An Engineering Example of Organophosphorus Recycling Inorganic Phosphorus in Wastewater

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Abstract. The organophosphorus pesticide wastewater with high value of COD and complex components was difficult to deal with. This paper presented a method for treating organophosphorus in wastewater, which could convert the organophosphorus in wastewater into inorganic phosphorus, then recycled the inorganic phosphorus and the conversion rate of organophosphorus and the recovery rate of inorganic phosphorus were high. The material content of organophosphorus and inorganic phosphorus in wastewater treated by this method was significantly reduced, and the environmental pressure was reduced. Meanwhile, the treatment conditions were moderate, and the cost of organophosphorus treatment in wastewater was reduced.

1. Introduction

Organophosphorous compounds are organic compounds containing carbon-phosphorus bonds, the structure contains alkyl, alkoxy, amino, organic or inorganic acid roots. At present, organophosphorus compounds are widely used in pesticide and pharmaceutical industry with heavy usage. The organic phosphorus intermediate or compound involved is dimethyl phosphite, trimethyl phosphite, methyl thiophosphoryl chloride, Dimethyl thiophosphoryl chloride, diethyl thiophosphoryl chloride, dimethyl dithiophosphate and diethyl dithiophosphate.

Related organophosphorus pesticides are phorate, special cube sulphur phosphorus, methamidophos, omethoate, profenofos, dimethoate, isocarbophos, fenitrothion, phoxim, ibp, malathion, acephate, chlorpyrifos-methyl, chlorpyrifos, triazophos, dipterex, dichlorvos, N-Phosphoryl methyl glycine, 4-hydroxyl (methyl) phosphonyl-D/L-hyperalanine.

The main harm of organic phosphorus to human body is that it can be combined with acetylcholinesterase in the body, so that acetylcholine cannot be hydrolyzed, resulting in symptoms such as blurred vision, headache, dizziness, fatigue, lacrimation, salivation, stomachache, emesis, chest distress, naupathia, feelgloomy, sweaty, corestenoma, convulsion, clouding of consciousness, pupillatonia, coma, pneumonedema, gastism, respiratory central failure and death. In the mean time, phosphorus is also one of the major pollution elements of eutrophication of water. Therefore, the national emission requirements for organophosphorus are extremely high. According to the "Integrated Wastewater Discharge Standard (GB8978-1996)", the primary standard organophosphorus

pesticides (with phosphorus) shall not be detected; the "Chemical Synthesis Pharmaceutical Industrial Water Pollutant Emission Standard (GB21904-2008)" stipulates that the total phosphorus must not exceed 1.0mg/L; the "Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant(GB18918-2002)" demands the total phosphorus in grade A shall not exceed 1.0mg/L.

At present, the treatment of organophosphorus is extremely difficult, and there are very few to meet the emission requirements, resulting in the malignant eutrophication of many water bodies in China. Meanwhile, many enterprises in the pesticide and chemical industry are facing closure, shutdown, transformation and merger due to the technical and economical problems of phosphorus disposal according to the Dodument No.57 issued by the general office of the ministry of environmental protection in 2013.

2. Organophosphorus Treatment in Pesticide Wastewater

The organophosphorus pesticide wastewater is of enormous amount, high toxicity and complex component, its chemical oxygen demand can reach tens of thousands of milligrams per liter. Therefore, treatment must be carried out before discharge. At present, the treatment technology of organophosphorus pesticide wastewater mainly includes physical treatment and chemical treatment. The physical processing methods include adsorption extraction gas extraction, flocculation and settling, etc. And chemical treatments include oxidation style, reduction method, hydrolysis and other methods.

Each organophosphorus pesticide wastewater treatment method has its advantages and disadvantages. Among them, the adsorption method is suitable for enterprises with low concentration and low production of wastewater while precipitation method is suitable for high concentration of phosphorus wastewater; the biological method is suitable for treating organic wastewater with low phosphorus concentration.

There are so many kinds of organophosphorus wastewater with different pesticide composition that a single treatment method is impossible to meet the emission standard. In practice, several methods are adopted synthetically to achieve better processing effect.

Invention patent CN201110310586.8 disclosed a processing method for the production of phosphorous fertilizer by a certain kind of pesticide. According to the method, in a temperature ranging from 250℃ to 1200℃, the production of phosphorous waste from the pesticide is oxidized to inorganic phosphorus in high-temperature by the contact of oxygen-containing gas, so as to realize the recovery of phosphorus. Such organic phosphorus waste is generally hazardous. According to "Hazardous Waste Incineration Pollution Control Standard" (GB18484-2001), the requirements for the incineration process such as incineration temperature, residence time, removal efficiency value, exhaust emissions (especially dioxins) is extremely strict, resulting in high operation cost. Due to the harsh operating conditions, there are very few hazardous waste incinerators with long-term stable operation.

Invention patent CN201310165774.5 unveiled a process extracting disodium hydrogen phosphate from glyphosate mother liquor. According to the method, the organic phosphorus in wastewater was converted to inorganic phosphorus by high temperature ranging from 180℃ to 280℃ and high pressure ranging from 3.0MPa to 9.0MPa. The inorganic phosphorus was removed by means of extraction, and the removal of organophosphorus, inorganic phosphorus and total phosphorus was finally realized.

The reason for adopting the above harsh reaction conditions is that the organic phosphorus is extremely difficult to degrade and has the flame-retardant property which prevent the transmission of free radicals such as .H, .OH and .O in combustion or oxidation reactions. The removal effect of organophosphorus is not satisfactory even under high temperature and pressure. At the same time, because of the harsh reaction conditions of high temperature and high pressure, this is leading to the greater technical, economical and security challenges such as equipment corrosion, operating difficulties, large investment and maintenance. Therefore, it is difficult for large-scale application in the organic phosphorus wastewater treatment both in the domestic and overseas.

At present, it is very urgent to develop the mild reaction conditions to convert the organic phosphorus in wastewater into inorganic phosphorus and finally remove the total phosphorus in wastewater.

3. Examples

3.1. Process of Treating Organic Phosphorus in Wastewater

Processing imported materials containing at least one kind of organophosphorus compound into the biochemical reaction unit. In the biochemical reaction unit, the organic phosphorus was converted into inorganic phosphorus under the condition that the mixture of organic phosphorus wastewater methane and oxygen-containing gas microorganisms fully mixed. Soon afterwards, the mixture entered the inorganic phosphorus recovery unit. After the separation of inorganic phosphorus and aqueous solution from wastewater and microorganisms, the inorganic phosphorus was recovered as by-product. The process is shown in Fig.1.

In the process, oxygen could promote the respiration of methane oxidizing bacteria. Methane was used as a substrate for the oxidation of methane and the organic phosphorus was converted into inorganic phosphorus with the catalysis of methane-oxidizing bacteria. In the process of using oxygen and methane, methane oxidizing bacteria produce a key enzyme named Methane Monooxygenase (MMO), which speeds up the conversion of organic phosphorus to inorganic phosphorus in biochemical reaction cells.

It has been found by many experiments that microbial bacteria, especially methane oxidative bacteria will devour organic phosphorus and inorganic phosphorus, synthesis of new offspring microorganisms when the phosphorus concentration in the form of organic phosphorus in wastewater is less than or equal to 5mg/L.

As a result of the need to remove the phosphorus by regularly eliminating the proliferation of microbial cells, the microbial content in the biochemical reaction cells gradually decreases. Organophosphorus inhibits the activity of methane oxidizing bacteria, thus gradually reducing the processing capacity of microorganisms to organophosphorus and inorganic phosphorus, finally unable to effectively treat organic phosphorus in wastewater.

The methane-oxidizing bacteria can catalyze the conversion of organic phosphorus to inorganic phosphorus when the total phosphorus concentration in wastewater is greater than 5mg/L and the organic and inorganic phosphorus would not be consumed to synthesize new progeny microorganisms. While removing organophosphates effectively, the recovery of inorganic phosphorus can be achieved and the economic benefits can be improved at the same time.

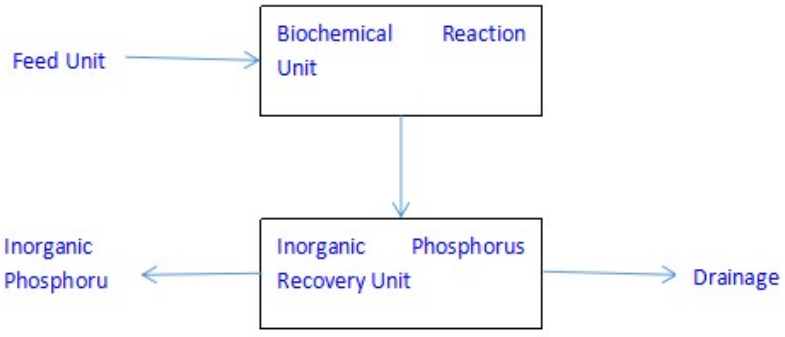

Figure 1. Process flow diagram of organic phosphorus recovering inorganic phosphorus in wastewate.

3.2. Process Parameters

The main process control parameters of inorganic phosphorus recovered from inorganic phosphorus wastewater are shown in table 1.

Table 1. Process Control Parameters of Organophosphorus Recovery in Wastewater.

Parameters	Methane-oxidizing Bacteria	DO	Mass Ratio of Phosphorus to Methane	Temperature	Processing Time
Unit	kg	mg/L		℃	h
Data	1	0.5-9.8	1:0.1-85	5-60	1-1000

3.3. Engineering Test

The wastewater of a fine chemical plant is rich in organic phosphorus and its total phosphorus concentration is about 90~100mg/L. Organic phosphorus concentration of total phosphorus concentration-inorganic phosphorus concentration was about 55~60mg/L. The waste water was directly connected to the biochemical reaction unit which has a push-flow structure. The biochemical reaction unit contains microorganisms, which are similar to activated sludge in the biochemical reaction cells. The microorganisms mainly include methane-oxidizing bacteria, and secondly, nitrobacterium, nitrococcus, denitrifying bacteria and anaerobic ammonium oxidation bacteria. And the concentration of suspended bacteria is about 6000mg/L. Methane gas comes from the enterprise's wastewater anaerobic facility, connecting to the biochemical treatment unit through the jet aeration. The oxygen-containing gas which is air in this example enters the biochemical reaction unit through the microporous aeration.

The microbial, wastewater and oxygen is mixed by oxygen-containing microporous aeration agitation and the microbial, wastewater and methane is mixed by methane jet-flow aeration agitation. The parameters of the biochemical reaction unit are shown in Table 2.

Table 2. Process Control Parameters of Organophosphorus Recovery in this Case.

Parameters	Methane-oxidizing Bacteria	DO	Mass Ratio of Phosphorus to Methane	Temperature	Processing Time
Unit	kg	mg/L		℃	h
Data	2.0-5.0	0.5-2	0.4-1.0	40	72

After the biochemical reaction, the waste water was discharged from the biochemical reaction unit and into the phosphorus recovery unit. Detected the organophosphorus concentration in biochemical reaction unit was 0 mg/L according to "Determination of Phosphate and Total Phosphorus in Water by Continuous Flow-Ammonium Molybdate Spectro photo metric method".(HJ 670-2013)

In the phosphorus recovery unit, the microorganisms and wastewater first entered the sedimentation tank. The precipitated biochemical sludge was returned to the biochemical reaction unit to continue to participate in the reaction, and the supernatant was then moved into the next section of the gas to further remove the microorganisms that were not effectively precipitated to get relatively clear and rich inorganic phosphorus wastewater.

The microorganisms in the waste water were separated and the wastewater flowed directily into the coagulation pond for precipitation, and the inorganic phosphorus was precipitated in the form of ferric phosphate by inorganic iron salts. Pump the precipitate into the filter press to get the pure phosphoric acid iron salt, and the precipitation supernatant and filter liquor was direct discharge as the qualified waste water.

The concentration of organophosphorus and inorganic phosphorus in phosphorus recovery unit were tested by method HJ670-2013, and the result showed that the concentration of organic phosphorus was 0mg/L and the inorganic phosphorus concentration was 0.1mg/L to 0.4mg/L. The change of inorganic phosphorus, organophosphorus and total phosphorus in wastewater before and after treatment is shown in table 3.

Table 3. Comparison of Phosphorus Content in Wastewater.

Inflow(mg/L)			Outflow(mg/L)			Removal Rate(mg/L)		
Inorganic Phosphorus	Organophosphorus	Total Phosphorus	Inorganic Phosphorus	Organophosphorus	Total Phosphorus	Inorganic Phosphorus	Organophosphorus	Total Phosphorus
10.0	0.0	10.0	0.5	0.0	0.5	95.0	-	95.0

In this experiment, the conversion rate of organophosphorus, inorganic phosphorus and total phosphorus was 100%, 160-180%, 99.6-99.9%, respectively.

In this example, the inorganic phosphorus concentration in the biochemical reaction unit was only 0.5mg/L when the intake port contained only 10mg/L inorganic phosphorus. It is shown that when the concentration of organophosphorus in wastewater is less than the concentration of inorganic phosphorus, the microorganisms such as methane-oxidizing bacteria will consume organophosphorus and inorganic phosphorus and synthesize new subgeneration microorganisms. In the end, organophosphorus and inorganic phosphorus can only be removed in the form of microorganism cells that emit or proliferate, rendering it unable to recycle inorganic phosphorus, and causing a lot of waste in phosphorus. Meanwhile, the content of methane oxidizing bacteria in biochemical reaction cells was always insufficient.

4. Conclusion

Compared with the existing technology, the effect of this method is as follows.

In this method, the wastewater containing organophosphorus whose concentration of organic phosphorus was greater than 5mg/L was injected into at least one biochemical reaction unit, so that the gas microorganism containing oxygen and methane and the wastewater containing the organic phosphorus were fully mixed in the biochemical reaction unit, so that the organic phosphorus was fully converted into inorganic phosphorus, which prevented the loss of inorganic phosphorus due to the removal of organophosphorus and inorganic phosphorus by the form of microbial cells that were excreted and proliferated. The phosphorus recovery unit can hardly detect organophosphorus in the water, which meets the national standard for the safe discharge of organophosphorus in wastewater, and effectively disposes the organic phosphorus in wastewater.

In phosphorus recovery unit, microbial separated from waste water containing inorganic phosphorus was flowing back into biochemical reaction cell to continue with biochemical reactions to ensure the microbes in the biochemical reaction unit, especially methane oxidizing bacteria is not easy to loss, in order to improve the efficiency of organic phosphorus into inorganic phosphorus.

In the phosphorus recovery unit, the inorganic phosphorus is separated from the wastewater and the recovery rate is high. It not only reduces the inorganic phosphorus content in wastewater, lowering its concentration less than 0.5mg/L to meet the national standard for the safety of inorganic phosphorus in wastewater, but also improves economic efficiency by recycling inorganic phosphorus in agricultural chemical industry and other industries.

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