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Dichloro-diphenyl-trichloroethane removal via nano zero-valent iron: determination of degradation mechanism using response surface methodology

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ABSTRACT

Most organochlorine pesticides (OCPs) are considered to be persistent organic pollutants (POPs) as they have characteristics which are resistant to biological degradation and are subject to bioaccumulation. Dichloro-diphenyl-trichloroethane (DDT) continues to be released into the environment because it is the main ingredient of various pesticides, even though its direct use is prohibited. In contrast to the works in the literature using very high concentrations of DDT, this study was carried out with low DDT concentrations that can be found in water. This study aimed to reveal the mechanism for removal by observing whether, other than adsorption, the mechanism of dechlorination was effective. In addition to scanning the GC-MS library, the effects of the variables of nano zero-valent iron (nZVI) concentration, initial DDT concentration and contact time were investigated. The study also examined the highest initial DDT concentration that could be used to achieve an effluent concentration below the carcinogenic effect limit for DDT of 0.23 μg/L. The highest concentration that could be degraded by nZVI was 88.33 mg/L. A contact time of 48.6 min and 550 mg/L adsorbent concentration were required to achieve the carcinogenic effect limit using nZVI.

Keywords: POPs; DDT metabolites; nZVI; OCPs

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1. Introduction

Chemical substances used against harmful insects, plant pathogens and weeds are generally called pesticides. Although pesticides were seen as life-saving products in the past, they have been shown to have significant toxic effects on humans and other living organisms, and especially, because of their persistence and accumulation in oil, by entering the food chain. These pesticide residues, which are resistant to biological degradation, can be transported long distances by release into the atmosphere, where they can persist for a long time. Because of their characteristics, it can be said that the health effects of these substances are not limited only to those working in the agricultural sector. In addition to pesticides, the Stockholm Convention prohibits the use and release of certain non-degradable industrial organic pollutants resulting from combustion used in insulation materials, including dioxins, furans and polychlorinated biphenyls (PCBs) [1].

Although the release of persistent organic pollutants (POPs) has been reduced due to restrictions, their release is still important over the long term due to their longer half-life. Although direct use of dichloro-diphenyl-trichloroethane (DDT) is prohibited, environmental release of DDT is continuing due to the fact that DDT is the main ingredient of various pesticides which have been in use since 2011 and are still being used. Dicofol is a derivative pesticide containing 0.3%–14.3% DDT that was actively used until it was banned in 2011 [2]. Moreover, according to a study conducted in Africa in 2017, although the use of DDT in agricultural areas has been banned, the high level of DDT in the sera of rats and mother's milk demonstrates that it has been used agriculturally [3].

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Although environmental remediation of POPs is mostly observed in environmental samples, studies on adsorption, chemical oxidation, anaerobic treatment, electro-oxidation and membrane processes in terms of water pollution are increasing daily [4–12]. One of the processes used in the removal of non-biodegradable pollutants is the use of nanoparticles and with the development of nanotechnology, studies are being carried out in increasing number. Titanium oxide-based, metal oxide-based and carbon-based nanoparticles are among the known nanoparticles that have been used in environmental studies [13–20]. Studies have been conducted on soil remediation, especially for non-degradable organic pollutants such as organic solvents, organochlorine pesticides and PCBs as well as heavy metals. With respect to water solubility, there are studies in the literature about the removal of DDT at high concentrations not found in environmental settings using nano zero-valent iron (nZVI) [16,21–25].

Considering the significant effects of DDT on human and environmental health, the aim was to reveal the mechanism of removal of this contaminant from the water via nanoparticles. This study aimed to investigate and optimize the removal of DDT using nZVI in terms of contact time, nZVI concentration and DDT concentration and to reveal the removal mechanism of DDT from an aqueous medium. Furthermore, the study aimed to calculate the highest possible initial DDT concentration which could provide an effluent DDT concentration at the carcinogenic effect limit of 0.23 μg/L [26]. After the treatment was investigated, by-products were also identified and the status of other pollution was determined.

2. Materials and methods

2.1. Materials

Iron sulfate ($FeSO_4.7H_2O$), sodium borohydride ($NaBH_4$) and ethanol, provided by Merck, were used for nZVI synthesis. Polyethylene glycol (PEG, 2000), purchased from Sigma-Aldrich, was also used for gas chromatography (GC) analysis. Acetone and methanol (Merck gas chromatography-electron capture detector [GC-ECD] Quality) and solid-phase extraction (SPE) cartridges were used for the determination of pesticides (Dionex - SolEx™ C18). Pesticide standards p,p′-DDT, p,p′-DDD and p,p′-DDE were supplied from AccuStandards and Tetrachloro-m-xylene was used as an internal standard.

2.2. Method

2.2.1. nZVI synthesis

Synthesis of nZVI can be performed by reacting a solution containing iron chloride or iron sulphate with a solution containing sodium borohydride in accordance with Eqs. (1) and (2).

$$4\ Fe^{2+} + BH_4^- + 3\ H_2O \rightarrow 4\ Fe^0 + H_3BO_3 + 7\ H^+ \tag{1}$$

$$Fe^0 + 2\ H^+ \rightarrow Fe^{2+} + 7H_2 \uparrow \tag{2}$$

The borohydride method was modified in our previous study [27]. According to the modified method, iron sulphate prepared at a concentration of 0.03 M by 17.25% ethanol was used for nZVI synthesis. The borohydride solution was added at a flow rate of 25 mL/min BH_4. The particle size and zeta potential of the nanoparticles synthesized by this method were measured as 88.2 nm and –15.05 mV, respectively (Fig. 1). The isoelectric point was found at pH 7.8, which is consistent with the literature [28,29]. Similar chain structure has been observed in the literature [28,30,31]. This nZVI chain structure originates from the magnetic characteristic [30,32]. The XRD pattern of the synthesized nZVI is shown in Fig. 2. A single peak was obtained at 44.7° 2θ degree in the sample, indicating zero-valent iron.

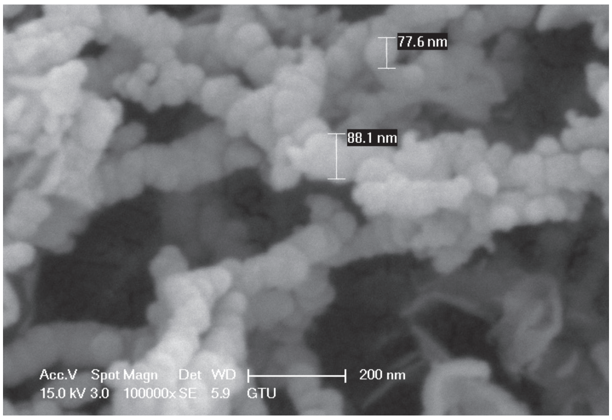

Fig. 1. SEM imaging of synthesized nZVI.

2.2.2. DDT analysis

Before injection for GC/ECD analysis, the samples were concentrated using SPE, which was applied as in the previous work [33]. A gas chromatograph (Clarus 500, PerkinElmer) with an ECD was used with the HP-5MS column having a length of 30 m, an inner diameter of 0.25 mm and a filler thickness of 250 μm via splitless injection. The carrier gas was high-purity helium with a flow rate of 1.2 mL/min, and high-purity nitrogen with a flow rate of 30 mL/min was used as a makeup gas. The method steps were as follows: (1) the injector temperature was set at 225°C and the detector temperature at 300°C, (2) the oven starting temperature was 50°C and after waiting for 1 min, the temperature was raised from 50°C to 170°C at 25°C/min and then from 170°C to 300°C at 5°C/min and held for 2 min at 300°C [34].

2.3. Response surface methodology

Response surface methodology (RSM) is a statistical technique that reveals the effect of process variables. Instead of carrying out excessive analyses for the systems affected by the different variables, it reduces the combinations of the variables to the minimum, revealing the optimum conditions within the variables.

In order to observe the effects of the variables and to find the optimum conditions, the second-degree polynomial regression model shown in Eq. (3) was applied.

$$y = a_0 + \sum a_i x_i + \sum a_{ij} x_i x_j + \sum a_{ii} x_i^2 \tag{3}$$

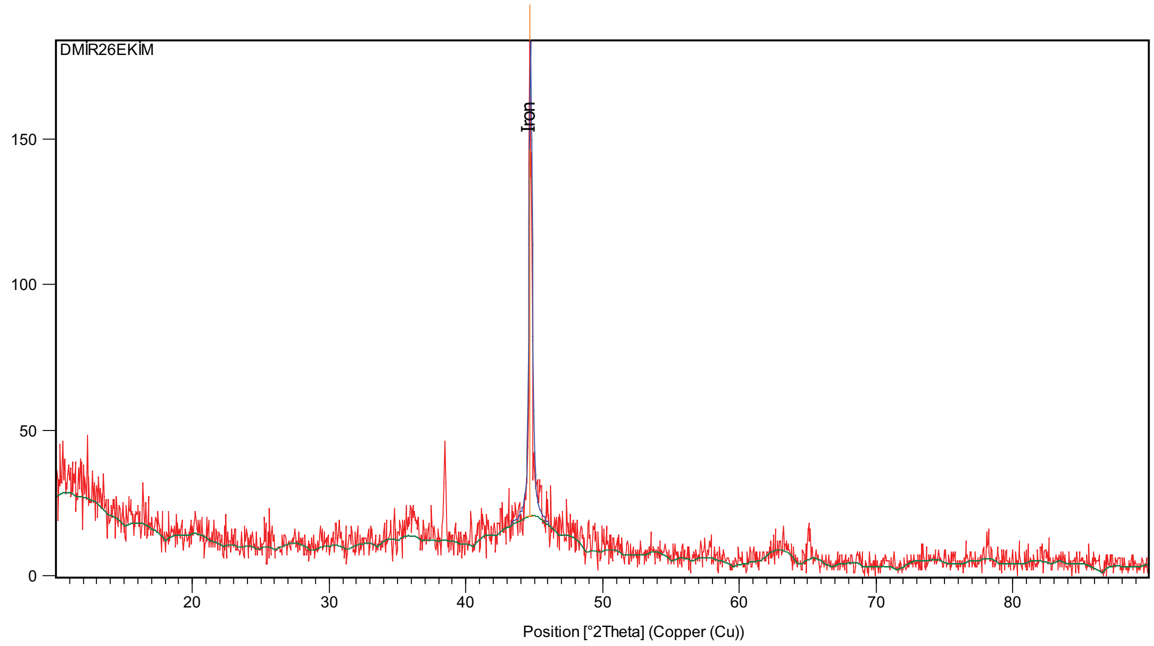

Fig. 2. XRD pattern of synthesized nZVI.

Here, y represents the response variables, a_o, the constant, a_{ij}, a_{ii} and a_i, the linear coefficients and x_i and x_j, the independent variables. The variables are encoded in Eq. (4).

$$\alpha = \frac{x_i - x_0}{\Delta x} \tag{4}$$

Here, α is the coded value of the independent variables, x_i is the actual value, x_o is the actual value at the midpoint, and Δx is the change in the variable x_i.

2.4. Experimental studies

Synthetic samples with DDT at concentrations of 5-250 µg/L were used in the optimization studies. In order to ensure tightness, all studies were performed using 250 mL amber glass serum bottles with Teflon lids. As a result of the literature search, it was observed that the concentration of 1 mg/L or higher had been used as the input concentration in the studies conducted with nanoparticles and water for pesticide removal [16,21–25]. In this study, the highest water soluble concentration of 250 µg/L of DDT was chosen. The experiment sets were carried out using an orbital mixer placed in the incubator. From the literature research, it was determined that changes in pH and ORP had been observed depending on the reaction time [35]. Thus, changes of pH and ORP were observed at different reaction times and at different inlet pH values.

3. Results and discussion

3.1. Effects of RSM variables on DDT removal

In order to determine the effect of nZVI on DDT removal and its mechanism in wide spectrum research, RSM was used with the matrix established to investigate the reaction time, the initial DDT concentration and the effect of the concentration of nZVI used. The details of the matrix and coded factors can be found in Table 1. As a result of our previous study, the effect of pH on DDT removal was not added as an independent variable [33]. According to our study, there was no significant change in removal efficiency over the wide pH range of pH 4–pH 10 [33]. Moreover, it was found that no ORP change was observed after 60 min, so the work was adjusted to a maximum reaction time of 61 min [33]. The lowest reaction time was chosen as 1 min. According to Eq. (4), α = ±2 and the longest reaction time was calculated as 61 min. The maximum initial DDT concentration was selected as approximately 250 µg/L, depending on the maximum water-soluble DDT concentration [36,37]. The lowest initial DDT concentration was selected as 10 µg/L, since the DDT and its metabolites were not expected to be below detection limits in the output samples.

Table 1
Working matrix

Independent variables	Coded factors					
	α	–2	–1	0	+1	+2
Reaction time, min	x_1	1	16	31	46	61
nZVI concentration, mg/L	x_2	50	175	300	425	550
Initial DDT concentration, µg/L	x_3	10	70	130	190	250

Three factors at five levels were chosen for DDT removal optimization and the factors coded according to Eq. (4) are given in Table 1. The coded factors for the study and the RSM responses are given in Table 2.

The effluent DDT concentration and the DDD and DDE concentrations were measured in the effluent samples. These results were evaluated as different responses in RSM and

Table 2
Coded factors for DDT removal via nZVI and RSM responses

Run	Reaction time	nZVI concentration	Initial DDT concentration	Effluent DDT concentration	DDT removal efficiency %	Eff. DDD concentration µg/L	Eff. DDE concentration µg/L
	x_1	x_2	x_3		y_1	y_2	y_3
1	–1	–1	–1	16.761	75.97	0.793	0.38
2	1	–1	–1	9.877	85.84	1.141	2.608
3	–1	1	–1	11.917	82.91	1.224	0.447
4	1	1	–1	3.065	95.61	0.535	1.562
5	–1	–1	1	85.746	54.98	1.82	0.808
6	1	–1	1	38.027	80.04	1.416	3.354
7	–1	1	1	56.789	70.18	2.916	1.853
8	1	1	1	24.469	87.15	1.132	1.567
9	–2	0	0	80.041	38.75	1.679	0.115
10	2	0	0	15.348	88.25	1.072	4.51
11	0	–2	0	27.693	78.81	0.528	1.877
12	0	2	0	11.702	91.04	0.8	1.758
13	0	0	–2	0.389	96.46	0.365	0.222
14	0	0	2	74.854	69.9	3.31	5.645
15	0	0	0	24.16	81.51	1.233	0.98133
16	0	0	0	24.832	81	1.107	1.0035
17	0	0	0	24.587	81.18	1.221	1.017
18	0	0	0	24.619	81.16	1.2	1.101
19	0	0	0	24.154	81.52	1.159	1.104
20	0	0	0	24.522	81.23	1.187	1.019

the graphs were drawn via the STATISTICA 8.0 program. Variance analysis (ANOVA) was carried out via Excel in order to investigate the statistical significance. Based on the ANOVA results, a polynomial equation was formed.

The DDT removal efficiency (y_1) was given via surface graphs according to the selected variables (Fig. 3). Fig. 3(a) shows the effect of reaction time (x_1) and nZVI concentration (x_2) on the DDT removal efficiency for the $\alpha = 0$ position of DDT concentration (x_3) corresponding to 130 µg/L and it can be seen that the effect of the concentration of nZVI (x_2) is considerably lower than the effect of the reaction time. As the reaction time increased, the removal efficiency increased from 40% ((–2, –2):(x_1, x_2)) to 95% ((+2, +2):(x_1, x_2)). For the reaction time at the point $x_1 = -0.5$ (23.5 min), removal efficiency could be increased from 70% to 80%, even if the concentration of nZVI was increased from a concentration of 50 to 550 mg/L. Approximately 40% of the DDT could be removed with a 1 min reaction time at point $x_1 = -2$. It was observed that the reaction time influenced the removal efficiency could be increased from 40% to 80% in parallel with the nZVI concentration at point $x_1 = -0.5$ (23.5 min).

In Fig. 3(b), the effect of reaction time (x_1) and the initial DDT concentration (x_3) can be seen at the point $\alpha = 0$ for nZVI concentration (300 mg/L). As expected, the increase in the reaction time (x_1) affected the DDT removal positively, whereas the increase in the initial DDT concentration (x_3) had a negative effect. A removal efficiency of higher than 80% was obtained as the reaction time increased, while at the lowest reaction time (1 min [$\alpha = -2$ for x_1]), the removal rate was about 20% for the highest initial DDT concentration ($\alpha = +2$ for x_3). At the points at which reaction time was higher than 40 min ($\alpha = +0.6$ for x_1), the removal efficiency was above 80%, whereas no significant change was observed with increase in reaction time. In addition, for initial DDT concentrations below 130 µg/L ($\alpha = 0$ for x_3), removal efficiencies higher than 90% were obtained, while for DDT concentrations higher than 130 µg/L, the removal efficiencies did not exceed 90% (Fig. 3(b)).

The effect of the nZVI concentration (x_2) and the initial DDT concentration (x_3) on DDT removal at the point $\alpha = 0$ for the reaction time (x_1) is shown in Fig. 3(c). Similar to Fig. 3(b), the increase in the concentration of nZVI (x_2) affected the DDT removal positively, whereas the increase in the initial DDT concentration (x_3) affected it negatively. It can be understood from the surface graph that the removal rate could not exceed 90% for cases where the initial DDT concentration was higher than 130 µg/L. Variance analysis was performed in accordance with the results in Table 2, and the results are given in Table 3. The regression coefficient (R^2) was obtained as 0.984, and according to these results, the second-order equation (Eq. (5)) was obtained at a 95% confidence interval.

$$y_1 = 81.424 + 10.225x_1 + 3.968x_2 - 6.319x_3 - 4.363x_1^2 \quad (5)$$

The coefficients that are effective according to Table 3 are x_1, x_2, x_3 and x_1^2. It is seen that the three selected independent variables are effective in DDT removal efficiency. The reaction time (x_1) and the concentration of nZVI (x_2) directly affect the recovery efficiency, while the initial DDT concentration

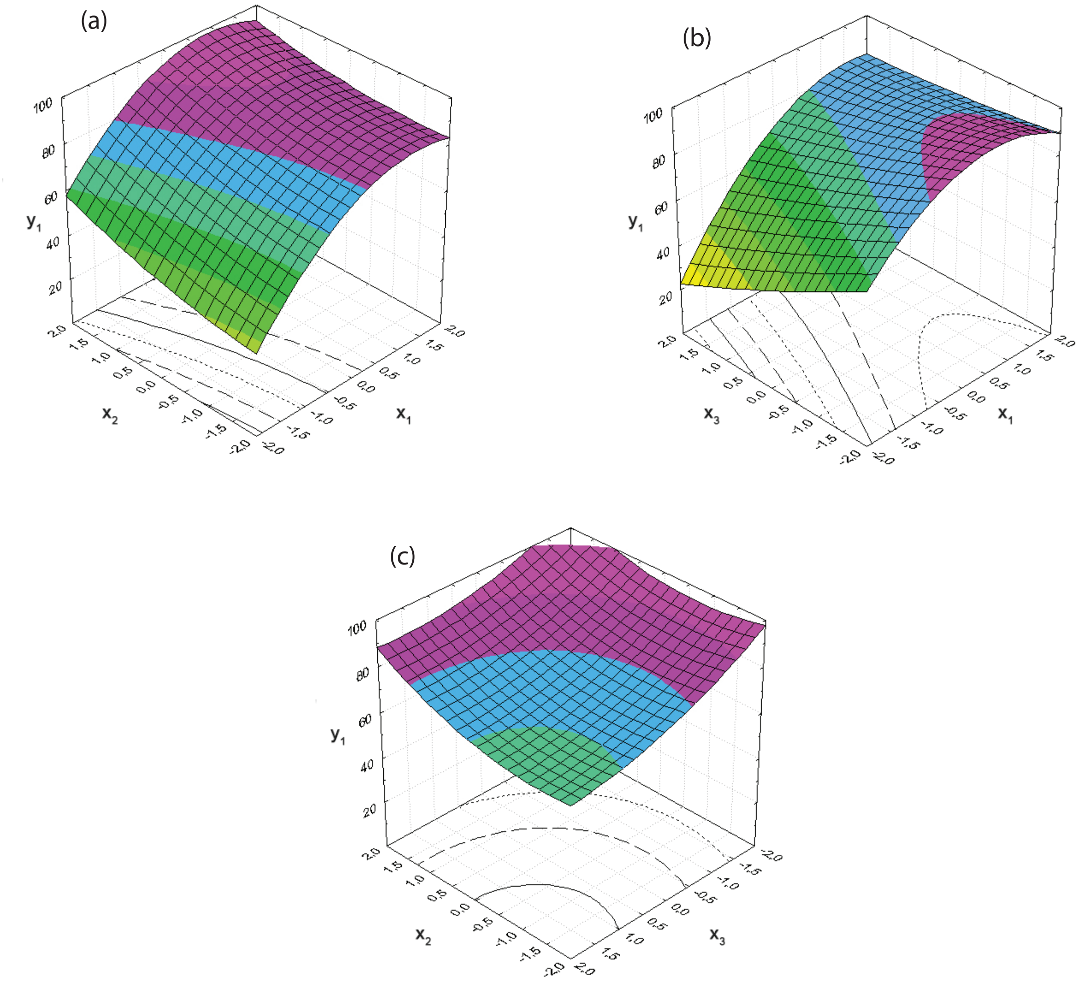

Fig. 3. DDT removal efficiency (y_1) depending on reaction time (x_1), nZVI concentration (x_2) and initial DDT concentration (x_3).

Table 3
Variance analysis (ANOVA) of DDT removal rate

	Coefficients	Standard error	*t* Stat	*p*-Value	Importance
Intersection	81.424	1.306	62.332	2.74 E-14	Very significant
x_1	10.225	0.819	12.488	2.01 E-07	Significant
x_2	3.968	0.819	4.846	0.60 E-03	Very significant
x_3	–6.319	0.819	–7.717	1.61 E-05	Very significant
$x_1 x_2$	–0.658	1.158	–0.568	0.583	–
$x_1 x_3$	2.433	1.158	2.101	0.062	–
$x_2 x_3$	0.7	1.158	0.605	0.559	–
x_1^2	–4.363	0.653	–6.680	5.50 E-05	Very significant
x_2^2	0.993	0.653	1.521	0.159	–
x_3^2	0.557	0.653	0.853	0.414	–

(x_3) affects it in reverse ratio and these findings overlap with the data obtained from the surface graphs.

Surface plots of the DDD concentration (y_2) in the effluent samples are given in Fig. 4. Fig. 4(a) shows the effect of the reaction time (x_1) and the concentration of nZVI (x_2) on the DDD concentration at the point $\alpha = 0$ which corresponds to the initial DDT concentration (x_3) of 130 µg/L. At the point $\alpha = –0.5$ for nZVI (x_2) (240 mg/L), the DDD concentration in the effluent increased as the reaction time increased. However, after the point $\alpha = 0$ for nZVI concentration (300–550 mg/L), the DDD concentration decreased with the increasing reaction time (x_1). This indicated that an nZVI

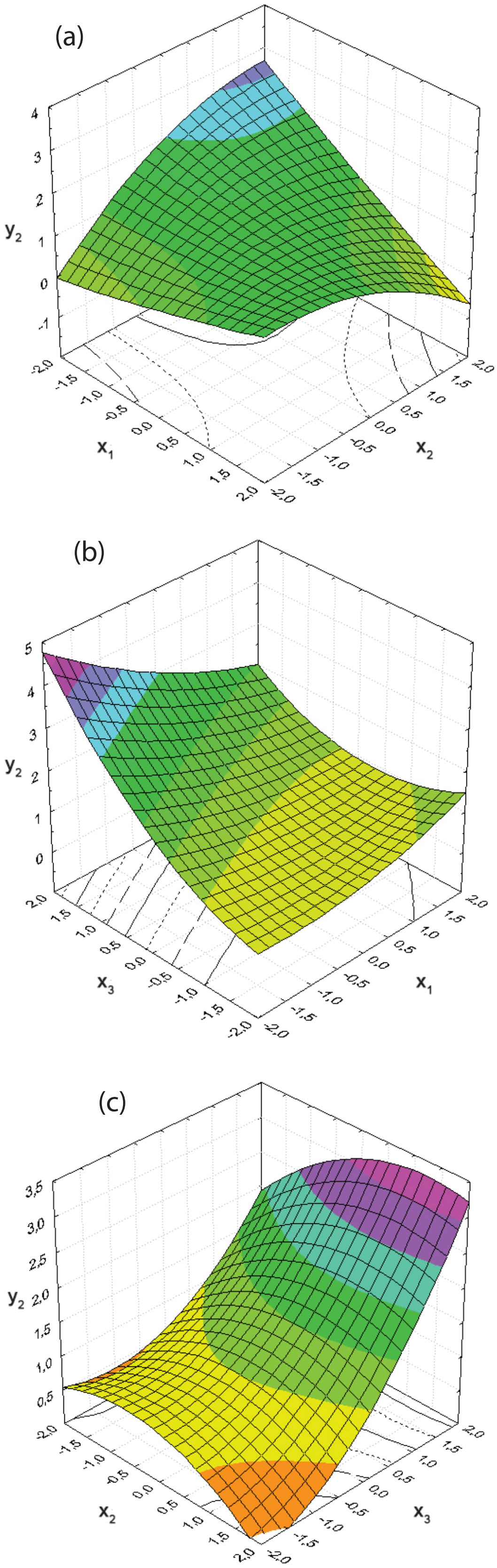

Fig. 4. Effluent DDD concentration (y_2) depending on reaction time (x_1), nZVI concentration (x_2) and initial DDT concentration (x_3).

concentration higher than 300 mg/L assists in the degradation of DDD, which is the oxidative product of DDT.

Fig. 4(b) shows the effect of the reaction time (x_1) and the initial DDT concentration (x_3) on the DDD concentration at the point $\alpha = 0$ which corresponds to 300 mg/L nZVI concentration (x_2). At low reaction times ($\alpha < 0$), the concentration of DDD increased as the concentration of DDT (x_3) increased, and as the reaction time (x_1) increased, the formation of DDD decreased. This indicated that DDD was oxidized as a pollutant in higher initial DDT concentrations.

In the surface graph given in Fig. 4(c), the DDD concentration (y_2) changes regarding the nZVI concentration (x_2) and the initial DDT concentration (x_3). It was observed that the DDD concentration decreased as the concentration of nZVI increased (x_2), but decreased at higher initial DDT concentrations (x_3) at the point $\alpha = +1$ (190 mg/L).

It can be inferred that as the initial DDT concentration (x_3) increased, its oxidative product DDD was oxidized by nZVI as a new pollutant in the system.

Variance analysis was performed on the obtained data and the results are given in Table 4. The regression coefficient (R^2) was obtained as 0.974, and the second-order equation (Eq. (6)) was obtained at a 95% confidence interval.

$$y_2 = 1.204 - 0.235\,x_1 + 0.593\,x_3 - 0.302\,x_1 x_2 - 0.231\,x_1 x_3 - 0.120\,x_2^2 + 0.173\,x_3^2 \tag{6}$$

According to Table 4, the coefficients determined via *p*-values which were effective included x_1, x_3, $x_1 \cdot x_2$, $x_1 \cdot x_3$, x_2^2 and x_3^2. It can be said that the parameters affecting DDD concentration were the three selected independent parameters, of which the most effective parameter was the initial DDT concentration (x_3). The reaction time (x_1) and the concentration of nZVI (x_2) caused the DDD concentration to be low in the effluent sample, while the initial DDT concentration (x_3) caused the DDD concentration to increase. This is consistent with the results obtained from the surface graphs.

The effect of the independent variables on the concentration of DDE occurring as a result of oxidation is given by the surface graphics in Fig. 5. The effect of the reaction time (x_1) and the concentration of nZVI (x_2) on DDE concentration is shown in Fig. 5(a). As the reaction time (x_1) increases, the DDE concentration in the output sample decreases. Furthermore, in Fig. 5(a), it is observed that for DDE formation, the effect of nZVI concentration (x_2) is higher than the effect of reaction time (x_1). As the concentration of nZVI increased, the concentration of DDE in the effluent decreased. Although the effluent DDE concentration was increased by increasing the reaction time at the point $\alpha = -1.5$ for the nZVI concentration (x_2) (115 mg/L), there was a decrease in DDE concentration due to oxidation at the higher nZVI concentration of 115 mg/L. Similar to the formation of the DDD concentration as seen in Fig. 4(a), DDE appeared to be degraded as a pollutant. Fig. 5(b) shows the effect of the initial DDT concentration (x_3) and reaction time (x_1) on the formation of the DDE concentration. It is clear from the graph that the initial DDT concentration (x_3) was much more effective than the reaction time (x_1). As the initial DDT concentration increased, the output DDE concentration also increased. A similar effect is seen in Fig. 5(c). As the initial DDT concentration (x_3) increased, the effluent DDE concentration increased. Fig. 5(c) shows the

Table 4
ANOVA analysis of DDD concentration

	Coefficients	Standard error	*t* stat	*p*-value	Importance
Intersection	1.204	0.090	13.314	1.093 E-07	Very significant
x_1	–0.234	0.057	–4.128	0.002	Significant
x_2	0.074	0.057	1.302	0.222	–
x_3	0.593	0.057	10.455	1.056 E-06	Very significant
$x_1 x_2$	–0.302	0.080	–3.769	0.0036	Significant
$x_1 x_3$	–0.231	0.080	–2.880	0.016	Significant
$x_2 x_3$	0.123	0.080	1.539	0.155	–
x_1^2	0.057	0.045	1.271	0.232	–
x_2^2	–0.120	0.045	–2.663	0.024	Significant
x_3^2	0.173	0.045	3.825	0.003	Significant

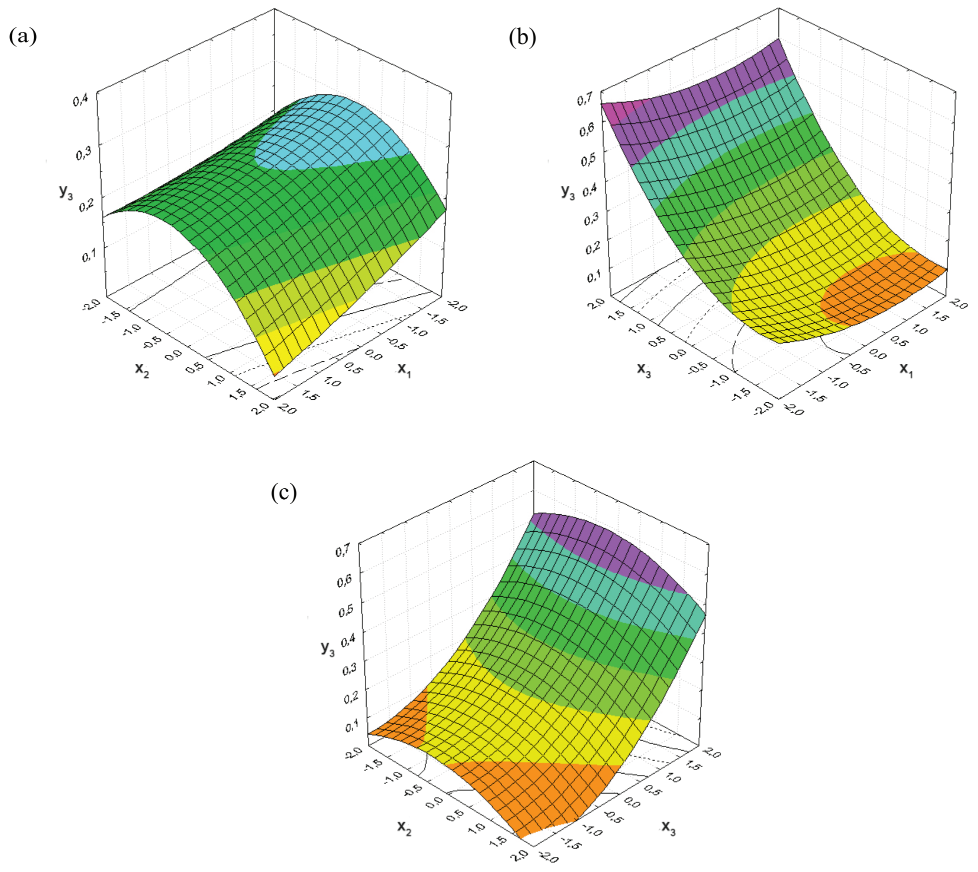

Fig. 5. Effluent DDE concentration (y_3) depending on reaction time (x_1), nZVI concentration (x_2) and initial DDT concentration (x_3).

effect of the concentration of nZVI (x_2) and the concentration of initial DDT (x_3) on the formation of the DDE concentration. The effluent DDE concentration increased with nZVI concentrations (x_2) lower than approximately 250 mg/L ($x_2 < -0.5$), while nZVI concentrations higher than 250 mg/L affected lower effluent DDE concentrations. Thus, as the effluent DDE was degraded with high nZVI concentrations, the oxidation of DDE was also higher than the formation of DDE.

When the surface graphs are compared, it is seen that the most effective parameter in the DDE concentration formed in the effluent sample was the initial DDT concentration (x_3) and the lowest effective parameter was the reaction time (x_1). Furthermore, when compared with DDD and DDE effluent concentrations, DDT appears to be more susceptible to DDD formation by nZVI dechlorination.

The ANOVA results obtained for DDE concentration are shown in Table 5. The regression coefficient was 0.967. Eq. (7) was obtained according to the ANOVA results.

$$y_3 = 0.212 + 0.211\,x_3 - 0.022\,x_2^2 + 0.032\,x_3^2 \qquad (7)$$

Table 5
ANOVA analysis of DDE concentration

	Coefficients	Standard error	*t* stat	*p*-value	Importance
Kesişim	0.212	0.018	11.693	3.726 E-07	Very significant
x_1	–0.020	0.011	–1.735	0.1134	–
x_2	–0.016	0.011	–1.427	0.1841	–
x_3	0.121	0.011	10.670	8.75 E-07	Very significant
$x_1 x_2$	–0.006	0.016	–0.385	0.708	–
$x_1 x_3$	0.002	0.016	0.128	0.900	–
$x_2 x_3$	0.001	0.016	0.066	0.949	–
x_1^2	0.009	0.009	0.982	0.349	–
x_2^2	–0.022	0.009	–2.382	0.038	Significant
x_3^2	0.032	0.009	3.505	0.005	Significant

According to the equation, the parameters affecting the formation of DDE were found to be nZVI concentration (x_2) and initial DDT concentration (x_3). When the *p*-values were taken into account, the effect of initial DDT concentration (x_3) was higher than that of other independent parameters. The DDE concentration in the effluent sample was higher in concentration with increasing initial DDT concentration (x_3). The DDE concentration was lower when the concentration of nZVI increased (x_2). This demonstrated that by increasing the nZVI concentration (x_2), DDE was degraded as a pollutant.

3.1.1. Optimization

This part of the study outlines the determination of the highest initial DDT concentration that could be reduced to the carcinogenic effect concentration of 0.23 µg/L in the effluent sample [26]. In accordance with this proposal, the highest initial DDT concentration was determined using the equation obtained for DDT removal (Eq. (5)) using the iteration technique in MathCad and Excel. The data obtained are shown in Table 6. When a water sample with an initial DDT concentration of 88.237 µg/L was treated with an nZVI concentration of 550 mg/L nZVI for about 49 min of reaction time, the effluent DDT concentration was reduced to below the carcinogenic effect limit of 0.23 µg/L.

3.1.2. Removal mechanism

In order to reveal the removal mechanism, the sample which was prepared and treated at the points (0,0,0): (x_1, x_2, x_3). The sample containing a DDT concentration of 130 µg/L was treated by an nZVI concentration of 300 mg/L for 31 min. The GC/MS library was scanned for the effluent sample. The oxidation products of DDT can be seen in Fig. 6. To illustrate the absence of contamination from a supernatant, the chromatogram of the MeOH used is also given in Fig. 6.

Table 6
Highest initial DDT concentration providing carcinogenic effect limit for the effluent

Variables	α	Variables	Uncoded form
x_1	1.172	Reaction time	48.6 min
x_2	2	nZVI concentration	550 mg/L
x_3	–0.695	Initial DDT concentration	88.33 µg/L
Removal rate		99.742%	
Effluent concentration		0.228 µg/L	

The proposed mechanism for dechlorination of DDT is given in Fig. 7. The results were similar to those of previous studies [38,39]. The first step for DDT dechlorination was the oxidation of DDE and DDD formation. According to the detected components in Fig. 6, DDE was oxidized to 1-chloro-2-2-bis(p-chlorophenyl) ethylene (DDMU) while DDD was converted to DDMU and/or 1-chloro-2-2-bis(p-chlorophenyl) ethane (DDMS). Both DDMS and 4,4′-Dichlorobenzophenone (DBP) were formed by oxidation of DDMU. In the next oxidation step, DDMS was first oxidized to 1,1-bis(chlorophenyl)ethane (DDNS) and then to 2,2-bis(p-chlorophenyl)ethanol (DDOH).

The oxidizing products DDOH and DBP were oxidized to DDM. Studies in the literature on the oxidation of DDT show that DDM formed by oxidation is oxidized to DBH, DM, BP and BH [38,39]. In this study, the ultimate oxidation products that could be determined were DDNS and DBP. With the data obtained, it can be said that in addition to the adsorption of nZVI, the DDT was oxidized. The nZVI molecules reacted with oxygen to form hydrogen peroxide, as seen in Eq. (8) [40].

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \quad (8)$$

The resulting hydrogen peroxide reacted with oxygen in the environment to react with unreacted zero-valent iron, as shown in Eq. (9).

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \quad (9)$$

and it caused the formation of hydroxyl radicals by the reaction of hydrogen peroxide and Fe^{2+} Fenton reactions (Eq. (10)).

$$Fe^{+2} + H_2O_2 \rightarrow Fe(III)(OH)_2 + OH\bullet \quad (10)$$

In addition to this mechanism, the dechlorination mechanism of nZVI can also be effective. As a result of the electron-donating of nZVI, the Cl bond of the Cl^- containing contaminant was replaced by the H bond (Eq. (11)) [28].

$$RCl + Fe^0 + H^+ \rightarrow RH + Fe^{2+} + Cl^- \quad (11)$$

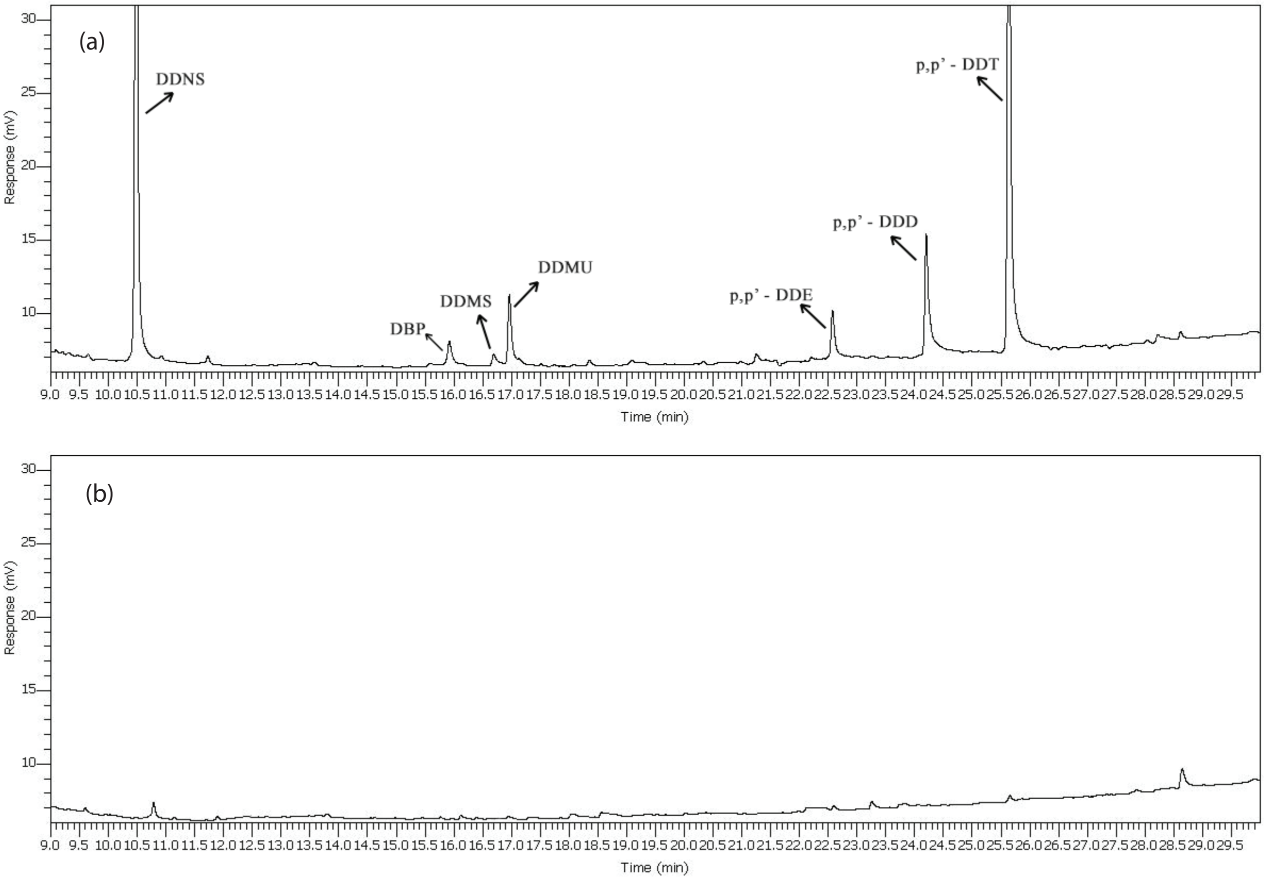

Fig. 6. GC/MS library scan.

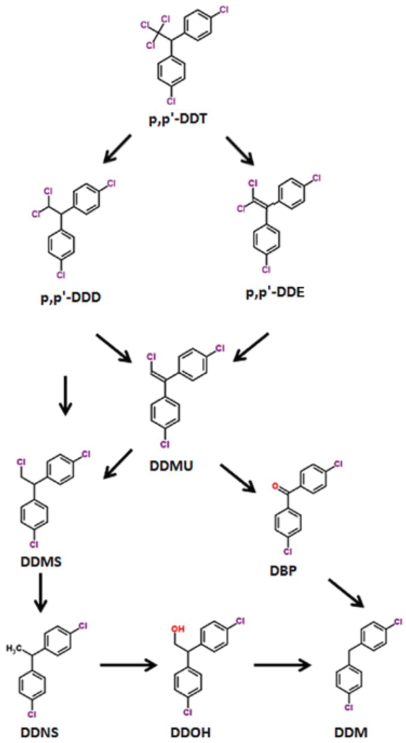

Fig. 7. DDT dechlorination mechanism [38,39].

4. Conclusion

According to the dechlorination process, the first step in the oxidation of DDT is the formation of its metabolites DDD and DDE. In addition, the selected independent parameters of initial DDT concentration, reaction time and the amount of nZVI were found to be effective for DDT degradation and the formation of DDD. The decrease in DDD and DDE concentrations due to increased reaction time demonstrated that dechlorination products in the system were also removed as pollutants. In order to oxidize the totally formed DDE concentration, a high nZVI concentration of 250 mg/L was required. In order to achieve the current carcinogenic effect limit of 0.23 μg/L in the effluent sample, the highest initial DDT concentration that could be degraded (88.33 μg/L) was treated at 48.6 min of reaction time with an nZVI concentration of 550 mg/L. According to the GC-MS screening of the dechlorination mechanism, the formation of dechlorination components such as DDD, DDE, DDMU, DDMS, DBP and DDNS was observed, while DDNS and DBP were formed as the lowest oxidation stage.

In order to reduce the cost of nanoparticle synthesis, the use of more accessible catalytic metals and the removal of persistent organics using bimetallic and trimetallic nanoparticles should be investigated along with the rate of hydroxyl radical formation and the removal of residual organic pollutants.

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Conflict of interest

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