



Titanium dioxide mediated photocatalytic degradation of methamidophos in aqueous phase

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ABSTRACT

In this paper, the photocatalytic degradation of methamidophos, an organophosphorous pesticide, was investigated in aqueous solution by using TiO_2 as a photocatalyst. The degradation was studied under different conditions such as the amount of the photocatalyst, illumination time, pH of the system, reaction temperature, initial concentration, electron acceptors, metal ions and presence of anions. The results showed that the photocatalytic degradation of methamidophos was strongly influenced by these parameters. The best conditions for the photocatalytic degradation of methamidophos were obtained. The optimum amount of the photocatalyst used is 12.0 g/L. The photodegradation efficiency of methamidophos increases with the increase of the illumination time. Alkaline media are favorable for the photocatalytic degradation of methamidophos. The degradation efficiency is enhanced by increasing reaction temperature, and the photodegradation efficiency decreases with the increase in the initial concentration of methamidophos. The photodegradation efficiency of methamidophos is accelerated by adding a small amount of H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, KBrO_3 , Fe^{3+} or Cu^{2+} . There are no obvious effects on the reactions with the addition of a small amount of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} or adding trace amount of SO_4^{2-} , Cl^- , Br^- . The possible roles of the additives on the reactions and the possible mechanisms of effect were also discussed.

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1. Introduction

In recent years, using a semiconductor as the photocatalyst to degrade various organic and inorganic pollutants in wastewater has become a kind of water treatment technology with the best prospect of exploitation and utilization [1,2]. Since pollutants could be completely degraded into harmless matters by photocatalysis method under normal temperature and air pressure, scientists predicted that in the near future photocatalysis will become one of the most effective means in dealing with various kinds of industrial wastewater [3,4]. Among various oxide semiconductor photocatalysts, TiO_2 has been proven to be the most suitable for widespread environmental applications due to its biological and chemical inertness, strong oxidizing power, and long-term stability against photocorrosion and chemical corrosion [5]. However, the efficiencies of the photocatalytic reactions using TiO_2 as a photocatalyst are not high. In order to increase the efficiencies of the photocatalytic reactions, some methods were used in the disposal of wastewater. One of them is to use some chemicals to promote photocatalytic reaction rate. H_2O_2 as an ideal chemical is often used, especially

in the photocatalytic oxidation [6,7]. Metal ions and anions are also used in both the photocatalytic oxidation and photocatalytic reduction [8,9].

Methamidophos (*O,S*-dimethyl phosphoramidothioate) is a highly efficient, broad-spectrum organophosphate insecticide, which is used in great quantities worldwide [10]. This non-selective pesticide has been used extensively for the control of a wide range of insects. It is a potent acetylcholinesterase inhibitor [11] used to control chewing and sucking insects and spider mites on ornamental plants, citrus fruits, stone fruits and other intensive agriculture crops. However, it contaminates the environment from various sources such as industrial effluents, agricultural runoff and chemical spills [12]. It creates a particular problem in some developing countries, where widespread ignorance about the pesticides' hazards has led to many deaths among agricultural workers. Recently, cleanup of pesticide-contaminated soil, surface water and air has become a major focus of research and policy debate. There are numerous techniques used for treating organically contaminated water and much attention has been given to employing the biological process. The organophosphate pesticides, however, are too toxic to be mineralized by the indigenous microorganisms which present in the aquifer matrix. Many reports on the photocatalytic oxidation of organophosphorous pesticides have been published [13,14]. Nevertheless, the photocatalytic degradation of methamidophos

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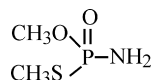
has been rarely investigated. At the same time, dissolved metal ions and anions are also very common in natural water and industrial wastewater. For example, metal ions such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , and anions such as SO_4^{2-} , Cl^- , Br^- are often contained in wastewater. They may significantly influence the photocatalytic reactions for removal of organic pollutants. Meanwhile, the pH values of the different wastewater are different, which also probably influence the photocatalytic reactions for removal of the pollutants [2]. Such studies will therefore be greatly useful in our quest for a better technological condition to dispose wastewater of the pollutants and purify environment.

In this paper, we selected a pesticide methamidophos as a model compound of organic pollutants and TiO_2 powder as a photocatalyst. The effects of various parameters, such as the amount of the photocatalyst, illumination time, reaction temperature, electron acceptors, metal ions, anions, and initial concentration, reaction pH on the photocatalytic degradation of methamidophos were studied. From the studies, the optimum conditions for photocatalytic degradation of methamidophos and the different effects of the parameters on the photocatalytic removal of methamidophos were obtained. The possible roles of the additives on the reactions and the possible mechanisms of effect were also discussed.

2. Experimental

2.1. Materials

The chemical structure of methamidophos (Pur. >95.0%) is shown as follows:



It was purchased from Lianyungang Liben Agro-chemical Co. Ltd., China. The TiO_2 used in the experiments was prepared by thermal decomposition and calcination of a colloidal solution made by hydrolysis of titanium tetraisopropoxide $[\text{Ti}(\text{iso-OC}_3\text{H}_7)_4]$ in our laboratory. From the analysis, it is known that the TiO_2 sample contains mainly anatase 80% and rutile 20% with the mean particle size of 30 nm and a BET surface area of $50 \text{ m}^2/\text{g}$. H_2O_2 , KBrO_3 , $\text{K}_2\text{S}_2\text{O}_8$, CuSO_4 , Na_2SO_4 , NaCl and other chemicals used in the experiments are of analytically pure grade. They were purchased from Shanghai and other China chemical reagent Ltd. without further purification. Deionized and doubly distilled water was used throughout this study. The various pH values of the reaction solutions were adjusted by dilute HCl and NaOH solutions.

2.2. Photoreaction apparatus and procedure

Experiments were carried out in a photoreaction apparatus. The schematic diagram is shown in Fig. 1. The photoreaction apparatus consists of two parts. The first part is an annular quartz tube. A 375 W medium pressure mercury lamp (Institute of Electric Light Source, Beijing) with a maximum emission at about 365 nm is laid in the empty chamber of the annular tube, and running water passes through an inner thimble of the annular tube. Owing to continuous cooling, the temperature of the reaction solution is maintained at approximately 30°C . The second part is an unsealed beaker of a diameter 12 cm. At the start of the experiment, the reaction solution (volume, 300 mL) containing reactants and photocatalyst was put in the unsealed beakers, and a magnetic stirring device was used to stir the reaction solution. The distance between the light source and the surface of the reaction solution is 11 cm. The UV irradiation intensity (the wavelengths below 400 nm) of the reaction solution surface is about $18,300 \mu\text{W}/\text{cm}^2$. The intensity is about

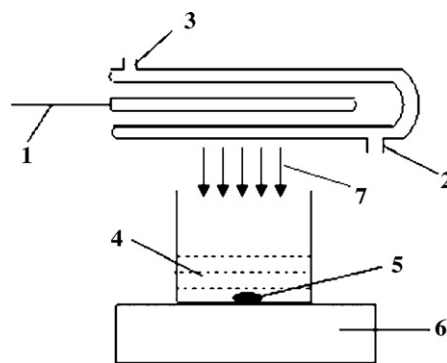


Fig. 1. Schematic diagram of photoreaction apparatus: (1) lamp; (2) water-cooling inlet; (3) water-cooling outlet; (4) reaction solution; (5) stirring rod; (6) magnetic agitator; (7) light.

6 times than that of solar UV irradiation. In the experiments, the initial pH of the reaction solution was 6.0, the illumination time was 30 min, and the amount of TiO_2 photocatalyst used was 6.0 g/L , except for experiments where the pH value, the illumination time and the amount of the photocatalyst used were varied. The initial concentration of methamidophos was $1.9 \times 10^{-4} \text{ mol/L}$. In order to disperse the photocatalyst powder, the suspensions were ultrasonically vibrated for 20 min prior to irradiation. After illumination, the samples (volume of each was 5 mL) were taken from the reaction suspension, centrifuged at 7000 rpm for 20 min and filtered through a $0.2\text{-}\mu\text{m}$ millipore filter to remove the particles. The filtrate was then analyzed. In order to determine the reproducibility of the results, at least duplicated runs were carried out for each condition for averaging the results, and the experimental error was found to be within $\pm 4\%$.

2.3. Analysis

One of the final degradation products of methamidophos is PO_4^{3-} . The generation of phosphate stoichiometrically represents the complete degradation of methamidophos, with one mole of phosphate generated for each mole of methamidophos. So the amount of methamidophos degraded is indirectly determined using the concentration of phosphate. The determination of PO_4^{3-} was performed colorimetrically by the molybdenum blue method [15]. The photodegradation efficiency for each sample was calculated from the following expression:

$$\eta = \frac{p_t}{p_0} \times 100\%$$

where η is the photodegradation efficiency of methamidophos; p_t is the amount of phosphate in solution after t illumination; p_0 is the whole amount of organophosphate in solution before illumination.

3. Results and discussion

3.1. Effect of the amount of TiO_2

It has been reported that photodegradation efficiency of organic pollutant is very slow under UV illumination in absence of TiO_2 or in the dark with TiO_2 , only under UV illumination in presence of TiO_2 are there an ideal result [16]. The above result is verified in our laboratory. In order to obtain the optimum TiO_2 suspension concentration, the effect of photocatalyst dosages on the degradation of methamidophos in aqueous solution was studied, and experiments were carried out employing different concentrations of TiO_2 varying from 2.0 to 20.0 g/L . The result is illustrated in Fig. 2.

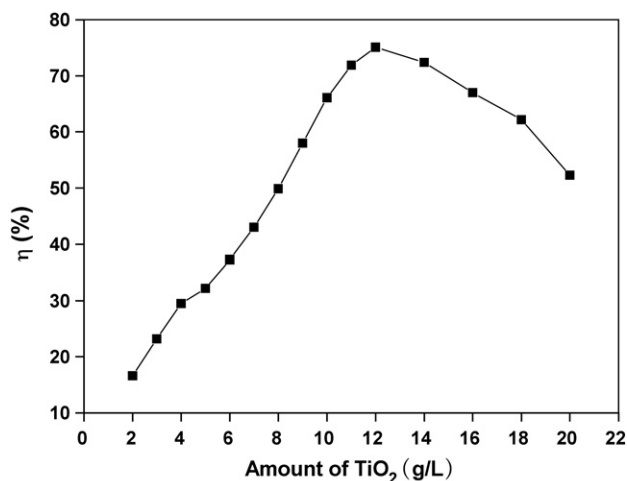


Fig. 2. Effect of the amount of TiO₂ on the photodegradation efficiency. Illumination time $t = 30$ min.

As can be seen from Fig. 2, it is obvious that when the illumination time is fixed at 30 min, the photodegradation efficiency is directly proportional to the mass of catalyst. As the concentration of the photocatalyst increases from 2.0 to 12.0 g/L, the photodegradation efficiency of methamidophos increases rapidly from 16.6% to 75.1%. Then the efficiency decreases slightly when the amount of TiO₂ is above 12.0 g/L.

It is believed that the increase in the number of TiO₂ particles will increase the number of photons absorbed and the number of the methamidophos molecules adsorbed. Therefore, the degradation efficiency can be enhanced with increasing TiO₂ concentration due to the increase in total surface area available for contaminant adsorption. And a further increase of the catalyst concentration beyond 12.0 g/L may cause light scattering and screening effects. The excessive TiO₂ photocatalyst leads to opacity of the suspension, which prevents the catalyst farthest in solution from being illuminated [7]. The scattering and screening effects reduce the specific activity of the catalyst [17]. At high catalyst concentration, particle aggregation may also reduce the catalytic activity [1]. So the photodegradation efficiency of methamidophos decreases. In this study, the optimum amount of catalyst is found to be 12.0 g/L for the degradation of methamidophos. In all the experiments, the height of the reaction solution is about 2.7 cm, and other solution heights may probably lead to different results due to other conditions, such as light scattering and screening.

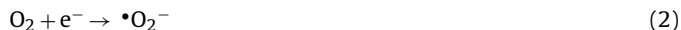
3.2. Effect of illumination time

The fixed amount of TiO₂ was 6.0 g/L. The relationship between the photodegradation efficiency of methamidophos and the illumination time was investigated. The result is shown in Fig. 3.

From Fig. 3, it can be seen that the photodegradation efficiency of methamidophos increases with the increase of the illumination time. The photodegradation efficiency of methamidophos increases from 19.6% to 87.7% when the illumination time increases from 10 to 110 min.

It is believed that the photocatalytic degradation reaction of organic pollutants occurs on the surface of TiO₂ [18], and O₂ and H₂O are necessary for the photocatalytic degradation. Under UV illumination, electron-hole pairs are created on the TiO₂ surface. Oxygen adsorbed on the TiO₂ surface prevents the recombination of electron-hole pairs by trapping electrons; Superoxide radical ions ($\bullet\text{O}_2^-$) are thus formed. $\bullet\text{OH}$ radicals are formed from holes reacting with either H₂O or OH⁻ adsorbed on the TiO₂ surface [3,8,19].

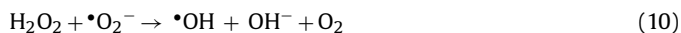
The entire course is as follows:



Correspondingly, H₂O₂ is formed by $\bullet\text{O}_2^-$.



$\bullet\text{OH}$ and O_2^{2-} are also formed by H₂O₂



The $\bullet\text{OH}$ and O_2^{2-} are widely accepted as primary oxidants in heterogeneous photocatalysis. The oxidizing power of the $\bullet\text{OH}$ radicals is strong enough to completely oxidize methamidophos adsorbed on the surface of TiO₂ into PO₄³⁻, H₂O and other mineral acids [20–22].

From Fig. 3, it also can be seen that when the illumination time is longer than 70 min, only small enhancement of photodegradation efficiency is observed. When the illumination time is 90 and 110 min, the photodegradation efficiency of methamidophos is 86.5% and 87.7%, respectively. The result does not seem to lead to full degradation. The possible reason is that there are a large number of small organic molecules produced by photodegradation with the increase of the irradiation time. The small organic molecules adsorb on the surface of TiO₂, resulting in the decrease in the amount of $\bullet\text{OH}$ radicals that attack the organophosphate, and therefore influence the photodegradation efficiency of methamidophos. At the same time, it had been reported that the organophosphorus pesticides can be completely photocatalytically degraded into PO₄³⁻ with the increase of the illumination time [2,3].

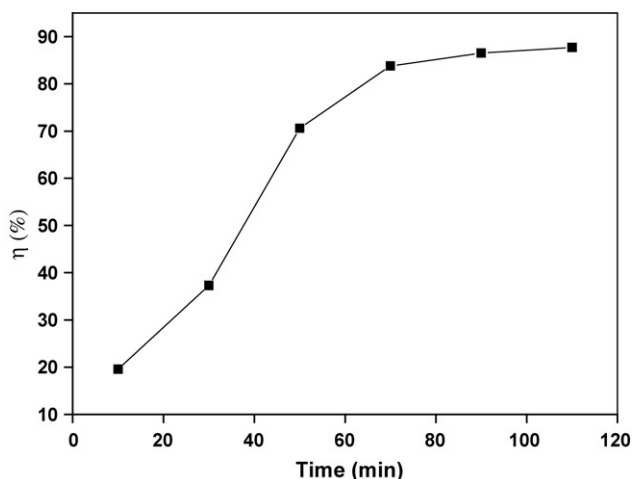


Fig. 3. Effect of illumination time on the photodegradation efficiency.

3.3. Effect of initial pH value

The pH value of the different wastewater is different, and it influences the photocatalytic reactions for removal of the pollutants. Similarly, the pH plays an important role in the degradation of methamidophos. The pH was measured by using precision pH meter of PHS-3C type. The effect of the initial pH value on the photodegradation efficiency of methamidophos is shown in Fig. 4.

From Fig. 4, it can be seen that the initial pH value has an important influence on the photodegradation efficiency of methamidophos. The photodegradation efficiency increases with the increase of the initial pH value. The photodegradation efficiency of methamidophos increases from 22.0% to 46.0% when the initial pH value increases from 2.0 to 12.0.

It is reported that in the illuminated TiO₂ system, the effect of pH on the photocatalytic reaction is generally attributed to the surface charge of TiO₂ [23]. The point of zero charge (pzc) of TiO₂ is 6.3. At pH values lower than 6.3 the catalyst's surface is positively charged and at higher pH values it is negatively charged [24]. Electrostatic attraction or repulsion between the catalyst's surface and the organic molecule is taking place, depending on the ionic form of the organic compound (anionic or cationic) and consequently enhances or inhibits the photodegradation efficiency, respectively.

From Fig. 4, it is observed that alkaline media are favorable for the photocatalytic degradation of methamidophos. The main reasons for enhancement of the efficiency are as follows: (i) The surface of the TiO₂ catalyst is negatively charged at higher pH value, when there exists a large quantity of OH⁻. It is favorable for holes to transfer from the inner part of granule to the surface. The elevated concentration of OH⁻ will increasingly scavenge photogenerated holes and concurrently yield highly oxidative •OH species through Eq. (4). On the contrary, at a low pH condition the catalyst's surface is positively charged and the degradation reaction mainly results from photogenerated holes, whose oxidizing ability is somewhat lower than that of •OH species [25]. (ii) The electrostatic attraction between the methamidophos molecules and the TiO₂ catalyst is greater at alkaline pH, the methamidophos molecules are allowed to reach easily the catalyst's surface [26]. (iii) It may be attributed to the adsorption capacity of methamidophos, which is higher than acidic pH and advantageous to get high quantum yield. Therefore, they are more favorable for efficient generation of •OH and O₂²⁻ in alkaline medium and achieve higher photodegradation efficiency [26].

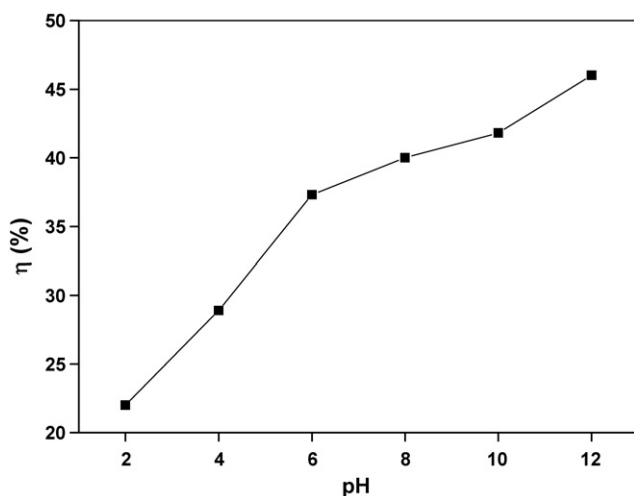


Fig. 4. Effect of initial pH value on the photodegradation efficiency. Illumination time $t = 30$ min.

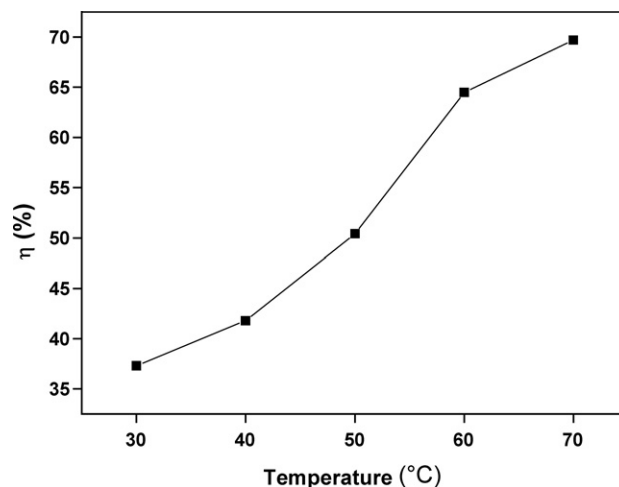


Fig. 5. Effect of temperature on the photodegradation efficiency. Illumination time $t = 30$ min.

3.4. Effect of reaction temperature

In order to evaluate the effect of reaction temperature on the photocatalytic degradation of methamidophos, experiments at different temperatures, varying from 30 to 70 °C, were carried out. The effect of temperature on the photodegradation efficiency of methamidophos is shown in Fig. 5.

As can be seen from Fig. 5, it is obvious that when the illumination time is fixed at 30 min, the increase of the temperature causes an increase in the degradation efficiency. The photodegradation efficiencies at 40 and 70 °C are 41.3% and 70.6%, respectively. The enhancement of the photodegradation is probably due to the increasing collision frequency of molecules. Irradiation is believed to be the primary source of electron–hole pairs at ambient temperature because the band gap is too high to overcome by thermal excitation [27].

From Fig. 5, it is clear that the value of 70 °C seems to fall dramatically off the rest of the data points, the possible reason is that the reaction solution evaporates more quickly when it is heated to 70 °C, which causes the solution to condense and the concentration becomes higher. Illumination for 30 min, the amount of evaporation is about 60 mL. On the contrary, the evaporated quantity of the solution is much less at low temperature.

3.5. Effect of initial concentration

The effect of initial concentration of methamidophos on the photocatalytic degradation was studied by varying the initial concentration over a wide range. The result is illustrated in Fig. 6.

From Fig. 6, it can be seen that photodegradation efficiency decreases with the increase in the initial concentration of methamidophos. The photodegradation efficiency of methamidophos decreases from 58.7% to 37.7% when the initial concentration increases from 5.9×10^{-5} to 1.9×10^{-4} mol/L. It was reported that the recombination of photogenerated electrons and holes at the surface of TiO₂ can complete within 10^{-9} s [28], which implies that the contaminants can not be degraded unless they are adsorbed on the surface of TiO₂. Thus surface adsorption process is of paramount importance in controlling the degradation of methamidophos. At a fixed concentration of TiO₂ and consequently constant total sites available for adsorption, the degradation efficiency tends to decrease with the increase in the initial concentration of methamidophos.

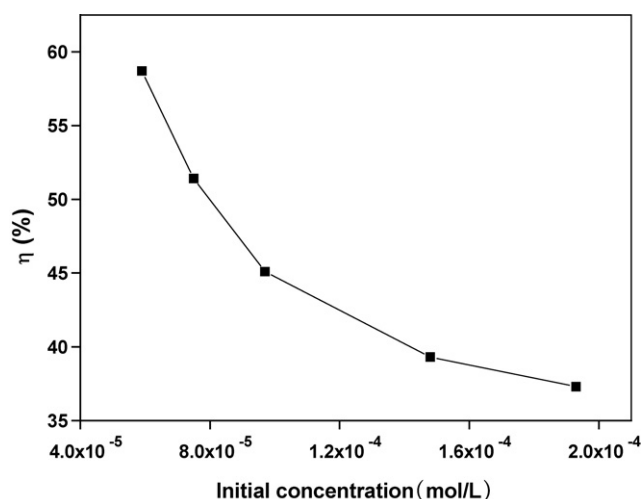


Fig. 6. Effect of initial concentration on the photodegradation efficiency. Illumination time $t = 30$ min.

3.6. Effect of electron acceptors

In the illuminated TiO_2 system, one practical problem is the undesired electron–hole pair recombination, which is the major energy-wasting step and leads to low quantum yield. So the prevention of electron–hole recombination appears to play an important role in photocatalysis. It is an extremely efficient measure by adding a proper electron acceptor or donor. The addition of the electron acceptor enhanced the degradation rate by (1) preventing the electron–hole recombination by accepting the conduction band electron; (2) increasing the hydroxyl radical concentration; and (3) generating other oxidizing species ($\text{SO}_4^{\cdot-}$) to accelerate the efficiency of intermediate compounds [29].

Molecular oxygen is usually used as an electron acceptor in heterogeneous photocatalytic reactions. The addition of an oxidant into a semiconductor suspension has been proven to enhance the photodegradation efficiency of a variety of organic pollutants [30–34]. In this study, the addition of other irreversible electron acceptors such as H_2O_2 , KBrO_3 , and $\text{K}_2\text{S}_2\text{O}_8$ on the photodegradation of methamidophos was evaluated.

3.6.1. Effect of H_2O_2

The effect of adding H_2O_2 on the photodegradation efficiency of methamidophos was investigated by varying the amount of H_2O_2 from 0.01 to 10.0 mmol/L. The result is shown in Fig. 7.

From Fig. 7, it can be seen that adding a small amount of H_2O_2 (up to 0.8 mmol/L) the photodegradation efficiency of methamidophos increases rapidly from 37.3% to 71.5%, but if the H_2O_2 concentration is larger than 0.8 mmol/L, the photodegradation efficiency decreases gradually. A similar observation has been reported in other organic pollutants [6,14,15]. The rate improvement at lower H_2O_2 dosages is probably due to the following reasons. First, direct photolysis of H_2O_2 by UV light can generate $\cdot\text{OH}$ radicals, which are likely to be the dominant rate-improving mechanism in this process (Eq. (11)). Another minor mechanism may partially contribute to the rate enhancement, in which H_2O_2 is suggested to be a better electron acceptor than oxygen. This would reduce the chances of the electron–hole pair recombination, as shown in Eq. (9). At high H_2O_2 dosages, however, the excess H_2O_2 molecules scavenge the valuable $\cdot\text{OH}$ that was generated by either the direct photolysis of H_2O_2 (Eq. (11)) or the photooxidation of OH^- by holes (Eq. (4)), and form a much weaker oxidant $\text{HO}_2\cdot$ (Eq. (13)). In addition, the high dose of H_2O_2 might absorb and attenuate the incident UV light

available for the photocatalysis process [14,29]. Therefore, the total oxidation capabilities of the system are largely reduced (Eq. (14)) and the rates retarded:

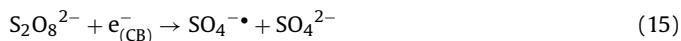


So the optimum concentration of H_2O_2 is 0.8 mmol/L for the photocatalytic degradation of methamidophos under the fixed condition described above.

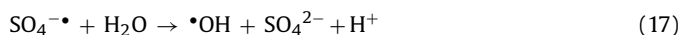
3.6.2. Effect of $\text{K}_2\text{S}_2\text{O}_8$

The effect of $\text{S}_2\text{O}_8^{2-}$ concentration on the photodegradation efficiency of methamidophos is shown in Fig. 7. From Fig. 7, it can be seen that adding a small amount of $\text{S}_2\text{O}_8^{2-}$ (up to 4.0 mmol/L) the photodegradation efficiency of methamidophos increases rapidly from 37.3% to 78.4%, however, if the $\text{S}_2\text{O}_8^{2-}$ concentration is larger than 4.0 mmol/L, only small enhancement of photodegradation efficiency was observed.

The enhancement of reaction rate is due to the inhibition of electron–hole recombination and production of other oxidizing species, namely, sulphate radical anion (Eq. (15)).



The sulphate radical anion $\text{SO}_4^{\cdot-}$ may react with photogenerated electron and with water molecule producing hydroxyl radical (Eqs. (16) and (17)).



The sulphate radical anion ($\text{SO}_4^{\cdot-}$) is also a very strong oxidant ($E^0 = 2.6$ eV). This radical anion also participates in the degradation process.

The inhibition of reaction occurs at a high dosage of $\text{S}_2\text{O}_8^{2-}$ due to the increase in concentration of SO_4^{2-} ion (Eq. (15)). The excess of SO_4^{2-} ion is adsorbed on the TiO_2 surface and reduces the catalytic activity. At the same time, the excess adsorbed SO_4^{2-} ion also reacts with the photogenerated holes (Eq. (18)) and hydroxyl radicals (Eq. (19)) [6,9,29,35].

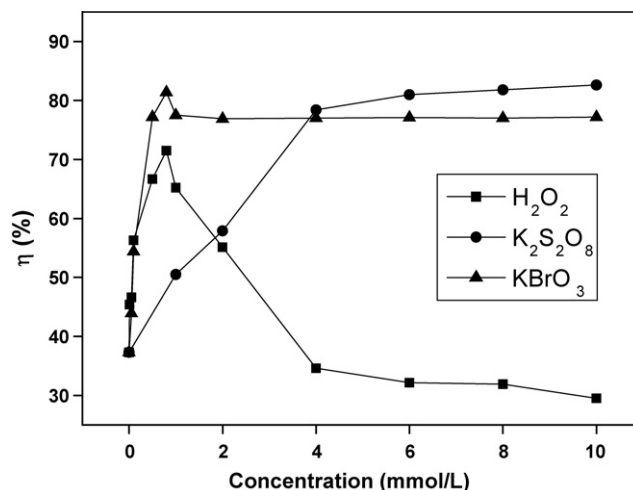


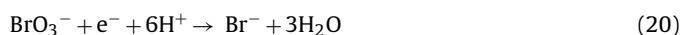
Fig. 7. Effects of H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and KBrO_3 concentrations on the photodegradation efficiency. Illumination time $t = 30$ min.

So the optimum concentration of $S_2O_8^{2-}$ is 4.0 mmol/L for the photocatalytic degradation of methamidophos. In the case of photocatalytic degradation, $S_2O_8^{2-}$ is the most effective additive for the photodegradation of methamidophos among the additives studied in this paper.

3.6.3. Effect of $KBrO_3$

$KBrO_3$ is an efficient electron acceptor which is often used as an additive to enhance photocatalytic degradation rate [9,29,35]. The effect of BrO_3^- on the photodegradation efficiency of methamidophos is shown in Fig. 7.

From Fig. 7, it can be seen that adding a small amount of BrO_3^- (up to 0.8 mmol/L) the photodegradation efficiency of methamidophos increases rapidly from 37.3% to 81.4%. The enhancement of photodegradation efficiency is due to the reaction between BrO_3^- ion and conduction band electron (Eq. (20)), which reduces the recombination of electron–hole and prolongs the life-time of the photogenerated holes.



When the amount of BrO_3^- is more than 0.8 mmol/L, no significant change in the photodegradation efficiency is observed. On the contrary, a slight decrease is taking place because the adsorption of Br^- ion on TiO_2 surface decreases the catalytic activity of TiO_2 [29,35]. So the optimum concentration of BrO_3^- is 0.8 mmol/L for the photocatalytic degradation of methamidophos.

3.6.4. Effect of SO_4^{2-} , Cl^- , Br^-

Anions such as SO_4^{2-} , Cl^- , Br^- , are often contained in wastewater. They may influence the photocatalytic reactions for removal of organic pollutants. So the effects of adding SO_4^{2-} , Cl^- and Br^- on the photodegradation efficiency of methamidophos were also investigated by varying the concentration from 0.001 to 0.1 mmol/L. The results showed that adding trace amounts of SO_4^{2-} , Cl^- and Br^- , no obvious effects on the photocatalytic efficiency of methamidophos were observed. On the contrary, when the $S_2O_8^{2-}$ concentration is larger than 4.0 mmol/L, the relevant concentration of SO_4^{2-} reaches the excess amount, which is probably high enough to influence the photocatalytic activity.

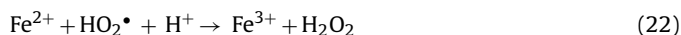
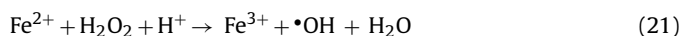
3.7. Effect of metal ions

3.7.1. Effect of Fe^{3+}

The role of Fe^{3+} as an additional electron acceptor in semiconductor-mediated photoreactions of certain organic compounds has been reported [3]. The effect of Fe^{3+} on the photodegradation efficiency of methamidophos was investigated by varying the amount of Fe^{3+} from 0.001 to 0.8 mmol/L. The result is shown in Fig. 8.

From Fig. 8, it can be seen that adding a small amount of Fe^{3+} (up to 0.5 mmol/L) the photodegradation efficiency of methamidophos increases rapidly from 37.3% to 55.0%. But if the Fe^{3+} concentration is larger than 0.5 mmol/L, the photodegradation efficiency decreases greatly.

Therefore, we assume that positively charged Fe^{3+} adsorbed on the TiO_2 surface is easily reduced by trapping electrons ($Fe^{3+} + e^- \rightarrow Fe^{2+}$). The amount of recombining electron–hole pairs thus decreases. It is favorable for the formation of $\bullet OH$ and O_2^{2-} on the surface of TiO_2 . At the same time, the following reaction occurs:



Eqs. (21) and (22) are favorable for the formation of $\bullet OH$ and O_2^{2-} . However, when the Fe^{3+} concentration is higher, the

$Fe(OH)^{2+}$ ion likely exists as the predominant monomeric iron(III)-hydroxy complex, which is also a major light absorbing species. The UV absorption spectrum exhibits a charge-transfer band ($\lambda_{max} = 295\text{--}297\text{ nm}$) with $\epsilon = 2050\text{ L mol}^{-1}\text{ cm}^{-1}$, which partly corresponding to the UV emission spectrum of the medium pressure mercury lamp in the 290–400 nm region [36,37].

So the optimum initial concentration of Fe^{3+} is 0.5 mmol/L for the photocatalytic degradation of methamidophos.

3.7.2. Effect of Cu^{2+}

It has been reported that adding a certain amount of Cu^{2+} can extremely enhance the photodegradation efficiency of an organic pollutant [3]. The effect of Cu^{2+} on the photodegradation efficiency of methamidophos was investigated by varying the amount of Cu^{2+} from 0.001 to 0.8 mmol/L. The result is shown in Fig. 8.

From Fig. 8, it can be seen that adding a small amount of Cu^{2+} (up to 0.006 mmol/L) the photodegradation efficiency of methamidophos increases rapidly from 37.3% to 67.0%, but if the Cu^{2+} concentration is larger than 0.006 mmol/L, the photodegradation efficiency decreases markedly.

Cu^{2+} behaves as electron scavenger ($Cu^{2+} + e^- \rightarrow Cu^+$), preventing the recombination of electron–hole pairs, thus increasing the chances of the formation of $\bullet OH$ and O_2^{2-} on the TiO_2 surface. This is favorable for the photocatalytic reactions. But when the Cu^{2+} concentration is higher, the photodegradation efficiency decreases. It may be attributed to the low reduction potential for Cu^{2+}/Cu^+ couple. As a result, Cu^{2+} ions are reduced to Cu^+ by electrons while Cu^+ ions thus formed are oxidized to Cu^{2+} by the photogenerated holes on the surface of TiO_2 particles or by $\bullet OH$ through the following reactions [38]:



Therefore, the Cu^{2+} – Cu^+ cycle does not produce any $\bullet OH$. Furthermore, it causes a decrease in the concentration of $\bullet OH$ in the photocatalytic system.

The same result has been reported that Cu^{2+} acts positively or negatively, depending on the concentration of Cu^{2+} [39]. When Cu^{2+} concentration is less than 0.006 mmol/L, it increases the rate, but a larger amount of copper was found to be detrimental under the reaction conditions used in this work. So the optimum initial concentration of Cu^{2+} is 0.006 mmol/L for the photocatalytic degradation of methamidophos.

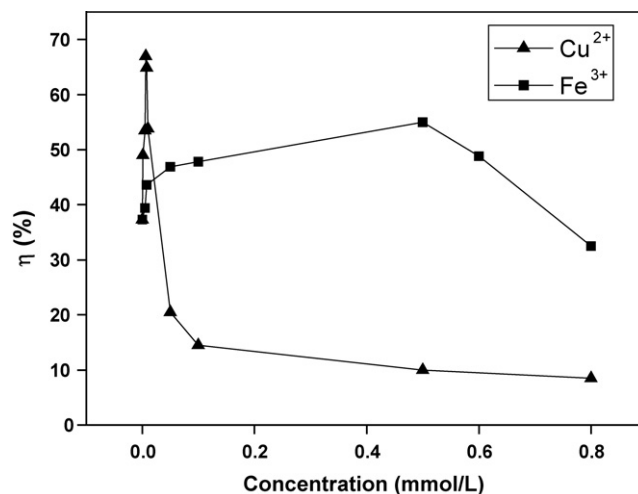


Fig. 8. Effects of Fe^{3+} and Cu^{2+} concentrations on the photodegradation efficiency. Illumination time $t = 30\text{ min}$.

3.7.3. Effect of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+}

The dissolved metal ions are rather common in natural water and industrial wastewater [16]. The effects of adding Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} on the photodegradation efficiency of methamidophos were also investigated by varying the concentration from 0.001 to 0.8 mmol/L. The results showed that adding a small amount of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , no obvious effects on the photocatalytic efficiency of methamidophos were observed.

4. Conclusions

Methamidophos was easily degraded by TiO_2 assisted photocatalysis in aqueous dispersion under irradiation by UV light. The best condition for degradation of 1.9×10^{-4} mol/L methamidophos at room temperature was determined. The optimum concentration of TiO_2 photocatalyst was 12.0 g/L. The photodegradation efficiency of methamidophos increased with the increase of the illumination time. Alkaline media were favorable for the photocatalytic degradation of methamidophos. The degradation efficiency was enhanced by increasing reaction temperature. And the photodegradation efficiency decreased with an increase in the initial concentration of methamidophos. The optimum concentrations of H_2O_2 , $\text{S}_2\text{O}_8^{2-}$ and BrO_3^- were 0.05, 0.5 and 0.5 mmol/L, respectively. The optimum initial concentrations of Fe^{3+} and Cu^{2+} were 0.05 and 0.004 mmol/L, respectively. No obvious effects on the photodegradation efficiency of methamidophos were found with addition of a small amount of SO_4^{2-} , Cl^- , Br^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} .

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