Combining bioadsorption and photoelectrochemical oxidation for the treatment of soil-washing effluents polluted with herbicide 2,4-D

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Abstract

BACKGROUND. The aim of this work is to evaluate the effectiveness of complete treatment of soil spiked with 2,4-D, consisting of the soil washing, followed by the bioadsorption with activated sludge and electrochemical and photoelectrochemical oxidation of resulting wastewater using BDD anodes combined with UV light irradiation.

RESULTS: Results show that 2,4-D is very efficiently removed from synthetic soil by soil-washing without the use of surfactants. The effluent can be treated by bioadsorption with fresh activated sludge coming from a municipal wastewater treatment plant and the maximum adsorption capacity is 0.012 mg 2,4-D/mg biomass. Despite the low contact time between the biomass and the soil-washing waste, results fits well to a Langmuir isotherm.

CONCLUSIONS: Photoelectrolysis with diamond anodes is more efficient than single electrolysis and influence of potential radicalary oxidants produced on the anode surface from sulfate and chloride and activated by UV light can explain the better results. Both, electrolysis

and photoelectrolysis can lead to the complete mineralization of the 2,4-D, regardless of the previous biomass/herbicide ratio applied in the previous bioadsorption process.

Keywords

2,4-D, bioadsorption, electrolysis, photoelectrolysis, soil washing

Highlights

- Bioadsorption of soil-washing effluents with fresh activated sludge can retain up to 0.012 mg 2,4-D/mg biomass
- Bioadsorption fits well to a Langmuir isotherm, despite the low contact time between sludge and 2,4-D
- Electrolysis and photoelectrolysis can fully mineralize the organic content of the effluent of the bioadsorption process
- UV irradiation improves the mineralization rate of electrolysis with diamond and is cost-effective

1. Introduction

The use of herbicides on large scale in agriculture to improve the quality and quantity of crops may cause serious pollution problems in soils. The environmental impact of herbicides is complex and diverse according to various factors, such as toxicity and ecotoxicity of parent molecules or by-product metabolites; synergetic effects with other pollutants, residence time

etc... [1, 2]. Especially 2,4-dichlorophenoxyacetic acid (2,4-D) is largely used in agriculture, as an herbicide to control broad leaf weeds, cereal crops, pastures and gardens [3, 4] due to its low cost and good selectivity. However, it may be easily transferred into surface and groundwater after application due to its high solubility and low soil sorption and high rate for leaching [4] which causes chronic poisoning effects on the human life [5]. 2,4-dichlorophenoxyacetic acid is classified as carcinogen and mutagen agent by the international agency for research on cancer. The World Health Organization recommended $70 \mu\text{g L}^{-1}$ as a maximum of 2,4-D concentration in drinking water [6]. In addition some chlorophenols like 2,4-dichlorophenol, monochlorophenols have been found to be produced as by products during the biodegradation of 2,4-dichlorophenoxyacetic acid [7, 8].

Surfactant-aided soil washing for removal of 2,4-D from soils could be one of the most competitive methods because of the simple process, low cost and mild operation conditions. [9-12]. In the case of organic pollutants, the use of surfactant solution is the major application which can give a soil completely remediated, but it generates highly polluted wastewater containing complex mixture of dissolved organics, surfactants and inorganic salts dissolved and exchanged from soil during the extraction process. To achieve wide-spread removal of organic and inorganic pollutants from wastewater, a more efficient and low-cost process must be found. Recently, the use of biological-based materials and their by-products as a biosorbent for the removal of organic and inorganic pollutants from different wastewater has attracted the attention of a number authors [13, 14]. It consists of the extraction of pollutants contained in the soil with a solution containing a biomaterial able to transfer the pollutants from the soil to liquid phase because of presence of carboxyl, hydroxyl and amino groups over their surfaces [15]. Consequently, this process remediates the soil and thus converts the problem of soil remediation into a potentially easier wastewater treatment problem. The major advantages of biosorption over conventional treatment methods include [16]: i) abundance of biosorbent,

1 being easily obtainable with high quantity and low cost; ii) low operating cost; iii) minimization
2 of the volume of chemical and/or biological sludge to be disposed of; iv) high efficiency in
3 detoxification of very diluted effluents, and consequently high purity in treated wastewater; the
4 removal from dilute solutions; v) no nutrient requirements; vi) the easy regeneration of
5 biosorbent. These advantages have served as the primary incentives for developing full-scale
6 biosorption processes to clean up heavy metal pollution.

7 Several methods including biodegradation processes, photocatalytic degradation, adsorption,
8 electrochemical degradation, have been developed to remove 2,4-dichlorophenoxyacetic acid
9 (2,4-D) from wastewater [1, 17-21]. However, this type of the effluent is difficult to treat by
10 conventional wastewater treatment methods. Additionally, these methods are relatively
11 expensive involving either elaborate and costly equipment or high costs of operation and energy
12 requirements. Advanced oxidation processes are one of the most effective processes for
13 cleaning polluted herbicide wastewater. These processes are highly efficient methods for
14 wastewater treatment due to its ability to mineralize a wide range of recalcitrant organic
15 contaminants by generating highly reactive hydroxyl radicals [18, 22-24]. Particularly, electro-
16 oxidation process has received increasing attention due to its ability to reach complete
17 mineralization of organics into carbon dioxide, water, and inorganics ions.

18 It must be noted that because of the low concentrations of pollutant, mass transport limitations
19 control the rate of oxidation and reduces the efficiency of the electrochemical process[25-30].
20 The combination of electrolysis with other processes such as Fenton oxidation, ultrasound
21 irradiation or UV light irradiation; that promotes the production of more efficient oxidants
22 increases the performance of the process[31]. In this work, electrooxidation process using boron
23 doped diamond (BDD) combined with UV light irradiation was selected for the treatment of
24 soil washing effluent from remediated soil polluted with 2,4-D.

Thus, the aim of this work is to evaluate the effectiveness of complete treatment of soil spiked with 2,4-D, consisting of the soil washing, followed by the bioadsorption with activated sludge and electrochemical and photoelectrochemical oxidation of resulting wastewater using BDD anodes combined with UV light irradiation.

2. Materials and methods

Chemicals. In this work, clay was selected as model of soil. 2,4-dichlorophenoxyacetic acid was selected as a model of organic compounds and it is was purchased from Fluka. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, NaCl, NaNO_3 , KI and CaCO_3 were purchased from Merck and Sigma-Aldrich. Deionized water was used to prepare all solutions.

Preparation of synthetic groundwater. Synthetic groundwater was used as the solvent of the soil washing process. According to literature, it was prepared by dissolving 6.671 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 1.318 g of NaCl, 1.302 g of NaNO_3 , 0.255 g of KI and 2.497 g of CaCO_3 in 10 dm^3 of deionised water.

Preparation of spiked soil. The preparation of soil has been described in the literature previously [9, 32, 33]. Polluted soil were prepared by dissolving 2,4-dichlorophenoxyacetic acid in deionized water (500 mg dm^{-3}) and then mixing this solution with clay soil. The spiked clay was aerated during 1 day to favor evaporation of the water and, in this way the 2,4-dichlorophenoxyacetic acid was homogeneously distributed on the clay surface. The resulting 2,4-dichlorophenoxyacetic acid concentration in the soil was around 0.1 g kg^{-1} of soil (average value of the 5 portion of spiked soil sampled).

Soil washing procedure. Soil washing with synthetic groundwater was carried out in stirred tank having 20 dm^3 of capacity and operated in discontinuous mode. 10 kg of polluted soil (0.1 g of 2,4-D kg^{-1} of soil) was stirred with 10 dm^3 groundwater during six hours at a stirring rate of 150 rpm. After the mixture let decanted during 24 hours to separate the soil form the aqueous

phase. These effluents consisted of aqueous mixtures of 2,4-D were finally treated by bioadsorption.

Bioadsorption of soil-washing effluents. Batch bioadsorption experiments were performed in order to evaluate the potential application of this technology for pesticides removal from liquid samples. In each experiment, fresh activated sludge from a conventional Wastewater Treatment Facility located in Ciudad Real, was added to lixivate of the soils polluted with herbicides. Before each test, the batch reactors were purged with nitrogen in order to remove the oxygen from the gas phase. Working in this way the removal of pesticide by means of aerobic oxidation of pesticide was avoided. The batch reactors were located in an incubator in order to maintain the temperature at about 20°C. The batch reactors were mixed by means of a magnetic stirrer rotating at 100 rpm in order to maintain the biomass suspended, but minimizing mass transfer between the liquid and gas phases. In order to evaluate the adsorption capacity of the biomass, several tests performed at different pesticide and biomass concentrations. Once finished the adsorption tests, after 6 h of contact time, the biomass was separated from the solutions by means of filtration through a glass fiber filter with a pore size of 45µm. Liquid phase was then treated by electrochemical and photoelectrochemical processes.

The pesticide recovered and sorbate uptake was calculated with reference to concentrations detected in non-inoculated media. The sorbate uptake was calculated using Eq. (1), where q corresponds to the sorbate uptake, V is the liquid volume (L), C_i and C_f are the initial and final pesticide concentrations and S is the sorbent amount (g).

$$q = \frac{V(C_i - C_f)}{S} \quad (1)$$

Electrochemical and photoelectrochemical oxidation of the bioadsorption effluents.

Electrochemical oxidation experiments were carried out in a bench-scale plant with a single compartment electrochemical flow. Bulk oxidations were performed in a single-compartment

cell, as described in previous works [32]. BDD and steel electrodes were used as anode and cathode, respectively. Characteristic of BDD are as follows: sp^3/sp^2 ratio: 225; boron content: 500 ppm; width of the diamond layer: 2.68 μm . For the electrochemical flow cell, inlet and outlet were provided for effluent circulation through the reactor; the simulated effluent was stored in a thermoregulated glass tank (2000 cm^3) and circulated through the cell using a peristaltic pump at a flow rate of 200 $dm^3 h^{-1}$. The electrical current was applied using a DC Power Supply (FA-376 PROMAX). Temperature was kept constant by means of a water bath. In the case of photoelectrochemical process the same procedure was applied combined by UV lamp (VL-215MC (Vilber Lourmat), $\lambda = 254$ nm, intensity of 930 $\mu W cm^{-2}$ and energy 4.43-6.20 eV irradiated 15 watts directly to the quartz cover light).

Analytical methods. Herbicide concentration during the soil washing and adsorption process was calculated by using the Lambert-Beer law and measuring the absorption at characteristic wavelength of 633 nm using a double beam UV–visible spectrophotometer Shimadzu UV-1800. The solution pH and the conductivity were measured with an InoLab WTW pH-meter and a GLP 31 Crison conductivimeter, respectively. Samples at different electrolysis and photoelectrolysis times were filtered with 0.20 μm Nylon filters before analysis. 2,4-D and all intermediates generated were identified by HPLC–UV (Agilent 1100 series). The analytical column used is type Phenomenex Gemini 5 μm C18 and it was maintained at room temperature. A gradient elution was applied using the mobile phase formed by 25 mM of formic acid water solution (Solvent A) and acetonitrile (Solvent B). A lineal gradient was obtained by initially running 10% of Solvent B ascending to 100% in 40 min. The injection volume was 20 μL and UV detector of HPLC–UV was performed at 291 nm. Ionic species (NO_3^- , SO_4^{2-} , Cl^-) were measured by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column (anionic species); mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, $1 \cdot 10^{-3}$

$^3 \text{ dm}^3 \text{ min}^{-1}$ (concentration accuracy: $\pm 0.5 \%$). The removal of total organic carbon (TOC) of 2,4-D solutions was determined with a Multi N/C 3100 Analytik Jena TOC analyzer.

3. Results and Discussion

Production of the soil-washing wastewater. Soil washing is typically a very effective technique for the remediation of soil. It consists of the extraction of the pollutant with a fluid (often known as soil washing fluid) that becomes wastewater and should be treated after their used, in order to be regenerated and further applied. Composition of the washing fluid could be tailored for the pollutant to be extracted and in the case of 2,4-D, taking into account its high solubility, groundwater seems to be a good candidate. For this reason, the tests were carried out with synthetic groundwater instead of using a surfactant solution, which is the case in most soil-washing processes with pesticides. Figure 1 shows the amount of pesticide extracted from the soil as a function of the ratio volume of water / mass of soil used in each soil-washing process.

Figure 1. Herbicide extracted from soil as a function of the washing fluid/ soil ratio

As it can be observed, in the water/soil range used, the herbicide is completely transferred to the liquid phase. This means that soil has no 2,4-D retention capability and low amounts of

synthetic groundwater will be enough to drag the pesticide. Based on these results, it was decided to use the ratio 1.0 L groundwater kg^{-1} soil to produce the soil-washing fluid used in this study which aims to evaluate the combined bioadsorption / electrochemical treatment of this effluent. Lower ratios were not used because of the unpractical separation of the liquid and solid phases.

Concentration of pesticide in the soil washing fluid is not negligible but significant and, as expected, a treatment is required in order to regenerate the washing fluid. This concentration is comparable to the concentration used in most studies reported in the literature about pesticide degradation [34, 35].

Bioadsorption of soil-washing fluids. Once the soil washing effluent was obtained, in order to optimize the pesticide removal performance of the bioadsorption process, several tests were performed at different biomass to herbicide ratios, ranging from 0 to 30 mg biomass/mg 2,4-D. Figure 2 shows the quality of the effluent generated in the bioadsorption process, as a function of the ratio biomass/herbicide used.

Figure 2. TOC (▲) and 2,4-D (Δ) concentration of the effluent of the bio-adsorption process obtained with different ratio biomass/herbicide.

As it can be observed, the higher the amount of biomass used, the lower is the amount of 2,4-D detected in the effluent of the bioadsorption process. On contrary, the total organic load (quantifies in terms of TOC) does not seem to depend significantly on the amount of biomass used. At this point, it is important to take in mind that bioadsorption is attained by mixing concentrated activated sludge with the soil-washing fluid and that mixed liquor contained other species different of 2,4-D, so not only 2,4-D is accounting for the TOC.

Short contact time between the biomass and the pollutant made adsorption to be the most important process expected. The concentration of 2,4-D adsorbed onto the biomass (calculated by mass balance taking into account the concentration of 2,4-D in solution before and after the addition of the biomass) is plotted versus the ratio biomass / herbicide in Fig. 3.

Figure 3. Effect of biomass loading on pesticide adsorption.

Increasing the biomass to pesticide ratio from 0 to 8 mg/mg does not increase the adsorption capacity of the herbicide by biomass. In this range, the adsorption capacity was maintained at its higher value, which seems to be about 0.012 mg 2,4-D/mg biomass. This phenomenon could be related to the saturation of the external binding sites of the biomass for herbicide sorption. These binding sites are located in the biomass surface, and when working with low biomass to

herbicide ratios can be saturated, acting as the limiting stage in the pollutant adsorption. From these results, it can be concluded that to reach the highest specific herbicide adsorption, the optimum biomass load to be dosed is about 8-10 mg biomass/mg of herbicide. Within this range, biomass is very efficiently used and it could be separated for a later slower biodegradation treatment very efficiently.

Taking into account the concentrations of herbicide in solution after the test and the concentration adsorbed onto the biomass, the pseudo-equilibrium isotherm obtained at room temperature (25°C) is shown in Figure 4. As already being pointed out, contact time between the pollutant and the biomass is short for a perfectly defined equilibrium, but longer times could mask the effects of bioadsorption by biodegradation.

Figure 4. Equilibrium isotherm of herbicide 2,4-D onto activated sludge biomass.

As it can be observed, a saturation adsorption isotherm is perfectly defined and data can be fitted well to a Langmuir isotherm with a regression coefficient of 0.943. The clear definition of the maximum adsorption capacity is an indicative of an almost steady-state adsorption process.

One important point for the later electrochemical treatment is to verify the concentration of the main anions contained in the effluent. As it is known, in order to be effective, electrochemical processes required electrolytes with suitable conductivity. If a low conductivity waste is treated, the energy consumption will be too high because of the concomitant higher ohmic losses of the electrochemical cell. On the other hand, the addition of salts to the effluent in order to increase conductivity is not a good practice, because it reduces unnecessarily the quality of the effluent and salts are extremely difficult to be removed after the treatment. Taking into account this information, Table 1 shows the concentration of the main anions detected in bioadsorption effluents.

Table 1. Concentration of several anions in the effluent of the bio-adsorption process.

Biomass/pesticide ratio	NO₃⁻ (mg/L)	SO₄²⁻ (mg/L)	Cl⁻ (mg/L)
1.67	1.93	255.19	153
3.00	3.05	254.43	140
6.00	13.57	250.99	124.4
10.00	24.04	255.53	110.9
16.67	35.37	250.30	97.40
30.00	42.56	221.29	81.00

As it can be observed, concentrations of sulfate, nitrate and chloride are important and depends on the biomass/herbicide ratio, because of the raw concentration of anions in the biomass and in the soil washing fluids. However, although low, they seem to be enough for an electrolytic process because they are in the range of water treatment, case that has been studied before by many groups [36-38].

Electrolysis and photoelectrolysis of the bioadsorption effluents. Figure 5 shows the changes in pollutant concentration and TOC during the electrolysis and photoelectrolysis of the effluent of the bioadsorption process using a biomass/herbicide ratio of 10. As it was pointed

out before, despite the low concentration of salts, the conductivity of the effluent of the bioadsorption process was appropriate for an efficient electrolysis, and thus the addition of higher concentration of salts was not required. Cell voltages during operation were kept constant (operating galvanostatically) at 9.0 V.

Figure 5. Changes in the TOC and 2,4-D concentration during the electrolysis (Δ TOC $\blacktriangle$ 2,4-D) and photoelectrolysis ($\square$ TOC $\blacksquare$ 2,4-D) of the effluent of the bio-adsorption process obtained with B/P: 10

As it can be observed, in both cases the herbicide is rapidly oxidized and applied electric charges below 6.0 Ah dm⁻³ are required to deplete its concentration down to undetectable values. On the other hand, higher values of electric charges are required to attain the complete mineralization of the organic load. These differences between pollutant removal and TOC are explained in terms of the formation of reaction intermediates. Another important observation is that UV light irradiation has a positive effect on both 2,4-D removal and mineralization, in

1 contrast to the inefficient 2,4-D degradation attained with single photolysis. In particular the
2 total applied charge required for the complete mineralization in the photoelectrolysis (9.0 kAh
3 m^{-3}) is less than half the required in the single electrochemical process (22.0 kAh m^{-3}). For a
4 cell potential of 7.0 V, this means a difference of 91 kWh m^{-3} . Taking into account, that light
5 irradiation power was 2 kW m^{-3} and duration of the treatment 8 hours, the 16 kWh m^{-3} clearly
6 shows the advantage of using photoelectrolysis for the treatment of soil-washing effluents with
7 an outstanding saving in operation cost.

8 Figure 6 shows the efficiency of the electrolysis and photoelectrolysis of the effluent of a
9 combined soil-washing bioadsorption process using different ratio biomass/herbicide. As it can
10 be observed, the energy efficiency in the mineralization does not depend significantly on the
11 ratio biomass/pesticide used in the bioadsorption process and it seems to be kept within a
12 constant value (around 5 mg (Ah) $^{-1}$) in the complete range of biomass/herbicide studied. On
13 contrary, the efficiency calculated for 2,4-D decreases at higher ratios biomass/herbicide ratios.
14 This fact can be explained in terms of mass transfer limitations, because the higher the ratio
15 biomass/herbicide used the lower is the concentration of 2,4-D.

16 This observation is even more relevant in photoelectrolysis tests, in which the oxidation rate of
17 2,4-D is even higher (see Figure 5). This is in accordance with previous works published in
18 literature [39, 40] in which it was observed that the use of UV light irradiation favors the
19 activation of oxidants electrogenerated during electrolysis with diamond anodes. However, it
20 is important to point out that in this work, electrolyte salts were not added, and ions present in
21 the effluents are exclusively those extracted from the soil during the soil-washing and the later
22 bioadsorption processes. As it was shown in Table 1, bioadsorption effluents contained sulfate,
23 nitrate and chloride in relevant concentration. Two of these anions are of extreme importance
24 in electrolysis: sulfate and chloride. Thus, during the electrolysis with diamond anodes of
25 sulfate solutions the oxidant peroxodisulfate is known to be produced [41, 42]. Its activation

with light to produce sulfate radicals has also been confirmed in the literature [39, 40, 43]. Regarding the electrolysis of chloride solutions a much more complex chemistry is known to occur, with the formation not only of gaseous chlorine and hypochlorite but also of undesirable chlorates and perchlorates. The higher efficiency obtained during UV irradiated electrolysis clearly indicates that large concentrations of oxidants are produced and activated under these conditions.

Figure 6. Efficiency of the electrolysis (Δ TOC ▲ 2,4-D) and photoelectrolysis (Δ TOC ▲ 2,4-D) in the treatment of the effluent of a combined soil washing bio-adsorption process

Fig. 7 compares the total amount of intermediates generated during electrolysis and photoelectrolysis of the effluents of the bioadsorption processes obtained with different ratios

biomass/herbicide. It has been preferred to show them as total chromatographic area in order to account for all of them with a single parameter. Anyhow, same intermediates were found in both processes, indicating that the primary mechanism of 2,4-D degradation is the same, regardless the irradiation of UV light. Main intermediates formed were hydroquinone and 4-chlororesorcinol, and 2-chlorophenol and 4-chlorophenol which are related to the presence of chlorine in the solution. This fact was previously studied in a work of this research group in which the mechanisms for the oxidation of 2,4-D were clarified for the electrolysis and photoelectrolysis of 2,4-D solutions with diamond anodes [44].

Figure 7. Total amount of intermediates (quantified as chromatographic area) during the electrolysis (part a) and photoelectrolysis (part b) of the effluents of the combined soil washing bio-adsorption process (Δ biomass/herbicide ratio 30; $\blacktriangle$ biomass/herbicide ratio 16.67; $\square$ biomass/herbicide ratio 10; $\blacksquare$ biomass/herbicide ratio 6; biomass/herbicide ratio 3; $\diamond$ biomass/herbicide ratio 1.67)

However, despite the intermediates are the same, the relative concentration of intermediates is different. In both electrolysis and photoelectrolysis, the concentrations of intermediates increase during the treatment achieving maximum concentration about 4 Ah dm^{-3} and 2 Ah dm^{-3} in electrolysis and photoelectrolysis, respectively, before being fully oxidized. The complete depletion of the aromatic intermediates is attained at about 12 Ah dm^{-3} and 7 Ah dm^{-3} , respectively. Total concentration of intermediates depends on the characteristics of the effluent electrolyzed. The lower the biomass/herbicide ratio, the higher is the total concentration of intermediates. This is a clear consequence of the higher concentration of 2,4-D in the effluents produced with lower biomass/herbicide ratio. In comparing electrolysis and photoelectrolysis, it can be clearly seen that the main difference is the faster removal of intermediates with UV irradiation. These results are in agreement with the results observed for TOC.

4. Conclusions

From this work, the following conclusions can be drawn:

- Bioadsorption is an effective treatment for the rapid removal of 2,4-D from soil-washing fluids. A maximum capacity of adsorption around $0.012 \text{ mg 2,4-D/mg biomass}$ can be attained and experimental results fits well to a Langmuir adsorption isotherm in spite of the low contact time between sludge and herbicide.
- A combination of bioadsorption onto activated sludge and electrolysis (or photoelectrolysis) with diamond anodes can attain the complete removal of herbicide 2,4-D from soil-washing wastewater. It can also attain the complete mineralization with the oxidation of all intermediates.

- Electrolytic removal of 2,4-D is attained regardless of the biomass/herbicide ratio used in the previous bioadsorption process. The lower the ratio, the higher the intermediates concentration observed.
- UV irradiation improves significantly the 2,4-D oxidation and the mineralization rate during the electrolysis of soil-washing effluent. In addition, due to the low energy dose as compared to the supplied with the electrochemical system becomes a promising cost-worthy technology.
- Intermediates are removed faster with UV irradiation and presence of ions that can be oxidized to higher oxidation state and produce radicals when exciting by UV light can explain the improvement.

Acknowledgements

The authors acknowledge funding support from the EU and Spanish Government through the MINECO Project CTM2013-45612-R, FEDER 2007-2013 PP201010 (Planta Piloto de Estación de Estación de Regeneración de Aguas Depuradas) and INNOCAMPUS.

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