SBCPD

PLANTA DANINHA

SOCIEDADE BRASILEIRA DA
CIÊNCIA DAS PLANTAS DANINHAS

<http://www.sbcpd.org>

ISSN 0100-8358 (print)
1806-9681 (online)

Literature Review

REMEDIATION OF SOILS CONTAMINATED BY PESTICIDES USING PHYSICOCHEMICAL PROCESSES: A BRIEF REVIEW

Remediação de Solos Contaminados por Agrotóxicos Utilizando Processos Físico-Químicos: Breve Revisão

BALDISSARELLI, D.P.[1]
VARGAS, G.D.L.P.[1]
KORF, E.P.[1]
GALON, L.[1]*
KAUFMANN, C.[1]
SANTOS, J.B.[2]

ABSTRACT - After years of pesticide application, often indiscriminately, damage has been caused to the environment, as well as to agronomic crops grown in contaminated areas. In water treatment, techniques based on physical and/or physicochemical processes are used, being formed secondary oxidizing agents responsible for the mineralization of contaminants present in the herbicides, thus causing the degradation process. However, few studies have demonstrated the effectiveness of these techniques in soils. The aim of this study was to review the existing studies, presenting the main techniques used for remediation of soils contaminated with pesticides. Emphasis was placed on electrokinetics, advanced oxidative processes, soil washing, chemical or solvent extraction, and combinations of these methods. According to the results of several studies, the combination of techniques, such as electrokinetics and soil washing processes, allows achieving a high efficiency when it is applied for the degradation of agricultural contaminants. The combination of electrolysis with other methods, such as the Fenton's reagent, ultrasound irradiation, and UV light, also present satisfactory results in removing pesticides in soil treatment. However, Fenton technology used alone is the most promising of the assessed techniques since it can be used for the remediation of several contaminants, especially pesticides, not harming the environment and allowing soil recovery.

Keywords: soil remediation, environmental sustainability, agricultural contaminants.

RESUMO - Após anos de aplicação, muitas vezes de forma indiscriminada, de agrotóxicos, danos foram causados ao ambiente, bem como às culturas agronômicas cultivadas em locais contaminados. No tratamento de água são utilizadas técnicas que se baseiam em processos físicos e ou físico-químicos, onde ocorre a formação de agentes oxidantes secundários responsáveis pela mineralização dos contaminantes presentes nos herbicidas, havendo assim o processo de degradação. No entanto, ainda existem poucos trabalhos que demonstram a eficácia dessas técnicas em solos. Dessa forma, objetivou-se fazer uma revisão sobre os trabalhos já existentes, apresentando as principais técnicas utilizadas para a remediação de solos contaminados com agrotóxicos. A ênfase foi dada para a eletrocinética, processos oxidativos avançados, lavagem de solo, extração química ou por solventes e para as combinações desses métodos. Verificou-se, pelos resultados apresentados nos diversos estudos, que a combinação de técnicas permite alcançar grande eficiência, como é o caso de processos eletrocinéticos e de lavagem de solo, quando aplicadas para a degradação de contaminantes agrícolas. As combinações da eletrólise com outros métodos, como reagente de Fenton, irradiação de ultrassom e luz UV, também apresentam resultados satisfatórios na

*** Corresponding author:**
<leandro.galon@uffs.edu.br>

Received: September 5, 2017
Approved: January 24, 2018

Planta Daninha 2019; v37:e019184975

[1] Universidade Federal da Fronteira Sul, Erechim-RS, Brasil; [2] Universidade Federal dos Vales do Jequitinhonha e Mucuri, Diamantina, MG, Brasil.

Doi: 10.1590/S0100-83582019370100054

remoção de agrotóxicos no tratamento do solo. Contudo, a tecnologia de Fenton utilizada isoladamente apresenta-se como a mais promissora das técnicas avaliadas, uma vez que pode ser usada para a remediação de diversos contaminantes, em especial os agrotóxicos, não agredindo o ambiente e permitindo também a recuperação do solo.

Palavras-chave: despoluição de solo, sustentabilidade ambiental, contaminantes agrícolas.

INTRODUCTION

Due to an increase in world population and consequent need in increasing food production, techniques used in agriculture have undergone changes in order to increase their efficiency. In order to guarantee a high productivity index of the main crops, the use of agrochemicals, applied in high quantities, is frequently used to control weeds, insects, and diseases that may adversely affect the growth and development of crops. In Brazil, the intensive use of pesticides began with the Green Revolution in the 1960s, and the country reached the position of the world's largest consumer of these products in 2008 (Gama et al., 2013), maintaining this index nowadays (Piccoli et al., 2016).

On the one hand, the use of pesticides allows a higher food productivity by minimizing pest attack, improving supply conditions (Ribeiro et al., 2011), on the other hand, its indiscriminate use and without following the technical recommendations cause serious impacts on the environment and health of the applicator and population (Cheng et al., 2016a; Araujo and Oliveira, 2017).

The high persistence, mobility, and toxicity of pesticides make the compounds stay in the environment longer, causing impacts to the physical and biotic environments. For this reason, the determination of the presence and concentration levels of these residues in several substrates is essential in environmental monitoring and control programs (Duarte et al., 2016).

Although the soil has a certain capacity of adsorption and the environmental conditions allow the degradation of compounds present in the agrochemicals (Steffen et al., 2011), their high toxicity and persistence make necessary an intervention in the area. This is the reason why many studies are seeking to apply physical and physicochemical techniques for removing contaminants, reducing the residual levels to safe and acceptable levels. Chemical oxidation, for example, aims to transform pollutants into water, carbon dioxide, and inorganic compounds or other less aggressive molecules through the mineralization process (Cheng et al., 2016a).

The use of the technique of advanced oxidative process, in particular the conventional Fenton, has the disadvantage of reducing soil pH, being preferred the adoption of the modified Fenton process, which can produce –OH at a near neutral pH (Cheng et al. al., 2016a). The ozonation process is suitable for the treatment of soils with large porous spaces and low moisture, and plasma oxidation is able to treat soils with pollutants at high concentrations. Electrochemically assisted technologies, such as electrokinetics, on the other hand, are limited to the application of an electric field between electrodes placed on the polluted soil, directly or indirectly contributing to the removal of soil contaminant (Lopez-Vizcaíno et al., 2017).

Thus, this study aimed to present and discuss the potentialities of using some physical and physicochemical techniques used to remediate soils contaminated with pesticides.

DEGRADATION OF CONTAMINANTS IN SOILS

Physicochemical processes

Advanced oxidative processes

Among the techniques for remediation of contaminated soils, the application of advanced oxidative processes (AOPs) presents a high potential and is the subject of several studies in the area, either as a pretreatment or as treatment. The purpose of this methodology is to degrade polluting compounds by mineralizing them into water molecules (H_2O), carbon dioxide (CO_2), and inorganic compounds or even inert components. Researches on AOPs in aqueous systems, soil and/or air are the focus of many studies, mainly because this technique is performed under ambient temperature and pressure (Cheng et al., 2016a).

Studies on advanced oxidation processes are still in the early stages. Most studies have been conducted on a laboratory scale and many improvements are needed before the technology can be extended to bank and pilot plant levels in terms of cost assessment and operating conditions (Morillo and Villaverde, 2017). AOPs have method versatility and the most frequently applied are the Fenton's reactions, photocatalysis, plasma oxidation, and ozonation. The use of these treatments in soils contaminated with pesticides is shown below.

Fenton processes

One of the best-known and most developed methods of advanced oxidative processes is the Fenton's reactions. These reactions are based on the oxidation of iron ions (Fe^{2+}) in a medium containing hydrogen (H_2O_2) to produce reactive hydroxyl radicals (•OH), which act by oxidizing organic pollutants in less aggressive products. In addition to H_2O_2, permanganate (MnO_4^-), persulfate ($S_2O_8^{2-}$), and ozone (O_3) can also be used in the reaction, but each oxidizing agent demonstrates some limits, such as concentration, reactivity, and persistence in the soil matrix (Vicente et al., 2012; Cao et al., 2013; Cheng et al., 2016b). Other catalysts, such as iron oxide (II) (FeO), iron oxide (III) (Fe_2O_3), and ferrous-ferric oxide (Fe_3O_4) have also been assessed and shown promising results.

Although it is considered an in situ (on-site) remediation of chemical oxidation because the chemical oxidizing agent is inserted on the surface of the contaminated soil, the use of the technique can also occur off-site (ex situ). This flexibility is one of the main advantages of the method, as well as being environmentally feasible, easy to handle (Cao et al., 2013), and applied under conditions of atmospheric pressure and ambient temperature (Cheng et al., 2016a). However, the main obstacle is an acid pH dependence ($pH < 4$) (Rosas et al., 2014), which makes it aggressive for microorganisms in the soil and may even alter its characteristics (Cheng et al., 2016a), hampering the cultivation of the vast majority of crops of agricultural interest.

Despite this applicability, soil remediation with Fenton's reagent is still little explored in the world, with the majority of studies being focused on aqueous media such as industrial effluents, groundwater, and wastewater (Rosas et al., 2014). Treatments using Fenton may be assisted by other oxidation systems. In the study of Cao et al. (2013), the Fenton process for soil remediation sought to degrade chlorinated pesticides, such as DDT (dichlorodiphenyldichloroethane) and DDE (dichlorodiphenyldichloroethylene), being investigated together with a zero valence iron (ZVI), EDTA (ethylenediaminetetraacetic acid), and air (ZVI/EDTA/Air). The highest pesticide removal occurred under conditions of 0.02 mM EDTA, 5 g L^{-1} ZVI, and the introduction of air at 1 L min^{-1}, at ambient temperature. The results demonstrated that the new Fenton-like ZVI/EDTA/Air system is efficient in soil remediation.

A similar system was used to remediate soil contaminated with 2,4-dichlorophenol (2,4-DCP). The removal was performed with the amino-ZVI/Air system, investigating the effects of EDTA and EDDS (ethylenediamine-N, N'-disuccinic). A 96% efficiency of in a 45 minute reaction was reached with the addition of 7.5 g L^{-1} ZVI, 0.4 mmol L^{-1} EDTA, and 1 L min^{-1} aeration, with EDDS inhibiting the degradation (Zhou et al., 2014).

Fenton process associated with steel slag converter degraded atrazine by 93.7% (Cheng et al., 2016b). This efficiency in removing atrazine from the soil was reached when the catalyst, which is the steel slag, was applied at a concentration of 80 g kg^{-1} and 10% H_2O_2 added every three hours. Because of this application, soil temperature reached 50 °C, the pH increased from 5.4 to 6.2, and the dissolved organic carbon increased from 0.339 to 1,206 g kg^{-1}.

Fenton's reaction with H_2O_2 as an oxidizing agent, trisodium citrate as a chelating agent, and Fe^{3+} as a catalyst reduced 80% of the diuron concentration in the soil (Vicente et al., 2012). This level of removal was reached after 50 hours of reaction at 20 °C, with the application of 600 mg kg^{-1} Fe (III), 3,000 mg kg^{-1} trisodium citrate, and 60,000 mg kg^{-1} hydrogen peroxide.

The versatility and efficiency of Fenton's reaction to the degradation of contaminants have stimulated the development of variations of this process, such as the processes of photo-Fenton, electro-Fenton, heterogeneous Fenton, among others. However, studies using these techniques for soil decontamination is still scarce.

Heterogeneous photocatalysis

Heterogeneous photocatalysis (HPC) is another branch of AOPs used in the degradation of contaminants. This technique uses transition metal oxides and sulfides, mainly titanate (TiO_2), zinc oxide (ZnO), zinc sulfide (ZnS), among others, as photosensitizers in photoinduced processes, as they have semi-filled valence band structures and empty conduction band (Castro et al., 2016). In addition, semiconductors through ultraviolet irradiation favor the displacement of electrons from the valence to the conduction band, originating hydroxyl radicals for deteriorating pollutant compounds (Santos et al., 2015a). However, recovering semiconductors to be reused is difficult and laborious. Another disadvantage of the heterogeneous photocatalysis is that its performance depends on the adsorption, morphology, surface, structure, particle size, among other characteristics of the used compound (Castro et al., 2016).

Xu et al. (2011) assessed the use of the $Fe_3O_4/SiO_2/TiO_2$ photocatalysis system in the decontamination of a soil polluted with glyphosate. The solid-gel method proved to be efficient when iron oxide particles acted as a colloid core for other catalysts. With two hours of treatment, 89% of the glyphosate was degraded with 0.5% $Fe_3O_4/SiO_2/TiO_2$, 30–50% soil water content, light intensity between 6 and 10 mW cm^{-2}. Under higher intensities, the reaction rate is higher. This efficiency was reached with photocatalyst doses of 0.4 g 100 g^{-1} of soil.

The effectiveness of this technique depends on "n" factors, being necessary to search for the most favorable conditions to remove the contaminant. Imidacloprid degradation, widely used in several crops for insect control, was assessed with the optimization of variables for photocatalytic mineralization in the study of Sharma et al. (2015). The experiments demonstrated that soil depth and light intensity affect positively, enhancing process efficiency, with the pH and concentration of imidacloprid being the most important variables. Degradations of 83% of this insecticide were reached with a light intensity of 30 W m^{-2} UV, soil depth of 0.2 cm, initial soil pH equal to 3.0, and imidacloprid concentration of 10 mg kg^{-1}.

Plasma oxidation and ozonation

Electrons with a high electric charge are generated with the plasma oxidation technique, providing energy and space for reactive molecules, such as oxygen, hydroxyl, ozone, and hydrogen peroxide, forming free radicals. The corona pulsed discharge and dielectric barrier discharge come from plasma oxidation at low temperatures (Wang et al., 2011; Aggelopoulos et al., 2015; Cheng et al., 2016a).

According to Cheng et al. (2016a), plasma oxidation and ozone can be applied to degrade various compounds, such as hydrocarbons, pesticides, among others. However, what limits the use of this method is the high energy required for producing the oxidizing compounds (Brillas et al., 2003). The dielectric barrier discharge plasma (DBDP) in a plane-to-grid reactor can be mentioned as an example of the application in soil remediation (Aggelopoulos et al., 2015). In this study, the authors assessed the mixture for the removal of non-miscible liquids (NML), being the model mixture consisting of n-C_{10}, n-C_{12}, and n-C_{16} those that showed good results (Aggelopoulos et al., 2015). These studies were carried out in small soil thicknesses, obtaining total removal of pollutants with a reaction time of 1–2 minutes, energy density of 6.0 kg soil kWh^{-1}, and applied a peak-to-peak voltage of 28 kV. Under these conditions, the pollutant is removed quickly and with a low energy consumption, which shows a promising and profitable future for soil decontamination with NML. Equivalent results were found in a metallic reactor developed by Aggelopoulos et al. (2015, 2016) also in a soil decontamination with NML.

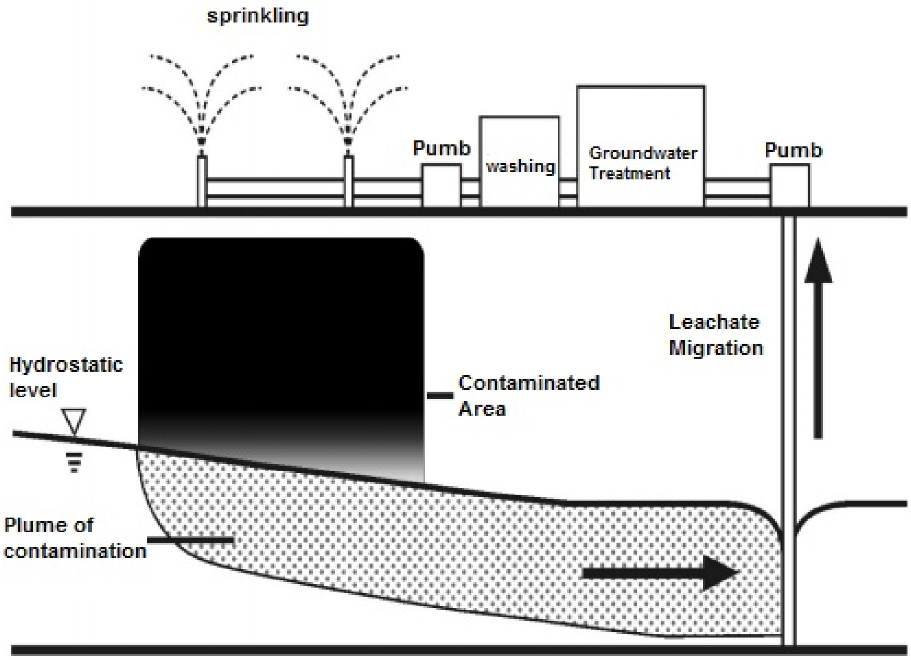
Plasma pulse discharge processes were applied to the degradation of pentachlorophenol (PCP) by Wang et al. (2013). The influence of high-energy electrons, initial concentration of PCP, oxygen concentration, and treatment time was analyzed and the results showed that the high energy of electrons interferes considerably with the process. With 1.9 x 10^{12} electrons per pulse, there was about 84% degradation of pollutant within 60 minutes of treatment. Furthermore, the degradation efficiency was negatively affected by the concentration of PCP and positively affected by time and oxygen (Wang et al., 2013). After the study, the authors carried out further investigations in order to understand the influence of gaseous ozone transport (Wang et al., 2014b) and soil depth (Wang et al., 2014c) on PCP degradation.

Wang et al. (2014a) found that the use of corona pulsed discharge plasma removed 86 and 94.1% of p-nitrophenol (PNP) and pentachlorophenol (PCP), respectively, from contaminated soils. The mixture of contaminants was treated under the conditions of discharge voltage of 18 kV, pulse frequency of 50 Hz, capacitance of 200 pF, and energy input per pulse of 0.018 J, with an initial concentration of pollutants of 600 mg kg^{-1} (50% of each pesticide). However, treatment efficiency decreases at higher concentrations, requiring more energy. By assessing the efficiency in the same treatment, but with different initial concentrations, the authors concluded that treatment efficiency decreases at higher concentrations, requiring more energy (Wang et al., 2014a).

However, the use of the dielectric barrier discharge plasma at atmospheric pressure by Wang et al. (2016) deteriorated approximately 94% of glyphosate present in the soil. This efficiency was obtained with a voltage of 18.0 kV, with an energy yield of 0.47 g kWh^{-1} during 45 minutes of the procedure. The total organic carbon (TOC), chemical oxygen demand (COD), PO_4^{3-}, and NO^{3-} confirmed the herbicide mineralization by DBDP.

Soil washing

Soil washing method uses physical or chemical techniques or even physical combined with chemical techniques to separate contaminants from soils and sediments, as in Figure 1. The initial contaminants are concentrated in a small volume of contaminated residues, being then recycled or discarded. This process can be used to treat numerous organic and inorganic contaminants and can be applied independently or in combination with other treatment technologies (Rosas et al., 2013). Soil washing is more appropriate for soils containing at least 50% sand and gravel (Morillo and Villaverde, 2017), given its higher permeability.



Source: Adapted of Fernandes et al. (2012).

Figure 1 - Soil remediation by washing.

Soil washing process for contaminant remediation, although effective, is widely used with surfactant solutions. Therefore, it cannot be considered as a finalistic technology since the pollutant is transported to a washing solution, thus generating the need for treatment of this aqueous residue. These solutions to be treated are a challenge because of the high concentration and diversity of pollutants they have. In addition, when these solutions contain a high xenobiotic load, conventional biological treatment becomes inefficient (Santos et al., 2015a).

Many technologies of combinations to the soil washing process have been studied in order to improve and reduce operating costs. Rosas et al. (2013) analyzed the effect of Fenton oxidation in the soil after washing the medium using a low oxidant concentration in the removal of p-cresol. These authors concluded that, in addition to being an adequate method for this treatment, Fenton oxidation can be used to treat the liquid residue generated after soil washing, being able to recover the solution of surfactant for use in a subsequent treatment, which reduces treatment costs.

The efficiency of the combination of soil washing and electrolysis with diamond electrodes to remove atrazine using sodium dodecyl sulfate (Santos et al., 2015b) as a surfactant can be cited. In this study, there was the total mineralization of the pesticide, obtained with a ratio of 0.5 g of surfactant kg^{-1} of soil and current of 30 mA cm^{-2} (Santos et al., 2015b). Another case also studied was the viability of β-methyl cyclodextrin (MCD) and sunflower oil solution to wash soils contaminated with organochlorine pesticides (OCP) (Ye et al., 2014). This method proved to be effective and environmentally feasible by combining ultrasound (35 kHz, 30 minutes) with 25 g L^{-1} MCD and 100 mL L^{-1} sunflower oil.

Chemical extraction – solvent extraction

The supercritical fluid extraction (SFE) can be applied to different contaminants present in the soil, such as pesticides, phenols, hydrocarbons, among others. This method is modern and has a high solvency and recovery capacity, being composed of a principal solvent agent, for instance, the methanol, often used as an aid to carbon dioxide (CO_2). The CO_2 passes through the contaminated soil, causing the toxic compound to solubilize and be collected for a proper disposal (Baig et al., 2011; Ferero-Mendieta et al., 2012; Bielská et al., 2013). Solvent extraction can be used to recover a wide variety of substances due to the high solvency power established by the method (Baig et al., 2011), applying it at slow soil desorption sites (Bielská et al. 2013).

The removal of pollutants by this technique is dependent on the type of extraction and soil properties (pH, moisture, organic matter content). Extractions involving carbon dioxide can be carried out under low temperatures and do not require a high-energy load, favoring the maintenance of soil characteristics, such as structures and nutrients (Baig et al., 2011; Ferero-Mendieta et al., 2012).

The selective extraction of several organic compounds using CO_2 as extraction fluid was analyzed (Bielská et al., 2013). The tests were carried out on three types of natural and artificial soils. After 56 days of testing, a decrease in the extraction was observed due to the formation of a recalcitrant fraction in the soil. The reduction of pollutant removal also occurred when the level of total organic matter and other soil properties in the analyzed soils was higher.

An alternative studied by Forero-Mendieta et al. (2012) for the removal of pesticides was the use of methanol (MeOH) as a co-solvent with CO_2. The study confirmed that the extraction system with the solvents SC-CO_2/MeOH is applicable to remove 31 pesticides, such as iprodione, tetradifon, cypermethrin, acephate, diazinon, metalaxyl, among others, with 15 MPa, 318 K, and 4 phases of 10 min in static mode, with an efficiency above 70%. In addition, the organic matter content did not adversely affect the efficiency of this technique.

The SFE can be coupled with the dispersive liquid-liquid microextraction (DLLM) for determining seven organophosphorus pesticides (o,o,o-triethyl phosphorothioate, thionazin, sulfotepp, disulfoton, methyl parathion, parathion, and famphur) in soil and sediments (Naeeni et al., 2011). Pesticide removals between 44.4 and 95.4% were reached with the supercritical CO_2 under the conditions of 150 bar, 60 ^{o}C, 10 minutes of static extraction, and 30 minutes of dynamic extraction. SFE-DLLM was proved to be appropriate for removing the mentioned compounds, with a good recovery both in the soil and in marine sediments.

A technique derived from solvent extraction was used by Chitescu et al. (2012) in the recovery and detection of various pharmaceutical products for animal use and fungicides in soil samples. Ultrasound extraction in the system had more than 70% removal in 68% of the studied compounds from soil samples using acetone/0.2 M citric acid (50:50).

The remediation of soil contaminated with DDT is investigated by several decontamination methodologies. Soil washing can also be one of the used methods, with the removal of up to 94% after five washing cycles, according to studies by Ye et al. (2013). The extraction was obtained with 100 mL L^{-1} petroleum ether (60-90 °C), washing time of 180 minutes at 50 °C, mixing speed of 100 RPM, and soil solution ratio of 10:1. A high removal efficiency of four chlorobenzenes was reached with ultrasound-assisted water extraction (UAWE) and solvent bar microextraction (SBME) from 1.0 g of sediment and 10 mL of ultrapure water at 100 W for 30 minutes at 30-35 °C (Wang et al., 2012).

Electrokinetics

This technique is also called electrokinetic soil processing or electromigration or, even, electrocorrection. This methodology consists of the application of a continuous and low-intensity current between electrodes in the soil. Electrodes should consist of an inert material such as graphite or platinum. When an electric current is applied, water electrolysis occurs, making the solution acid close to the anode. The acid front of the anode moves to the cathode by migration, which leads to desorption of soil contaminants (Gomes et al., 2012). This technique allows directing the movement of pollutants and concentrate them in a small area (Gomes et al., 2012; Bocos et al., 2015), but an energy consumption of 10–15% of the total cost is the main difficulty imposed for its application (Souza et al., 2016b).

The efficiency of this technique in degrading metals and organic pollutants (phenol, atrazine, DDT, BTEX) depends on the involved contaminants, the used method, and soil properties, such as pH, buffering capacity, permeability, adsorption capacity, among others, as well as pesticide characteristics (Ma et al., 2010; Santos et al., 2016).

Among the various soil decontamination methods, electrokinetic remediation is considered a tool of least disturbance in the environment and economically feasible. Therefore, it is an in situ treatment technique, especially in permeable subsoils. In electrokinetics, two types of processes may occur: electromigration and electro-osmosis. The charged ions are removed by electromigration to the anode, while non-polar contaminants are removed by electro-osmosis to the cathode (Ma et al., 2010; Li et al., 2011; Bocos et al., 2015; Santos et al., 2016). This technology is particularly useful for fine granulometry soils with a low hydraulic conductivity and large specific surface areas, being able to treat fine and low permeability materials (Morillo and Villaverde, 2017).

The removal of molinate and bentazon from the soil using electrokinetics was studied by Ribeiro et al. (2011). Both the pesticides were moved by electrokinetics: the molinate presented as main removal path the catholyte, while the bentazon moved to both electrodes. Higher intensities of current exerted on the medium direct the movements of transport and degradation of the bentazon to the anode due to the occurrence of electromigration.

For some compounds, such as pentachlorophenol (PCP), electrokinetics is not efficient in removing this compound from the soil and requires extra elements. Electrokinetics, along with the permeable reactive barrier (PRB), transports the contaminants to destruction. The installation of a PRB containing lead and iron particles, for instance, between the anode and the cathode for pollutant degradation increases the recovery efficiency of PCP, both as the compound itself and as phenol, maintaining the pH lower than 10.0 (Li et al., 2011).

Some pilot studies were developed to assess electrokinetics as a means of remediation of soils contaminated with pesticides, such as those assessed by Santos et al. (2016) and Risco et al. (2016a,b). The use of electrodes surrounding the contaminated area is an alternative of remediation of 2,4-dichlorophenoxyacetic acid (2,4-D), as reported for a simulated leak of this pesticide. This treatment reduced the concentration of 2,4-D by 80% in 60 days (from 20 to 4.1 mg kg^{-1}), with an electrode configuration in the form of a hexagon (Risco et al., 2015).

The influence of electrode configuration on 2,4-D degradation in the soil was assessed in pilot studies (Risco et al., 2016a, b). For this, parallel lines with opposite electrodes, i.e. anodes on one side and cathodes on the other side, were used and removed more than 52% of the pollutant by electrokinetic and hydraulic flows for 40 days (Risco et al., 2016a). In a subsequent study, electrode configuration of soil treatment with electrokinetics was altered to improve oxyfluorfen removal (Risco et al., 2016b). The formulation with one anode and six cathodes (1A6C) was more efficient than one cathode and six anodes (1C6A), with an oxyfluorfen degradation rate of 41.3 and 27.0%, respectively, after 35 days. In both conformations, there was oxyfluorfen removal and aid in soil pH control since this technique acidifies or alkalinizes the soil in areas near the electrodes. Santos et al. (2016) did not use the same electrode conformation and obtained about 80% removal of oxyfluorfen and atrazine. In addition, sodium dodecyl sulfate, a solubilizer that aided in the electro-osmotic flow of molecules to the collection wells of the liquid, was added.

The comparison of efficiency between a conventional electric system and a wind system in the 2,4-D removal was assessed by Souza et al. (2016a), using the electrokinetic technique. After 15 days of testing, the conventional energy source was more efficient than the renewable energy source with the removal of 90.2 and 53.3%, respectively, of 2,4-D from the soil. On the other hand, solar-powered electrodes removed 73.6% of 2,4-D from the soil. The variable power supply of the wind turbine and photovoltaic panel and a higher electric charge justify the lower efficiency of the wind energy to remove the pesticide from the soil (Souza et al., 2016b).

Analysis of techniques and possibilities of applications

Table 1 shows some studies that include the combination of techniques for the degradation of pesticides, in addition to the used conditions and the best results pointed out by the authors for contaminant removal. Table 2 shows some advantages and disadvantages of remediation techniques of soils contaminated with pesticides, being these techniques presented in isolation or combined with others.

Although isolated remediation techniques presented significant results of pesticide removal from the soil, the combination of techniques also demonstrated a considerable removal efficiency when analyzing the combination of techniques and its advantages and disadvantages. In this sense, the association of electrokinetic processes and soil washing present good results when applied to the degradation of agricultural contaminants. In addition, the combination of electrolysis with other methods, such as Fenton's reagent, ultrasound irradiation, and UV light, also show efficiency for removing pesticides in soil treatment due to contaminant oxidation.

Moreover, the remediation of soils contaminated with pesticides by advanced oxidative processes, especially soil remediation by the Fenton technique, is the most advantageous among the studied techniques. This assertion is justified once the Fenton technique can be used to degrade a wide range of contaminants, including almost all types of organic contaminants, and applied both at the area of contamination and out of it. In addition, this technique is considered environmentally adequate, has a shorter treatment time than other techniques, its production of hazardous sludge is minimal, and the generated byproducts are harmless or biodegradable, in addition to presenting a low operation cost and easy implementation.

Final considerations

Therefore, the ideal is the development of technologies that remove the pollutant from the soil, allowing its recovery. Soil washing and electrochemically assisted processes are considered promising technologies when applied together. The former is used for the recovery and restoration of ecosystems of the contaminated soil and the latter is used for the treatment of soils contaminated with pesticides, as well as remediate different types of pollutants. However, the Fenton technology used in isolation is the most promising among all those assessed since it is not necessary to use a large quantity of oxidizing agent and the time in the remediation process is only a few hours, which is considered a rapid treatment. In addition, it can be used for

Table 1 **-** Combination of techniques for removing pesticides from soil

Method	Pollutant	Condition	Better removal results (%)	Reference
Pb/Fe nanoparticles stabilized in carboxymethylcellulose and electrokinetics	Pentachlorophenol	Anolyte and catholyte: 0.025 M Na_2SO_4 and 0.025 Na_2CO_3, pH 8.0; Center: nano-CMC stabilized Pb/Fe, pH 5–6; 14 days	70%	Yuan et al. (2012)
Electrokinetics-Fenton and hydrogen peroxide	Pyrimethanil	H_2O_2 (10% w/v), 0.1M $NaSO_4$, 3 V/cm, 27 days, 0.2M citric acid to maintain the pH at 5.0	59%	Bocos et al. (2015)
Electrokinetics and bamboo activated carbon	2,4-dichlorophenol	10.5 days; inversion of polarity at 24 h intervals; electrodes: 0.01M KNO_3; 1.0 V/cm	76%	Ma et al. (2010)
Nanoscale of zero valence iron (nZVI)	DDT	Use of two types of Fe (type B, produced using borohydride precipitation, and type T, produced by reduction of the gaseous phase of iron oxides into H_2)	Soil paste – nZVI-B (22.4%); nZVI-T (9.2%)/ Soil column – nZVI-B (25.4%)/ nZVI-T (not significant)	El-Temsah, et al. (2016)
Hytrel polymer adsorption and polymer regeneration solvent extraction (methanol)	4-chlorophenol (4CP) and pentachlorophenol (PCP)	5% w/w Hytrel polymer (polymer/soil ratio), 25 ºC and 24 hours. 4CP with 500 rpm PCP with 320 rpm	97% (4CP) and 80% (PCP)	Angelucci and Tomei (2015)
Non-thermal pulsed discharge plasma and TiO_2 photocatalysis	p-nitrophenol	Pulse frequency of 100 Hz; capacitance of 200 pF; energy input of 0.023 J; impulse voltage of 20 kV; 10% moisture; air injection of 0.5 L min^{-1}; 2% TiO_2 by weight of soil; 10 min reaction	88.8%	Wang et al. (2011)
Electrokinetics-nZVI	Molinate		97.5%	Gomes et al. (2014)
Photocatalysis – biological treatment	Chlorothalonil	pH 7.0; 30 ºC; CDS-8 bacteria (*Pseudomonas* sp.); disturbed soil; 20 mg kg^{-1} TiO_2	97.55%	Wu et al. (2016)
Soil washing with tetrapolyphosphate and zero valence iron ZVI/Air	Pentachlorophenol	2 mmol/L tetrapolyphosphate and 48 h; pH 11; 5 g/L ZVI, air flow at a rate of 1.5 L min^{-1}; 25 ºC; 180 min	85.1%	Cao et al. (2015)
Soil washing with co-doped La-B and photocatalysis with TiO_2 nanoparticles	Hydrophobic pentachlorophenol			Li et al. (2011)

Table 2 **-** Advantages and disadvantages of remediation techniques of soils contaminated with agrochemicals

Technique	Advantage	Disadvantage
Fenton[2]	- Do not transfer pollutants from one phase to another (as in chemical precipitation and adsorption); - Do not produce massive quantities of hazardous sludge; - Easy to implement; - Able to degrade a wide range of contaminants (including agrochemicals) - By-products are generally harmless or biodegradable; - Iron is highly abundant and non-toxic; - Treatment time shorter than other techniques; - Insensitive to external disturbances, e.g. contaminant load; - Heat released from reactions improves the mass transfer, reaction rate, and microbial activity.	- Reduction of soil pH; - A large amount of oxidant is required for soil with a high organic matter content or additional substances; - Harmless organic materials in soils can also be oxidized throughout the oxidation; - The oxidizing agent must be introduced near the contaminated areas; - Immobilization of inorganic reactive species on the treatment wall.
Heterogeneous photocatalysis using TiO_2[2]	- Safety; - High photocatalytic activity; - Low cost.	- Only occurs on the soil surface; - Removal efficiency decreases as the soil layer becomes thicker; - Lack of visible light activity; - The use of a UV lamp can be expensive due to the limited lamp life.
Plasma oxidation[2]	- Able to remove almost completely the pollutants from the soils in minutes; - It is possible to treat soils with pollutants of high concentration.	- Some active species of short duration would disappear before entering the soil layer and participate in the degradation of pollutants; - High energy densities are required to treat a heavily polluted soil.
Ozonation[2]	- Rapid treatment time; - High degradation efficiency.	- Suitable only for the treatment of soils with a low moisture content.
Soil washing[3]		- Contaminants are not destroyed and an additional treatment is required to remove the target compounds from wastewater.
Soil washing combined with photo-Fenton[3]	- Efficiently removes several contaminants from soil.	
Electrokinetics[1]	- Strict control over the direction of water movement and dissolved contaminants; - Retention of contaminants within a confined area; - Low energy consumption; - Possibility of treating soils of low permeability, inaccessible to other remediation techniques.	
Electrokinetics combined with surfactants[1]	- Decrease the surface tension of the liquid; - Improve contaminant solubility.	- The consumption of surfactants depends on their type and other environmental factors.
Electrokinetics combined with cyclodextrins[1]	- Chemical stability and reliable electro-osmotic flow.	- The inclusion compounds between complexing agents and organochlorines may be less soluble.
Electrokinetics combined with soil pH control[1]	- Maintain the pH of the anolyte and catholyte within appropriate intervals.	- Depending on the method used to control the pH, the addition of some acids may represent environmental problems.
Electrokinetics combined with Fenton[4]	- Low concentrations of iron in the solution; - Easy recycling of the iron catalyst; - Self-regulating capacity of iron ion concentration.	- pH scale typically sharp and preferable (i.e. 3–5 in most cases).
Electrokinetics combined with permanganate oxidant[4]	- High oxidation potential; - Great stability; - Strong ability to oxidize a variety of organic chemicals; - Efficacy over a wide range of pH; - Easy to distribute and detect its color.	- Production of Mn^{2+}, which may result in the formation of precipitated MnO_2.
Electrokinetics combined with ozone[4]	- Generation of water-soluble products; - Better bioavailability.	- Great harm to human health if leaks occur.

[1] Gomes et al. (2012); [2] Cheng et al. (2016a); [3] Villa et al. (2010); and [4] Ren et al. (2014).

remediating several contaminants, especially pesticides, not harming the environment and allowing soil recovery.

REFERENCES

Aggelopoulos CA, Svarnas P, Klapa MI, Tsakiroglou CD. Dielectric barrier discharge plasma used as a means for the remediation of soils contaminated by non-aqueous phase liquids. Chem Eng J. 2015;270:428-36.

Aggelopoulos CA. et al. Parametric analysis of the operation of a non-thermal plasma reactor for the remediation of NAPL-polluted soils. Chem Eng J. 2016;301:353-61.

Angelucci DM, Tomei MC. Regeneration strategies of polymers employed in ex-situ remediation of contaminated soil: Bioregeneration versus solvent extraction. J Environ Manag. 2015;159:169-77.

Araujo IMM, Oliveira AGRC. Agronegócio e agrotóxicos: impactos à saúde dos trabalhadores agrícolas no nordeste brasileiro. Trab Educ Saúde. 2017;15:117-29.

Baig MN, Leeke GA, Hammond PJ, Santos RCD. Modelling the extraction of soil contaminants with supercritical carbon dioxide. Environ Pollut. 2011;159(7):1802-9.

Bielská L, Smídová K, Hofman J. Supercritical fluid extraction of persistent organic pollutants from natural and artificial soils and comparison with bioaccumulation in earthworms. Environ Pollut. 2013;176:48-54.

Bocos E et al. Removal of PAHs and pesticides from polluted soils by enhanced electrokinetic-Fenton treatment. Chemosphere, 2015;125:168-74.

Brillas E, Calpe JC, Cabot PL. Degradation of the herbicide 2,4-dichlorophenoxyacetic acid by ozonation catalyzed with Fe^{2+} and UVA light. Appl Catal B-Environ. 2003;46:381-91.

Cao M, Wang L, Ai Z, Zhang L Efficient remediation of pentachlorophenol contaminated soil with tetrapolyphosphate washing and subsequent ZVI/Air treatment. J Hazard Mater. 2015;292:27-33.

Cao M, Wang L, Wang L, Chen J, Lu X. Remediation of DDTs contaminated soil in a novel Fenton-like system with zero-valent iron. Chemosphere. 2013;90(8):2303-8.

Castro DC, Cavalcante RP, Jorge J, Martines MAU, Oliveira LCS, Casagrande GA, et al. Synthesis and characterization of Mesoporous $Nb_2O_5$and Its application for photocatalytic degradation of the herbicide methylviologen. J Brazil Chem Soc. 2016;27:1-11.

Cheng M, Cheng M, Zeng G, Huang D, Lai C, Xu P, et al.Degradation of atrazine by a novel Fenton-like process and assessment the influence on the treated soil. J Hazard Mater. 2016b;312:184-91.

Cheng M, Zeng G, Huang D, Lai C, Xu P, Zhang C, et al. Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review. Chem Eng J. 2016a;284:582-98.

Chitescu CL, Oosterink E, Jong J, Stolker AAM. Ultrasonic or accelerated solvent extraction followed by U-HPLC-high mass accuracy MS for screening of pharmaceuticals and fungicides in soil and plant samples. Talanta. 2012;88:653-62.

Duarte JS, Dores EFGC, Villa RD. Microextração líquido-líquido dispersiva assistida por vortex e ultrassom aplicada à determinação de agrotóxicos triazinas, triazinonas e o triazol flutriafol em água. Quim Nova. 2016;39:1-7.

Ferero-Mendieta JR. et al. Extraction of pesticides from soil using supercritical carbon dioxide added with methanol as co-solvent. J Supercrit Fluids. 2012;68:64-70.

Fernandes FRC, Bertolino LC, coordenadores. Projeto Santo Amaro –BA: aglutinando ideias, construindo soluções–diagnósticos. 2ª.ed. Rio de Janeiro: CETEM/MCTI; 2012. 252p.

Gama AF, Oliveira AHB, Cavalcante RM. Inventário de agrotóxicos e risco de contaminação química de recursos hídricos no semiárido Cearense. Quim Nova. 2013;36:462-7.

Gomes HI, Fan G, Mateus EP, Dias-Ferreira C, Ribeiro AB. Assessment of combined electro–nanoremediation of molinate contaminated soil. Sci Total Environ. 2014;493:178-84.

Gomes HI, Ferreira CD, Ribeiro AB. Electrokinetic remediation of organochlorines in soil: Enhancement techniques and integration with other remediation technologies. Chemosphere. 2012;87(10):1077-90.

Li Z, Yuan S, Wan J, Long H, Tong M. A combination of electrokinetics and Pd/Fe PRB for the remediation of pentachlorophenol-contaminated soil. J Contam HydroL. 2011;2(1-4):99-107.

Lopez-Vizcaíno R, Risco C, Isidro J, Rodrigo S, Saez C, Cañizares P, et al. Scale-up of the electrokinetic fence technology for the removal of pesticides. Part II: Does size matter for removal of herbicides? Chemosphere. 2017;166:549-55.

Ma JW, Wang FY, Huang ZH, Wang H. Simultaneous removal of 2,4-dichlorophenol and Cd from soils by electrokinetic remediation combined with activated bamboo charcoal. J Hazard Mater. 2010;176(1-3):715-20.

Morillo E, Villaverde J. Advanced technologies for the remediation of pesticide-contaminated soils. J Sci Total Environ. 2017;586:576-79.

Naeeni MH, Yamini Y, Rezaee M. Combination of supercritical fluid extraction with dispersive liquid-liquid microextraction for extraction of organophosphorus pesticides from soil and marine sediment samples. J Supercrit Fluids. 2011;57(3):219-26.

Piccoli C, Cremonese C, Koifman RJ, Koifman S, Freire C. Pesticide exposure and thyroid function in an agricultural population in Brazil. Environ Res. 2016;151:389-98.

Ren L, Lu H, He L, Zhang Y. Enhanced electrokinetic technologies with oxidization–reduction for organically-contaminated soil remediation. Chem Eng J. 2014;247:111-24.

Ribeiro AB, Mateus EP, Rodríguez-Maroto JM. Removal of organic contaminants from soils by an electrokinetic process: The case of molinate and bentazone. Experimental and modeling. Sep Purif Technol. 2011;79(2):193-203.

Risco C, López-Vizcaíno R, Sáez C, Yustres A, Cañizares P, Navarro V, et al. Remediation of soils polluted with 2,4-D by electrokinetic soil flushing with facing rows of electrodes: A case study in a pilot plant. Chem Eng J. 2016a;285:128-36.

Risco C, Rodrigo S, López-Vizcaíno R, Yustres A, Sáez C, Cañizares P, et al. Electrochemically assisted fences for the electroremediation of soils polluted with 2,4-D: A case study in a pilot plant. Sep Purif Technol. 2015;156(Part 2):234-41.

Risco C, Rubí-Juárez H, Rodrigo S, López-Vizcaíno R, Saez C, Cañizares P, et al. Removal of oxyfluorfen from spiked soils using electrokinetic soil flushing with the surrounding arrangements of electrodes. Sci Total Environ. 2016b;559:94-102.

Rosas JM, Vicente F, Saguillo EG, Santos A, Romero A. Remediation of soil polluted with herbicides by Fenton-like reaction: Kinetic model of diuron degradation. Appl Catal B-Environ. 2014;144:252-60.

Rosas JM, Vicente F, Santos A, Romero A. Soil remediation using soil washing followed by Fenton oxidation. Chem Eng J. 2013;220:125-32.

Santos EV, Sáez C, Martínez-Huitle CA, Cañizares P, Rodrigo MA. The role of particle size on the conductive diamond electrochemical oxidation of soil-washing effluent polluted with atrazine. Electrochem Comm. 2015b;55:26-9.

Santos EV, Souza F, Saez C, Cañizares P, Lanza MR, Martinez-Huitle CA, et al. Application of electrokinetic soil flushing to four herbicides: A comparison. Chemosphere. 2016;153:205-11.

Santos LM, Amorim KP, Andrade LS, Batista OS, Trovó AG, Machado AEH. Dye degradation enhanced by coupling electrochemical process and heterogeneous photocatalysis. J Brazil Chem Soc. 2015a;26(9):1-7.

Sharma T, Toor AP, Rajor A. Photocatalytic degradation of imidacloprid in soil: application of response surface methodology for optimization of parameters. RSC Adv. 2015;5:25059-65.

Souza FL, Llanos J, Sáez C, Lanza MR, Rodrigo MA, Cañizares P. Performance of wind-powered soil electroremediation process for the removal of 2,4-D from soil. J Environ Manage. 2016a;171:128-32.

Souza FL, Saéz C, Llanos J, Lanza MRV, Cañizares P, Rodrigo MA. Solar-powered electrokinetic remediation for the treatment of soil polluted with the herbicide 2,4-D. Electrochim Acta. 2016b;190:371-7.

Steffen GPK, Steffen RB, Antoniolli ZI. Contaminação do solo e da água pelo uso de agrotóxicos. Tecno-Lógica. 2011;15:15-21.

Vicente F, Santos A, Sagüill EG, Martínez-Villacorta AM, Rosas JM, Romero A. Diuron abatement in contaminated soil using Fenton-like process. Chem Eng J. 2012;183:357-64.

Villa RD, Trovó AG, Nogueira RFP. Soil remediation using a coupled process: soil washing with surfactant followed by photo-Fenton oxidation. J Hazard Mater. 2010;174(1-2):770-5.

Wang L, Wang L, Chen J, Du W, Fan G, Lu X. Ultrasonic-assisted water extraction and solvent bar microextraction followed by gas chromatography–ion trap mass spectrometry for determination of chlorobenzenes in soil samples. J Chromatogr A. 2012;1256:9-14.

Wang TC, Lu N, Li J, Wu Y. Plasma-TiO_2 catalytic method for high-efficiency remediation of p-nitrophenol contaminated soil in pulsed discharge. Environ Sci Technol. 2011;45(21):9301-7.

Wang TC, Qu G, Li J, Liang D. Remediation of p-nitrophenol and pentachlorophenol mixtures contaminated soil using pulsed corona discharge plasma. Sep Purif Technol. 2014a;122:17-23.

Wang TC, Qu G, Li J, Lu N. Transport characteristics of gas phase ozone in soil during soil remediation by pulsed discharge plasma. Vacuum. 2014b;101:86-91.

Wang TC, Ren J, Qu G, Liang D, Hu S. Glyphosate contaminated soil remediation by atmospheric pressure dielectric barrier discharge plasma and its residual toxicity evaluation. J Hazard Mater. 2016;320:539-46.

Wang TC. et al. Evaluation and optimization of multi-channel pulsed discharge plasma system for soil remediation. Vacuum. 2014c;103:72-7.

Wang TC. Qu G, Li J, Lu N. Kinetics studies on pentachlorophenol degradation in soil during pulsed discharge plasma process. J Electrostat. 2013;71(6):994-8.

Wu M, Deng J, Li J, Li Y, Li J, Xu H. Simultaneous biological-photocatalytic treatment with strain CDS-8 and TiO_2 for chlorothalonil removal from liquid and soil. J Hazard Mater. 2016;320:612-9.

Xu X. Ji F, Fan Z, He L. Degradation of glyphosate in soil photocatalyzed by fe3o4/sio2/tio2 under solar light. Int J Environ Res Public Health. 2011;8(4):1258-70.

Ye M, Sun M, Hu F, Kengara FO, Jiang X, Luo Y, et al.. Remediation of organochlorine pesticides (OCPs) contaminated site by successive methyl-]”-cyclodextrin (MCD) and sunflower oil enhanced soil washing - Portulaca oleracea L. cultivation. Chemosphere. 2014;105:119-25.

Ye M, Yang X-L, Sun M-M, Bian Y-R, Wang F, Gu C-G. et al. Use of organic solvents to extract organochlorine pesticides (ocps) from aged contaminated soils. Pedosphere. 2013;23:10-19.

Yuan S, Long H, Xie W, Liao P, Tong M. Electrokinetic transport of CMC-stabilized Pd/Fe nanoparticles for the remediation of PCP-contaminated soil. Geoderma. 2012;185-186:18-25.

Zhou H, Sun Q, Wang X, Wang L, Chen J, Zhang J, et al. Removal of 2,4-dichlorophenol from contaminated soil by a heterogeneous ZVI/EDTA/Air Fenton-like system. Sep Purif Technol. 2014;132:346-53.