

Removal of HCH and DDX from historical polluted soils by zerovalent iron technology

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Abstract

This paper presents the remediation of polluted soils with chlorinated pesticides (HCH, DDX) by zerovalent iron technology (ZVI). We performed soil remediation tests with iron (two grinding sizes), three doses, with iron and acetic acid (two doses for each dose of iron and for each type of grinding iron size). In the study was applied 99 tests (samples). The diminishing of HCH and DDX concentrations in treated samples is more significant with the increasing of iron and acetic acid doses, for the same contact time: 99% HCH and 91% DDX for large iron particles and 95% HCH and 82% DDX for small iron particles.

Keywords: POPs, HCH, DDX, soil remediation, ZVI

INTRODUCTION

Persistent organic pollutants (POPs) constitute a large class of organic substances with toxic action and cumulative. Another aspect is the migration in soil and groundwater. They have different physical-chemical properties, which control this behavior. Their sources and pathways for release into the global environment depending on local industrial development and environmental regulations. Stockholm Convention (UNEP, 2001) and its update since 2019 put HCH and DDX on the list of persistent organic pollutants (POPs) [1, 2].

The former industrial production of HCH and DDT still create present pollution problems in many countries including Romania.

Lindane was synthesized for the first time in 1825 by Michael Faraday [3] and deeply used as a broad-spectrum organochlorine insecticide since the 1940s [4,5]. HCH is a monocyclic chlorinated hydrocarbon. Technical HCH is a mixture of various stereo-isomers, gamma-HCH (γ HCH) being the most well-known [6, 7] with application in agriculture as pesticide.

Industrial chlorination of benzene leads to a mixture of about 14% γ HCH and 86% of inactive-isomers: 65÷70% alpha-HCH (α HCH), 14÷15% beta-HCH (β HCH), approximately 7% delta-HCH (δ HCH), 1÷2% epsilon HCH (ϵ HCH) and 1÷2% other components [6,7].

For each ton of lindane 8-12 tons of HCH-residuals were produced and there are 5-10 million tons of HCH-waste which still exist around the world [8, 9].

In the province of Overijssel, Spain around 200000 tons of HCH-contaminated soils have been excavated and treated in the last 20 years from 400000 tons of HCH-contaminated soils and 3500 tons of pure HCH-waste [10,11].

Public concern of environmental and health problems caused by the insecticide 1,1,1-trichloro-2,2-bis(4-chlorophenyl)-ethane (DDT), due to its toxicity, hydrophobicity, persistence, and bioaccumulation in nature, has resulted in global legal restrictions on its production, commercialization, and use [6]. DDT residues and its two major intermediates 1,1-dichloro-2,2-bis(4-chlorophenyl) ethylene; (DDE) and 1,1-dichloro-2,2-bis(4-chlorophenyl) ethane (DDD), are still found in diverse agricultural, urban, and industrial soils [12,13].

Some studies have focused on the remediation of HCHs in the aqueous phase, dealing with groundwater treatments applied in situ [14] or on-site [15÷17]. However, only a few works are found in the literature concerning the remediation of soils contaminated by HCH wastes [18÷20]. The objective of these treatments is the chemical or biological degradation of HCHs. They were carried out to the remediation of soils artificially spiked with HCH isomers and soils with real HCH contamination [21, 22].

In recent decades, the use of the ZVI method to clean up water, soil and, sludge contaminated with DDT and other pesticides has received considerable attention, especially to treat high concentrations of these compounds.

Zero-valent iron (ZVI) technology was studied over the past decade for its potential to remediate a wide variety of environmental contaminants both in superficial and groundwater [23]. The use of ZVI over other metals is a preferred choice due to its high abundance, low cost, and benign environmental impact [23÷25]. Among other pollutants, ZVI showed high efficiency in the treatment of chlorinated organic compounds such as HCH isomers [3, 5, 14, 24÷34].

Most of the reported works are focused on the degradation of lindane and the use of ZVI nanoparticles [3÷5, 24, 26, 27, 29÷32] or the combination of ZVI with other metals, Pd being the most studied [19, 21, 24]. In the presence of ZVI nanoparticles, lindane can be eliminated in 24 hours reaction time when this pollutant is dissolved in water [3] or present in spiked soils [5]. In the case of using bimetallic Pd-Fe nanoparticles [24, 26, 29] or more complex systems, like carbon-supported Cu-ZVI nanoparticles [3] or carboxymethylcellulose Fe/Ni nanoparticles [32], the reaction times for lindane dichlorination can be even decreased. It has been reported that anaerobic conditions favor lindane degradation in the presence of stabilized iron nanoparticles [26], and the temperature has a beneficial effect on the pollutant degradation rate [29], whereas lindane degradation decreases with pH increasing, initial lindane concentration, and in the presence of cations [29]. Several degradation pathways for lindane degradation have been proposed based on the detection of certain reaction intermediates during lindane dichlorination reactions in the presence of ZVI nanoparticles [4, 24, 31, 32].

Although encouraging results in HCH treatment in the presence of these materials have been achieved, the low stability of iron nanoparticles due to aggregation [4, 24, 26, 31] and the unaffordable cost of noble metals like Pd [25] has encouraged the use of ZVI in the form of microparticles during the last years, with lower cost and higher stability [14, 33÷35].

Even though promising results have been obtained with ZVI in the degradation of HCHs in the aqueous phase, the use of this material for soil remediation entails additional problems. The application of ZVI in the form of microparticles on contaminated soils would yield low HCH conversion due to the hindered contact between the solid phases (soil and ZVI microparticles) [36÷38]. Using ZVI nanoparticles for soil remediation is limited by problems of agglomeration and the high cost associated. Furthermore, if HCH granules are present in the soil, a remarkable decrease in the efficiency of the dechlorination treatment is expected, due to the expected poor contact between the two solid phases [39÷41].

The aim of the paper was to investigate removal of HCH and DDX from historical polluted soils using zerovalent iron technology with two sizes particles of zerovalent iron.

EXPERIMENTAL PART

Tests for pollutants removal

Two different soil samples were taken for physical-chemical tests: S1 (0÷30 cm depth) and S2, sample collected from 0÷200 cm depth, near to HCH isomers landfill (10 m), from a peasant yard. Both samples were collected in the proximity of the former chemical pesticides plant.

Soil samples were dried, grinded, and sieved. Finally, particle size was below 1.5 mm. Brown bottles were used and orbital shaker. The experiments of soil treatment using ZVI method were performed in the following conditions: were tested 9 specific operating conditions for each contact time, tested at 2 types particle size of iron (ips). Each experimental test was performed for 4 different period (7, 14, 21 and 28 days). Thus, were performed soil tests with iron (two grinding size) at three doses, with

iron and acetic acid (two doses for each dose of iron and for each type of grinding iron size). In total, was performed 99 tests.

In table 1 are presented the main operated conditions for each test (each bottle contains 50 g of dried soil and 150 ml of water).

Table 1. Experimental parameters for micro-pollutants removal

Test no.	Contact times (days)	Fe doses (% weight to d.w.)	Glacial acetic acid doses (mL/100 g soil sample)
1	7, 14, 21 and 28	1	-
2	7, 14, 21 and 28	2	-
3	7, 14, 21 and 28	5	-
4	7, 14, 21 and 28	1	0.5
5	7, 14, 21 and 28	1	1.0
6	7, 14, 21 and 28	2	0.5
7	7, 14, 21 and 28	2	1.0
8	7, 14, 21 and 28	5	0.5
9	7, 14, 21 and 28	5	1.0

Analytical methods

The analytical determination of HCH isomers and DDX concentrations was carried out in accordance with SR ISO 10382 [42], using an Agilent 8890A (Agilent Technologies) equipped with TR-1701 column (30m x 250 μ m x 0.250 μ m) and μ ECD detector. The soil samples were dried in open space, grounded and homogenized before extraction with hexane. 1 μ L of extract was injected at 260 $^{\circ}$ C and chromatographically separated by maintaining the oven at 50 $^{\circ}$ C for 3 minutes, then raising the temperature with 10 $^{\circ}$ C/minute up to 260 $^{\circ}$ C, where the temperature was maintained for 15 minutes.

RESULTS AND DISCUSSION

Initial organochlorinated concentrations in soil samples were as following:

S1: 3643 α HCH μ g/kg dry weight (d.w.), 5223 β HCH μ g/kg d.w., 4377 γ HCH μ g/kg d.w., 1988 δ HCH μ g/kg d.w., Σ HCH = 15231 μ g/kg d.w.; 79.4 DDE μ g/kg d.w., 86.8 DDD μ g/kg d.w., 97.3 DDT μ g/kg d.w., Σ DDX = 263.5 μ g/kg d.w.; initial dry substances 95%.

S2: 1989 α HCH μ g/kg d.w., 30823 β HCH μ g/kg d.w., 618 γ HCH μ g/kg d.w., 591 δ HCH μ g/kg d.w., Σ HCH = 34022 μ g/kg d.w.; 131000 DDE μ g/kg d.w., 62000 DDD μ g/kg d.w., 611230 DDT μ g/kg d.w., Σ DDX = 804230 μ g/kg d.w.; initial dry substances 86%.

First step of the results analysis was to find the residual concentrations of HCH isomers and DDX concentrations during 28 days of ZVI treatment (sampling after 4, 14, 21 and 28 days).

S1 experimental results

The experimental data are presented in table 2. In case of first sampling point, test #9 shows the lower values both for HCH isomers and DDX after 28 days: Σ HCH = 283 μ g/kg d.w. and Σ DDX = 38 μ g/kg d.w. comparing with test 1 (Σ HCH = 4534 μ g/kg d.w. and Σ DDX = 145 μ g/kg d.w.) which means that acid add and high doses of zerovalent iron are determinant factors for better micro-pollutants removal.

The tendency of HCH and DDX concentrations is increasing because of better solubilization of pollutants during the time: Σ HCH = 32 μ g/kg d.w. after 7 days contact time and Σ HCH = 283 μ g/kg d.w. for the same test 9. Similarly, in case of DDX the total concentration raised from 13 μ g/kg d.w. to 38 μ g/kg d.w.

For the same S1, the evolution of HCH and DDX concentrations is similar for the same doses of zerovalent iron but with lower particle size.

Table 2. Residual micro-pollutants concentrations depending on performing test for S1 samples

Iron particles dimension, μm	Contact time (days)	Test 1		Test 9	
		ΣHCH , $\mu\text{g/kg d.w.}$			
465	7	988	58	32	13
	14	1516	72	39	14
	21	4519	140	193	29
	28	4534	145	283	38
215	7	5074	133	715	29
	14	4622	190	634	69
	21	6332	135	788	44
	28	6015	128	749	42

In case of test 9, the concentrations were lower than test #1 for both micro-pollutants categories: $\Sigma\text{HCH} = 749 \mu\text{g/kg d.w.}$ and $42 \mu\text{g/kg d.w.}$ and $\Sigma\text{DDX} = 6015 \mu\text{g/kg d.w.}$ and $128 \mu\text{g/kg d.w.}$ respectively.

The influence of particle size is significant: in the same experimental conditions of test #9, the concentrations of HCH and DDX were higher in case of zerovalent iron with smaller particle size: $\Sigma\text{HCH} = 283 \mu\text{g/kg d.w.}$ (465 μm particle size) vs. $749 \mu\text{g/kg d.w.}$ (215 μm particle size) and $\Sigma\text{DDX} = 38 \mu\text{g/kg d.w.}$ (465 μm particle size) vs. $42 \mu\text{g/kg d.w.}$ (215 μm particle size).

Half particle size of zerovalent iron do not lead to decrease of micro-pollutants concentration but on contrary in case of these tests probably because of competition between a higher active particle surface and the clogging phenomena.

The removal efficiencies of HCH isomers and DDX for first sampling location (figures 1 and 2) increased with iron doses and acetic acid from test 1 to test 9 and the values were slightly higher for 465 μm particle size dimension (99% efficiency for test 9, 81% efficiency for test 1 for ΣHCH , figure 1 and 91% efficiency for test 9, 82% efficiency for test 1 for ΣDDX , figure 2). The acetic acid has a determining role, starting with test 4.

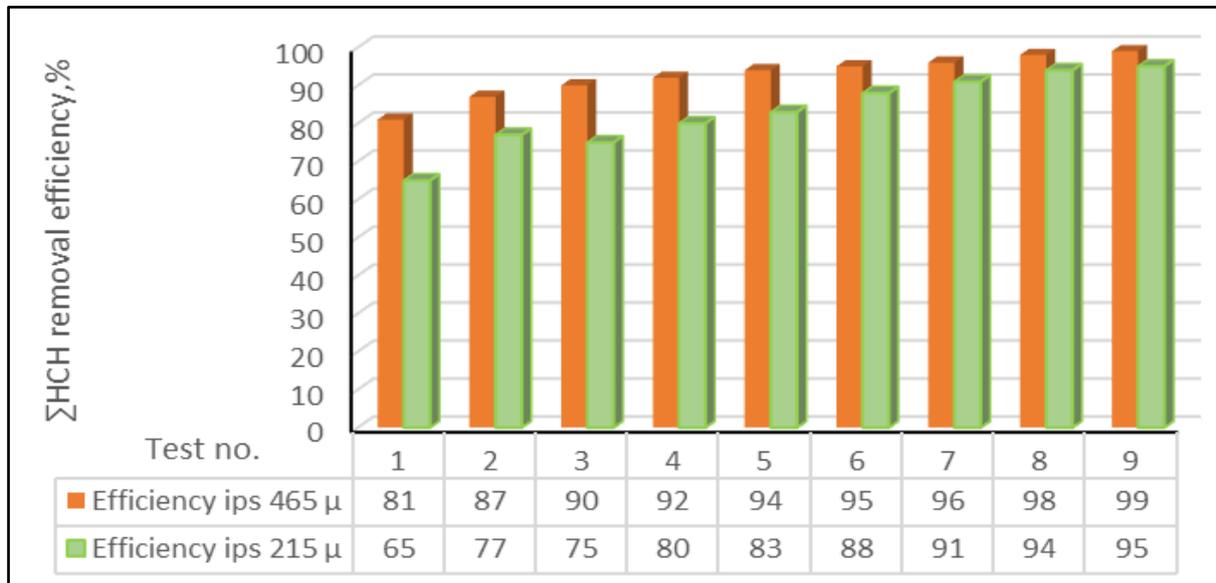


Fig. 1. Removal efficiency of HCH for all nine tests and two different ips for S1 experiments

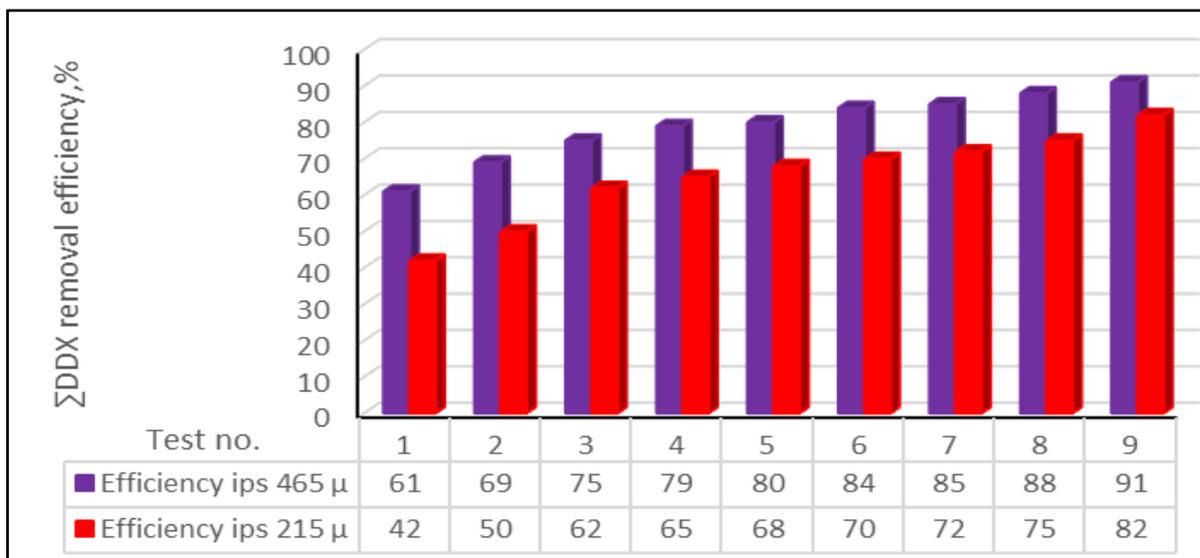


Fig. 2. Removal efficiency of DDX for all nine tests and two different ips for S1 experiments

The analyses of residual concentration for HCH isomers and DDX compounds (figures 3 and 4) emphasize the following resistance to the treatment: β HCH > α HCH > γ HCH > δ HCH (figure 3); DDT > DDD > DDE (figure 4).

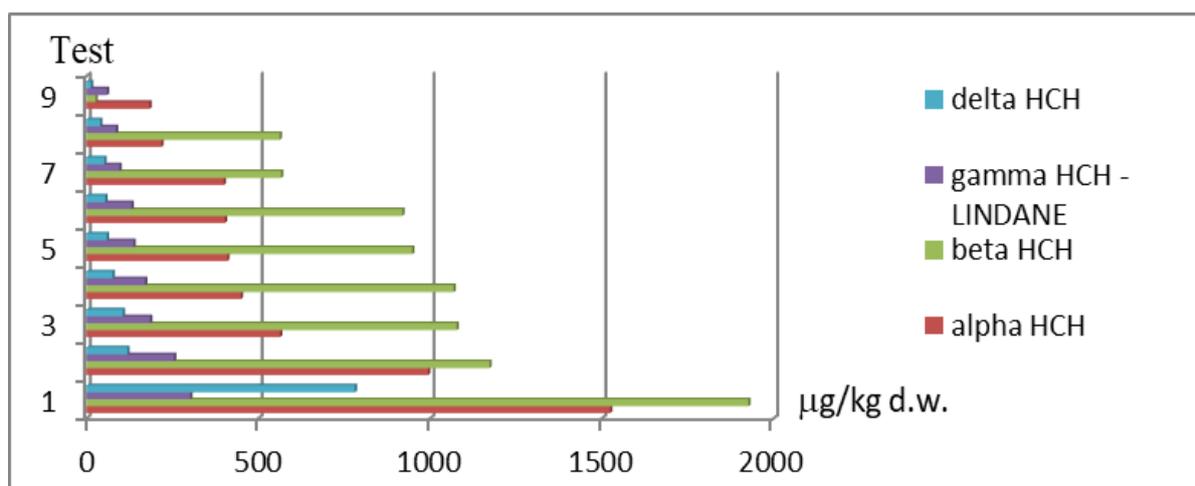


Fig. 3. HCH residual concentration after 28 days of ZVI treatment (ips 465 μ) in S1 samples

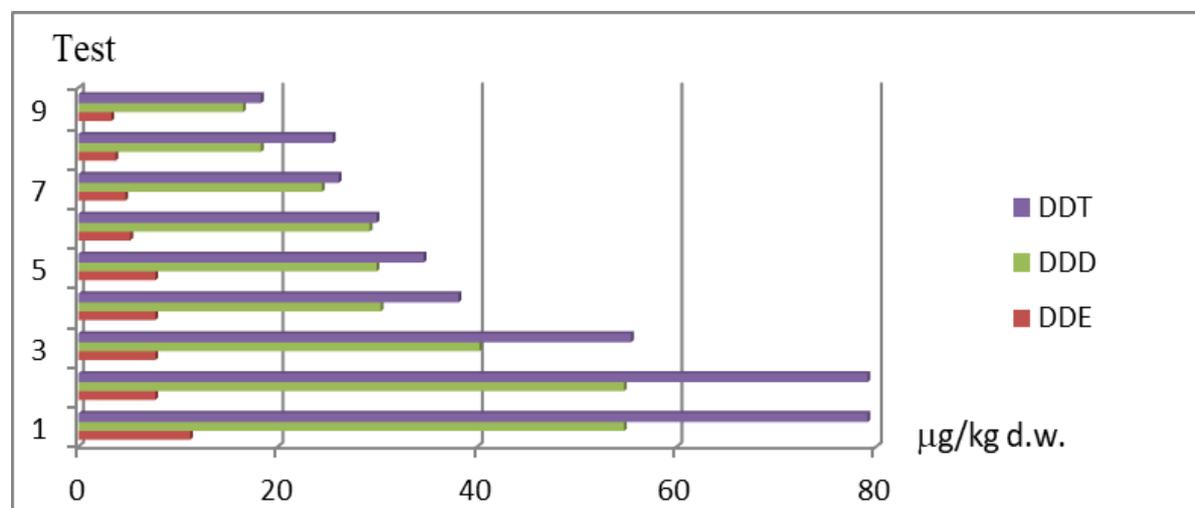


Fig. 4. DDX residual concentrations after 28 days of ZVI treatment (ips 465 μ) in S2 samples

S2 experimental results

In case of the S2 sampling point, test 9 shows the lower values both for HCH isomers and DDX after 28 days: $\sum\text{HCH} = 1014 \mu\text{g/kg d.w.}$ and $\sum\text{DDX} = 5768 \mu\text{g/kg d.w.}$ comparing with test 1 ($\sum\text{HCH} = 12480 \mu\text{g/kg d.w.}$ and $\sum\text{DDX} = 41931 \mu\text{g/kg d.w.}$).

The tendency of HCH and DDX concentrations is decreasing: $\sum\text{HCH} = 1610 \mu\text{g/kg d.w.}$ after 7 days contact time and $\sum\text{HCH} = 1014 \mu\text{g/kg d.w.}$ for the same test 9. Similarly, in case of DDX the total concentration raised from $6732 \mu\text{g/kg d.w.}$ to $5768 \mu\text{g/kg d.w.}$. Because of the different structure and composition of these samples the evolution of treatment process is different for 28 days contact time but is similar for 14 and 21 days.

For the sampling point 2, in case of test 9, the concentrations were lower than test 1 for both micro-pollutants categories: $\sum\text{HCH} = 973 \mu\text{g/kg d.w.}$ and $11981 \mu\text{g/kg d.w.}$ and $\sum\text{DDX} = 5537 \mu\text{g/kg d.w.}$ and $40254 \mu\text{g/kg d.w.}$ respectively.

The influence of particle size is significant: in the same experimental conditions of test 9, the concentrations of HCH and DDX were smaller in case of zerovalent iron with smaller particle size after 28 days: $\sum\text{HCH} = 1014 \mu\text{g/kg d.w.}$ ($465 \mu\text{m}$ particle size) vs. $973 \mu\text{g/kg d.w.}$ ($215 \mu\text{m}$ particle size) and $\sum\text{DDX} = 5768 \mu\text{g/kg d.w.}$ ($465 \mu\text{m}$ particle size) vs. $5537 \mu\text{g/kg d.w.}$ ($215 \mu\text{m}$ particle size) but the evolution is ascending if we compare the results for 21 days.

The following date is a synthesis of removal efficiencies of HCH and DDX for each test and sampling point (table 3).

Table 3. Residual micro-pollutants concentrations depending on performing test for S2 samples

Iron particles dimension, μm	Contact time (days)	Test 1		Test 9	
		$\sum\text{HCH}$, $\mu\text{g/kg d.w.}$			
465	7	7926	31742	1610	6732
	14	13714	669517	3629	28359
	21	27393	78754	2767	43221
	28	12480	41931	1014	5768
215	14	13165	642736	3483	27225
	21	26297	75604	2656	41492
	28	7610	40254	1993	5537

The evolution of HCH and DDX residual concentrations was quite similar in case of S2 samples (figures 5 and 6).

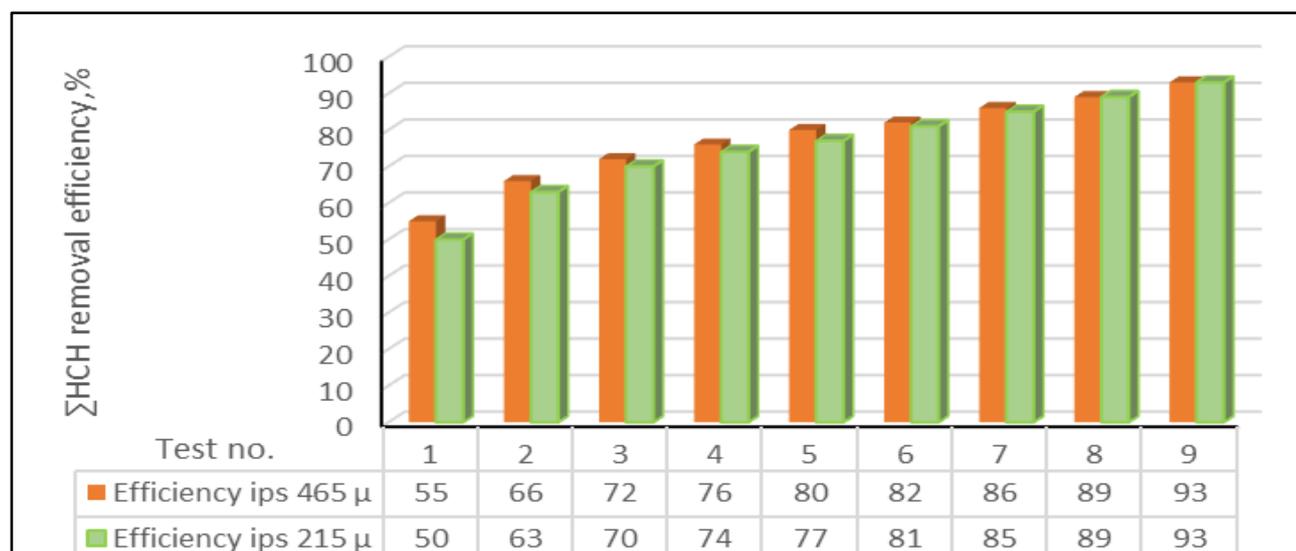


Fig. 5. Removal efficiency of HCH for all nine tests and two different ips for S2 experiments

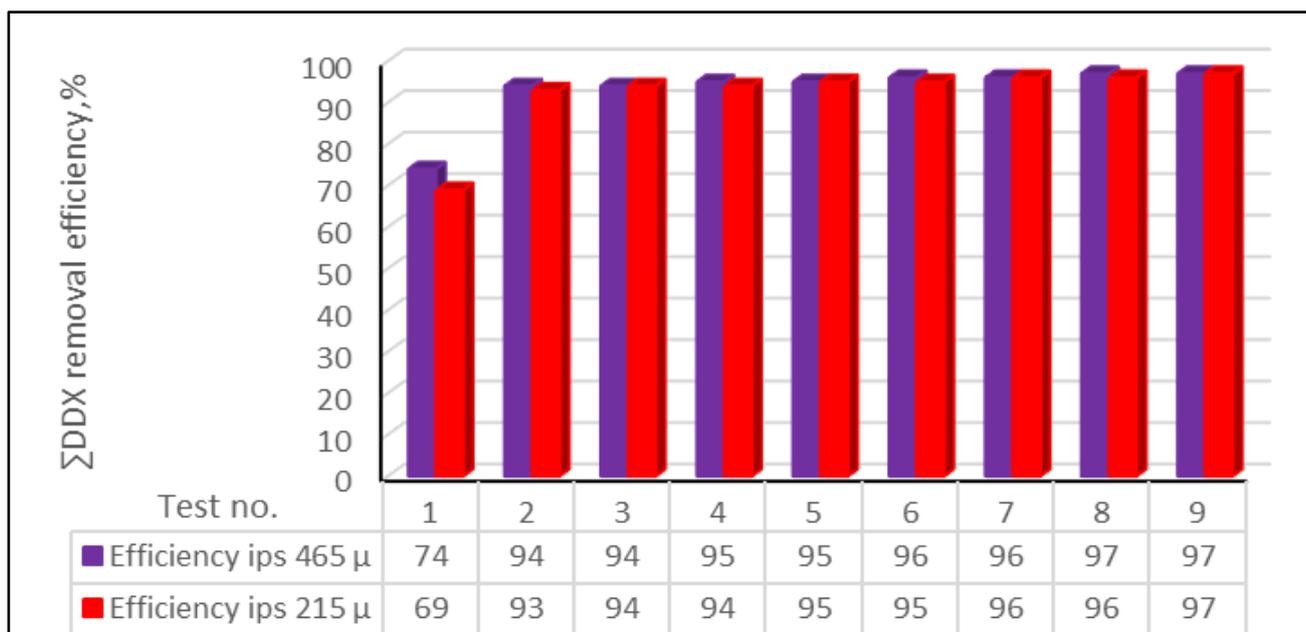


Fig. 6. Removal efficiency of DDX for all nine tests and two different ips for S2 experiments

The most important difference was referring to the very close or identical values of removal efficiencies. The best results were for test 9 in case of $\Sigma\text{HCH}=93\%$ for both micro-pollutants classes and $95\div 97\%$ for tests 5÷9 in case of ΣDDX .

CONCLUSIONS

Considering the aspects related to POPs removal by ZVI technology the following aspects must be emphasized. The heterogeneity of contaminated soil (non-uniformity of POPs distribution on/into soil particles) influences the pollutants concentrations levels.

Nonlinear variation of HCH isomers and DDX concentrations in time for the treated soil samples was observed. Decreasing of ΣHCH and ΣDDX contents in treated soil, from both locations was correlated with the increasing of iron and acetic acid doses, for the same contact time.

The average reduction yields of POPs concentrations (ΣHCH , ΣDDX) were high for all experiments (over 80-95% for DDX and HCH respectively).

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