

Treatment of organophosphate-contaminated wastewater by acidic hydrolysis and precipitation

Zhiqian Jia^{*}, Yue Li, Shu Lu, Haizhu Peng, Jianying Ge, Shideng Chen

Beijing Research Institute of Chemical Industry, Beijing, China

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Abstract

Wastewater from commercial manufacture of organophosphate (OP) pesticide of *O*-methyl-*O*-(2-isopropyl salicylate) thiophosphorusyl amide contains large amounts of organophosphate, organic sulfides, COD and $\text{NH}_3\text{-N}$. A treatment process including acidic hydrolysis and precipitation was explored in this paper. The effects of initial pH values, hydrolysis temperature and hydrolysis time on the removal of pollutants were investigated. The experimental results showed that, in the hydrolysis, with the decreasing initial pH value, the removal of OP, sulfide and COD rose whereas the $\text{NH}_3\text{-N}$ removal declined. Increased hydrolysis temperature and time favored the removal of all the pollutants. 15.0 wt% $\text{Ca}(\text{OH})_2$ was sufficient for the removal of inorganic phosphorus and residual $\text{NH}_3\text{-N}$ in the precipitation step. With this chemical process, the removal of total phosphorus (TP), organophosphate, sulfides and $\text{NH}_3\text{-N}$ exceeded 90%, and the removal of COD was about 60%. The BOD_5/COD value was greatly improved from 0.05 to 0.3, and the bio-degradability of the wastewater was greatly improved. The NH_3 generated in the process was absorbed with water and might be reused in the manufacture of the pesticide. The results showed that this comprehensive process is effective for the treatment of this typical unbio-degradable pesticide wastewater.

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1. Introduction

O-methyl-*O*-(2-isopropyl salicylate) thiophosphorusyl amide (i.e. Bayer 93820, Scheme 1), synthesized firstly in 1967 by the Bayer Co., is an important organophosphate (OP) pesticide and has high activities in killing insects and acarids. In China, there are about 10 factories manufacturing the pesticide, and the annual production of the pure oil attains about 5000 t [1].

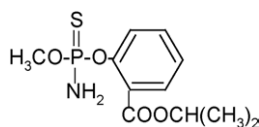
The manufacturing process includes two steps. Firstly, *O*-methyl-dichloro-thiophosphate reacts with 2-isopropyl salicylate and produces *O*-methyl-monochloro-thiophosphate. Then, *O*-methyl-monochloro-thiophosphate reacts with ammonia and generates the pesticide (Scheme 2). Lastly, the pesticide is rinsed with water and pure pesticide oil is obtained [2].

For every tonne of pesticide oil manufactured, about 1.5 t of wastewater is discharged. The wastewater contains COD ($\sim 50,000 \text{ mg dm}^{-3}$), $\text{NH}_3\text{-N}$ ($\sim 40,000 \text{ mg dm}^{-3}$), organophosphate ($\sim 10,000 \text{ mg dm}^{-3}$) and sulfide compound (S^{2-} , $\sim 10,000 \text{ mg dm}^{-3}$). The BOD_5/COD value is usually less than 0.1, displaying as a typical unbio-degradable organic wastewater. Physico-chemical approaches are usually indispensable for the treatment of concentrated organic wastewater [3]. As for organophosphate wastewater, wet oxidation, photo-Fenton [4], membrane anodic Fenton [5], combination of supercritical carbon dioxide extraction (at 90°C and 325 atm) and degradation with Fenton's reagent [6], heterogeneous photocatalytic oxidation [7–11], etc., have been employed. Nevertheless, the conditions of wet oxidation and supercritical carbon dioxide extraction are usually severe. The cost of Fenton approach is often very high. Photocatalytic oxidation is generally suitable for the degradation of dilute wastewater. In addition, to date there are only a few reports concerned with the treatment of real organophosphate wastewater.

For the wastewater from commercial manufacture of *O*-methyl-*O*-(2-isopropyl salicylate) thiophosphorusyl amide, the

^{*} Corresponding author. Present address: Department of Chemistry, Beijing Normal University, Xijiekou Street, Haidian District, Beijing 100875, China. Tel.: +86 10 58210560.

E-mail address: jzq5000@yahoo.com.cn (Z. Jia).



Scheme 1.

removal of organophosphate, total phosphorus (TP), sulfide, $\text{NH}_3\text{-N}$ and COD should be taken into account comprehensively. To treat this wastewater at milder conditions, in this paper, a comprehensive process including acidic hydrolysis at atmospheric pressure and precipitation was explored. The effects of initial pH values, hydrolysis temperature and time on the removal of pollutants were investigated. With this process, the removal of OP, TP, S^{2-} and $\text{NH}_3\text{-N}$ exceeded 90%, and the removal of COD attained about 60%. The bio-degradability of the wastewater was greatly improved.

2. Experimental

2.1. Wastewater qualities

The wastewater was sampled from a pesticide factory of Shandong Province, China. The wastewater displays yellow–green color with strong ammonia and sulfide smells, and contains a small amount of white precipitates and suspends. As shown in Table 1, the wastewater is basic (pH 9.1) and contains many kinds of pollutants with high concentration.

2.2. Experimental methods

In the acidic hydrolysis, a certain amount of H_2SO_4 was added into the wastewater to adjust the initial pH value. Then the wastewater was heated in the flask with total reflux operation for a certain time. The sulfide and ammonia generated in the reaction were absorbed with 30% (w/w) NaOH solution and water, respectively.

The analyses were conducted according to the national standards for wastewater analysis [13]. Chloride was determined by AgNO_3 titration. After dissolved in $\text{HNO}_3\text{-HCl}$ acid, TP and OP were assessed by ammonium molybdate with spectrophotometer. Sulfide, COD and BOD_5 were detected with iodimetry, potassium dichromate and dilution inoculation methods, respectively. $\text{NH}_3\text{-N}$ was determined by titration. 2-Propanol

Table 1
Wastewater qualities

pH	9.1
COD (mg dm^{-3})	53545
TP (mg dm^{-3})	11125
OP (mg dm^{-3})	10735
Sulfides (mg dm^{-3})	14631
$\text{NH}_3\text{-N}$ (mg dm^{-3})	39297
Cl^- (mg dm^{-3})	48884
BOD_5 (mg dm^{-3})	2446
BOD_5/COD	0.05

and methanol in the wastewater were assessed with gas chromatograph (SP-3402, Beijing Instrument Co.) with fixed phase of PEG-6202, carrier gas of nitrogen, FID detector, column temperature of 65°C , vaporization chamber temperature of 150°C and detection chamber temperature of 140°C .

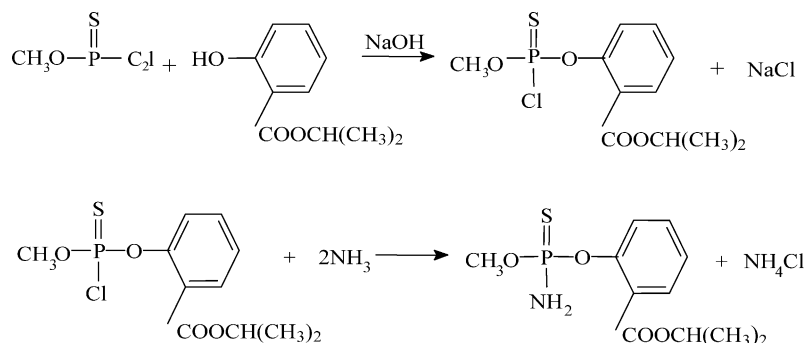
3. Results and discussions

3.1. Effects of hydrolysis temperature

H_2SO_4 was added into 0.25 dm^3 wastewater in a flask to adjust the initial pH value to be 2.5. Then the hydrolysis reaction was conducted at $75(\pm 1)^\circ\text{C}$, $85(\pm 1)^\circ\text{C}$, $95(\pm 1)^\circ\text{C}$ and the boiling point of the wastewater, respectively, for 0.5 h. It was found that the boiling point rose to 108°C due to the existence of inorganic salts (e.g. NaCl) and H_2SO_4 . Fig. 1a shows that with the increasing temperature from 75°C to 108°C , the removal of OP rose pronouncedly from 13% to 55% because hydrolysis is an endothermal reaction and the elevated temperature shifts the reaction balance to the right side. Meanwhile, according to the van't Hoff rule, the increased temperature also promotes the reaction rates, leading to the increment of the OP removal after hydrolysis for the same time (0.5 h). In the later experiments, all the reactions were conducted at the boiling point.

3.2. Effects of initial pH values

The initial pH value of the wastewater was adjusted to be 0.8, 2.0, 2.5, 3.6, 4.2 and 6.2 with H_2SO_4 , respectively. Then the wastewater was heated till boiling for 0.5 h under stirring. The experimental results (Fig. 1b) show that, with



Scheme 2.

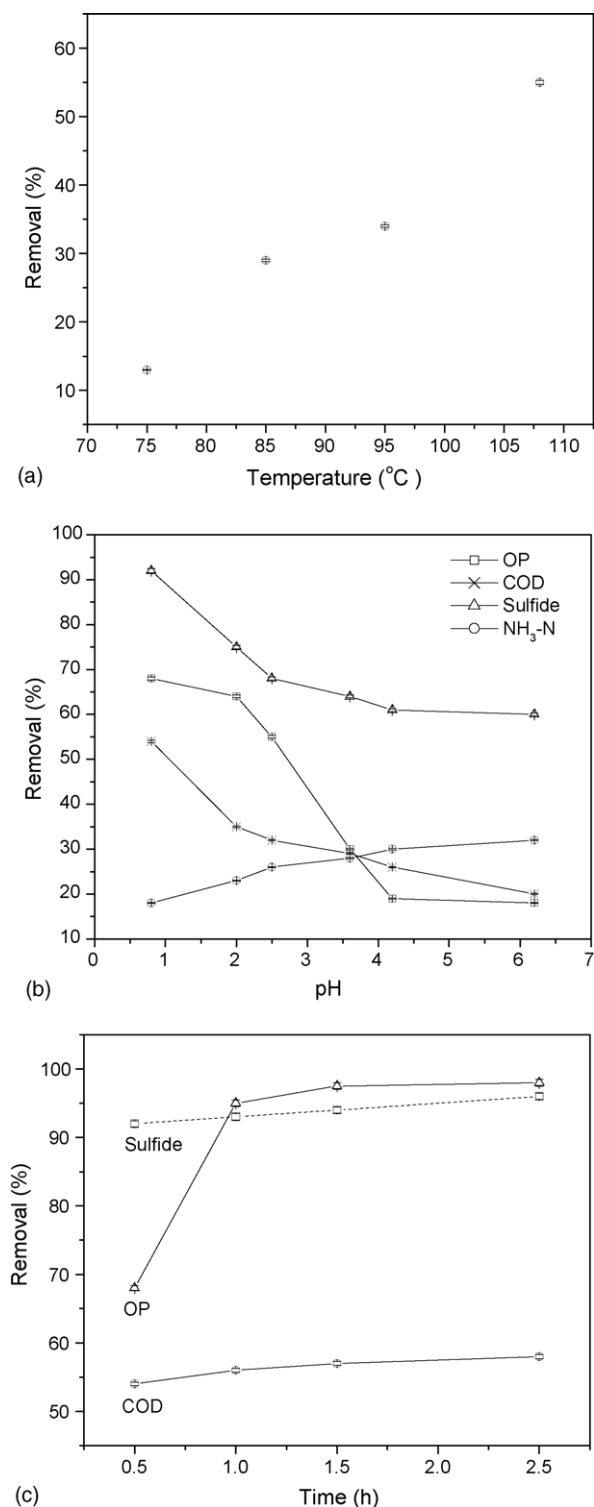
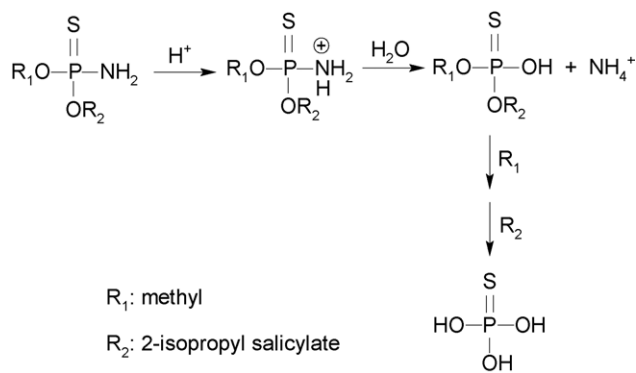


Fig. 1. Effects of operation parameters on the removal of pollutants: (a) effects of reaction temperature on the removal of OP, (b) effects of initial pH values and (c) effects of reaction time.

the increasing pH value from 0.8 to 6.2, the removal of OP, sulfide and COD decreased (e.g. the OP removal declined from 68% to 19%, and the sulfide removal decreased from 92% to 60%), whereas the removal of NH₃-N rose from 18% to 32% because high OH⁻ concentration favored the reaction of



Scheme 3.

$\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 \uparrow + \text{H}_2\text{O}$. The removal of COD was mainly ascribed to the volatilization of the sulfide.

In the wastewater, the pollutants include the pesticide, raw materials (e.g. dichloro-thiophosphate, 2-isopropyl salicylate) as well as the intermediate products (e.g. *O*-methyl-monochloro-thiophosphate). For the pesticide, the N atom of the molecule protonates at acidic conditions so that the P atom is readily attacked by the nucleophile (e.g. H₂O), leading to the breakage of P–N bond and the generation of NH₄⁺ and *O*-methyl-*O*-(2-isopropyl salicylate) thiophosphate [14]. Then *O*-methyl-*O*-(2-isopropyl salicylate) thiophosphate continues hydrolysis, resulting in the loss of methyl and 2-isopropyl salicylate and the formation of thiophosphoric acid (Scheme 3). The gas chromatograph analysis showed that, after hydrolysis at pH 0.8 for 0.5 h, the methanol concentration in the wastewater increased from 0.35% to 0.96% and the 2-propanol concentration rose slightly from 0.10% to 0.12%.

3.3. Effects of hydrolysis time

The hydrolysis was conducted at the initial pH value of 0.8 and the boiling point for 0.5 h, 1.0 h, 1.5 h and 2.5 h, respectively. Fig. 1c shows that the removal of OP was about 68% at 0.5 h and attained 97% at 1.0 h. Then the uprising of the OP removal became slowly. The effects of hydrolysis time on the removal of sulfide and COD were not very apparent. At 1.0 h, the respective removal of sulfide and COD attained 93% and 56%, and the NH₃-N removal was about 20%.

3.4. Removal of total phosphorus and residual NH₃-N

After hydrolysis at initial pH value of 0.8 and the boiling point for 1.0 h, about 97% organophosphates were converted into inorganic phosphorus compounds. In addition, only about 20% NH₃-N was removed. To further remove the inorganic phosphorus and the residual NH₃-N, Ca(OH)₂ powder with weight percent of 6.0%, 9.0%, 15.0% and 20.0% was added into the wastewater, respectively. Then the wastewater was heated till boiling for 0.4 h under stirring. The NH₃ generated was absorbed with water to obtain ammonia, which might be reused in the manufacture of the pesticide. In this process, the inorganic phosphorus reacted with Ca²⁺ and formed Ca₃(PO₄)₂ precipitates,

Table 2
Effects of Ca(OH)₂ addition amounts

Ca(OH) ₂ (%)	Initial pH	End pH	TP (mg dm ⁻³)	OP (mg dm ⁻³)	NH ₃ -N (mg dm ⁻³)	R _{TP} (%)	R _{OP} (%)	R _{NH₃-N} (%)
6.0	9.6	8.7	866	609	29747	92.2	94.3	24.3
9.0	10.3	8.9	487	487	16472	95.6	95.5	58.1
15.0	11.0	11.0	257	257	1391	97.7	97.6	96
20.0	11.0	11.0	252	252	1035	97.8	97.7	97

which could act as a flocculant to remove the residual OP and COD.

Table 2 shows that with the increase in the amount of Ca(OH)₂, the initial pH values ascended from 9.6 to 10.3, 11.0 and 11.0, and the end pH value rose from 8.7 to 8.9, 11.0 and 11.0, respectively. Meanwhile, the corresponding removal of NH₃-N was 24.3%, 58.1%, 96% and 97%, and the TP removal was 92.2%, 95.6%, 97.7% and 97.8%, respectively. When the Ca(OH)₂ addition was 15%, all the residual TP was OP (257 mg dm⁻³), and the BOD₅/COD of the wastewater was determined to be 0.3. So it seemed that 15.0% Ca(OH)₂ was sufficient for the treatment.

3.5. Comprehensive treatment process

From the above results, the treatment process can be summarized as follows: firstly, hydrolysis was conducted at the initial pH value of 0.8 and the boiling point for 1.0 h. The sulfide and NH₃ generated were absorbed with 30% (w/w) NaOH solution and water, respectively. In this process, the removal of OP, sulfide, COD and NH₃-N was about 97%, 93%, 56% and 20%, respectively. Then 15% Ca(OH)₂ powder was added into the wastewater, and the water was heated till boiling for 0.4 h to precipitate the inorganic phosphorus and to remove the residual NH₃-N. The NH₃ gas generated was absorbed with water. After the treatment, the discharged wastewater contained OP < 260 mg dm⁻³, S²⁻ < 1100 mg dm⁻³, NH₃-N < 1400 mg dm⁻³ and COD < 22,000 mg dm⁻³. The BOD₅/COD value increased from 0.05 to 0.3, indicating that the bio-degradability of the wastewater was greatly improved.

It should be noted that there are also several problems existing in this treatment process. Firstly, the treatment conditions are still somewhat severe (pH 0.8, boiling). It is suggested to use waste acid to replace H₂SO₄ in adjusting the initial pH value of the wastewater to reduce the cost. Waste alkaline is also preferred to Ca(OH)₂ powder. In the engineering design, steel tanks lined with polytetrafluoroethylene (PTFE) can be employed for the acidic hydrolysis and precipitation. In addition, the sulfide absorbed in the NaOH solution needs further treatment. The remaining sulfide and COD in the wastewater also need special consideration.

4. Conclusions

- The wastewater from the commercial manufacture of *O*-methyl-*O*-(2-isopropyl salicylate) thiophosphorusyl amide

was treated with the acidic hydrolysis and precipitation process. In the hydrolysis, with the decreasing initial pH value, the removal of OP, sulfide and COD rose whereas the NH₃-N removal declined. Increased hydrolysis temperature and time favored the removal of all the pollutants. In the precipitation step, 15.0% Ca(OH)₂ was sufficient for the removal of the inorganic phosphorus and the residual NH₃-N.

- With the above process, the removal of TP, OP, sulfide and NH₃-N exceeded 90%, and the COD removal attained about 60%. The BOD₅/COD value increased from 0.05 to 0.3, and the bio-degradability of the wastewater was greatly improved.
- The results showed that this comprehensive process is simple and effective for the treatment of this typical unbio-degradable pesticide wastewater.

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