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Research Progress on Propellant Wastewater Treatment Methods

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Abstract. The main treatment techniques of propellant wastewater, including red smoke nitric acid oxidant wastewater, hydrazine fuel wastewater, mixed amine and fuel wastewater, were reviewed. The mechanism, treatment effect, advantages and disadvantages of various methods were summarized and analyzed. The physical method is inefficient, the chemical method is prone to secondary pollution, and the biodegradation method has a long period. From an economic and safety point of view, the method of biodegradation or physico-chemical-biological joint treatment is more effective.

1. Introduction

Rocket propellant is a general term for the production of high-temperature and high-pressure gas reaction substances for jet rocket engines, including combustion agents, oxidants, and unit propellants. Rocket propellant consists of oxidants and combustion agents, in which oxidants are mainly nitro oxidants, often referring to red smoke nitric acid and nitrous oxide. The combustion agent, also known as fuel, is mainly hydrazine fuel, mixed amine fuel and special fuel. Propellant can be divided into liquid and solid according to their state. Because liquid propellant has the characteristics of rapid chemical reaction, high specific impulse and easy storage, countries around the world often launch communications satellites, near-Earth orbit satellites and interstellar detectors by large thrust vehicles, in which propellant is always liquid. In fact, the first stage of the multi-stage launch vehicle uses liquid engines more in developed countries, and the second stage uses solid engines. However, Shenzhou series of spacecraft and various satellites use liquid propellant as rocket engine fuel in our country [1].

According to statistics, the amount of wastewater generated by a rocket launch is 300-600 tons [2], mainly from the process of storage, transportation, recharging, filling and launching of liquid propellants. The sewage contains a large amount of toxic substances, such as dimethyl hydrazine, nitrous oxide, nitromethane, hydrocyanic acid, organonitrile, cyanic acid, formaldehyde, dimethylamine, amines, etc.. It may cause serious harm to the surrounding atmosphere, crops, soil and surface water, and also contaminate groundwater through infiltration into soil without treated. To this end, the National Environmental Protection Agency and the Technical Supervision Bureau jointly formulated the emission standard for aerospace propellant wastewater pollutants. Its main technical indicators are shown in table 1.



Table 1. Emission standard for aerospace propellant wastewater pollutants.

No.	Item	Max. permissible emission concentration(mg/L)	No.	Item	Max. permissible emission concentration(mg/L)
1	pH	6~9	8	aniline	2.0
2	BOD ₅	60	9	hydrazine	0.1
3	COD _{Cr}	150	10	MMH	0.2
4	SS	200	11	UDMH	0.5
5	NH ₃ -N	25	12	triethylamine	10
6	cyanide	0.5	13	DETA	10
7	methanal	2.0			

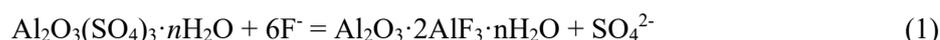
Common wastewater treatment methods such as oxidation, coagulation, adsorption, ion exchange, and biological methods all can be used for propellant wastewater treatment. Furthermore, other deep treatment methods have become increasingly popular, for example, electrochemistry, supercritical oxidation, and electron-fenton oxidation. Therefore, the present treatment situation of propellant wastewater is introduced in order to provide technical support for the research of "three wastes" management of liquid propellant.

2. Treatment of red smoke nitric acid oxidant wastewater

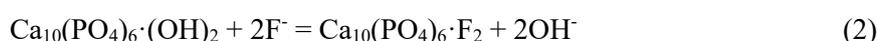
Red smoke nitric acid is an orange-red liquid that is easy to flow and consists mainly of 75% nitric acid, 22% nitrous oxide and a small amount of water, phosphoric acid and hydrofluoric acid. The mixture is highly corrosive and oxidizing. It is a Class III medium toxicant and its toxicity mainly comes from volatilized nitrogen dioxide. The main components of red smoke nitric acid are nitrous oxide, phosphoric acid, and hydrofluoric acid, which are all acidic substances. So, using acid-base neutralization method can make the nitric acid, nitrous oxide, and phosphoric acid convert into nontoxic salts, and meeting the requirements of wastewater discharge.

Alkali substances commonly used in acid-base neutralization methods include sodium hydroxide, calcium hydroxide, sodium carbonate, and calcium carbonate. Luo Yuehui studied that use sodium carbonate as a neutralizer, which could be used as a solution or be placed directly in solid form [3]. The reaction speed was fast and no precipitation occurs. After neutralization, hydrofluoric acid converted to fluorine ions, which is still an important mutagenic pollutant. Therefore, according to the pH of the solution treated with sodium carbonate, calcium chloride or calcium hydroxide is chosen as a precipitator. If the solution pH<8, using calcium hydroxide may play a dual role in regulating pH and precipitating fluorine ions. Zheng Hongjian suggested that a waste liquid treatment system, including shower tower, wastewater collection pool and reaction pool, could be constructed near the oxidizer storage [4]. Before treatment, a certain amount of water was injected into the pool, and then the wastewater and calcium hydroxide were put into batches until all the acidity and toxicity in the waste liquid were neutralized.

Fluorinated wastewater can also be treated by adsorption. Fluorine can be adsorbed on the surface of the adsorbent to produce insoluble fluoride. The main adsorbents used are activated aluminum oxide, calcium perphosphate and magnesium hydroxide. Active alumina has a large specific surface area and strong ion exchange capability. The exchange adsorption reaction with fluorine ions is as follows:



When calcium perphosphate is used as an adsorbent, the hydroxyl group undergoes the following exchange reaction with dissolved fluorine in water:



After the adsorbent is swapped and saturated, the sodium hydroxide solution is used for its regeneration, and the regeneration effect is good and economical. Therefore, the adsorption method is one of the more promising methods for the purification of fluorinated oxidant wastewater [5].

3. Treatment of hydrazine fuel wastewater

Hydrazine fuel generally refers to hydrazine (N_2H_4), methyl hydrazine (CH_3NHNH_2) and partial dimethyl hydrazine $[(\text{CH})_2\text{NNH}_2]$. It is a flammable, toxic, colorless and transparent liquid with a strong fishy taste, and is soluble in polar solvents such as water and alcohol. It also has strong hygroscopic properties, and can be combined with water vapor in the atmosphere easily. The pollution of hydrazine to water bodies mainly comes from two aspects. First, the running, draining, dripping, leaking of hydrazine tanks and pipelines, and washing wastewater. The second is the sewage produced by the hydrazine fuel and nitrous oxide combustion products entering the diversion tank through fire cooling water during rocket launch and test [6]. At present, the treatment methods of hydrazine wastewater mainly include catalytic oxidation, ozone oxidation, membrane biological reaction, and emerging supercritical water oxidation.

3.1. Catalytic oxidation

The concentration of dimethyl hydrazine has reached 6.0 % in propellant wastewater and has not been effectively treated. At present, a lot of research on this has been studied, but still in the experimental stage. The main reason is that there are too many oxidation intermediates to meet the emission standards.

Zhang Guangyou employed three catalysts of nanometer titanium dioxide, copper ion doped titanium dioxide and nanometer zinc oxide to treat the partial dimethyl hydrazine wastewater [7]. The influence of catalyst concentration, degradation time, pH and temperature on degradation efficiency was investigated. The order of degradation efficiency of the three photocatalysts is: $\text{Cu}^{2+}/\text{TiO}_2 > \text{ZnO} > \text{TiO}_2$. The results showed that adding Cu^{2+} to the reaction system could greatly increase the degradation rate of dimethyl hydrazine, because Cu^{2+} was an effective recipient of electrons. Its competition for electrons reduced the simple combination of photo-electrons (e^-) and photo-cavitation (h^+) caused by light on the TiO_2 surface. So, more OH^\cdot and oxygen anion O_2^{2-} on the TiO_2 surface came into being, increasing the degradation rate of partial dimethyl hydrazine significantly [8].

However, the suspension system has problems such as the easy condensation of catalysts and the difficulty of recovery, which will cause a great waste of raw materials. In order to solve the problem of catalyst fixation, Liang Liang used activated carbon fiber (ACF) as a carrier to load nanometer TiO_2 by sol-gel method. It not only solved the problem of difficulty in loading TiO_2 , but also ACF adsorbed pollutants in wastewater [9]. Thus the catalytic efficiency was increased. Wang Feng designed a single stage fixed bed reactor. Using $\text{CuO}/\text{Al}_2\text{O}_3$ as a catalyst and O_2 as an oxidant, the conversion rate of partial dimethyl hydrazine with 6.0% concentration reached 99.99% [10]. Although the treated sewage concentration was significantly reduced, however, the indicators still failed to meet the emission standards because the reaction material didn't have enough time to stay in the reactor. The deep oxidation required a longer stay time. Therefore, it is necessary to increase the stay time and depth of oxidation by connecting two or more reactors.

Not only that, foreign researchers but also carried out many studies on catalytic oxidation. For example, the catalytic oxidation reaction with $\text{Cu}/\text{Fe-ZSM}$ as a catalyst depends to a large extent on the pH of the system. Dimethyl hydrazine can be degraded to non-toxic 1, 1, 5, 5-tetramethylamine under acidic conditions, but under alkaline conditions, additional toxic pollutants-dimethylnitrosamine and dimethyl formamide are produced [11]. This puts forward harsh requirements for sewage treatment. Ismagilov studied the catalytic reaction mechanism of $\text{Cu}_x\text{Mg}_{1-x}\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, and also obtained a similar conclusion that at high concentrations and low temperatures, the reaction produced dimethylamine and methylene dimethyl hydrazine, thus further deep treatment was required [12].

3.2. Ozone oxidation

Ozone mainly undergoes the following three reactions in water: (1) oxidation-reduction reaction; (2) cycloaddition reaction; (3) electrophilic substitution reaction. In some cases, ozone may produce free radicals that react with most organic matter in the water. Therefore, the method can be used to treat hydrazine wastewater with a removal rate of about 99%. The reaction process and mechanism of ozone and dimethyl hydrazine are quite complex. A series of intermediate products, such as methylamine,

dimethylamine, and formaldehyde, are generated during the reaction process. Formaldehyde is also generated by further oxidation of methylamine and dimethylamine.

Since formaldehyde is also a serious pollutant and its concentration is low, generally about 10mg/L. It is quite difficult to simply oxidize formaldehyde in wastewater with ozone. Research results showed that formaldehyde reacted with ozone under ultraviolet light to produce formic acid and oxygen, and formic acid could be further oxidized to CO₂ and H₂O₂ [13]. This method was simple and easy to handle. The treated sewage can be discharged directly and is suitable for automatic control.

3.3. Membrane biological reaction Method (MBR)

MBR is a water treatment method combined with membrane separation technology and biological treatment technology. Due to its high sludge concentration, the treatment effect of wastewater can be greatly improved. Xia Benli investigated the effects of water retention time, dissolved oxygen, pH and sludge concentration on the treatment of hydrazine wastewater by integrated MBR [14]. The results showed that the removal efficiency of COD and dimethyl hydrazine were 95% and 99.4%, respectively. Liu Yuan combined the EOW and MBR process to treat the dimethyl hydrazine wastewater, which obtained fine effect [15]. EOW is an acidic oxidation potential water, rich in reactive oxygen species and a certain amount of effective chlorine. It has a very high redox potential and low pH. So it can reduce the partial dimethyl hydrazine in raw water from 300 mg/L to 0.3 ~ 1.5 mg/L, near the limit of the pollutant discharge standard.

3.4. Supercritical water oxidation (SCWO)

When water is in a state of high temperature and high pressure above its critical point (374.3°C, 22.1MPa), its physicochemical properties change significantly. It can be miscible with organic matter, oxygen, nitrogen, carbon dioxide and other gases in any proportion, becoming an excellent reaction medium. Since SCWO is a homogeneous reaction, there is no phase mass transfer resistance, and organic matters can be oxidized to CO₂, N₂, and H₂O in short time. Ge Hongguang suggested that the reaction temperature and residence time were the main factors affecting the removal of dimethyl hydrazine [16]. The increase of temperature and the extension of residence time would significantly increase the removal rate of hydrazine, and the removal rate could reach 99.8%. Zhang Li developed the automatic duct-type continuous reaction system independently, which accurately measured and automatically controlled the temperature, pressure, and residence time of the reaction [17]. So that the COD removal rate reached 99.9% or more, meeting the requirements of the propellant water pollutant discharge standard.

It can be seen that using SCWO reaction method to treat aerospace propellant wastewater requires only a simple structure of small reaction equipment that can achieve the purpose of complete oxidation and decomposition of a large number of refractory wastewater, and has a broad development prospects.

4. Treatment of mixed amine and fuel wastewater

Mixed amine is mainly composed of triethylamine and dimethylamine, each accounting for about 50%. Fuel is a mixture of hydrocarbons. Both of them are flammable and reduced, which may react strongly with oxidants. Mixed amine and fuel have certain toxicity. Their toxicity is mainly caused by aniline and aromatic hydrocarbons. According to the nature of the fuel, waste liquids and wastewater can be treated by adsorption, chlorination, ozone oxidation, and fuel regeneration methods.

Dimethyl aniline has large molecular weight, weak polarity and strong hydrophobicity. It is easily adsorbed by activated carbon. However, triethylamine has small molecular weight, large polarity, and certain water solubility. Its adsorption capacity of activated carbon is lower than that of paraxylene aniline. After treated, mixed amine wastewater with a concentration of 1000~1500 mg/L could decrease to: triethylamine 2mg/L, and dimethyl aniline 0.5mg/L [5].

Ion exchange resin was also used to adsorb triethylamine in wastewater [18]. The results showed that the removal rate of triethylamine with the initial concentration of 1500mg/L was 96.3% and 99.5% under static and dynamic adsorption conditions, respectively. The size of the cation effect was Ca²⁺>Mg²⁺>K⁺>Na⁺.

The chlorination method relies on the action of hypochlorous acid, which has a strong oxidizing property. It undergoes a strong redox reaction with the fuel in the wastewater to destroy the macromolecules in the fuel and oxidize it into small molecules and non-toxic oxidation products. Xiong Jian optimized the experimental parameters of the treatment of triethylamine wastewater by sodium hypochlorite [19]. It was determined that the removal rate of triethylamine after the reaction of 5min could reach 99.3% at a concentration ratio of 6:1 between sodium hypochlorite and triethylamine. Luo Yuehui applied the chlorination method to the treatment of the troops waste liquid, and the technological processes such as collection pools, reaction pools, and observation pools were designed to meet the standards for industrial wastewater discharge, especially for the rapid treatment of troops wastewater in remote mountainous areas [3].

The ozone oxidation method is the current method used by the troops to purify the treatment vehicle. This method is simple, fast and movable, but the disadvantage is that the amount of wastewater treatment is affected by the amount of ozone generation. The treatment volume of general wastewater treatment vehicles is only 0.3~0.4 m³/h.

If the amount of fuel wastewater production is reduced, it is also a good treatment measure. For this reason, Zheng Hongjian proposed to convert waste liquid into sustainable fuel by regenerative method [4]. The main reason for fuel scrapping, on the one hand, is due to the strong hygroscopicity, which causes the water content of fuel to exceed the standards of use. On the other hand, due to the large amount of volatilisation of triethylamine in the mixed amine, its content is lower than the standard for use. Therefore, to regenerate, only the water content of the fuel is reduced and the content of triethylamine is increased. Calcium hydride (CaH₂) dehydration or molecular sieve dewatering is usually used. The residues produced during dehydration are still toxic due to the attachment of xylene aniline and triethylamine, and should be treated by combustion.

5. Conclusion

With the rapid development of the national space industry and the emphasis on the ecological environment and human health, it is of far-reaching significance to develop efficient, economical and harmless propellant wastewater treatment technologies. Physical methods can be used for pre-treatment or in-depth treatment of wastewater, but they can not fundamentally control pollution. The chemical method has better effect, but it is easy to cause secondary pollution and has higher cost. It is an ideal method to treat organic wastewater with low running cost, high safety and simple operation, but slow treatment speed is the key to limit the practical application of biological method. Therefore, the reduction and elimination of the intermediate products produced during the treatment process and the combination of multiple technologies are the important development directions for the treatment of propellant wastewater in the future.

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