of the gravity flux. When the EOF is in the same direction of the gravity flux (Scheme 1), it could be expected a better performance. However, there is also another competing process which may affect results: the strength of the electrostatic attraction / repulsion forces(Mahmoud et al., 2011; Mahmoud et al., 2010; Sun et al., 2017). In this way, the lower z-potential observed in the bottom of the cell in Scheme 2 favors the more effective dewatering by gravity, because of the lower electrostatic attraction between the surface of the flocs and the layer of water surrounding it (which is around 30% lower as compared with the non-electrified sludge and 80% lower than in the case of sludge electrified with Scheme 1)(Vijh, 1999; Vijh and Novak, 1997).

Figure 4. Amount of water recovered (in weight percentage) in both analyzed tests: anode upstream and cathode downstream (●) and anode downstream and cathode upstream (×), and water released (in mL) in the entire experiment (inset).

Figure 5 shows the dewatering of the sludge in terms of weight loss associated to dewatering. As seen, the final water content of sludge that underwent Scheme 1 is lower than that of the sludge processed with Scheme 2. As indicated in the phenomenological model shown in part b of the Figure, the gravity and the electroosmotic fluxes are in the same direction and although electrostatic interactions in the bottom of the cells should favor the dewatering reached by Scheme 2, the opposite directions of the gravitational and the electrophoretic fluxes lead to the accumulation of water near to the cathode that was unable to exit the cake.

Figure 5. a) Total weight loss (in %) achieved according with the electric potential applied in anode upstream and cathode downstream configuration (Scheme 1) and anode downstream and cathode upstream electrode configuration (Scheme 2), and b) schematic representation of the gravitational and electrophoretic flux in the experimental setup according with the electrode configuration.

The influence of pH and the amounts of iron (Fe) and oxyfluorfen drained with the released water were also analyzed for the two electro-dewatering schemes tested. Results obtained in Scheme 1 are shown in Figure 6. As expected because of position of the cathode, pH in the outlet of this cell became more alkaline as the electric field increased. Thus, during the non-electrochemical dewatering (gravity and pressure driving forces), the pH of the water was near to neutrality, increasing with the application of electric fields event up to 12. Cathodic water reduction to hydrogen and hydroxyl ions (Eq. 1) allows to explain these changes which, in turn, may also affect iron and oxyfluorfen released (Lopez-Vizcaino et al., 2011).

It was observed a slight release of iron (around 50 mg/L) when the first potential was applied to the electro-dewatering cell, conditions at which the pH was not so alkaline still and which can be explained because of the transport of the positively charged species attracted by the cathode by electromigration. After that, iron released from the cell was almost nil, regardless of the applied electric field. Regarding oxyfluorfen, it only escapes from the sludge during the pressure-driven stage (only around 8 mg/L) and, over the electrochemical stages, the concentrations of oxyfluorfen measured into the obtained water were negligible with measured values close to zero, which might also be explained in terms of the pHs, because it is well known that iron remains in flocs at values higher than 6, and that this electrode configuration basified the environment leading to an improve capture of oxyfluorfen into the

iron flocs, preventing the drain of the organochlorine compound(Canizares et al., 2007; Canizares et al., 2006).

Figure 6. Electrochemical dewatering of an oxyfluorfen polluted sludge, placing the anode upstream and the cathode downstream and applying ascendant electric fields (1, 2, 4 and 16 V cm⁻¹), the graphic shows the influence of electrochemical dewatering on pH (+) and the release of oxyfluorfen (●) and Fe (×).

Results obtained in the cell operated according to Scheme 2 are shown in Figure 7. In this case, the electrode closer to the outlet is the anode. This explains the observed acidification up to values close to 3.0, once the electric potential (1.0 V cm⁻¹) was applied, which can be explained in terms of the oxidation of water to oxygen and protons (Eq. 2)(Lopez-Vizcaino et al., 2011).

This acidification led to the release of an important amount of oxyfluorfen (428.05 mg/L) and iron (360 mg/L) during the electrochemical stage, caused by the decrease of the pH. Obviously, no release of iron or oxyfluorfen were noticed in the preceding phases (gravity and pressure driven dewatering)

Figure 7. Electrochemical dewatering of an oxyfluorfen polluted sludge, placing the anode downstream and the cathode upstream and applying ascendant electric fields (1, 2, 4 and 16 V cm^{-1}), the graphic shows the influence of electrochemical dewatering on pH (+) and the release of oxyfluorfen (●) and Fe (x).

Finally, the distribution of oxyfluorfen in the final cake was also studied for both schemes, trying to determine if oxyfluorfen was successfully oxidized in the nearness of the BDD anode. To do this, the cake was divided into three portions: two portions next to the electrodes and the middle zone. Results are shown in Figure 8, where it can be noticed that in Scheme 1, concentrations are much lower than expected taking into account the almost null release of oxyfluorfen during the dewatering, indicating that extensive electrochemical oxidation may be happening in the system (Gronchi et al., 2017; Larue et al., 2006). In fact, oxyfluorfen is known to be very easily oxidizable by electrolysis and results obtained here are in agreement with previous works in which the oxidation of oxyfluorfen in aqueous dispersions was evaluated (Dos Santos et al., 2017a; dos Santos et al., 2017b; dos Santos et al., 2016). Thus, the final concentration of oxyfluorfen is around 500 mg oxyfluorfen / g of dewatered sludge, being more concentrated in the area close to the anode. Transport of oxyfluorfen micelles to the anode is favoured by electrophoresis, taking into account that micelles of oxyfluorfen in the commercial formulation are negatively charged (Risco et al., 2016). This explains this profile of concentration. Opposite, in Scheme 2, the concentration of oxyfluorfen is much higher, even taking into account the important release observed during the application of

electric fields. The values observed are around 13000 mg/L. In this case, the low electric field was not able to attain an important electrolytic removal of the herbicide, and the amounts released are rapidly flushed because of the proximity of the anode with the outlet of the cell.

Figure 8. Oxyfluorfen content in the final dewatered cake in three different areas: are close to the anode, area located at the middle zone of the final cake and area close to the cathode in both tests: a) Scheme 1 (anode upstream and cathode downstream) and b) Scheme 2 (anode downstream and cathode upstream).

4. Conclusions

The application of electric fields during the dewatering of sludge polluted with oxyfluorfen enhances the removal of water from the sludges and it can result in the electrolytic removal of the pollutant. The electro-dewatering cell design has an important influence on the performance of the process. When the anode was placed upstream and the cathode downstream (so-called in this work as Scheme 1), it was observed that it was required an increasing gradient (1.0 to 16.0 V cm^{-1}) of the imposed electric field to achieve the complete dewatering of the final cake which, in addition, is more important than in the reverse configuration. On the other hand, when anode was placed downstream and cathode upstream (Scheme 2), the electric field intensity needed for the complete dewatering of the cake was lower (1 V cm^{-1}), although more water is retained in the system at the end of the dewatering process.

The electro-dewatering cell also attains an electrolytic removal of the oxyfluorfen, being much more efficient the operation Scheme 1 in which the cathode is placed next to the outlet.

This scheme, in addition, prevents loses of oxyfluorfen because of the more efficient control of the pH.

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Conflicts of interest

The authors confirm that this article's content has no conflict of interest. Also, we declare that all authors have participated in the elaboration of this manuscript.

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