



DEGRADATION OF DDT, ENDRIN, AND ENDOSULFAN IN POLLUTED-SOILS BY ZERO-VALENT IRON (Fe^0) AND ZERO-VALENT IRON-COPPER ($\text{Fe}^0\text{-Cu}^0$) TREATMENTS

DEGRADACIÓN DE DDT, ENDRINA, Y ENDOSULFAN EN SUELOS CONTAMINADOS MEDIANTE TRATAMIENTOS CON HIERRO CERO VALENTE (Fe^0) Y HIERRO-COBRE CERO VALENTE ($\text{Fe}^0\text{-Cu}^0$)

I. Ortíz^{1*}, A. Velasco²

¹*Departamento de Procesos y Tecnología. Universidad Autónoma Metropolitana-Cuajimalpa (UAM-C), Av. Vasco de Quiroga 4871, Col. Santa Fe, Delegación Cuajimalpa de Morelos, 05348, Mexico City, Mexico.*

²*Posgrado en Ciencias Naturales e Ingeniería. Universidad Autónoma Metropolitana-Cuajimalpa (UAM-C), Av. Vasco de Quiroga 4871, Col. Santa Fe, Delegación Cuajimalpa de Morelos, 05348, Mexico City, Mexico.*

Received: August 31, 2018; Accepted: November 13, 2018

Abstract

The remediation of polluted soils containing DDX (DDT, DDE, and DDD), endrin, and endosulfan was assessed using zero-valent iron (Fe^0) and iron-copper Fe^0/Cu^0 at microcosms and bench-scale batch experiments. The treatments allowed for the reduction of the initial concentrations of DDX (30 mg/kg), endrin (150 mg/kg), and endosulfan (40 mg/kg) at both scales, indicating their suitability. However, in the case of DDX-polluted soil, the accumulation of the intermediate compound DDNS was registered. In microcosms experiments, the highest degradation percentage for DDX was obtained using a Fe^0/Cu^0 ratio of 10/3 (w/w). The degradation observed in the bench-scale reactor was improved for endrin and endosulfan-polluted soils, while degradation of DDX was similar to that found in microcosms experiments. The Fe^0/Cu^0 system mainly improves the degradation rates of DDD, DDE, and endrin, reducing the time of treatment from 8 to 4 days. The selection of the remediation strategies using Fe^0/Cu^0 or Fe^0 should weigh the cost of copper versus the time of treatment since the extent of remediation was similar for most experiments, except for DDD and DDE. Since the degradation of pesticides was not fully completed and the accumulation of intermediates compounds was observed, further investigation is required.

Keywords: galvanic corrosion; organochlorine pesticides; zero-valent iron; polluted soil; reducing dehalogenation.

Resumen

Se evaluó la remediación de suelos contaminados con DDX (DDT, DDE y DDD), endrina y endosulfan utilizando hierro cero valente (Fe^0) y acople galvánico Fe^0/Cu^0 en experimentos por lote a escala microcosmos y laboratorio. Los tratamientos permitieron la disminución de las concentraciones iniciales de DDX (30 mg/kg), endrina (150 mg/kg) y endosulfan (40 mg/kg) en ambas escalas, lo que indica su efectividad. Sin embargo, en el caso del suelo contaminado con DDX, se registró la acumulación del intermediario DDNS. En microcosmos, el mayor porcentaje de degradación de DDX se obtuvo a una relación Fe^0/Cu^0 de 10/3. A escala laboratorio, se registró una mayor degradación en los suelos contaminados con endrina y endosulfan, mientras que la degradación de DDX fue similar a la obtenida en microcosmos. El sistema Fe^0/Cu^0 favoreció principalmente las tasas de degradación de DDD, DDE y endrina, reduciendo el tiempo de tratamiento de 8 a 4 días. En la selección del uso del Fe^0/Cu^0 o Fe^0 debe ponderarse el costo del cobre versus el tiempo del tratamiento, dado que la eficiencia de remediación fue similar para la mayoría de los experimentos, excepto para DDD y DDE. Se requiere mayor investigación respecto a la acumulación de compuestos intermediarios.

Palabras clave: corrosión galvánica, plaguicidas organoclorados, hierro cero valente, suelo contaminado, deshalogenación reductiva.

* Corresponding author. E-mail: irmene@correo.cua.uam.mx
<https://doi.org/10.24275/uam/izt/dcbi/revmexingquim/2019v18n3/Ortiz>
issn-e: 2395-8472

1 Introduction

The Stockholm Convention on Persistent Organic Pollutants (POP), which was adopted in 2001 and went into effect in 2004, requires its parties to take measures to eliminate or reduce the release of these compounds into the environment (UNEP 2011). Organochlorine pesticides such as DDT and endrin were included in the initial 12 compounds regulated by the Stockholm Convention, and more recently, in 2011, endosulfan was also included (UNEP 2011). Despite the actions to protect the environment from these pollutants, they are frequently present in agricultural and industrial soil and sediments worldwide (Weber *et al.* 2010; Velasco *et al.* 2014; Bussian *et al.* 2015). This has been attributed to the production, storage, distribution, and use of these compounds in past decades since they are highly persistent in the soil, e.g. DDT has a half-life of 2-15 years (ATSDR 2002).

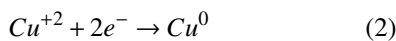
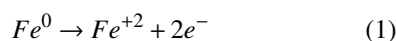
Diverse remediation strategies that include thermal, physicochemical and biological have been developed to treat water, sediment and soil contaminated with organochlorine compounds around the world (McDowall *et al.* 2004). The physicochemical treatment with Fe⁰ has been used mainly in the treatment of organochlorine compounds, such as carbon tetrachloride, trichloroethane, trichloroethylene, tetrachloroethylene, the isomers of hexachlorocyclohexane (α , β , γ and δ) chlorpyrifos, and DDT, in water, sediments and scarcely in soil (Satapanajaru *et al.* 2005; Boparai *et al.* 2008; Cao *et al.* 2010; Ghazali *et al.* 2010; Yang *et al.* 2010). In these systems, the organochlorine pesticides degradation is based on the reductive dehalogenation of contaminants attached to the iron corrosion by the oxidation of the metallic iron to divalent or trivalent iron (Ghazali *et al.* 2010). The increasing interest in the use of Fe⁰ treatments is due to their simplicity and effectiveness (Marican and Durán-Lara 2018). Furthermore, this treatment is cheaper than other physicochemical processes, since the metallic iron can be obtained as a low-cost byproduct (Satapanajaru *et al.* 2005).

Remediation technologies using micro and nanoparticles of Fe⁰ have been reported in the last decades (Han *et al.* 2016). Although nanoparticle size promotes rapid electron transference to contaminants due to its large surface area and high reactivity, its application represents potential adverse effects towards indigenous microbial communities shifts the

taxonomic composition (Lefevre *et al.* 2016).

On the other hand, the galvanic corrosion has been used to improve reductive dehalogenation process. Some studies have shown that the bimetallic couple between iron and other metals, such as palladium, nickel, and copper, among others, favors the degradation of diverse organochlorine compounds by increasing the iron corrosion (Aginhotri *et al.* 2011; Gunawardana *et al.* 2011). These bimetallic systems consisted of a core metal and shell metal with different oxidation potential (coating metals). The core metal is a less noble metal with lower oxidation potential (e.g., iron, magnesium), which acts as anode and provides the reducing power (e.g., palladium and platinum) for reductive dechlorination when it corrodes while the shell metal acts as cathode where reduction process occurs (Gunawardana *et al.* 2011). Furthermore, some shell metals act as catalytic metal that involves the formation of atomic hydrogen and its reaction with contaminant to improve reductive dechlorination. Complete dechlorination of DDT, endosulfan and lindane using magnesium/palladium system in water has been reported (Gautam and Sumathi 2006; Aginhotri *et al.* 2011). However, the use of this specific bimetallic system increases the cost of the treatment, in comparison with the use of non-catalytic metal couple.

The use of coating non-catalytic bimetallic system (iron/copper) has received increasing attention to support the degradation of diverse chlorinated hydrocarbons (Zheng *et al.* 2009; Liu *et al.* 2015), mainly due to low cost and high effectiveness to enhanced reactivity toward chlorinated organic compounds generated by the formation of galvanic couple with reactions shown in Eqs. (1) - (2).



The standard redox values of Eqs. (1) and (2) are $E_0 = -0.440V$ and $E_0 = +0.340V$, respectively. The evaluation of this bimetallic system on degradation pesticides has been conducted mainly in water, sediments, and scarcely in soil (Zheng *et al.*, 2009; Liu *et al.*, 2015).

The objective of this work was to evaluate the effect of Fe⁰ and galvanic couple Fe⁰/Cu⁰ (no coating bimetallic nor nanoparticles) treatments on the degradation of organochlorine compounds polluted-soils at microcosms- and bench-scale.

2 Materials and methods

2.1 Soil samples

Three soil samples identified as SG, SE, and SF were used: 1) SG soil was collected from a former pesticides factory in the state of Guanajuato, Mexico; 2) SE soil was collected from a chemical compounds factory in the State of Mexico; and 3) SF soil was sampled from a floriculture region also from the State of Mexico. The three specific pesticides were selected because they are regulated by the Stockholm Convention and they have been frequently detected in industrial and agricultural soils in Mexico (Velasco *et al.*, 2014).

The samples were homogenized by mechanical means and sieved to obtain a particle size < 0.54 mm (mesh #30) and then dried at room temperature to express all the concentrations on a dry basis.

Identification and quantification of pesticides contained in the soil were performed using a standard mixture of 17 organochlorine compounds (UltraScientific US-112B) according to the methodology described in the analytic methods section. The characteristics and concentrations of soil samples are shown in Table 1 and discussed later in this paper.

The SF soil (where isomers of endosulfan were present at quite low concentrations) was amended with commercial endosulfan (Tridane 350®, containing 33.24% of endosulfan, in a ratio of 7:3 of α - and β -isomers) and identified as SF-S. The spiking process was carried out as follows: the amount of commercial pesticide to obtain a concentration of approximately 40 mg/kg in soil was calculated and dissolved in CH_2Cl_2 ; this solution was spiked by drops into a thin layer of soil; the solvent was evaporated at room temperature; the soil was homogenized; and finally, the concentration was verified.

2.2 Metals

Zero-valent iron. The iron husks (burrs with a particle size < 0.6 mm) were collected from the metal workshop of the University. They were washed 3 times with n-hexane to avoid residual oil, after which water was used to rinse them and a magnet bar was used to separate the iron from other materials. Finally, the iron particles were sieved (mesh #40) to obtain a particle size < 0.42 mm. The iron particles were activated by contact with a solution of H_2SO_4 (10% v/v) for 2 min, and after that, they were rinsed with water and dried

for 2 h at 90 °C. The iron particles were stored in a hermetic container until use.

Iron powder reagent (J.T. Backer, USA) was also used as a control in the microcosms experiments. Once the results showed that there was no significant variation attributable to the origin of the iron, only residual iron from the metal workshop was used.

Zero-valent copper. Industrial grade copper for microcosms scale experiments was obtained by rubbing a commercial copper tube (particle size < 0.149 mm, mesh #100). Copper was part of the reactor structure in the bench-system, described later in this paper.

2.3 Analytical methods

Pesticides in the soil samples were extracted by sonication using as solvent a 1:1 n-hexane-ketone mixture (Method 3550C) (US-EPA 2007a) as described previously by Velasco *et al.* 2014. Extraction of a soil sample with known concentrations of pesticides (provided by the Mexican governmental laboratory, CENICA) rendered >90% of recovery. This procedure was routinely performed to assure the proper extraction of the compounds.

The identification of organochlorine compounds was performed using gas chromatography coupled with a mass spectrum detector (Agilent 6890N, MSD 5975B, USA) accordingly to the Method 8270D (US-EPA 2007b). Identification of compounds was performed by mass scan (50 to 450 z/m at 70 eV) and comparison with NIST05 Mass Spectral library. For positive identification of a compound, a minimum of 90% of quality was fixed. On the other hand, gas chromatography with electron capture detector (Varian 3400, USA) was used for quantification of pesticides (Method 8081B) (US-EPA 2007c). A detailed description of chromatography conditions used for identification and quantification can be found in Velasco *et al.* (2014).

The daily verification of calibration was used to assure the quality and reproducibility of quantification. Also, the line base of GC/MS was verified by measuring blank samples (hexane), with each batch consisting of 15 samples. The detection limit of the compounds was 0.2 $\mu\text{g/L}$, this value was obtained by evaluation of progressively more dilute concentrations of analytes (UltraScientific US-112B, USA).

The presence of H_2 in the headspace at the microcosms experiments (hermetic bottles) was evaluated in 100 μL of gaseous phase samples by gas chromatography equipped with a thermal conductivity

detector (GOW MAC Series 550, USA) using a silica-gel 60/80 column, 180 x 1/8 x 0.0850. The injector, column, and detector temperatures were 75, 30, and 120 °C, respectively. Nitrogen was used as carrier gas.

X-ray diffraction (XRD) powder analyses were obtained using EMPYREAN X-ray diffractometer (PANalytical, Netherlands), equipped with Cu-K α radiation and PIXcel detector. The analyses were carried out using the following conditions: 45 kV, 40 mA and measurement range (2θ): 10 to 70°.

2.4 Microcosms batch experiments

The experiments were carried out in amber flasks (240 mL) sealed with hermetic valves (Mininert, VICI precision sampling Inc. Baton Rouge, Louisiana, USA) using 3 g of dry soil and 3 mL of water and 2.5, 5 and 10% (w/w) of Fe⁰. In SE and SF-S soil, only the addition of 10% (w/w) of Fe⁰ was tested. In all cases, controls without iron were performed. The microcosms were incubated at 30 °C and 100 rpm. The initial pH value was adjusted, when needed, based on experiments to assess the effect of initial pH on biodegradation described in section 2.5.

There were also evaluated the ratios of Fe⁰/Cu⁰ to the soil of 10/1.5, 10/3 and 10/5 (w/w). Additional microcosms controls without Cu⁰ were performed. All the experiments and controls were carried out in duplicate and two measurements were done per each sample.

2.5 Experiments to assess the effect of initial pH value on degradation

The initial pH values of the soils were fixed at 4.5, 7 and 9 pH values adding solutions of 10% v/v of H₂SO₄ or 10% wt/v of NaOH. The experiments were conducted as described in section 2.4. The pH values were selected according to the original values of the soils (Table 1) and considering the range of pH values reported previously (Yao *et al.* 2006; Ghazali *et al.* 2010). Soil pH was measured using pH meter (OAKTON, USA) according to standard procedures (Method 9045D) (US-EPA 2004).

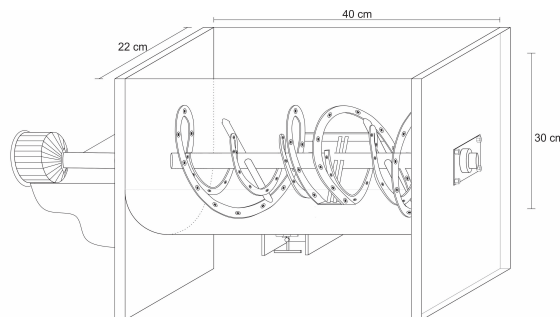


Fig. 1 Experimental bench-scale system for Fe⁰/Cu⁰ treatment.

2.6 Bench-scale batch experiments

The bench-scale reactor was designed to allow the galvanic couple of Fe⁰/Cu⁰. It consisted of a rotary helical mixer of 21 L stainless steel provided with copper-washers along the blades (Fig. 1). The treatment was performed with 2 kg of soil and 1.6 L of H₂O and added with 10% (w/w) of Fe⁰ microparticles (< 0.42 mm). A discontinuous mixing speed of 45 rpm with on/off cycles of 1:1 h from. Four-day treatments were evaluated according to the optimal reaction time registered in microcosms experiments. Treated soil samples were collected and storage at 5 °C every day during the treatment. Then residual pesticides in the soil samples were extracted and analyzed. Two measurements were done per each sample. No duplicate experiments were carried out.

2.7 Statistical analysis

The statistical treatments of the data were performed by analysis of variance (ANOVA) with the statistical functions of KaleidaGraph software.

3 Results and discussion

3.1 Soil characterization

The initial analysis of the soil samples allowed for the identification of the compounds contained in each soil and their concentrations (Table 1). The industrial soil SG was classified as sandy-loam and had a low organic load (0.13%) and a pH value of 4.5. This industrial soil was polluted with DDX, that is, DDT and its main intermediates, DDD and DDE, by anaerobic and aerobic pathways respectively (Bosch *et al.* 2015). The concentrations found indicate that SG would be considered as DDT and DDD-polluted soil, according

to the preliminary remediation goals (PRG) in the USA that establish value limits of 7.0 (DDT) and 7.2 (DDD) mg/kg for industrial soil and 1.7 and 2.0 mg/kg for residential soil. The DDE initial concentration was lower than the PRG for industrial and residential soil values of 5.1 and 1.4 mg/kg, respectively (US-EPA 2010).

On the other hand, the industrial soil SE was a sandy-clay-loam soil highly polluted with endrin and the intermediate of degradation, endrin aldehyde. The SE soil contained 1.21% organic matter and had a basic pH of 9.55. This soil exceeded the limit concentration of 18 mg/kg of endrin in residential soil, while the intermediate endrin aldehyde is not currently regulated (US-EPA 2010).

In the sandy-loam agricultural soil SF, the organic matter content was 4.17% and it had a pH value of 6. The α - and β -isomers of endosulfan were identified in this soil. However, these concentrations were an order of magnitude lower compared to the other soil samples, so the soil was spiked with commercial endosulfan, as described in section 2.1. Nevertheless, the resultant total concentration (α - and β - isomers) in the soil was under the concentration limit of 360 mg/kg for residential soil (US-EPA 2010).

The physicochemical properties of the soil samples are showed in Table 2. The SG soil (industrial soil) the cation exchange capacity was 1.24 cmol/kg and field capacity of 18.6% while the SF/SF-S soil (agricultural soil) the cation exchange capacity was (34.9 cmol/kg) and field capacity was (37.9%). These

data agree with the reports of soils with a higher clay fraction and organic matter have a higher CEC, while soils with high sand content have low CEC and low field capacity (Pansu and Gautheyrou 2006; Fan *et al.* 2015). On the other hand, the main exchangeable cations were $\text{Ca} > \text{K} > \text{Mg}$ in the soils tested, whereas the main micronutrients available were Fe and Mn in SG soil and Zn in SF/SF-S soil. A similar level of Cu^0 was registered in the three soils. The high concentration of Fe and Mn in GS soil maybe is related to the source of soil (former pesticide factory).

3.2 Degradation in microcosms batch experiments

3.2.1 Effect of initial pH value on degradation

The results for experiments with Fe^0 (10%) and Fe^0/Cu^0 (10/3) for SE and SG after 8 days of treatments at initial values of pH of 4.5, 7 and 9 are showed in Table 3. The lowest degradation of all compounds was observed at pH 9. Whereas at pH of 4.5 and 7 not significantly difference in degradation was observed. Diverse studies have indicated that degradations rates increased at pH range between 4 and 7, due to an excess of H^+ for reductive reaction and the prevention of iron surface passivation (Yao *et al.* 2006; Ghazali *et al.* 2010). Based on the above results, in the microcosms batch experiments, the initial pH value was adjusted to 4.5 and in the bench-scale reactor, the pH was adjusted to neutral.

Table 1. Initial characterization of soils

Soil	Pesticides concentration [mg/kg] ^a	CAS number	OM [%]	pH	Texture and composition [%]
SG	DDT: 25.58 ± 2.2 DDD: 3.35 ± 0.22 DDE: 1.08 ± 0.04	50-29-3 72-54-8 72-55-9	0.13	4.45	Sandy-loam Sand [60.9] Silt [30.7] Clay [8.4]
SE	Endrin: 150.3 ± 7.2 Endrin aldehyde: 5.6 ± 0.7	72-20-8 7421-93-4	1.21	9.55	Sandy-clay-loam Sand [59.5] Silt [20.0] Clay [20.5]
SF	α -endosulfan: 0.077 ± 0.009 β -endosulfan: 0.179 ± 0.032	959-98-8 33213-65-9	4.17	6.79	Sandy-loam Sand [59.5] Silt [26.0] Clay [14.5]
SF-S	α -endosulfan: 28.87 ± 5.46 β -endosulfan: 12.66 ± 4.83	959-98-8 33213-65-9	4.17	6.50	

a. dry basis. OM- Organic matter.

Table 2. Physicochemical properties of soil samples.

Parameters	Soil		
	SG	SE	SF/SF-S
CEC (cmol kg ⁻¹)	16.2	24.4	34.9
EC (dS m ⁻¹)	1.24	3.51	0.7
FC (%)	18.6	26.3	37.9
N (mg kg ⁻¹)	14.6	24.6	59
P (mg kg ⁻¹)	161.4	28.6	295.9
Ca (mg kg ⁻¹) ^a	4366	5216	3610
K (mg kg ⁻¹) ^a	918	3252	1196
Mg (mg kg ⁻¹) ^a	491	391	331
Mn (mg kg ⁻¹) ^b	47.62	4.9	35.17
Fe (mg kg ⁻¹) ^b	152.34	13.8	25.9
Cu (mg kg ⁻¹) ^b	2.69	2.23	1.88
Zn (mg kg ⁻¹) ^b	2.65	2.6	7.94

CEC-Cation exchange capacity. EC-Electric conductivity. FC-Field capacity (water holding capacity). a. extracted with ammonium acetate. b. extracted with diethylene triamine penta-acetic acid (DTPA: chelating agent).

Table 3. Effect of initial pH of SG and SE soils on removal of pollutants.

Compound	Treatment	pH 4.5	pH 7.0	pH 9.0
		Residual concentrations (mg/kg)		
Soil SG	Ratio % (w/w)			
DDT	Fe ⁰ 10	2.32 ± 0.11	3.46 ± 1.14	5.35 ± 1.48
	Fe ⁰ /Cu ⁰ 10/3	0.83 ± 0.19	1.31 ± 0.68	2.15 ± 1.40
DDD	Fe ⁰ 10	2.18 ± 0.56	2.54 ± 0.28	2.96 ± 0.45
	Fe ⁰ /Cu ⁰ 10/3	0.39 ± 0.06	0.44 ± 0.23	0.81 ± 0.15
DDE	Fe ⁰ 10	0.66 ± 0.12	0.79 ± 0.07	1.02 ± 0.20
	Fe ⁰ /Cu ⁰ 10/3	0.41 ± 0.08	0.57 ± 0.07	0.65 ± 0.12
Soil SE				
Endrin	Fe ⁰ 10	41.40 ± 2.1	43.28 ± 1.7	154.78 ± 4.3
	Fe ⁰ /Cu ⁰ 10/3	29.48 ± 1.27	32.29 ± 1.34	148.5 ± 2.3
Endrin aldehyde	Fe ⁰ 10	2.81 ± 0.41	3.13 ± 0.32	5.86 ± 0.61
	Fe ⁰ /Cu ⁰ 10/3	0.44 ± 0.43	1.37 ± 0.16	4.54 ± 0.66

Initial concentrations (mg/kg): DDT: 25.58±2.2; DDD: 3.35±0.22; DDE: 1.08±0.04; Endrin: 150.3±7.2; Endrin aldehyde: 5.6±0.7.

3.2.2 DDX degradation in soil SG

In all cases, the Fe⁰ and Fe⁰/Cu⁰ treatments improved the degradation of DDX compared to the controls after 8 days of treatment (Fig. 2). However, depending on the compound, the effect was different. The degradation of DDT was significantly enhanced ($p < 0.05$) by the addition of 10% and 5% compared to the 2.5% of Fe⁰: elimination observed was 72.9%, 63.4%, and 16.6%, respectively, while in the control

elimination was negligible (1.3%) (Fig. 2a). The Fe⁰/Cu⁰ treatments increased the degradation of DDT above 85% and up to 96% using 5% and 10% of Fe⁰ combined with any dose of Cu⁰ tested (Fig. 2a).

On the other hand, the addition of 10% of Fe⁰ significantly increased ($p < 0.05$) the degradation of DDD up to 50.8% while degradation was around 28% with both 5% and 2.5% of Fe⁰ (Fig. 2b). The degradation using 5/1.5 of Fe⁰/Cu⁰ was similar to that

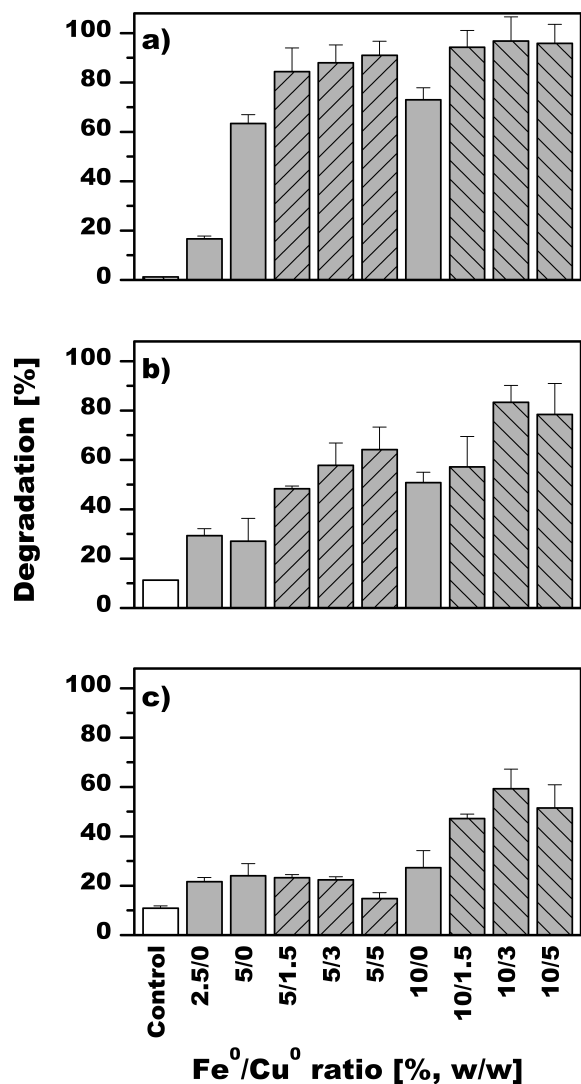


Fig. 2 Degradation of a) DDT; b) DDD; and c) DDE after 8 days of treatment of soil SG with Fe⁰ and Fe⁰/Cu⁰ in microcosms batch experiments. Initial concentrations were 25.58 ± 2.2 of DDT; 3.35 ± 0.22 of DDD; and 1.08 ± 0.04 of DDE.

obtained in the system with 10% of Fe⁰ (Fig. 2b). Higher doses of Cu⁰ (5/3 and 5/5) slightly increased the DDD degradation, but not significantly ($p > 0.05$). The dose of 10/3 of Fe⁰/Cu⁰ resulted in the highest observed degradation of DDD (around 83%).

In the case of DDE, the degradation was around 22% for all Fe⁰ ratios tested (Fig. 2c), which is contrary to the study by Yang *et al.* (2010). They reported that the increment of Fe⁰ in soil treatment markedly increased the degradation of DDE. They obtained 60% elimination in 40 days with the addition

of 5% of Fe⁰ in a soil containing 5 mg/kg of DDE (Yang *et al.* 2010).

In the Fe⁰/Cu⁰ treatments, the effect of Cu⁰ was negligible with the use of 5% of Fe⁰ with any dose of Cu⁰, and the DDE degradation obtained was comparable to that observed in Fe⁰ treatments. However, the addition of 10% of Fe⁰ combined with any dose of Cu⁰ resulted in a significant increased degradation of DDE of up to 60% at Fe⁰/Cu⁰ ratio of 10/3 (Fig. 2c) with a significantly difference compared with the use of 5% of Fe⁰ with any dose of Cu⁰.

The soil treated with 10% of Fe⁰ achieved the PRG for industrial soil in the USA of 7 mg/kg and 2 mg/kg for DDT and DDD, respectively (US-EPA 2010). Nevertheless, based on the results of this study, the higher dose of Fe⁰ with the medium dose of Cu⁰ (10/3) would be the best combination for treatment of the SG soil, considering that: i) the soil contained a mixture of the three compounds, DDT, DDD, and DDE; ii) the highest degradation percentages were obtained for the three compounds; iii) the strongest effect of Cu⁰ was on DDE and DDD degradation; iv) DDE has been reported as more recalcitrant than the DDT itself; v) the residual concentrations of DDX achieved the PRG for residential soil (US-EPA 2010).

Regarding the transformation and production of intermediates, the accumulation of DDE and DDD has been reported in Fe⁰ systems in water and soil by Pirnie *et al.* 2006; Yang *et al.* 2010. In the present study, no accumulation of DDD or DDE was observed under the conditions tested but five different intermediates were detected (Table 4). The main intermediate found was DDNS, which was identified in all the Fe⁰ treatments but not in the initial or the final control samples. These compounds (Table 4) have been reported as products of DDT degradation mainly under anaerobic conditions (Cao *et al.* 2010), which in our case could be related to the poor mixing conditions in the experiments. DDMU has been related to the aerobic pathway of DDT and DDE transformation (Singh *et al.* 2013), while the presence of DDMS and DDNS has been related to the transformation of DDT to DDD and its posterior transformation by reducing dechlorination under anaerobic conditions (Gautam and Sumathi 2006; Cao *et al.* 2010). The hydrogen production was also detected in the gas phase in all Fe⁰ and Fe⁰/Cu⁰ treatments, suggesting that DDNS accumulation could be associated with a mechanism similar to that proposed by Gautam and Sumathi 2006. They proposed the formation of DDNS via catalytic hydrogen transfer for the removal of alkyl chlorine atoms from DDT in a bimetallic Mg⁰-Zn system.

Table 4. Identification of intermediates in DDT-polluted soil treated with Fe and Fe-Cu.

RT [min]	CAS Number	Compound	Acronym
19.25	0101-76-8	bis(p-chlorophenyl)methane	[DDM]
20.34	4/4/47	1,1-bis(p-chlorophenyl)ethane	[DDNS]
20.43	2642-81-1	2,2-bis(p-chlorophenyl)ethylene	[DDNU]
23.66	2642-80-0	1-Chloro-2,2-bis(p-chlorophenyl)ethane	[DDMS]
23.98	1022-22-6	1-Chloro-2,2-bis(p-chlorophenyl)ethylene	[DDMU] ^a

a. Found also in controls. Identification quality > 98%.

The toxicology and recalcitrance of DDNS have been not reported, and further studies should be performed to assess it. Probably, a secondary treatment should be required. For example, Velasco *et al.* (2017) reported that a sequence of ZVI treatment followed by biostimulation can improve the remediation of DDT and its intermediate compounds.

3.2.3 Endrin degradation in soil SE

After 8 days of treatment, the addition of 10% (w/w) of Fe⁰ successfully degraded 77.1% and 63% of the initial endrin and endrin aldehyde concentrations of 150.3 ± 7.2 and 5.6 ± 0.7 mg/kg, respectively, compared with the lower degradation (41.9% and 18.7%) obtained by the addition of 5% (w/w) of Fe⁰, while in the controls degradation was 1% and 3.8%, respectively (Fig. 3a and 3b). The Fe⁰/Cu⁰ treatment effect on degradation was not significantly different for both compounds compared to the addition of 10% of Fe⁰. In Fe⁰/Cu⁰ treatments, using 5% of Fe⁰ with 3% and 5% of Cu⁰, the degradation obtained was similar to the values obtained with 10% of Fe⁰. However, the final concentration of endrin in the best case of Fe⁰/Cu⁰ (10/5) was still above the PRG level for residential soil of 18 mg/kg (US-EPA 2010).

Residual endrin in environmental matrices is reported much less frequently than DDT or other organochlorine pesticides because its relatively small-scale use and limited accumulation in biota this has resulted in less attention on its remediation (Zitko 2003). Treatments of bioremediation and natural attenuation have been tested, primarily (Xiao and Kondo 2013). However, the production or accumulation of intermediates was not observed.

3.2.4 Endosulfan degradation in soil SF-S

Due to the marginal effect of copper on the previous experiments, only the degradation of endosulfan

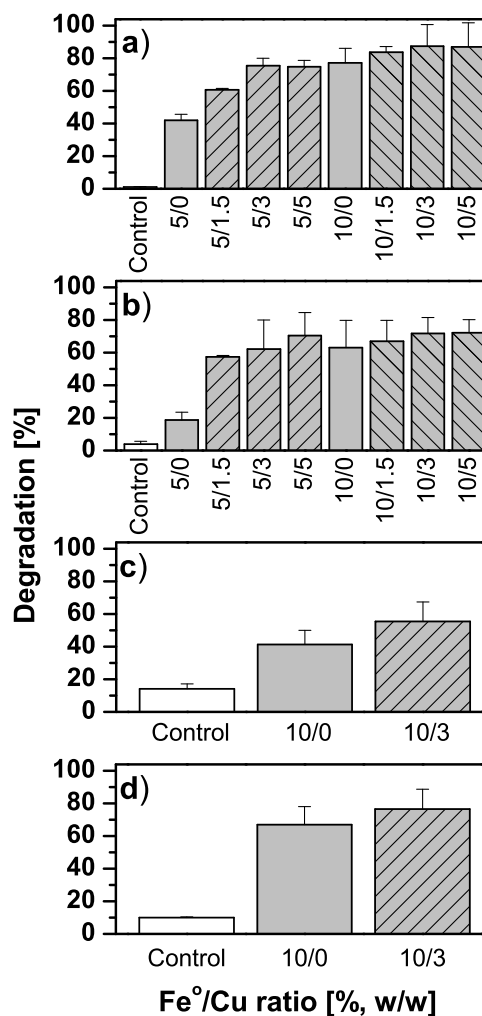


Fig. 3 Degradation of a) endrin; b) endrin aldehyde; c) α -endosulfan; and b) β -endosulfan after 8 days of treatment of SE and SF-S soils with Fe⁰ and Fe⁰/Cu⁰ in microcosms batch experiments. Initial concentrations [mg/kg] were 150.3 ± 7.2 of endrin; 5.6 ± 0.7 of endrin aldehyde; 28.87 ± 5.46 of α -endosulfan; and 12.66 ± 4.83 of β -endosulfan.

isomers with the addition of 10% of Fe^0 and a ratio of 10/3 of Fe^0/Cu^0 over 8 days of treatment is presented in Fig. 3c and 3d. The Fe^0 treatment significantly improved ($p < 0.05$) the degradation of both isomers compared to the controls (from 10% to 67% and from 14% to 41%) (Fig. 3). The Fe^0/Cu^0 treatment slightly improved the degradation obtained with Fe^0 , but no significant difference was observed; the α isomer was degraded up to 76.6% while the degradation of β -endosulfan was 55.4% in the Fe^0/Cu^0 system. These results agree with the literature where the β -isomer has been reported to degrade more slowly than the α -isomer, which could be related to its higher toxicity and chemical stability compared to the α isomer (Kwon *et al.* 2002; Weber *et al.* 2010). Consequently, the reported half-life in soils for α -endosulfan and for β -endosulfan is 60 days and 800 days, respectively (Kwon *et al.* 2002; Kataoka and Takagi 2013). Furthermore, it must be considered that the commercial endosulfan used contains the two parent isomers in a ratio of 7:3, meaning that the initial concentration of α isomer was 2.33 times higher.

There are relatively few studies that have examined the persistence of endosulfan in soil under field application where degradation rates strongly depend on the soil conditions, particularly soil water content and ambient temperature (Weber *et al.* 2010). Although some reports consider the addition of particles or nanoparticles of Fe^0 as an effective treatment for organochlorine compounds in aqueous media (Feitz *et al.* 2005; Cong *et al.* 2010), to our knowledge this is the first report of endosulfan treatment in soil by Fe^0 and Fe^0/Cu^0 . The existing studies are related to the degradation of endosulfan in water. For example, the complete dechlorination of endosulfan (30 mg/L) using the bimetallic system $\text{Mg}(0)/\text{Pd}(+4)$ ratio 5/0.5 was reported in aqueous media by Aginhotri *et al.* (2011), while Cong *et al.* (2015) reported degradation > 90% of endosulfan by zero-valent zinc treatment in water and soil with initial concentrations of 40 mg/L in liquid and 40 mg/kg in soil. Also, the $\text{Mg}(0)/\text{ZnCl}(2)$ bimetallic system has been tested for endosulfan elimination in aqueous media (30 mg/L) with 96% removal (Begum and Gautam 2011).

3.2.5 Length of treatment

Since DDX degradation was incomplete, experiments for 16 and 40 days were also performed to evaluate further degradation of DDX, obtaining slightly better or equivalent degradation to those obtained after 8

days. After treatments of 40 days using 2.5%, 5%, and 10% (w/w) of Fe^0 , the DDT degradation was 30.2%, 69.8%, and 82.7%; DDD degradation was 12.3%, 33.6%, and 62.1%; and DDE degradation was 4.1%, 23.2%, and 33.9%. The length of treatment of water using Fe^0 is in the range of 10 to 40 days (Ghazali *et al.* 2010; Yang *et al.* 2010).

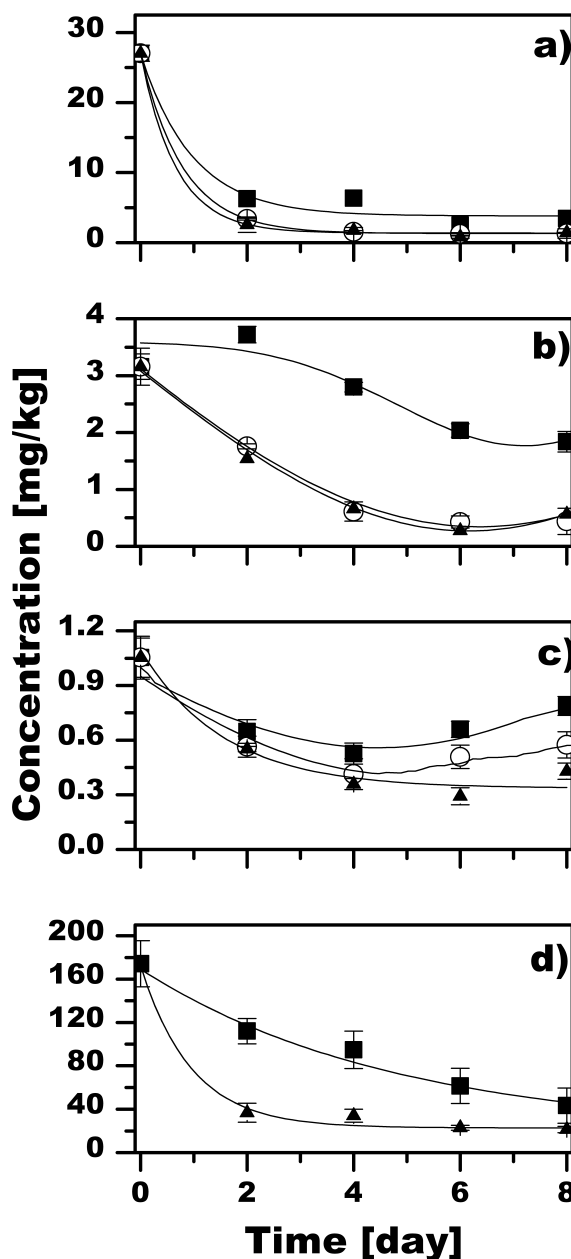


Fig. 4 Profiles of consumption of a) DDT; b) DDD; c) DDE; and d) endrin with the treatments: (■) Fe^0 10%; (○) Fe^0/Cu^0 10/3; (▲) Fe^0/Cu^0 10/5 in microcosms batch experiments.

Selected experiments (10% of Fe⁰, 10/3 and 10/5 of Fe⁰/Cu⁰) to evaluate the residual concentration of the pesticides at different times of treatment were conducted for DDX and endrin (Fig. 4). The DDT degradation rates were similar in these cases ($p > 0.05$), and only the final degradation was marginally enhanced in the galvanic couple systems (Fig. 4a). On the contrary, as discussed above, the effect of the systems (Fe⁰/Cu⁰) significantly enhanced the DDD percentage of degradation and the rate of degradation. The DDD degradation rate increased from 0.187 to 0.480 mg/kg/d, while degradation increased from 41.7 to 84% in Fe⁰/Cu⁰ systems compared to the Fe⁰ treatment (Fig. 4b). Also, the rate of endrin degradation was favored in the galvanic couple systems from 31.09 to 65.45 mg/kg/d while degradation was enhanced from 75.2% to 87.8%. The ANOVA analysis showed that the endrin degradation obtained in the treatment with Fe⁰ and Fe⁰/Cu⁰ (10/5) was significantly different. Increasing concentration of DDE was observed for Fe⁰ (10%) and Fe⁰/Cu⁰ (10/3) after four days, due to DDT degradation to DDE (Fig. 4c). The improved DDE degradation in the Fe⁰/Cu⁰ treatments was related to the consumption of DDE produced by the degradation of DDT, avoiding its accumulation in the media (Fig. 4c). In all cases, the rate of degradation tended to be constant after four days, and the pesticides were not completely depleted. The limit in the degradation could be associated with the reactions or with the mass transport phenomena. In the first case, this could be the result of the passivation of the superficial area contact of Fe⁰ due to the oxidation, while in other cases; this could be associated with the strong bond of the pesticide with the material organic content of the soils, thus limiting the diffusive transport.

Results shown in Fig. 4 indicate that a shorter time of treatment could be satisfactory for DDT in any case and for endrin in Fe⁰/Cu⁰ treatments. However, time of treatment should be weighed versus the cost that copper will present in the system and the PRG required. Also, the degradation or accumulation of intermediates should be considered.

Based on these results, experiments in the bench-scale reactor were performed for 4 days and the results are presented in the next section.

3.3 Degradation in Bench-scale batch experiments

The DDT, DDE, and DDD degradation attained in this system was 86.3%, 76.7%, and 65.5%, respectively (Fig. 5a, 5b, and 5c), these results were comparable to

those in the microcosms experiments with the addition of 10/3 of Fe⁰/Cu⁰ in four days. Degradation rates were also similar to those experiments, indicating the scalability of the process. However, the final concentration for DDD was below the PRG for residential use, but DDT only accomplished the PRG for industrial use.

On the other hand, the treatment of SE soil in this reactor attained 87.1% and 93% of degradation for endrin and endrin aldehyde, respectively (Fig. 5d and 5e). For endrin, the percentage and rate of degradation were similar to that in the microcosms but for endrin aldehyde, the degradation was 33% higher than that obtained in the microcosms experiments. This indicates that mixing favored its degradation, and therefore transport phenomena could be the limiting process of overall degradation rate in the experiments where the sludge was under slow agitation (100 rpm). The treatment proposed could be suitable for remediation of this highly polluted soil. However, a secondary treatment is recommended to accomplish the PRG of 18 mg/kg for endrin in residential soil.

In the case of SF-S, α - and β -endosulfan were degraded up to 86.9% and 90.3%, respectively, which is higher than those found in the microcosms experiments (Fig. 5f). Remediated soils were analyzed to confirm their stability after 4 and 12 months and no changes in the residual concentration of pesticides or intermediates were detected.

Furthermore, the XRD analysis showed that soil SG contain anorthite (CaAl₂Si₂O₈), quartz (SiO₂), gypsum (Ca(SO₄)₂·2H₂O) and lepidocrocite (γ -FeOOH), and jarosite (KFe₃³⁺(OH)₆(SO₄)₂). However, the presence of iron (III) goethite (γ -FeOOH) was evident in treated soil, due to the oxidation of zero-valent iron in presence of oxygen (air) because the bench-scale reactor was no hermetic closed.

This was also correlated with the changes in the color of the soil from brown to green to reddish with the time of treatment suggesting the production of oxides during corrosion of Fe⁰. The green color could be associated with green rusts, while reddish-brown soil color was due to the formation of oxy-hydroxide compounds as goethite. Some studies have indicated that green rusts are formed in both biotic and abiotic corrosion processes of iron or steel, which can be further oxidized to iron oxy-hydroxide when exposed to air (O'Loughlin *et al.* 2003). Several studies have also indicated that green rusts which are mixes of Fe (II) and Fe (III) hydroxides with chemical structure $[\text{Fe}_{(6-x)}^{\text{II}}\text{Fe}_x^{\text{III}}(\text{OH})_{12}]^{x+}[(\text{A})_{x/n}\text{yH}_2\text{O}]^{x-}$ are abiotic agents that may enhance the reductive dechlorination

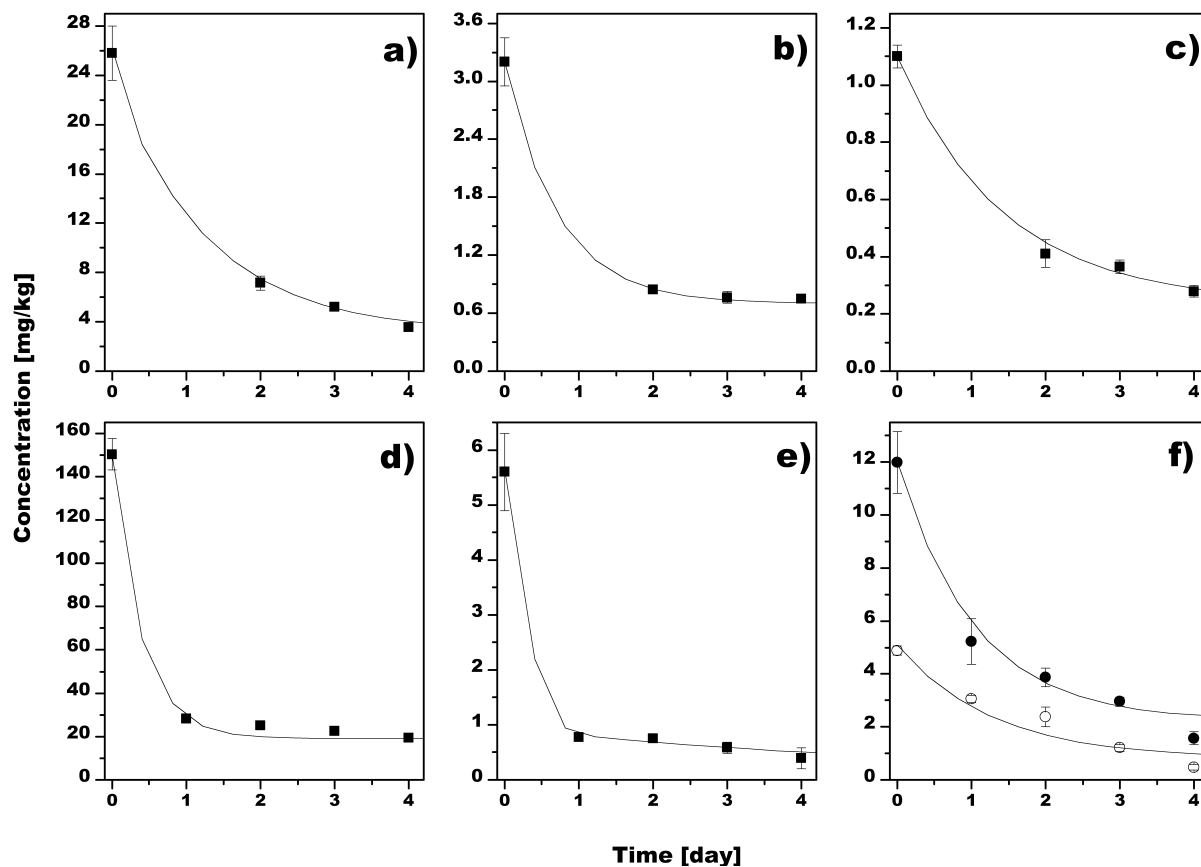


Fig. 5 Degradation of a) DDT; b) DDD; c) DDE; d) endrin; e) endrin aldehyde; and f) endosulfan: α - isomer (\bullet); and β -isomer (\circ) with Fe^0/Cu^0 in bench-scale batch experiments.

(Maithreepala and Doong 2005; O'Loughlin *et al.*, 2003). This suggested the presence of green rusts in the systems and its possible relation to the reductive dechlorination of the compounds tested.

Conclusions

The Fe^0 and Fe^0/Cu^0 treatments allowed for the reduction of higher concentrations of DDX, endrin, and endosulfan, in both microcosms experiments and a helicoidal-mixing bench-scale reactor, indicating the potential scale-up of the treatments. In microcosms experiments, the effect of copper was marginal for DDT degradation, but DDD and DDE degradation were enhanced. Endrin and DDD degradation rates were also enhanced by the presence of Cu^0 in microcosms experiments, while degradation of endrin aldehyde and endosulfan degradation improved in the bench-scale reactor compared to the microcosms

experiments due to the favored mixing conditions.

Furthermore, the production of intermediates (in the case of DDX-polluted soil) and the low removal efficiency (in the case of endrin-polluted soil), indicate that a secondary treatment should be considered. The cost of Cu^0 should be also evaluated and contrasted with the values and time required for remediation.

Acknowledgements

The authors would like to thank Dilyn Myers, from the Fulbright-García Robles scholarship program at the UAM-C for reading the manuscript and for her useful suggestions, as well as to Dra. Teresa Pi Puig from the Geology Institute at Universidad Nacional Autónoma de México (UNAM) for her assistance with X-ray diffraction analysis. Antonio Velasco is grateful to CONACYT for the scholarship no. 92139 and Posgrado de Ciencias Naturales e Ingeniería de la UAM-C.

References

- ATSDR, Agency for Toxic Substances and Disease Registry. (2002). Toxicological profile for DDT, DDD and DDE. US Department of Health and Services, Atlanta. Disponible en: www.atsdr.cdc.gov/ToxProfiles/TP.asp?id=81&tid=20
- Aginhotri, P., Mahidrakar, A.B., Gautam, S.K. (2011). Complete dechlorination of endosulfan and lindane using Mg(0)/Pd(+4) bimetallic system. *Water Environment Research* 83, 865-873.
- Begum, A. y Gautam, S.K. (2011). Dechlorination of endocrine disrupting chemicals using Mg(0)/ZnCl(2) bimetallic system. *Water Research* 45, 2383-2391.
- Boparai, H.K., Shea, P.J., Comfort, S.D., Machacek, T.A. (2008). Sequencing zerovalent iron treatment with carbon amendments to remediate agrichemical-contaminated soil. *Water Air & Soil Pollution* 193, 189-196.
- Bosch, C., Grimalt, J.O., Fernández, P. (2015). Enantiomeric fraction and isomeric composition to assess sources of DDT residues in soils. *Chemosphere* 138, 40-46.
- Bussian, B.M., Pandelova, M., Lehnik-Habrink, P., Aichner, B., Henkelmann, B., Schramm, K.W. (2015). Persistent endosulfan sulfate is found with highest abundance among endosulfan I, II, and sulfate in German forest soils. *Environmental Pollution* 206, 661-666.
- Cao, F., Li, F.B., Liu, T.X., Huang, D.Y., Wu, C.Y., Feng, C.H., Li, X.M. (2010). Effect of *Aeromonashydrophila* on reductive dechlorination of DDTs by zero-valent iron. *Journal of Agricultural and Food Chemistry* 58, 12366-12372.
- Cong, L.J., Guo, J., Liu, J.S., Shi, H.Y., Wang, M.H. (2015). Rapid degradation of endosulfan by zero-valent zinc in water and soil. *Journal of Environmental Management* 150, 451-455.
- Cong, X., Xue, N.D., Wang, S.J., Li, K.J., Li, F.S. (2010). Reductive dechlorination of organochlorine pesticides in soils from an abandoned manufacturing facility by zero-valent iron. *Science of the Total Environment* 408, 3418-3423.
- Fan, T.T., Wang, Y.J., Li, C.B., Zhou, D.M., Friedman, S.P. (2015). Effects of soil organic matter on sorption of metal ions on soil clay particles. *Soil Science Society of America Journal* 79, 794-802.
- Feitz, A.J., Joo, S.H., Guan, J., Sun, Q., Sedlak, D.L., Waite, T.D. (2005). Oxidative transformation of contaminants using colloidal zero-valent iron. *Colloids and Surfaces A* 265, 88-94.
- Gautam, S.K., Sumathi, S. (2006). Dechlorination of DDT mediated by bimetallic systems. *Environmental Technology* 27, 387-394.
- Ghazali, M., McBean, E., Shen, H., Dastous, P.A. (2010). Impact of iron concentration and pH on zero-valent iron dechlorination of DDT for brownfields. *Remediation Journal* 20, 97-107.
- Gunawardana, B., Singhal, N., Swedlund, P. (2011). Degradation of chlorinated phenols by zero valent iron and bimetallics of iron - A review. *Environmental Engineering Research* 16, 187-203.
- Han, Y., Shi, N., Wang, H., Pan, X., Fang, H., Yu, Y. (2016). Nanoscale zerovalent iron-mediated degradation of DDT in soil. *Environmental Science Pollution Research* 23, 6253-6263.
- Kataoka, R., Takagi, K. (2013). Biodegradability and biodegradation pathways of endosulfan and endosulfan sulfate. *Applied Microbiology and Biotechnology* 97, 3285-3292.
- Kwon, G.S., Kim, J.E., Kim, T.K., Sohn, H.Y., Koh, S.C., Shin, K.S., Kim, D.G. (2002). *Klebsiella pneumoniae* KE-1 degrades endosulfan without formation of the toxic metabolite, endosulfan sulfate. *FEMS Microbiology Letters* 215, 255-259.
- Lefevre, E., Bossa, N., Wiesner, M.R., Gunsch, C.K. (2016). A review of the environmental implications of in situ remediation by nanoscale zero valent iron (nZVI): behavior, transport and impacts on microbial communities. *Science of the Total Environment* 565, 889-901.

- Liu, X., Fan, J.H., Ma, L.M. (2015). Simultaneously degradation of 2, 4-Dichlorophenol and EDTA in aqueous solution by the bimetallic Cu-Fe/O₂ system. *Environmental Science Pollution Research* 22, 1186-1198.
- Marican, A., Durán-Lara, E.F. (2018). A review on pesticide removal through different processes. *Environmental Science Pollution Research* 23, 2051-2064.
- Maithreepala, R.A., Doong, R.A. (2005). Enhanced dechlorination of chlorinated methanes and ethenes by chloride green rust in the presence of copper (II). *Environmental Science & Technology* 39, 4082- 4090.
- McDowall, R., Boyle, C., Graham, B. (2004). Review of emerging, innovative technologies for the destruction and decontamination of POPs and the identification of promising technologies for use in developing countries. Final - GF/8000-02-02-2205. Auckland, New Zealand. 138 p. Disponible en: www.basel.int/techmatters/review_pop_feb04.pdf
- O'Loughlin, E.J., Kemner, K.M., Burris, D.R. (2003). Effects of Ag(I), Au(III), and Cu(II) on the reductive dechlorination of carbon tetrachloride by green rust. *Environmental Science & Technology* 37, 2905-2912.
- Pansu, M., Gautheyrou, J. (2006). Cation Exchange Capacity. In *Handbook of Soil Analysis* (Pp. 709-754). Springer, Berlin, Heidelberg.
- Pirnie, E.F., Talley, J.W. y Hundal, L.S. (2006). Transformation of DDT and its metabolites by various abiotic methods. *Journal of Environmental Engineering ASCE* 132, 560-564.
- Satapanajaru, T., Anurakpongsatorn, P., Songsasen, A., Boparai, H., Park, J. (2005). Using Low-cost Iron byproducts from automotive manufacturing to remediate DDT. *Water Air & Soil Pollution* 175, 361-374.
- Singh, S.P., Bose, P., Guha, S., Gurjar, S.K., Bhalekar, S. (2013). Impact of addition of amendments on the degradation of DDT and its residues partitioned on soil. *Chemosphere* 92, 811-820.
- UNEP, United Nation Environmental Program. (2011). The new POPs under the Stockholm Convention. Disponible en: www.chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx
- US-EPA, US Environmental Protection Agency. (2004). Soil and Waste pH. Method 9045D, Washington, DC.
- US-EPA, US Environmental Protection Agency. (2007a). Ultrasonic Extraction, Method 3550C, Washington, DC.
- US-EPA, US Environmental Protection Agency. (2007b). Semivolatile Organic Compounds, Method 8270D, Washington, DC.
- US-EPA, US Environmental Protection Agency. (2007c). Organochlorine Pesticides by Gas Chromatography, Method 8081B, Washington, DC.
- US-EPA. (2010). Regional Screening Levels (RSL) for Chemical Contaminants at Superfund Sites. Disponible en: www.epa.gov/region9/superfund/prg/
- Velasco, A., Hernández, S., Ramírez, M., Ortiz, I. (2014). Detection of residual organochlorine and organophosphorus pesticides in agricultural soil in Rio Verde region of San Luis Potosi, Mexico. *Journal of Environmental Science and Health Part B* 49, 498-504.
- Velasco, A., Aburto-Medina, A., Shahsavari, E., Revah, S., Ortiz, I. (2017). Degradation mechanisms of DDX induced by the addition of toluene and glycerol as cosubstrates in a zero-valent iron pretreated soil. *Journal of Hazardous Materials* 321, 681-689.
- Weber, J., Halsall, C.J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., Bidleman, T. (2010). Endosulfan, a global pesticide: A review of its fate in the environment and occurrence in the Arctic. *Science of the Total Environment* 408, 2966-2984.
- Xiao, P., Kondo, R. (2013). Degradation characteristics and mechanism of endrin by a white rot fungus, *Phlebia acanthocystis* TMIC34875. *Chinese Journal of Applied Environmental Biology* 19, 119-125.

- Yang, S.C., Lei, M., Chen, T.B., Li, X.Y., Liang, Q., Ma, C. (2010). Application of zerovalent iron (Fe(0)) to enhance degradation of HCHs and DDX in soil from a former organochlorine pesticides manufacturing plant. *Chemosphere* 79, 727-732.
- Yao, F.X., Jiang, X., Yu, G.F., Wang, F., Bian, Y.R. (2006). Evaluation of accelerated dechlorination of p,p-DDT in acidic paddy soil. *Chemosphere* 64, 628-633.
- Zheng, Z., Yuan, S., Liu, Y., Lu, X., Wan, J., Wu, X., Chen, J. (2009). Reductive dechlorination of hexachlorobenzene by Cu/Fe bimetal in the presence of nonionic surfactant. *Journal of Hazardous Materials* 170, 895-901.
- Zitko, V. (2003). Chlorinated pesticides: Aldrin, DDT, endrin, dieldrin, mirex. In *The Handbook of Environmental Chemistry* (Pp. 49-50). Springer-Verlag Berlin Heidelberg.