EFFECT OF INORGANIC IONS ON THE OXIDATION OF DICHLORVOS INSECTICIDE WITH FENTON'S REAGENT

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ABSTRACT

This study analyzes the oxidation of dichlorvos with Fenton's reagent in solutions containing various ions. Results show that the larger the added amount of ferrous ions, the higher the elimination rate of dichlorvos and the oxidization rate after the addition of ferric ions is far smaller than that of adding ferrous ions. Anions suppress the decomposition of dichlorvos in the following sequence: $H_2PO_4^-$ > > Cl^- > NO_3^- ~ ClO_4^- . It can be seen that the Fenton reaction is extremely sensitive to anions, and phosphate ions in particular will seriously suppress the Fenton system's ability to oxidize dichlorvos.   The main reason for the suppression of phosphate ions is that phosphate ions will produce a complex reaction together with ferrous ions and ferric ions, which then lowers its ability to catalyze hydrogen peroxide. ©1997 Elsevier Science Ltd
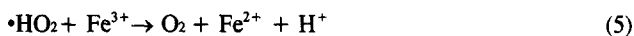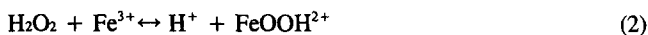
INTRODUCTION

The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants[1,2].   In 1894, H.J.H. Fenton [3] presented the theory that ferrous ions could catalyze   hydrogen peroxide to oxidize tartaric acid.   Others also gradually discovered that a combination of hydrogen peroxide and ferrous ions induced oxidization in various organic matter, thus these two agents were co-named "Fenton's reagent"[4-6].   Hydroxyl radicals are substances with extremely high oxidizing

powers. Therefore, the Fenton system is endowed with powerful oxidizing abilities, and can oxidize hard-to-decompose organic compounds, such as chlorophenols and pesticides fairly well in a short period of time [2,4].

The Fenton reaction is when ferrous ions react with hydrogen peroxide and produce hydroxyl radicals, the reaction is as shown Equ. 1 [5-7]:

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+} \tag{1}$$
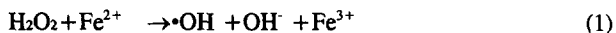
Moreover, the newly formed ferric ions may catalyze hydrogen peroxide, causing it to be decomposed into water and oxygen. Ferrous ions and radicals are also formed in the reactions. The reactions are as shown in Equ. 2 ~ 5 [5-7]:

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH^{2+} \tag{2}$$

$$FeOOH^{2+} \rightarrow \cdot HO_2 + Fe^{2+} \tag{3}$$

$$\cdot HO_2 + Fe^{2+} \rightarrow \cdot HO_2^- + Fe^{3+} \tag{4}$$

$$\cdot HO_2 + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \tag{5}$$

Pignatello et al.,[7] point out that the reaction rate of Equ. 2 is slower than that of Equ. 1, because ferrous ions are being consumed more rapidly than they are being produced.

Current studies done on the Fenton method present fairly good results when applying the Fenton's reagent on toxic chemical and dyed waste water treatment[4]. Because a large quantity of anions are often present in waste water, and its influence on the Fenton reaction is yet unknown. Therefore, this study will select Fe^{2+}, and four anions, namely ClO_4^-, NO_3^-, Cl^- and $H_2PO_4^-$, to investigate the effect of ion species on the Fenton reaction. Additionally, the influence of $[Fe^{2+}]$ on oxidation of dichlorvos is also investigated.

EXPERIMENTAL

The original dichlorvos solution was manufactured by the Bayer company (purity, 96.33%). Ferrous sulfide and hydrogen peroxide (purity 30%) were manufactured by the Merck company. The standard dichlorvos solution is a R.D.H. production (purity > 99%), and the rest of the used agents are at least reagent grade.

A dichlorvos solution was prepared by stirring an excess amount of dichlorvos in pure water at room temperature. More dilute solutions were obtained by mixing a stock solution

with pure water. Take an appropriate amount of dichlorvos solution, place in a 100 ml measuring bottle, add ferrous and the background ions, dilute with pure water to 100ml, and adjust the pH . After the pH adjustment finished, the solution was poured into a 250ml flask, and then placed in a thermal oscillator tank at 30°C. The reaction was initiated after hydrogen peroxide is added. Samples were regularly taken and the residual quantity of dichlorvos were measured.

Dichlorvos was analyzed by a HP 5980II gas chromatography with a electron capture detector and also a Sopleco PTE-5 column (0.53mm in inside diameter, 15m long). The chlorine ion was determined with a Dionex-4500i ion chromatograph.

RESULTS AND DISCUSSION

The oxidation of dichlorvos with Fenton's reagent is a two-stage reaction. The first stage is a Fe^{2+}/H_2O_2 reaction in which Fe^{3+} and $\cdot OH$ are produced rapidly (see Equ.1) and dichlorvos swiftly decomposes. In the second stage, dichlorvos decomposes somewhat less rapidly because of less Fe^{2+} and $\cdot OH$ formed (see Equ.2-5), and it is a Fe^{3+}/H_2O_2 reaction [7,8]. Comparing the catalysis activity between ferrous ions and ferric ions is another way of proving the two-stage reaction. Although both ferrous ions and ferric ions can produce oxidizing abilities by reacting with hydrogen peroxide, there is an apparent distinction in their oxidization rate. The way in which adding equal amounts of ferrous ions, ferric ions and a combination of the two, which influences dichlorvos degradation is shown in Figure 1. The sequence of oxidation rate is $Fe^{2+} >$ $(Fe^{2+}+Fe^{3+}) > Fe^{3+}$; the elimination efficiencies in 90 minutes are 97.4%, 87% and 51.6%. It can be derived from this result that the oxidization rate after the addition of ferric ions is far smaller than that of adding ferrous ions.

The oxidization potential of hydrogen peroxide is 1.77V[9], therefore, adding hydrogen peroxide only into the solution will not effectively oxidize dichlorvos. Ferrous ions can catalyze hydrogen peroxide to produce hydroxyl radicals, the main species which oxidizes dichlorvos. Because the amount of ferrous ions added directly affects the production of hydroxyl radicals, its influence on the decomposition rate of dichlorvos is also great. In this experiment, we used a solution of $[H_2O_2]=5\times10^{-3}M$ to proceed with reaction and observe the change the dichlorvos concentration undergoing when different amounts of ferrous ions are added.
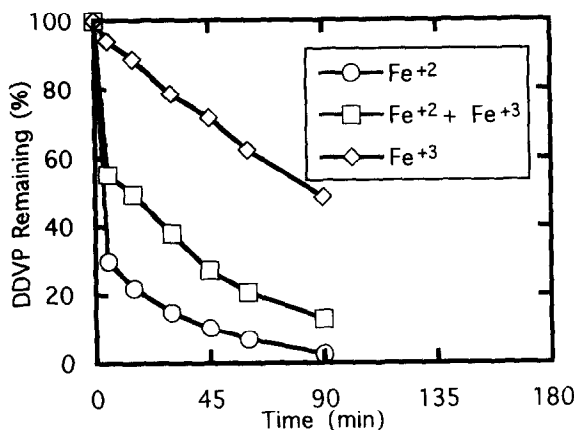
Figure 1. Comparison of Fe^{2+} and Fe^{3+} on the Oxidation of Dichlorvos

[Dichlorvos]$=2.26 \times 10^{-4}$ M, $[H_2O_2]=5.0 \times 10^{-3}$ M,

$[NaClO_4]=0.2$ M, pH$=3$

As shown in Figure 2, the larger the added amount of ferrous ions, the higher the elimination rate of dichlorvos. When $[Fe^{2+}]=5 \times 10^{-4}$M, the elimination ratio of dichlorvos reaches 99.8% after 60 minutes of reaction. When the added amount of ferrous ions is cut down to 5×10^{-5}M, the elimination ratio of dichlorvos merely reaches 40% after 60 minutes of reaction. It may also be observed in Figure 2 that when only hydrogen peroxide is added and ferrous ions are left out, dichlorvos hardly decomposes at all in the duration of 90 minutes.

Solution pH gradually lower during the decomposing process of dichorvos. The relationship between the dichlorvos remaining and pH are as shown in Figure 3. When the elimination ratio of dichlorvos reaches 97.5%, the pH drops from 3 to 2.74. It can be derived from this result that hydrogen ions are released during the reaction process.

Figure 4 is a diagram of the relationship between dichlorvos residual quantity and chlorine ion productivity at pH 3. The amount of chlorine ions produced will increase as dichlorvos decomposes. It can be seen that the production quantity of chlorine ions is almost two times of the decomposition quantity of dichlorvos.
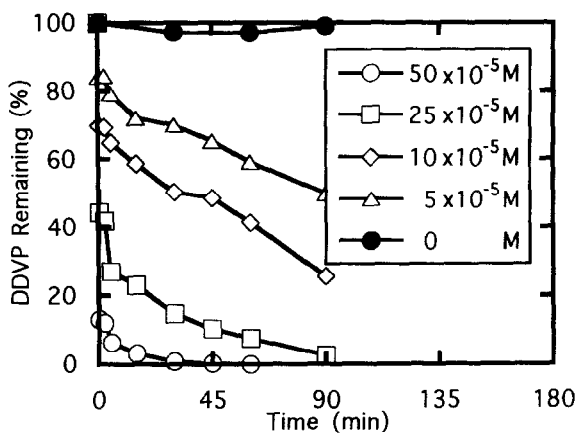
Figure 2. Effect of Fe^{2+} on the Rate of Dichlorvos Oxidation
[Dichlorvos]$=2.26x10^{-4}$ M, $[H_2O_2]=5.0x10^{-3}$ M,
$[NaClO_4]=0.2$ M, Initial pH$=3$
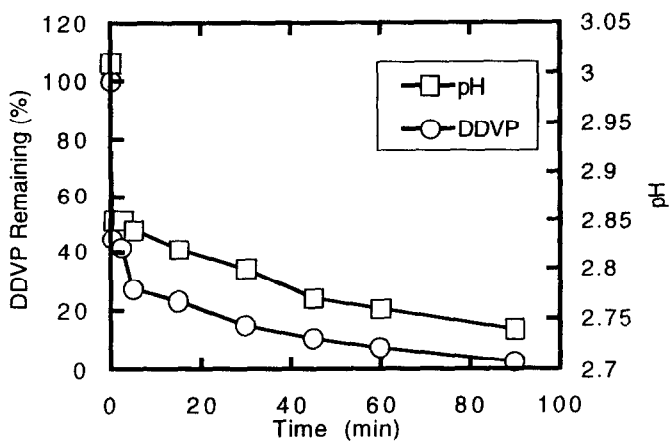
Figure 3. Variation of [Dichlorvos] and pH in the Fenton Reaction
[Dichlorvos]$=2.26x10^{-4}$ M, $[H_2O_2]=5.0x10^{-3}$ M,
$[Fe^{2+}]=2.5x10^{-4}$ M, $[NaClO_4]=0.2$ M, Initial pH$=3$
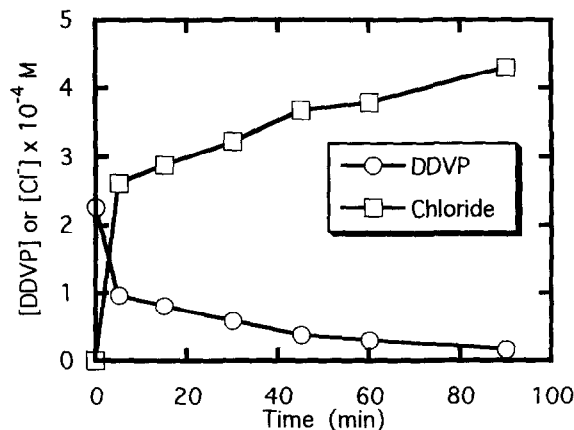
Figure 4. Comparing Dichlorvos Oxidation and Chloride Formation

[Dichlorvos]$=2.26 \times 10^{-4}$ M, [H$_2$O$_2$]$=5.0 \times 10^{-3}$ M,

[Fe^{2+}]$=2.5 \times 10^{-4}$ M , [NaClO$_4$]$=0.2$ M, Initial pH$=3$

The Fenton reaction is extremely sensitive to the anions which remain in the solution. These anions come from several sources: (1) the counter ions of hydrogen ions and ferrous ions, (2) the ions produced from dichlorvos decomposition, and (3) background ions. This study selects ,namely ClO$_4^-$, NO$_3^-$, Cl$^-$, H$_2$PO$_4^-$, four types of background ions to be examined . The counterions of hydrogen ions and ferrous ions are ClO$_4^-$ and SO$_4^{2-}$. Because the background ions have a high concentration (the concentration of background ions is approximately 0.2M), which is far higher than the concentration of hydrogen ions and ferrous ions (approximately 1.25×10^{-3}M), the effect of counter ions on the reaction is not mentioned here. Likewise, the effect which anions released from dichlorvos decomposition on the reaction rate may also be omitted. Figure 5 shows that the effect of background ions on the dichlorvos oxidation. The anions suppress the decomposition of dichlorvos in the following sequence: H$_2$PO$_4^-$ > > Cl$^-$ > NO$_3^-$ ~ ClO$_4^-$.

On the whole, there are two reasons why ClO$_4^-$ and NO$_3^-$ have less effect on dichlorvos decomposition than Cl$^-$ and H$_2$PO$_4^-$ solution: (1) ClO$_4^-$ and NO$_3^-$ will not produce a complex reaction with ferric ions, therefore, the reaction between ferric ions and hydrogen peroxide is not
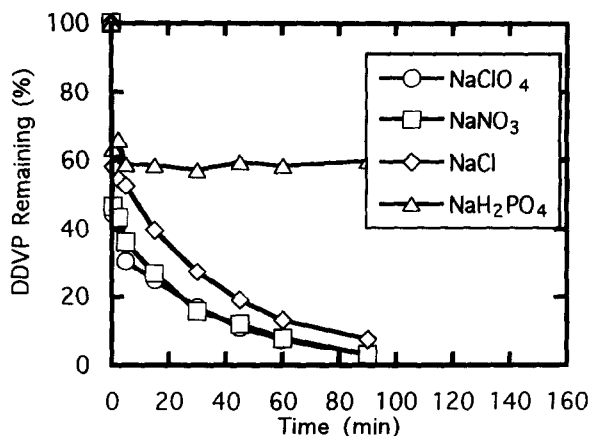
Figure 5. Effect of Inorganic Anions on Dichlorvos Oxidation

[Dichlorvos]=2.26×10^{-4} M, [H_2O_2]=5.0×10^{-3} M,

[Fe^{2+}]=2.5×10^{-4} M , [$NaClO_4$]=0.2 M, Initial pH=3

suppressed. (2) Because and NO_3^- will not react with hydroxyl radicals, the decompositon rate of dichlorvos is not inhibited. The dichlorvos decomposition in Cl^- solution is slower than that in the ClO_4^- and NO_3^- solution. The reason is that Cl^- may undergo a complex reaction with ferric ions. The reaction is as shown in Equ.7~9 [10].

$$Fe^{3+}+Cl^- \rightarrow FeCl^{2+} \qquad (7)$$

$$FeCl^{2+}+Cl^- \rightarrow FeCl_2^+ \qquad (8)$$

$$FeCl_2^++Cl^- \rightarrow FeCl_3 \qquad (9)$$

The ferric complexs can not react efficiently with hydrogen peroxide. It will impede the reaction of producing hydroxyl radicals, thus the decomposition rate of dichlorvos is slowed down. Another reason is that Cl^- will interact with hydroxyl radicals (as in Equ.10)[7], so that Cl^- will compete with organic compounds for hydroxyl radicals and slow down the decomposition rate of dichlorvos.

$$\cdot OH + Cl^- + H^+ \rightarrow Cl^- + H_2O \tag{10}$$

The form which phosphate ions take on in a solution is determined by the cation species and the pH of the solution. From the pH-phosphate distribution diagram[11], it can be seen that when pH = 3, phosphate primarily exists in the form of $H_2PO_4^-$ which will react with ferrous and ferric ions to form complex compounds, as shown in Equ. 11 ~ 12 [10, 11]:

$$Fe^{2+} + H_2PO_4^- \rightarrow FeH_2PO_4^+ \qquad K = 10^{2.75} \tag{11}$$

$$Fe^{3+} + H_2PO_4^- \rightarrow FeH_2PO_4^{2+} \qquad K = 10^{5.84} \tag{12}$$

When $[H_2PO_4^-] = 0.2$ M, then

$$[FeH_2PO_4^+]/[Fe^{2+}] = 113 \tag{12}$$

$$[FeH_2PO_4^{2+}]/[Fe^{3+}] = 6.1 \times 10^4 \tag{13}$$

Thus, ferrous ions mainly exist in the form of $FeH_2PO_4^+$ in the first stage of Fenton's reagent oxidizing dichlorvos. When the added amount of ferrous ions is 2.5×10^{-4}M, only 2.2×10^{-6}M of ferrous ions will remain, and all of the rest is $FeH_2PO_4^+$. In the second stage, it mainly exists as $FeH_2PO_4^{2+}$, if there is 2.5×10^{-4}M of Fe^{2+} added initially in the solution, then only 4.1×10^{-9}M of free frric ions will remain. In the first stage, the dichlorvos remaining of the solution containing $H_2PO_4^-$ reaches 36.7%. This would not be possible if only 2.2×10^{-6}M of free ferrous ions remained in the solution, because when ferrous ions are 5×10^{-5}M, the dichlorvos remaining in the first stage is 15.8%, as seen in Figure 2. It may be derived that $FeH_2PO_4^+$ possibly reacts with hydrogen peroxide and produces radicals. It is still possible to oxidize dichlorvos in the first stage. In the second stage, $FeH_2PO_4^{2+}$ reacts slowly, or does not react at all with hydrogen peroxide. Besides, the concentration of the free ferric ions remaining in the solution is too low, so that the decomposition reaction of dichlorvos can not be observed.

CONCLUSION

The molecular formula of dichlorvos is $C_4H_7Cl_2O_4P$, chlorine ions are released when dichlorvos is being oxidized by the Fenton system. With the increase in dichlorvos elimination, the production of chlorine ions increases as well, and the chlorine ions production is almost two

times of the dichlorvos elimination.   Increasing the amount of ferrous ions may increase the rate of dichlorvos decomposition.   When $[Fe^{2+}]$ increases from $5 \times 10^{-5}M$ to $5 \times 10^{-4}M$, the remaining of dichlorvos increases from 50% to 100% in 90 minutes.

The background ions used in this research affect the decomposition rate of dichlorvos greatly by examining with four anions.   Their order of sequence according to the reaction rate is: $H_2PO_4^- > > Cl^- > NO_3^- \sim ClO_4^-$.   When the background ion used is $H_2PO_4^-$, dichlorvos is hardly decomposed at all during the second stage.   The reason for this is that ferric ions undergo a complex reaction with $H_2PO_4^-$, causing ferric ions to lose the power to catalyze hydrogen peroxide. However, $FeH_2PO_4^+$ possibly reacts with hydrogen peroxide and produces radicals. It is still possible to oxidize dichlorvos.

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