

Abiotic Degradation of the Herbicide Oxadiazon in Water

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The performance of abiotic degradation of oxadiazon was investigated by applying zerovalent iron (ZVI), potassium permanganate (KMnO₄) and titanium dioxide (TiO₂) in the contaminated water. Experimental conditions allowed the disappearance of oxadiazon in the abiotic system. The degradation of this herbicide was monitored in buffer solutions having pH 3, 5 and 7 in the presence of iron powder in which the maximum degradation rate was achieved at acidic condition (pH 3) by 2% of ZVI treatment. The oxidative degradation of oxadiazon was observed in aqueous solution by KMnO₄ at pH 3, 7 and 10 in which the highest disappearance rate was found at neutral pH when treated with 2% of KMnO₄. The catalytic degradation of oxadiazon in TiO₂ suspension was obtained under dark and UV irradiation conditions. UV irradiation enhanced the degradation of oxadiazon in aquatic system in the presence of TiO₂. Conclusively, the remediation strategy using these abiotic reagents could be applied to remove oxadiazon from the contaminated water.

Key words: *oxadiazon, degradation, zerovalent iron, potassium permanganate, titanium dioxide.*

The ubiquitous use of herbicide in agricultural production has resulted in extensive water contamination. The application of herbicides and their apparent hazard to human health have promoted investigations concerning their impact on water environment. The oxadiazole herbicide oxadiazon [5-*tert*-butyl-3-(2,4-dichloro-5-isopropoxy-phenyl)-1,3,4-oxadiazol-2(3*H*)-one, Ronstar[®]] has routinely applied for the control of weeds in various agricultural crops like rice, cotton, soybean, potato, peanut and onion. The intensive use of this agrochemical combined with its relatively long half-life has a strong impact on the aquatic system^{1,2}. For this reason, innovative methods are needed to remediate herbicide-contaminated water in affected areas. As environmentally benign and economically feasible novel strategy, chemical approaches for the destruction of organic contaminants in water system commonly utilize reduction or oxidation schemes to degrade organic compounds. The use of zerovalent metals, especially iron, has produced success in the treatment of contaminated water indicating an accepted remediation technology. Zerovalent iron (ZVI) is capable of reductively degrading a wide range of organic contaminants including chlorinated aliphatic and aromatics abiotically³⁻⁵. The oxidation of organic contaminants by potassium permanganate (KMnO₄) is also a promising alternative chemical approach for the remediation of contaminated water. Permanganate, as a metal-oxo reagent, usually attacks organic contaminant powerfully due to the inherent nonspecificity of reactive oxygen species⁶.

Advanced methods are in demand for the effective treatment of pesticide-contaminated water. A lot of researches have been addressed to point out the prominent role of a special class of oxidation techniques defined as advanced oxidation processes (AOPs). Some studies^{7,8} have concentrated on this goal pointing out that these processes, although making use of different reacting systems, are characterized by the production of •OH radicals. Among the AOPs, titanium dioxide (TiO₂) as a heterogeneous photocatalyst is the irradiation of semiconductor slurries by UV irradiation in order to generate highly reactive intermediates, especially •OH radical as a very strong oxidizing agent that initiates a sequence of reactions resulting in partial or total destruction of most the organic contaminants^{9,10}.

Considering the above facts, this study has been designed to detoxify water contaminated with the herbicide oxadiazon using various abiotic reagents. The objectives of the present study were to investigate the potential use of abiotic reagents such as ZVI, KMnO₄ and TiO₂ for the degradation of the herbicide oxadiazon in water.

Materials and Methods

Agrochemical and chemicals. The herbicide oxadiazon (99.95% purity) was provided by Rhone-Poulenc, Inc., Agro-Division, France. ZVI powder was purchased from Fisher Scientific, USA. Potassium permanganate (KMnO₄) was obtained from Duksan Pharmaceutical Co. Ltd., Korea. Titanium dioxide (TiO₂) was purchased from Sigma Chemical Co., USA. All other chemicals were of reagent grade supplied by Sigma Chemical Co., USA, Junsei Chemical Co. and Kanto Chemical Co., Japan.

Zerovalent iron treatment. Oxadiazon was dissolved in acetone to prepare 1,000 mg/l stock solution, which was

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diluted to obtain the desired concentrations. Oxadiazon (2 mg/l) was dissolved in 100 ml of citrate-phosphate buffer solution with 5% of acetone and a 10 ml water sample was treated with ZVI at rates of 0.5, 1 and 2% at different pH (3, 5 and 7) conditions. This reaction mixture was incubated in shaking incubator (SW-90F, Sangwoo Scientific Co., Korea) for 1, 4, 8, 12 and 24 h at room temperature. After a specified time, the reaction mixture was partitioned with hexane. After dehydration with anhydrous sodium sulfate, the remaining concentration of oxadiazon was analyzed by gas chromatograph (GC).

Potassium permanganate treatment. Oxadiazon stock solution was prepared in acetone and the required concentration of this stock solution was mixed with buffer solution. The pure oxadiazon-in-buffer solutions having pH range of 3 to 10 were shaken vigorously and allowed to stand for at least 24 h. The pH values of these solutions were adjusted whenever necessary. The aliquot (10 ml) was treated with KMnO_4 at rates of 0.5, 1 and 2% at various pH (3, 7 and 10) conditions separately. This reaction mixture was incubated in shaking incubator (SW-90F, Sangwoo Scientific Co., Korea) for 0.5, 1, 7 and 14 d at room temperature. After a specified time, the samples were partitioned by hexane. After dehydration with anhydrous sodium sulfate, the remaining amount of oxadiazon was analyzed by GC.

Titanium dioxide treatment. The degradation experiment was performed on 10 ml of aqueous medium containing 2 mg/l of oxadiazon and different amounts of TiO_2 (100 and 500 mg/l) at natural pH. The suspensions were allowed to stand in the dark for 60 min under stirring to reach adsorption equilibrium onto semiconductor surface. This reaction mixture was incubated for 0.5, 1, 2, 3 and 5 h under dark and UV irradiation conditions. After a specified time, the reaction mixture was partitioned with hexane. After dehydration with anhydrous sodium sulfate, the concentration of remaining oxadiazon was analyzed by GC.

Analytical technique. The herbicide oxadiazon of treated water samples was analyzed by gas chromatograph (Varian CP-3800, USA) equipped with an electron capture detector. Analytical conditions for GC were as follows: column, 30 m \times 0.25 mm i.d. capillary column DB-1; temperature, column oven 240°C, detector block 300°C; carrier N_2 gas flow rate, 1.0 ml/min and injection volume, 1.0 μl .

Degradation kinetic parameters. The reaction rate constant (k) and half-life ($t_{1/2}$) were calculated by using the first-order rate equation (Eq. 1) as described by Leifer¹¹.

$$C_t = C_0 e^{-kt} \quad (1)$$

Where, C_t represents the concentration at time t
 C_0 represents the initial concentration and
 k is the rate constant.

When the concentration was reduced to 50% of its initial amount, the half-life ($t_{1/2}$) was obtained by the following equation (Eq. 2):

$$t_{1/2} = 0.693/k \quad (2)$$

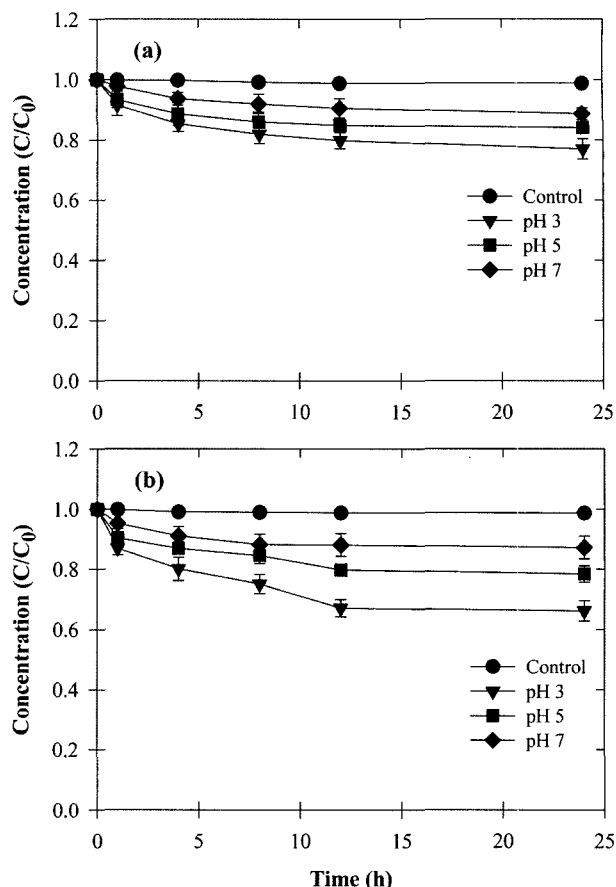


Fig. 1. Degradation of oxadiazon by 1% (a) and 2% (b) of ZVI treatments. Error bars indicate standard deviation of mean.

Where, k is the degradation constant.

Results and Discussion

Degradation of oxadiazon by zerovalent iron. In the aquatic system, the degradation rate of oxadiazon was studied by the addition of 0.5, 1 and 2% of ZVI at different pH (3, 5 and 7) conditions. At acidic condition (pH 3), 23.0 and 33.8% of oxadiazon was degraded within 24 h by treatments of 1 and 2% of ZVI, respectively (Fig. 1). The highest degradation rate of oxadiazon was achieved at a reaction time after 12 h with increasing the amount of ZVI. For the comparative studies of pH, the maximum degradation rate was observed within 24 h at acidic condition (pH 3) as compared to other pH (5 and 7) conditions (Fig. 2). The obtained results suggested that a chemical method of zerovalent iron (Fe^0) reduction had been explored for the removal of this herbicide from water by the oxidation of ZVI as shown in the following equation¹²:



Weber¹³ stated that a two-electron transfer generally occurred directly at the iron surface oxidizing iron (Fe^0) to ferrous iron (Fe^{2+}) resulting degradation as mentioned in Eq. 4.

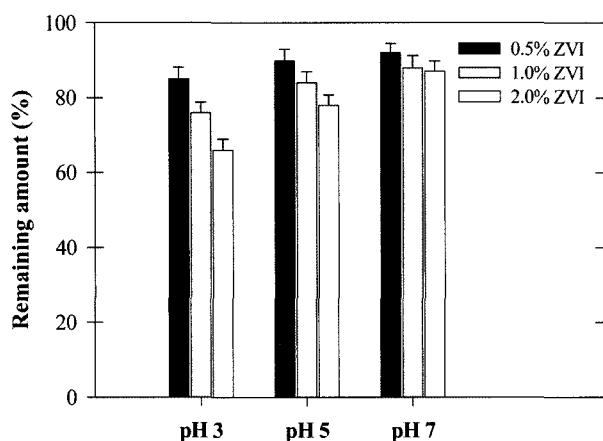
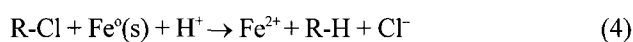
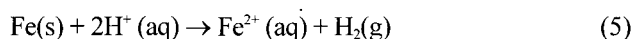


Fig. 2. Degradation of oxadiazon by ZVI treatment at various pH conditions. Error bars indicate standard deviation of mean.



It is clear from this finding that pH played a vital role in the degradation rate of oxadiazon *via* metallic iron. The rate of this process increased as the solution pH decreased. Dombek *et al.*¹⁴ reported that a low pH of the reaction solution probably allowed more of the iron surface to remain available for reaction with molecule *via*:



Conversely, the ferrous and hydroxyl ions formed ferrous hydroxide and then precipitated at the elevated pH of solution. The precipitation of ferrous hydroxide on the surface of ZVI could hinder the transport of the target contaminants and block the reactive sites on ZVI and hence, decreased the overall reaction rate. Monson *et al.*¹⁵, Joo *et al.*¹⁶ and Gibb *et al.*¹⁷ investigated the reductive degradation using ZVI (Fe^0) as an electron donor for the remediation of water contaminated with herbicides.

The reaction rate constant (k) and half-life ($t_{1/2}$) during ZVI treatment have been presented in Table 1. The calculated results revealed that the half-life of oxadiazon decreased by increasing the amount of ZVI but decreasing pH of the

Table 1. Degradation kinetic parameters (reaction rate constant and half-life) during ZVI treatment

pH	ZVI (%)	k (h^{-1})	$t_{1/2}$ (h)
3	0.5	4.8×10^{-3}	144.4
	1.0	6.7×10^{-3}	103.4
	2.0	0.012	57.8
5	0.5	2.9×10^{-3}	239.0
	1.0	4.0×10^{-3}	173.2
	2.0	6.1×10^{-3}	113.6
7	0.5	2.8×10^{-3}	247.5
	1.0	3.2×10^{-3}	216.6
	2.0	3.7×10^{-3}	187.3

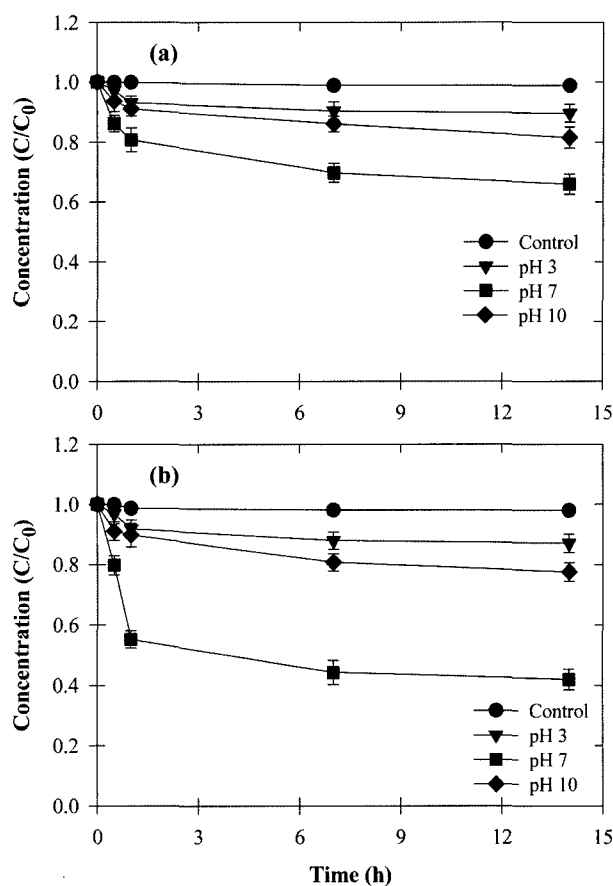


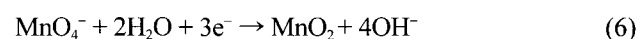
Fig. 3. Degradation of oxadiazon by 1% (a) and 2% (b) of KMnO_4 treatments. Error bars indicate standard deviation of mean.

solution. These results were in agreement with experimental findings of Chen *et al.*⁵ and Siantar *et al.*¹⁸.

Degradation of oxadiazon by potassium permanganate.

In the aqueous phase, the disappearance rate of oxadiazon was examined by treatments of 0.5, 1 and 2% of KMnO_4 at different pH (3, 7 and 10) conditions. At a neutral pH, 34.0 and 58.1% of oxadiazon was degraded within 14 d by treatments of 1 and 2% of KMnO_4 , respectively (Fig. 3). The maximum degradation rate of oxadiazon was obtained within 14 d with increasing the amount of KMnO_4 . Considering the pH of solution, the highest degradation rate was obtained at a neutral pH within 14 d as compared to other pH (3 and 10) conditions (Fig. 4).

In oxidation with KMnO_4 , pH was considered as a primary variable because it influenced the redox potential in a system in which the couples of manganese ions involved in the overall reaction¹⁹. At neutral pH condition, the maximum degradation of oxadiazon might be due to mechanistic factors in contrast to the overall free energy change of the oxidant. Under this condition, the redox reaction with the potentials of various couples of manganese ions has been involved in the following equation²⁰:



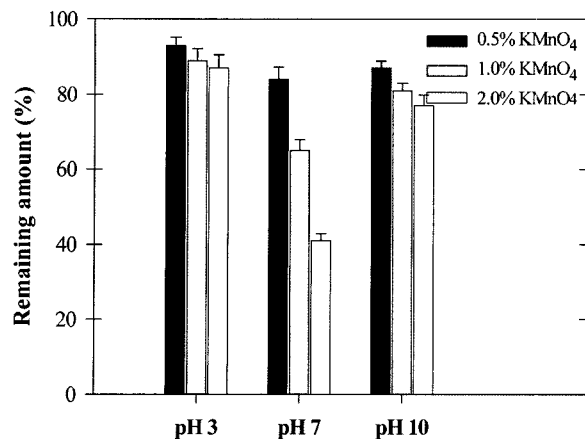


Fig. 4. Degradation of oxadiazon by KMnO_4 treatment at different pH conditions. Error bars indicate standard deviation of mean.

Table 2. Degradation kinetic parameters (reaction rate constant and half-life) during KMnO_4 treatment

pH	KMnO_4 (%)	k (d^{-1})	$t_{1/2}$ (d)
3	0.5	3.2×10^{-3}	216.6
	1.0	6.1×10^{-3}	113.6
	2.0	8.0×10^{-3}	86.6
7	0.5	7.7×10^{-3}	90.0
	1.0	2.5×10^{-2}	27.7
	2.0	6.1×10^{-2}	11.4
10	0.5	6.9×10^{-3}	100.4
	1.0	1.2×10^{-2}	57.8
	2.0	1.5×10^{-2}	46.2

The reaction rate constant (k) and half-life ($t_{1/2}$) during KMnO_4 treatment have been reported in Table 2. The obtained results indicated that the half-life of oxadiazon decreased by increasing the amount of KMnO_4 , but its half-life was lower in neutral pH compared to other pH conditions.

Degradation of oxadiazon by titanium dioxide. Figure 5 illustrated that the disappearance of oxadiazon was obtained in the presence of TiO_2 at rates of 100 and 500 mg/l for 0.5, 1, 2, 3 and 5 h under dark and UV irradiation conditions. As compared to dark condition, 42.6 and 64.0% of oxadiazon was degraded from aqueous solution within 5 h under UV irradiation by treatments of 100 and 500 mg/l TiO_2 , respectively. The dark reaction produced slight mineralization of oxadiazon. Konstantinou *et al.*²¹⁾ observed a similar trend of catalytic degradation of herbicides using same amounts of TiO_2 in aqueous suspension. It is noted that when aqueous TiO_2 suspension was irradiated with UV light, the generated electrons reduced organic substrate or reacted with electron acceptors such as the adsorbed molecular O_2 on the Ti(III) -surface. The photogenerated holes oxidized either the organic molecule directly, or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface to $\cdot\text{OH}$ radicals. Accordingly, the relevant reactions at the semiconductor surface have been

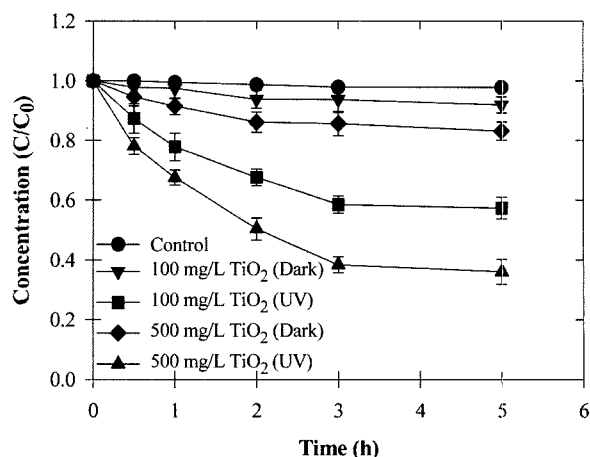
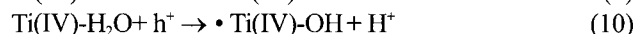
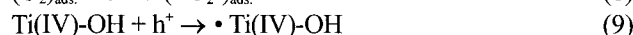


Fig. 5. Disappearance of oxadiazon by TiO_2 treatment. Error bars indicate standard deviation of mean.

Table 3. Degradation kinetic parameters (reaction rate constant and half-life) during TiO_2 treatment

Reaction	TiO_2 (mg/l)	k (h^{-1})	$t_{1/2}$ (h)
Dark	100	0.014	49.5
	500	0.027	25.7
UV irradiation	100	0.092	7.5
	500	0.178	3.9

cited in Eqs. 7 to 12.



The resulting $\cdot\text{OH}$ radical, being strongly active and non-selective degrading agent, oxidized this organic xenobiotic in aqueous solution. The detailed above mechanism was described in the literatures of Konstantinou and Albanis¹⁰⁾, Heltz *et al.*²²⁾ and Herrmann²³⁾.

The kinetics of oxadiazon disappearance in the presence of TiO_2 has been shown in Table 3. The reaction rate constant (k) values confirmed the positive influence of the increased number of TiO_2 active sites on the kinetics. The recorded half-life indicated that the photocatalytic degradation of this herbicide was occurred prominently in TiO_2 suspensions as compared to dark condition.

In conclusion, the enhanced degradation with TiO_2 was a feasible and fast treatment for the removal of this herbicide from the contaminated water as compared to ZVI and KMnO_4 treatments. It is suggested that the association of enhanced degradation by advanced oxidation process using TiO_2 with ZVI was considered to be suitable for the remediation of water environment contaminated with oxadiazon.

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