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WASTEWATER TREATMENT IN HYDRAZINE HYDRATE PRODUCTION

Thesis

CENTRIA UNIVERSITY OF APPLIED SCIENCES

Degree Programme Environmental Chemistry and Technology

MAY 2021



ABSTRACT

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Degree programme Environmental Chemistry and Technology		
Name of thesis WASTEWATER TREATMENT IN HYDRAZINE HYDRATE PRODUCTION		
Centria supervisor Mikko Kuusisto	Pages 40	
<p>As an important fine chemical raw material, hydrazine hydrate has a wide range of uses, not only for the synthesis of rocket fuel, foaming agent, herbicide, but also for the synthesis of medical drugs. Usually ketone, sodium hypochlorite, and ammonia are used as raw materials to synthesize hydrazine hydrate, but the wastewater during the production process contains a variety of organic matter, has peculiar smell, and contains 15-20% sodium chloride. Therefore, sewage treatment is relatively difficult. While processing sewage, if the sodium chloride in the sewage can be recycled, it not only effectively reduces the treatment cost of hydrazine hydrate production sewage, but also solves the environmental pollution caused by high salt content.</p> <p>In this thesis, several methods to produce hydrazine hydrate are introduced, such as the Raschig method, the urea method, the ketazine method, and the hydrogen peroxide method. The basic process of these methods and some improvement measures about these methods will be introduced. In addition, some wastewater treatment methods in the production of hydrazine hydrate are also introduced, including evaporation and distillation, oxidation, and nanofiltration membrane methods.</p>		
Key words hydrazine hydrate, wastewater treatment		

CONCEPT DEFINITIONS

$\text{N}_2\text{H}_4\text{H}_2\text{O}$	Hydrazine hydrate
NaClO	Sodium hypochlorite
NH_3	Ammonia
NaOH	Sodium hydroxide
NaCl	Sodium chloride
NH_2CONH_2	Urea
NH_2Cl	Dichloramine
KMnO_4	Potassium Permanganate
H_2O_2	Hydrogen peroxide
N_2	Nitrogen
MnSO_4	Manganese sulfate
MnO_2	Manganese dioxide
MgSO_4	Magnesium sulphate
$\text{Ca}(\text{ClO})_2$	Calcium hypochlorite
$\text{C}_3\text{H}_6\text{O}$ $(\text{CH}_3)_2\text{C} = \text{O}$	Acetone
$(\text{CH}_3)_2 = \text{N} - \text{N} = \text{C} (\text{CH}_3)_2$	Ketazine
Na_2CO_3	Sodium carbonate
Ca_2CO_3	Calcium carbonate
$\text{Ca}(\text{OH})_2$	Calcium hydroxide

ABSTRACT

CONCEPT DEFINITIONS

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1 INTRODUCTION

Hydrazine hydrate is an important industrial raw material, it is mainly used in the production of dehydrating agents, foaming agents, pharmaceutical intermediates, purification and separation agents and rocket fuel. With the development of science and technology and the continuous improvement of human living standards, the application fields of hydrazine hydrate are also expanding. Due to the increasing demand for hydrazine hydrate, there are great amount chemical plants producing hydrazine hydrate in China. People are paying more attention to the environmental pollution caused by the wastewater and waste gas discharged by the factories.

The methods for producing hydrazine hydrate include the Raschig method, the urea method, the ketazine method, and the hydrogen peroxide method. At present, the production of hydrazine hydrate in China mostly uses the urea method and the ketazine method. There is also a more advanced method--hydrogen peroxide method. Compared with other methods, the urea method has more mature and simple technology, urea method has adopted by most hydrazine hydrate production enterprises in China. However, the urea method has high energy consumption and generates a large amount of wastewater and waste gas. So, most countries have given up the urea method. Due to its low energy consumption, low wastewater and waste gas consumption and high hydrazine hydrate production yield, the ketazine method has become the preferred process for hydrazine production in developed countries. It is also the development direction of the upgrading and transformation of China's hydrazine industry.

Otherwise, the wastewater in the production process is high-salt, high-toxic, high-COD organic. If it is discharged without any form of treatment, it will not only cause harm to the environment but also affect human health. This also goes against the theme of sustainable development in the world today. So, how to treat the wastewater and in which way to treat the wastewater becomes important. The treatment and reuse of wastewater should focus on solving three problems: removing organic matter to reduce COD, ammonia nitrogen removal, brine purification and recovery. Researchers in China and abroad also study wastewater treatment from the above three goals. Common wastewater treatment methods include oxidation method, evaporation method and nanofiltration membrane method. The wide application of these technologies provides help for wastewater treatment.

2 USES OF HYDRAZINE HYDRATE

Hydrazine hydrate has 35%, 40%, 55%, 64%, 80%, 85% and 100% specifications according to its concentration. Among them, 80% hydrazine hydrate is immiscible with solvents such as ether and chloroform, but it is miscible with water and ethanol. It is a colourless and transparent liquid. It has a certain ammonia smell and strong corrosiveness and permeability. Hydrazine hydrate can react with carbon dioxide in the air to form white mist. High-concentration hydrazine hydrate not only has weak alkalinity and strong reducibility (reacts violently with oxidants and may even cause spontaneous combustion and self-explosion), but it is also a toxic substance. Its toxicity can accumulate, and if it is accidentally touched, it will cause harm to human skin and eyes. (Dai 2008.)

Hydrazine hydrate is an important fine organic synthetic raw material commonly used by chemical companies and has a wide range of uses. For example, the strong reducibility of hydrazine hydrate allows it to be used as an antioxidant. It can be used in the deoxidation process of power boiler water or as a cleaning agent in the electroplating industry. In chemical production, hydrazine hydrate can be used to produce different types of foaming agents. In medicine, it is a key component in the production of certain medicines. In addition, in the high-tech field, high-purity hydrazine hydrate is also required to produce rocket fuel and certain explosives. (Dai 2008.)

2.1 Rocket propellant and explosives

Hydrazine, monomethyl hydrazine, unsymmetrical dimethylhydrazine, and methylhydrazine sulphate are all good rocket fuels with good storability. When in use, gas is generated by catalytic decomposition. Hydrazine has the longest history of military application. The initial industrial production of hydrazine was to provide fuel for military rockets. Hydrazine is a self-igniting fuel, that is, it can ignite spontaneously when it meets an oxidant, or it can automatically catalyse and decompose when it encounters a catalyst. (Dai 2008.)

2.2 Foaming agent

There are more than a thousand kinds of chemicals that have been tried and explored as blowing agents in the world, but only a dozen kinds of blowing agents have finally been confirmed and widely used. Among them, azodicarbonamide, azidomethyl and amide (blowing agent AC) are the most useful foaming agent. 2-methylpropionitrile (ABIN) is a high-efficiency, non-polluting organic foaming agent, which can be prepared from hydrazine hydrate, acetone, hydrogen cyanide, and chlorine through condensation, cyanidation, and oxidation. 2-methylpropionitrile blowing agent is an exothermic blowing agent, which decomposes rapidly when reaching a certain temperature, and the amount of gas generation is relatively stable. Now a wide variety of blowing agents are compounded based on these structures. (Dai 2008.)

2.3 Antioxidant

The reaction of hydrazine hydrate and β -(3,5-di-tert-butyl-4-hydroxyphenyl) methyl propionate produces β -(3,5-di-tert-butyl-4-hydroxyphenyl) propionyl hydrazide, then combine the β -(3,5-di-tert-butyl-4-hydroxyphenyl) propionyl hydrazide with the β -(3,5-di-tert-butyl-4-hydroxyphenyl) propionyl chloride to produce 1,2-bis(β -3,5-di-tert-butyl-4-hydroxyphenyl) propane. Hydrazine can be used as an antioxidant and a metal deactivator, also known as a metal chelating agent, which has the effect of preventing metal ions from causing oxidation of the polymer. (Dai 2008.)

2.4 Chemical additives

One or more of hydrazine and cyanamide, lime nitrogen, sodium cyanamide, and thiol thiourea can generate aminoguanidine. It can be diazotized in neutral solution and thermally coupled with general dye intermediates to form a series of azo dyes, which have good dyeability to silk and sheep wool. In addition, starting from hydrazine and its derivatives, a series of chemical additives such as antioxidants, metal purifying agents, imaging agents, chain terminators, and epoxy curing agents can be synthesized. (Dai 2008.)

2.5 Synthetic medicine

Hydrazine is a good intermediate in the pharmaceutical industry. Anti-tuberculosis drugs produced by hydrazine include isoniazid thiourea. Anticancer drugs produced by hydrazine include hydrazone and allopurinol. Antibacterial anti-inflammatory drugs produced by hydrazine include sulfamethazine phthalazine and cephalosporins. Antipsychotic depression agents produced by hydrazine include pentylenetetrazol and isoxazole. Glaucoma drugs produced by hydrazine include acetazolamide and methyl acetamide. Malaria and haemostatic drugs produced by hydrazine include primaquine diphosphate and euthanasia. In addition, some medicines produced by hydrazine include isoniazid phosphate, primaquine, procarbazine and prop amidrazone. (Dai 2008.)

2.6 Synthetic pesticide

Hydrazine hydrate is an important intermediate in the production of pesticides and can be used to prepare insecticides, acaricides, fungicides, herbicides, and plant growth regulators. The main applications include the reaction of hydrazine hydrate and tert-butyl chloride to produce tert-butyl hydrazine. Hydrazine hydrate reaction with o-chlorobenzaldehyde can prepare the acaricide Mitejing. Hydrazine hydrate as raw material can also produce a series of organophosphorus pesticides. In terms of herbicides and plant growth regulators, hydrazine hydrate can be used to prepare herbicides such as metaphor, benzalkonium, and wild quat. Plant growth regulators such as maleic hydrazide, paclobutrazol and uniconazole are also prepared from hydrazine hydrate. (Dai 2008.)

3 HYDRAZINE HYDRATE PRODUCTION TECHNOLOGY IN CHINA AND ABROAD

At present, there are many methods for preparing hydrazine hydrate in China and abroad, mainly including four methods: Raschig method, urea method, ketazine method and hydrogen peroxide method. Foreign manufacturers mostly use the ketazine method and the hydrogen peroxide method. Most domestic manufacturers now adopt the urea method. In addition, Japan's Hayashihiro Company has published an air oxidation method, which is currently in the laboratory test stage and is still far from industrial production. (Dai 2008.)

3.1 Raschig method

In the 1960s, the main production method of hydrazine hydrate at abroad was the Raschig method. This process was first used in industrial production in 1906. It produced hydrazine hydrate by reacting NaClO with NH₃. The reaction equation is as follows:



The mass fraction of NaOH used in the reaction was 8%. When Cl₂ was introduced to produce NaClO, NaOH was surplus, and pure water was used to absorb NH₃ into an aqueous solution. The mixing mass ratio of NH₃ and NaClO solution is 20:1, and the reaction temperature is controlled to 170°C. The reaction can be carried out under pressure and completed within a few seconds. Adding gelatine to the reaction system helps to increase the yield. In addition to hydrazine hydrate, the distillate in the reaction tower also contains NaCl and NaOH, unreacted ammonia and a small number of by-products. After flash vaporized under normal pressure, the ammonia and the bottom liquid are separated through the ammonia separation tower, and the bottom liquid enters the evaporation tower. After sodium chloride and sodium hydroxide are separated, the water is discharged from the top of the tower, and on the bottom obtained hydrazine hydrate. The process flow is as follows:

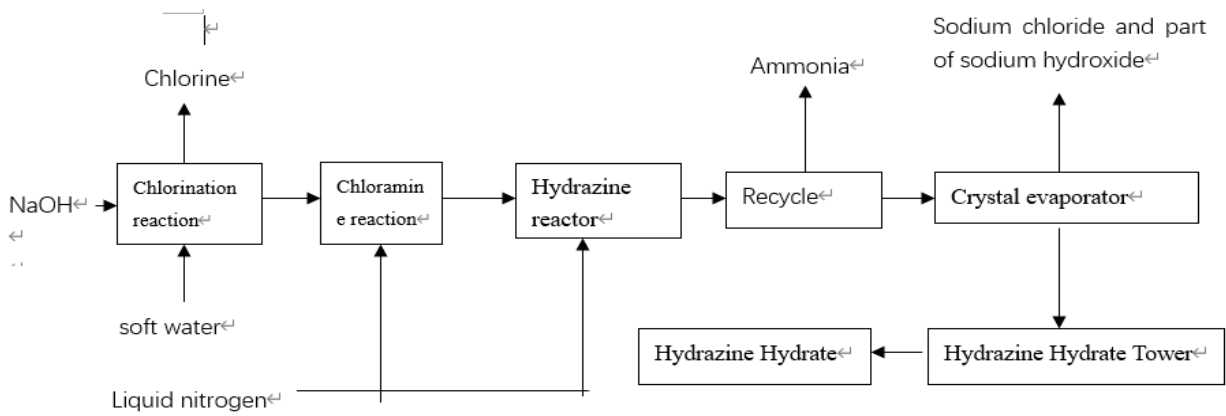
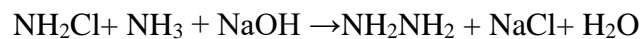
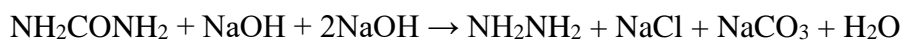


FIGURE 1 Raschig process flow diagram (adapted from Dai 2008.)

Although the Raschig process is mature and reliable, the raw materials are readily available and the price is relatively cheap, it has fatal shortcomings. Since hydrazine can be oxidized and decomposed by chloramine, the yield of hydrazine is very low. The yield of the entire process is only 65%, so its raw material consumption is large, and the product cost is high. The concentration of hydrazine in the reaction solution is low (about 3% to 4%), and salts such as sodium chloride and ammonium chloride are formed, with large evaporation and high energy consumption. A large amount of excess ammonia needs to be recovered, and equipment and operating costs increase. Compared with the urea method, the Raschig method has lower raw material costs, but the equipment investment and energy consumption are higher. When the production scale is large, the total cost is lower than that of the urea method. FBC Company in 1974, the United States Unirol (u-nroyal) and Fairmont, France PCUK, and other companies in 1981 abolished this method. (Zhou 1995,1-6.)

3.2 Urea method

The urea method is also called the schestakof method. At the beginning of the industrialization of the Raschig method, French chemists proposed the reaction of preparing hydrazine from urea. The reaction equation of the urea method is as follows:



This reaction is Hofmann amide degradation reaction. In this reaction, a hydrogen atom on the nitrogen atom in the molecule of urea (carbonamide) is replaced by chlorine to form N-chloramide. N-chloramide loses hydrogen chloride under the action of alkali and produces an intermediate containing six valence electrons and a monovalent nitrogen atom, this intermediate called azene. Due to the structure of arene, it is a very active reaction intermediate and can take place many types of reactions at the same time. Due to the extremely short time of existence of azene, it is generally produced during the reaction, and then the next step of the reaction is carried out. Under the action of alkali, it rearranges to form isocyanate, which is hydrolysed to form hydrazine hydrate and salt. (Ruan 1998,27-31.)

The urea process is essentially an improvement of the Raschig process, using urea instead of ammonia as the nitrogen source, and the process does not have the problem of large-scale circulation of excess reactants. Firstly, Cl₂ and NaOH are used to react to produce NaClO solution, and then urea, NaClO, NaOH solution are oxidized under the action of oxidants such as KMnO₄ and H₂O₂, then after evaporated, desalted, and refined to obtain the finished product. The process flow as follows: (Li 2006,50.)

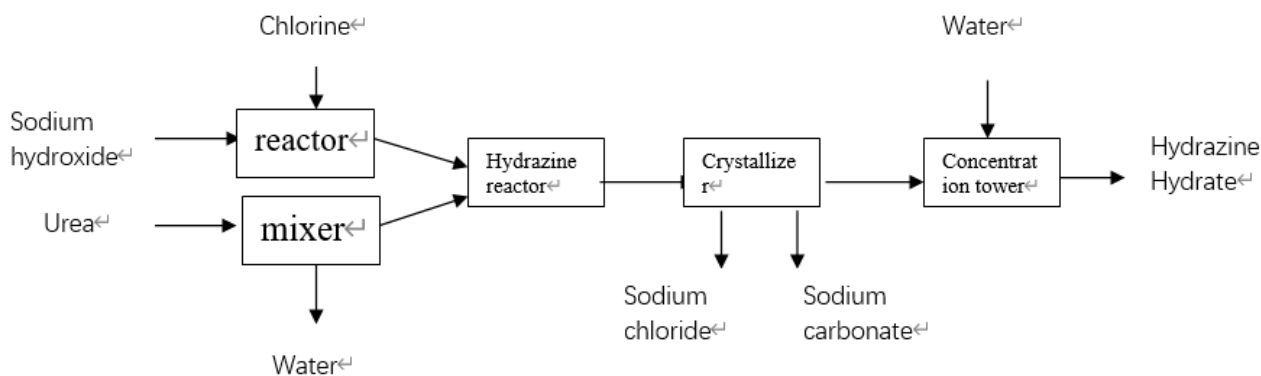
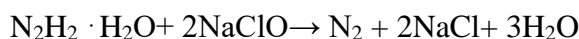


FIGURE 2 Urea method process flow diagram (adapted from Dai 2008)

The process is simple, and the method is mature. When MgSO₄ is used as the catalyst, the reaction time is 1 to 2 minutes, the temperature rises rapidly to 100°C, and the yield is about 70%. This method uses urea instead of ammonia, which simplifying equipment and saving investment. However, since the reactant NaClO is a strong oxidizing agent and the product is a strong reducing agent, there is a side reaction in which hydrazine hydrate is oxidized by NaClO during the reaction: (Ye & Xu 1998,17-21.)



Because the side reactions are very intense, spraying accidents may occur when ingredients or improper operations taken place. Therefore, the yield of urea oxidation method is low, generally 70% to 80%. To suppress side reactions, it is necessary to maintain a very low hydrazine concentration (generally 2% to 3% by mass). The amount of by-product salt and alkali is 12 times that of hydrazine. Soda ash is recovered by freezing crystallization and evaporated under stirring (5-layer tank). The medium desalination and subsequent distillation to concentrate hydrazine consume a lot of heat and mechanical energy, so there are restrictive factors such as high energy consumption, high raw material costs, and environmental protection issues. (Ye & Xu 1998, 17-21.)

There are some technical transformations about the urea method: Sodium hypochlorite raw material is prepared with a packed absorption tower. The tank reactor is changed to a tubular heating reactor to synthesize hydrazine hydrate, which improves the yield. The five-layer evaporator Intermittent evaporation was changed to a special new type of evaporator for continuous evaporation. The liquid phase was changed to gas phase into the tower for concentration, which reduced steam consumption. Production of high concentration sodium hypochlorite in the preparation process of sodium hypochlorite. Cooling and recycling of crude hydrazine hydrate solution Sodium carbonate decahydrate, the by-product sodium chloride is recovered, so that the by-product can be comprehensively utilized. The application of advanced production equipment and optimization of the production process, it is estimated that the production cost per ton of 80% hydrazine hydrate can be further reduced to about 10,000 yuan. (Wu & Xu 1995.)

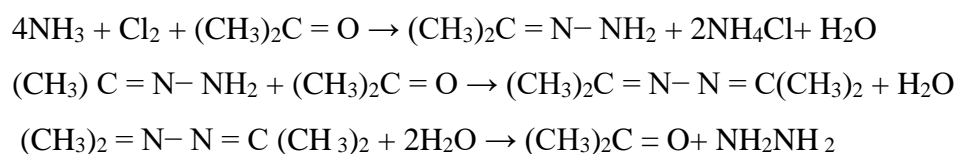
The purpose of improving the process in recent years is to suppress side reactions and increase the yield of hydrazine hydrate. Additives such as gelatine, protein glue, KMnO_4 and MnSO_4 can be added to the reaction medium. KMnO_4 and MnSO_4 are the most widely used in China. However, these two additives are dark red when dissolved in the urea solution, which is difficult to control in actual operation. At the same time, MnO_2 is formed by the reaction of manganese salt, which causes fouling and even blockage of pipelines, which is liable to cause environmental pollution. Now MgSO_4 additives have been used instead of manganese salt. (Dai 2008.)

The method has simple equipment, small investment, mature technology and low technical requirements, and it is suitable for small-scale production. Because the price of raw materials used in this method is higher than other methods, and the energy consumption is high, it cannot compete with other methods

in large-scale production. Urea method has been basically eliminated in foreign countries, but the urea method still the main production method to produce hydrazine hydrate in China. (Dai 2008.)

3.3 Ketazine method

The ketazine method, also known as the Bergbau-Bayer-Whifel method, was first patented by Bergbau-Forschung, an affiliate of the German Coal Mining Association, and was later improved by the Bayer and Huifen parent companies. Research began in the early 1960s and industrialization in the 1970s. This method is an improvement of the Raschig method. The difference is that acetone is introduced into the reaction system, so that the active hydrazine generated by the reaction immediately forms a less active acetone azine with acetone, and the acetone azine is hydrolysed under certain conditions to regenerate hydrazine and acetone. The reaction formula is: (Ye & Xu 1998,17-21.)



The method mainly includes the following steps. In the presence of aliphatic ketones, ammonia is oxidized with NaClO to obtain hydrazone, azine or isohydrazone. The composition of the product depends on the pH of the system, the ratio of ketones and the reaction conditions. In the presence of excess ketone, hydrazone and isohydrazone can be converted to ketazine. After the oxidant is completely consumed, the intermediate is concentrated and then hydrolysed into hydrazine and hydrazine salt. Ammonia water and NaClO solution are used to synthesize a hydrazine hydrate solution at a pressure of 4MPa and a temperature of 140°C. The excess ammonia is removed by air stripping, and then evaporative desalting and rectification are performed to obtain the product hydrazine hydrate. (Ye & Xu 1998,17-21.)

In the Japanese process, in the presence of ketones, Ca (ClO)₂ reacts with ammonia to produce ketazine, which is then hydrolysed to obtain calcium ketone of hydrazine hydrate. In this method, ammonia and ketones can be recovered and recycled. The waste brine containing CaCl₂ is treated with Na₂CO₃ to obtain Ca₂CO₃, which is precipitated and converted into Ca (OH)₂ by high temperature calcining and water dissolution, and then recycled. Therefore, this method has the advantages of high raw material utilization rate and few by-products. (Masatomi Otsuka, Naruto Et al 1969.)

The basic flow of the Bayer process is as follows. Chlorine is continuously added to the dilute sodium hydroxide solution to form a sodium hypochlorite solution (oxidant). The latter, dilute ammonia and acetone are added to the ketazine reactor at a molar ratio of $\text{NaClO}:\text{CH}_3\text{COCH}_3:\text{NH}_3=1:2:20$. It reacts under low pressure at 30-40°C to produce ketazine dilute synthetic liquid. After the synthetic liquid is separated and recovered by the ammonia recovery tower to recover excess ammonia, it is heated into the ketazine tower. The azeotrope of ketazine and water (95°C, containing 55.5% of ketazine) is separated from the top of the tower. The bottom of the tower is basically salt (NaCl) water with a small amount of hydrazine and related organic matter, which must be treated and discharged. The azeotrope of ketazine is sent to the hydrolysis tower under pressure, where the hydrolysis reaction occurs at a pressure of about 1.0 MPa to produce hydrazine hydrate and acetone. Acetone is condensed and separated from the top of the tower, and then returned to the azo reactor, and a 10% hydrazine hydrate solution is obtained at the bottom of the tower. The solution is then concentrated by a hydrazine hydrate tower to become 68% hydrazine hydrate. When using methyl ethyl ketone, the process consumption quota is 320kg/ton of pure hydrazine, while using pentanone the process consumption quota can be reduced to 100kg/ton of pure hydrazine. The total yield of this method is 90%. (Yan & Zhang 2006,13-15.)

The characteristic of this method is the formation of the intermediate product ketazine. Ketazine has the characteristic of not being further oxidized, thus completely overcoming the shortcomings of hydrazine being decomposed and lost in the Raschig process, resulting in a breakthrough increase in yield (total yield based on chlorine can reach 98%). Because the ketazine is relatively stable, the concentration of the reaction product can be increased, and the hydrazine content in the dilute hydrazine solution obtained by hydrolysis can be increased to more than 10%, so the amount of evaporation and concentration is greatly reduced, and the energy consumption is greatly reduced. In addition, there are also other methods (Fusen Process, Mitsubishi Gas Chemical Process) that use other fatty ketones. Although the process conditions are different, the process principles and processes are the same. (Yan & Zhang 2006,13-15.)

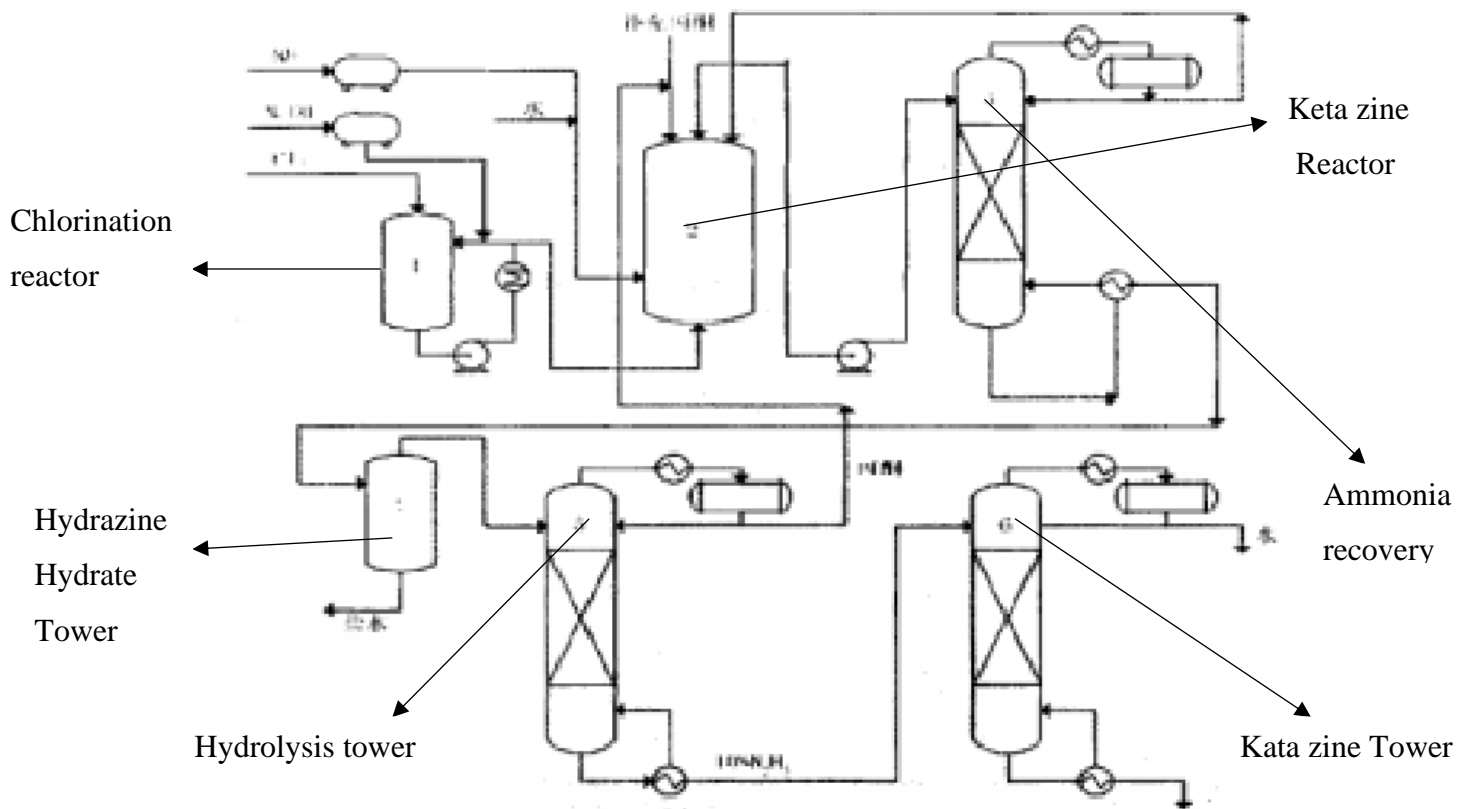


FIGURE 3 Kata zine method to produce hydrazine hydrate (adapted from Dai 2008.)

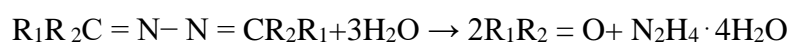
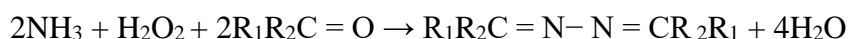
To overcome the shortcomings of the Bayer process such as the large amount of ammonia and the low concentration of the hydrolysed product. The Southwest Research Institute of Chemical Industry of China developed a catalytic oxidation process for hydrazine production. The chemical industry uses rare earth silica gel hypochlorite as the catalyst to overcome the shortcomings. The addition amount of the catalyst is 0.1%-4% of the mass of NaClO , the molar ratio of butanone, ammonia and NaClO is (2~8): (2~12):1, the reaction produces butanone azine and butanone azine it is separated from water and hydrolysed to obtain hydrazine hydrate. This method uses a catalyst to increase the yield of butanone azine by 8% to 12% under the condition of reducing the amount of ammonia. The hydrolysis efficiency of butanone azine is greater than 99%, and the yield of hydrazine hydrate is greater than 98%, which greatly reduces Energy consumption. However, the process is still in the pilot stage and has not yet been industrialized. (Zheng 2005,17-21.)

Compared with the Raschig process, the Bayer process has the outstanding advantages of high yield, less investment, and low cost. Therefore, since the launch of the Bayer process, new plants have adopted the ketazine route without exception. But at the same time, it also brings problems to the treatment of

salty wastewater and organic waste, which causes pollution to the environment, which is its shortcoming. (Zheng 2005,17-21.)

3.4 Hydrogen peroxide method

Hydrogen peroxide method was successfully developed by French PCUK in the early 1980s (also known as the PCUK method) and built an industrial plant. So far, the plant capacity has expanded to 12,000 tons/year. The ownership has been reorganized and the plant has been renamed several times. The Japanese MGC company also developed this method and built a device. The current device capacity has reached 12,000 tons/year. This method has two main reactions. One is to oxidize NH_3 with H_2O_2 in the presence of methyl ethyl ketone and a catalyst to generate ketazine (also known as azine); the other is to hydrolysis the latter to generate hydrazine hydrate and methyl ethyl ketone, and the ketone is recycled. The main reaction is as follows: (Kuriyama, Nagata & Yoshida, 1996.)



In the synthesis process, ketones are added to generate intermediate ketazine instead of hydrazine directly, which can prevent the hydrazine (reducing agent) from reacting with the oxidizing agent and being consumed, which can increase the yield. Methyl ethyl ketone is often used in industry because its ketazine is almost insoluble in water. After the reaction, the ketazine can be separated from the aqueous medium by a simple standing sedimentation method. In order to obtain a higher concentration of ketazine solution, a higher concentration of hydrogen peroxide should be used, and its mass fraction is mostly 70%. The hydrolysis reaction is carried out in 2 steps and the reaction is reversible. In order to break the balance and make the hydrolysis reaction proceed smoothly, the hydrolysis is often carried out in a rectification tower, and the generated ketone is removed in time. The process route is shown in Figure 4: (Hu 2005,1-5.)

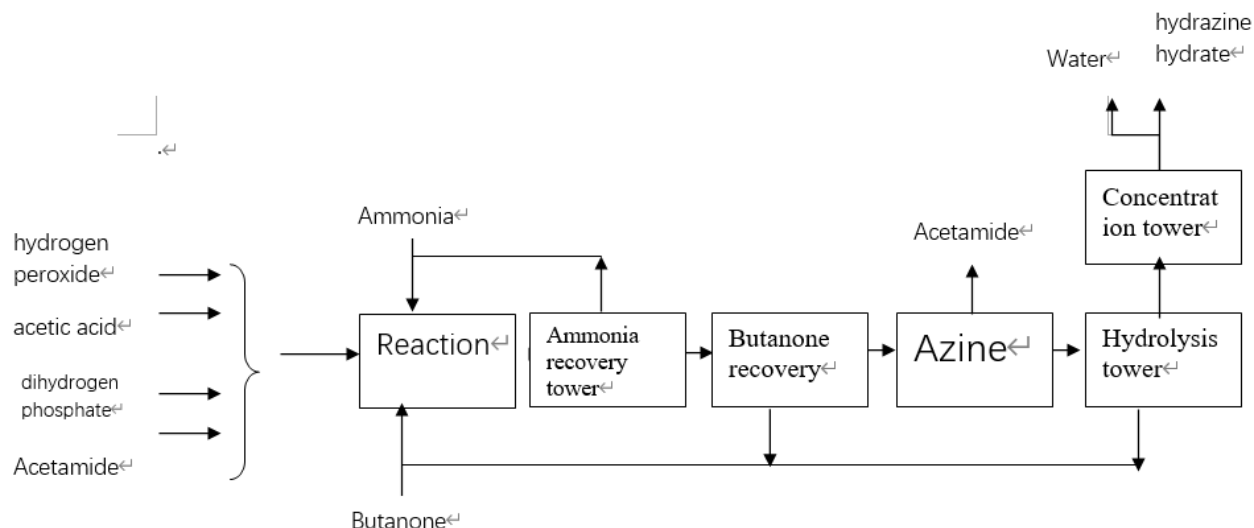


FIGURE 4 Hydrogen peroxide method to produce hydrazine hydrate (adapted from Dai 2008.)

The economic comparison between the hydrogen peroxide method and the Raschig method and the ketazine method mainly depends on the relative prices of chlorine and NaOH. The yield of this method is 75%, and if there is a cheap source of H₂O₂, this method is quite attractive. This method uses methyl ethyl ketone, which is more expensive than acetone, but the generated ketone azine is insoluble in water and easy to separate and does not need to be rectified, so the energy consumption is lower than that of the ketazine method. The advantages of the hydrogen peroxide method are no salt by-products, no environmental pollution, and less excess ammonia. Nitrogen recovery uses phase separation operation, energy consumption is lower than other methods, and product quality is improved. Another important advantage of this method is to replace chlorine with H₂O₂, to avoid a series of problems such as corrosion and pollution caused by chlorine and NaCl. (Dai 2008.)

Although the hydrogen peroxide method is relatively mature, it still has many shortcomings, such as the high energy consumption in the hydrolysis process of the rectification tower. The concentration of the hydrazine hydrate solution obtained in the hydrolysis tower is relatively low (up to 40%). In addition, there are many factors affecting the hydrolysis process, leading to unstable operation in industrial production and unbalancing to achieve larger-scale production (the maximum production scale so far is 12,000 tons/year). Although the catalytic distillation hydrolysis process has been successful in small trials, however, it has not been industrialized due to catalyst and separation issues. (Dai 2008.)

3.5 Analysis of current production status and prospects in China

At present, there are more than 20 hydrazine hydrate production plants in China, and the common specifications for the mass fraction of hydrazine in the commercially available hydrazine hydrate are 15%, 20%, 35%, 40%, 51.1%, 54.4%, 64% and 80%. Most Chinese manufacturers use the urea method to produce hydrazine hydrate. The major manufacturers in China that produce and sell hydrazine hydrate are Sichuan Yibin Tianyuan Co Ltd, hanghai Xiangyang Chemical Plant, Juhua Group Company, and Beijing Chemical Plant. Among them, Sichuan Yibin Tianyuan Co Ltd. has a scale of hydrazine hydrate about 5,000 tons per year, and the company plans to expand its production from 5,000 tons per year to 10,000 tons per year. (Xue 2002,31.)

Zhuhua Group has a production capacity of 10,000 tons/year of 80% of hydrazine hydrate, reducing costs and realizing all domestic equipment. The company plans to expand the production capacity of hydrazine hydrate production equipment to 20,000 tons/year. The company has self-developed frozen desalination, the new process of continuous evaporation and desalination has improved the shortcomings of intermittent production in the urea process and realized continuous production. Tianjin Soda Plant and Bayer of Germany jointly built a project with an annual output of 12,000 tons of hydrazine hydrate, making Binhai New Area the largest hydrazine hydrate production base in China. Qinghai Liming Chemical Plant, Puyang Zhong yuan Chemical Group Co Ltd, Shandong Yantai, Jiangxi have all planned hydrazine hydrate projects with an annual capacity of more than 5,000 tons. (Xue 2002,31.)

The international chemical giant LANXESS signed a cooperation agreement with Shandong Weifang Yaxing Chemical Co., Ltd. on September 28, 2004, to establish its first joint venture in China. The joint venture established the only production base in China capable of producing high-quality hydrazine hydrate with a mass fraction of 64%, and successfully started the operation in the second half of 2006, with an annual production capacity of 12,000 tons. (Xue 2002,31.)

At present, the Chinese market's demand for hydrazine hydrate is about 52,000 tons/year (based on 40%), while the actual output of the Chinese device is about 30,000 tons/year, and there is still a market gap of about 20,000 tons/year. All companies must import a certain amount of hydrazine hydrate, and the price of hydrazine hydrate continues rise. In August 2004, in response to the relatively large amount of international hydrazine hydrate dumping to China over the years, the Ministry of Commerce has issued the anti-dumping policies. The promulgation of anti-dumping policies has led to an increase in China's demand for hydrazine hydrate. The supply of hydrazine hydrate exceeds supply, and the price

fluctuates sharply. The price of hydrazine hydrate has soared from 13,000 to 14,000 yuan/ton in 2003 to 30,000 yuan/ton. With the rapid development of engineering plastics, pharmaceuticals, and pesticides in China, and the increasing demand for boiler deoxidizers, hydrazine sales have maintained a strong growth momentum. Therefore, it is imperative to vigorously develop the production of hydrazine hydrate. (Xue 2002,31.)

3.6 Analysis of the problems in the process of hydrazine hydrate in China

Looking at the current situation in China, the main problem in the production of hydrazine hydrate in China is that there are many manufacturers and scattered distribution points. Most companies have adopted the urea method to produce hydrazine hydrate. While producing hydrazine hydrate, a large amount of sodium chloride and soda ash will be by-produced. The previous concentration process is five-layer tower evaporation process. The dilute hydrazine liquid enters the five-layer tower to vaporize the hydrazine and the remaining residue is washed with boiling water, but the washing liquid containing salt and soda ash also contains a small amount of hydrazine hydrate and cannot be directly used. The wastewater has long been directly discharged into rivers and lakes. The wastewater not only seriously pollute freshwater resources, but also waste precious resources, restricting the further development of China's hydrazine hydrate industrial production. (Dai 2008.)

Take Xiangyu Company of Zhuhua Group as an example, its production capacity has reached 12,000 tons/year, and the by-product salt residue has reached 60,000 tons/year. The salt residue contains about 70% sodium chloride, about 15% sodium carbonate, about 3% sodium hydroxide, about 12% water, and the total amine reached more than 5000ppm. The conventional treatment method is to burn heavy oil to produce high-temperature calcined salt residue, by using this method, the amine content is reduced to less than 200ppm, which can theoretically be reused in the caustic soda electrolysis device, but due to the relatively high sodium carbonate and water content in the salt residue, it is easy to agglomerate, and the amine content is very unstable after calcination, which makes it difficult to guarantee the quality of the electrolyte. In addition, in recent years, the price of crude oil has continued to increase, and this method is uneconomical. It is very difficult to export salt residues, and the pressure given by the environmental protection prevents direct discharge of 16 salt residues. The problem of salt residues has become the primary problem for the further expansion of the production capacity of hydrazine hydrate. (Dai 2008.)

4 WASTEWATER OF HYDRAZINE HYDRATE

In the hydrazine hydrate production process, the wastewater produced will contain sodium chloride, a small number of ketones and ammonium ions. These compounds will cause high ammonia nitrogen and COD content in the wastewater. If it is improperly treated and discharged into the water body, it will seriously pollute the environment, and the lost sodium chloride is also a waste of resources. (Tian 2013.)

4.1 Wastewater characteristics

There are many kinds of organic matter in wastewater, with high COD content, but low BOD content and poor biodegradability, so it cannot be directly treated by biological methods. There are many kinds of substances that cause wastewater to produce peculiar smell, and it is difficult to completely remove peculiar smell with a single treatment method. The purity and content of sodium chloride are high, and it has a high recovery value. But if it is recycled, organic matter must be removed. (Tian 2013.)

4.2 The harm of wastewater to the environment

The wastewater produced in the process of synthesizing hydrazine hydrate contains a large amount of sodium chloride, a small amount of ammonium salts, ketones and other substances, and the content of COD is high. After this wastewater is discharged into the water body, although the concentration of chloride ions will be reduced due to the physical dilution and degradation process, but even a very low concentration of chlorine is harmful to aquatic organisms. Chlorine has strong killing power and has toxic effects on most aquatic organisms. Moreover, the reaction of chlorine with organic matter in the water body can form many chlorinated by-products, and most of these substances are also harmful to aquatic organisms. In addition, the salt content of wastewater is high, and biological cells will also be dehydrated and die in a high-salt environment. Therefore, if such wastewater is treated improperly, it will seriously pollute the water body. (Tian 2013.)

On the other hand, the ammonia nitrogen and organic matter contained in the wastewater may also cause the deterioration of the water body. The ammonia nitrogen and organic matter in the water body will be oxidized by microorganisms in the water under the action of dissolved oxygen in the water. The larger

content, the more dissolved oxygen will be consumed. Under normal circumstances, the amount of dissolved oxygen in a natural water body is in a dynamic equilibrium state of oxygen consumption and oxygen enrichment. When a large number of oxygen-consuming pollutants are discharged into the water body and the self-purification capacity of the water body is exceeded, the water body will be in an oxygen-deficient state, and the survival of aerobic organisms such as fish in the water will be affected, and even cause death due to long-term lack of oxygen. (Tian 2013.)

4.3 China Wastewater Treatment Policy

As one of the important links of environmental treatment, industrial wastewater treatment plays an important role in industrial production. In October 2010, in the Decision on Accelerating the Cultivation and Development of Strategic Emerging Industries, the State Council of China proposed that energy conservation and environmental protection should be identified as one of the seven strategic emerging industries, and that energy-efficient technologies, equipment and products should be promoted to achieve breakthroughs in key technologies in key areas to improve the overall level of energy efficiency. (Tang,2020.)

In April of 2015, China's state council issued the "water pollution prevention plan of action" (article 10 of "water"), this is the first time in China's industrial water treatment to regulate. The "water pollution prevention plan of action" puts forward the assessment requirements for industrial wastewater treatment from various angles, such as proposed governance non-ferrous metal, printing and dyeing, coking, API manufacturing top ten key industries. In addition, 238 strong measures are proposed to deal with pollution in industrial agglomeration areas. While China pays more attention to reducing total pollutant discharge, it also pays more attention to improving water environment quality and preventing and controlling environmental risks. (Tang,2020.)

In October 2017, in the report of the 19th National Congress of the Communist Party of China, the government required to improve the pollution emission standards, strengthen the responsibility of polluters, improve the system of environmental credit evaluation, mandatory disclosure of information, severe punishment and heavy punishment, which will play a guiding role in the development of the industrial wastewater treatment industry. (Tang,2020.)

On the other hand, in the environmental protection tax law, the Chinese government has also issued relevant policies. In December 2017, the State Council of China promulgated the "Regulations for the Implementation of the Environmental Protection Tax Law of the People's Republic of China", requiring taxpayers to pay an environmental protection tax at a reduced rate of 75.0% if the concentration of taxable water pollutants is lower than the national and local pollutant discharge standards by 30.0%. If the concentration of pollutants is below the national or local pollutant discharge standards by 50.0%, the environmental protection tax will be levied at a reduced rate of 50.0%. After the implementation of this policy, the collection of pollutant discharge fees was abolished, which is of great significance for protecting and improving the environment, reducing pollutant discharge and promoting ecological civilization construction. (Tang,2020.)

5 TREATMENT TECHNOLOGY OF HYDRAZINE HYDRATE HIGH-SALT WASTEWATER

The high concentration of salt and organic matter in hydrazine hydrate wastewater will inhibit the degradation process of micro-organisms and affect microbial metabolism and cause toxic effects. Therefore, there are certain advantages to treat this wastewater with physicochemical methods.

5.1 Evaporation and distillation method

Evaporation refers to a relatively low temperature (50 to 150°C). Part of the water in the high-salt wastewater is vaporized to achieve the effect of solid-liquid separation. This method can make the salt removal rate in wastewater up to 100% (or 100% salt recovery). This method is generally used as a pre-treatment process for high-salt organic wastewater. Distillation uses the different boiling points of different components in the liquid phase to separate and purify the liquid mixture. (Tang 2020.)

5.1.1 Current Status about Evaporation and Distillation method

Hunan Zhuhua Group has tried to evaporate the waste brine to produce salt residue in the exploration of the reuse of hydrazine hydrate waste brine. After calcination, the solid salt obtained meets the requirements of chlor-alkali electrolysis brine reuse, but the cost is significantly higher. Lai Zhenghua uses a vacuum deoxidation process to remove ammonia, hydrazine hydrate, acetone, and other low-boiling substances in the hydrazine hydrate wastewater at 85-90°C and returns to the ketone hydrazine section, and then uses NaClO oxidation to realize the recovery of waste brine, which is treated for electrolysis Chlor-alkali production to makes full use of salt resources. Li Baibang stripped the waste brine of hydrazine hydrate under normal pressure or reduced pressure and added acetone to convert hydrazine into ketazine and form the lowest azeotrope with water and collect the light components of organic matter back to ketazine system. Then the brine is concentrated by the evaporator, and the water obtained by evaporation reaches the process water standard. After the concentrated brine is cooled, it is added with NaClO for reaction and blown off by compressed air. (Tang 2020.)

Cheng Di developed a process for distilling hydrazine hydrate wastewater to produce industrial salt, effectively combining distillation with oxidation technology and catalytic reduction technology. The leftover liquid is centrifuged to obtain the crude salt and the filtrate. The filtrate is refluxed for oxidation reaction; the pH of the fraction is adjusted to 3~5 and the reducing agent is added to react. The COD removal rate of wastewater is 85%. 90%, the removal rate of ammonia nitrogen is 99%. At the same time, the biodegradability of wastewater is improved, and the obtained refined salt TOC is ≤ 10 mg/L, which meets the standard of chlor-alkali industry. Fang Peng distilled the oxidation-treated hydrazine hydrate wastewater through a multi-effect evaporator and the purity of NaCl recovered from the tail water reached 98.9%. Li Qunsheng and others took the hydrazine hydrate wastewater of Yibin Tianyuan Group as the research object. The combined process of reactive distillation, stripping and rectification are adopted. The recovery of ammonia and acetone through this process brings considerable economic and environmental benefits. (Tang 2020.)

Evaporation and distillation have a good purification and concentration effect on hydrazine hydrate waste brine or waste solid salt, but the equipment is relatively complex and powerful. It is suitable for treating small amount of hydrazine hydrate wastewater. Usually, it is necessary to cooperate with the oxidation method to achieve a better treatment effect. (Tang 2020.)

5.1.2 Evaporation and distillation related equipment---high temperature multi-effect evaporator

The multi-effect evaporator has significant advantages, mature technology, high efficiency, and low energy consumption. It can be used to treat high-salt wastewater generated in the chemical industry and recover the salt in the wastewater. (Zheng 2005,5-7.)

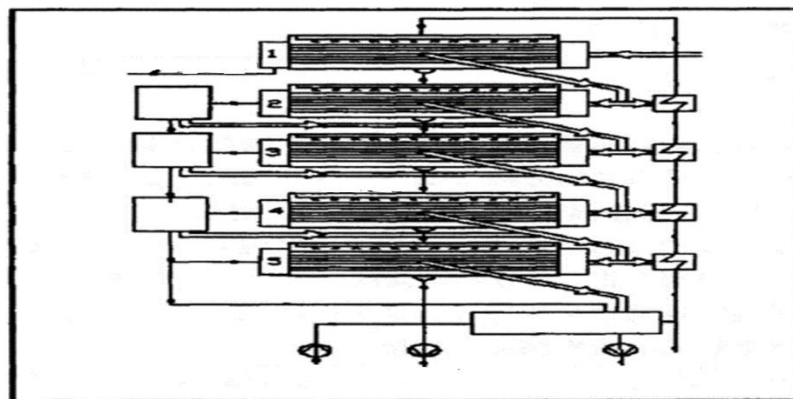


FIGURE 5 Schematic diagram of high temperature multi-effect evaporator (adapted from Tian 2013.)

The high-temperature multi-effect evaporator is composed of several evaporators connected in series and use high temperature of the steam, that is why it called this name. Using sea water as a raw material to explain its working principle. The seawater enters the condenser for heat exchange, a part of the seawater is discharged as cooling seawater, and the rest is pumped into the preheater to be heated step by step. When it reaches the first layer of evaporator, the temperature is close to the boiling point and is evenly distributed by the porous distributor. The spray enters the next layer of evaporator. (Tian 2013.)

At the same time, when high-temperature steam is introduced into the first layer, the water will quickly evaporate and generate secondary steam. After evaporation and concentration, the concentrated liquid will enter the next layer under the action of gravity. On the second floor, these concentrated liquids will be evaporated by the high-temperature steam introduced into the layer to produce steam. Part of the produced steam is introduced into the next effect as heating steam, and the other part is used by the preheater. (Tian 2013.)

The condensed water produced after the heating steam is condensed into the flash tank of this layer. Because the pressure in the flash tank is very low, the condensed water evaporates rapidly, and the generated steam is introduced into the next layer as a part of the heating steam. The wastewater after evaporation and concentration enters the next layer, and so on, until the last layer. The condensed fresh water of the heat exchanger and the fresh water of the flash tank are collected into the freshwater tank to achieve the purpose of desalination and concentration. (Tian 2013.)

Similarly, when the high-salt hydrazine hydrate production wastewater is added to the raw water tank of the high-temperature multi-effect evaporator, according to its working principle, a small amount of low-boiling acetone and ammonium salt are steamed out and can be reused as raw materials after condensation. In the hydrazine hydrate production system, this can not only reduce the production cost of hydrazine hydrate, but also reduce the processing burden for the subsequent recovery of sodium chloride. The concentrated solution containing organic matter and sodium chloride is further processed to recover sodium chloride. (Tian 2013.)

5.2 Oxidation Method-- Fenton Oxidation Technology

The oxidation method uses strong oxidants to oxidize and decompose pollutants in wastewater to reduce COD (Chemical Oxygen Demand), and convert large molecules, difficult to degrade, highly toxic organic substances into small molecules, easily degradable, and low-toxic substances. When using oxidation method to treat hydrazine hydrate wastewater, considering the recovery of salt, to avoid the introduction of impurities, chlorine-based oxidants are often used. Available chlorine (ClO^-) has strong oxidizing properties and can oxidize organic matter such as hydrazine hydrate in wastewater. The reaction between hydrazine hydrate and available chlorine is very fast and sufficient and not affected by OH^- . (Tang 2020.)

5.2.1 Current Status about Oxidation Method

As early as 1994, Hunan Zhuhua Group used NaClO to decompose hydrazine in hydrazine hydrate wastewater. N_2 was used to blow off ammonia nitrogen in the reaction tank, and the treated brine was reused for electrolysis. It is a preliminary attempt to reuse hydrazine hydrate wastewater, but the operation was not ideal due to the high ammonia nitrogen content. Huanghui added an appropriate amount of acetone to the hydrazine hydrate wastewater to react with the hydrazine hydrate to generate ketazine. Then NaClO oxidation was used to remove impurities such as ammonia nitrogen, hydrazine hydrate, ketone hydrazine and other impurities in the wastewater. At the same time, compressed air was used to remove the ammonia nitrogen and hydrazine hydrate. The removal rate of ammonia nitrogen and hydrazine hydrate reached 96.3% and 99%. The recovered brine reached chlor-alkali production raw material requirements. Jie Jia and Tan Yong used ClO_2 oxidation combined with rotating foam separation to remove ammonia nitrogen and COD, and the removal rates reached 98.1% and 99.8%. (Tang 2020.)

Chen Hua used a combination of physical and chemical methods to treat urea-process hydrazine hydrate wastewater, first added chlorine to oxidize, then used Na_2SO_3 to reduce free chlorine, and finally added acid to neutralize to reduce the total amount of ammonium in the wastewater. Fang Peng used the ultrasonic stripping- NaClO oxidation process to treat the hydrazine wastewater produced by the ketone dinitrogen process and optimized the process conditions. The removal rate of COD, ammonia nitrogen and hydrazine were all above 96%, and the cost was about RMB 30/t. Yibin Tianyuan Group hydrolysed the waste brine under high temperature and high pressure, then added NaClO and stirred to obtain refined brine with ammonia nitrogen ≤ 30 mg/L and acetone ≤ 30 mg/L for reuse in the chlor-alkali industry.

Shandong Yaxing Company used a bubbling-oxidation process to reduce the organic content in the waste brine to less than 200 mg/L under high temperature conditions. Starting from production, China Salt Lake Nan Zhuzhou Chemical Group Co., Ltd. Combined the dilute brine dichlorination system with the hydrazine hydrate production wastewater treatment and used the free chlorine in the dilute brine to oxidize the hydrazine hydrate wastewater, which not only improved the capacity of the chlorine system, but also made the hydrazine hydrate discharge of wastewater up to standard, saving operating costs. (Tang 2020.)

The chlorine oxidation method is simple in operation and low in cost. It can effectively remove hydrazine hydrate and other organic substances to reduce COD. It is used in large quantities in the treatment of hydrazine hydrate high-salt wastewater, but the effect of removing ammonia nitrogen is not ideal. It usually requires a combination of blow-off, gas-liquid separation, pH adjustment. The method promotes the removal of ammonia nitrogen, and the recovered brine that meets the ammonia nitrogen standard meets the standard of chlor-alkali industrial brine. (Tang 2020.)

5.2.2 Introduction to Fenton Oxidation Technology

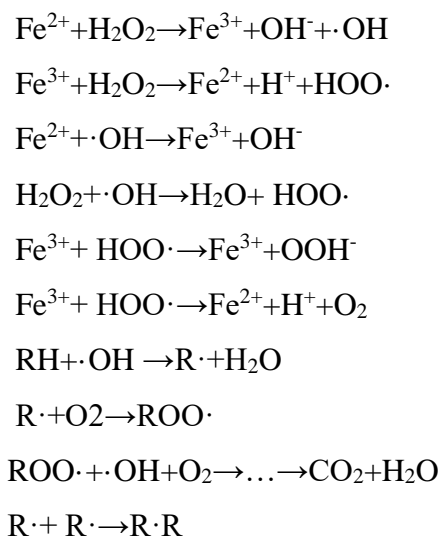
Fenton oxidation technology is one of the commonly used advanced oxidation technologies. Compared with other advanced oxidation technologies, it has the advantages of convenient operation, faster reaction speed, low price and no pollution, and its application prospects are broad. The key role in the Fenton oxidation reaction is the hydroxyl radical $\cdot\text{OH}$, which has strong oxidizing properties and can oxidize most difficult-to-degrade organic substances. It is produced by a series of catalytic reactions between divalent iron and hydrogen peroxide. When it is applied to organic wastewater with poor biochemical properties and hard to degrade, the biodegradability of wastewater can be improved by controlling the appropriate H_2O_2 dosage, pH of the solution, reaction temperature and Fe^{2+} concentration. Especially, it can be used in the field of organic wastewater that cannot be treated by conventional chemical oxidation and achieves a good treatment effect through Fenton oxidation reaction. (Lei 2003.)

5.2.3 Mechanism of Fenton's reagent oxidation technology

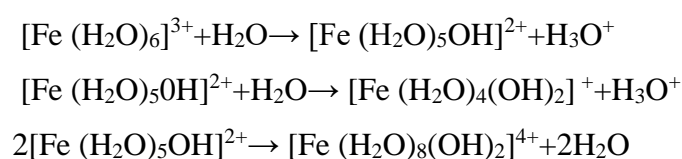
Fenton's reagent is a mixed system composed of H_2O_2 and Fe^{2+} , which can uniquely oxidize organic wastewater, and can also be used in conjunction with other processes such as coagulation. The role in

water treatment mainly includes oxidation and coagulation of organic matter. In addition to the oxidation effect of H_2O_2 as a strong oxidant, H_2O_2 reacts under the catalysis of Fe^{2+} to produce hydroxyl radicals $\cdot OH$ with strong oxidizing ability. It acts on organic matter and undergoes an oxidation reaction to completely oxidize the organic matter to carbon dioxide, and water or other easily degradable small molecules; coagulation is reflected in the catalyst iron salt, Fe^{2+} reacts under certain conditions to form $Fe(OH)_3$ colloid and molten iron complex, which can exert its flocculation and adsorption functions to achieve reduce the effect of organic matter. (Lei 2003.)

There are many studies on Fenton oxidation technology used in the treatment of refractory organic wastewater. As a very important part of advanced oxidation technology, its application value is also increasing. The degradation mechanism of the Fenton reaction is complicated. At present, it is generally agreed that under the condition of pH less than 7, the Fenton reagent mainly undergoes the following reactions: (Kammeyer 2001,277-285.)



The above reaction is a manifestation of the theory of hydroxyl oxidation. It can well explain the oxidation mechanism of Fenton's reagent, but some phenomena in the actual wastewater treatment process may need coagulation theory to support. Studies have shown that due to the presence of iron salts, Fenton reagent can produce iron complexes with flocculation under certain conditions. The main reaction formula is as follows: (Kammeyer 2001,277-285.)



It can be concluded from the above reaction formula that in addition to oxidation, Fenton reagent can also exhibit flocculation function, which can better explain the advantages of Fenton oxidation in treating refractory wastewater. (Sheng 1997,2050-2056.)

5.2.4 Advantages of Fenton oxidation technology

Compared with conventional water treatment oxidation methods, the characteristics of Fenton oxidation method are as follows. Under the catalysis of Fe^{2+} , many hydroxyl radicals with strong oxidizing ability can be generated, which can oxidize most organic substances. The oxidizing ability (2.80V) is second only to fluorine (2.87V). Fenton oxidation method oxidizes organic matter thoroughly. It can be used as an independent treatment unit or combined with other treatment processes. For example, as a pre-treatment process, it can improve the biochemical properties of wastewater, and the product is not harmful to the environment and has no secondary pollution. The reaction is convenient and easy to control, the speed is fast, and the efficiency is high, which can meet the processing requirements to the greatest extent in a short time. In addition to strong oxidation, it also has a coagulation effect that conventional oxidation technology does not have, which is more conducive to the removal of organic matter. (Kammeyer 2001,277-285.)

5.2.5 The main influencing factors of Fenton oxidation effect

According to the mechanism of the Fenton reaction, the key to oxidation is the concentration of $\cdot\text{OH}$, and the concentration of $\cdot\text{OH}$ depend on the concentration of H_2O_2 and Fe^{2+} in the solution. Therefore, the factors affecting the oxidation effect of Fenton reagent mainly include the pH value of the raw water, water temperature, and H_2O_2 dosing amount and Fe^{2+} dosing amount. The specific influence of each factor on the oxidation effect is as follows. The influence of pH value of raw water. The influence of pH value on the Fenton oxidation reaction is realized by the state of Fe^{2+} — Fe^{3+} complex system. Too high or too low pH is not conducive to the progress of the reaction. Research shows that the most suitable pH range is between 3 and 5. When the solution is highly alkaline, the Fe^{2+} and Fe^{3+} in the solution will precipitate in the form of oxychloride and lose its catalytic ability. Only under acidic conditions can $\cdot\text{OH}$ be produced, but if the pH is too low, too much H^+ in the solution will hinder the reduction of Fe^{3+} and reduce the catalytic reaction rate. To proceed efficiently, the pH of the initial solution must be maintained between 3 and 5. (Tian 2013.)

Within a certain range, the increase in temperature is conducive to the generation of $\cdot\text{OH}$, and $\cdot\text{OH}$ has high activity. Fenton's reagent has a good oxidation effect and can remove organic matter more effectively. At the same time, H_2O_2 is easy to decompose at high temperature, which is not conducive to the generation of OH , Fenton oxidation is reduced, and the treatment effect becomes worse. Zhang Tiekai and others used Fenton's reagent to treat certain refractory organic wastewater. The test results show that the most suitable reaction temperature is between 30°C and 50°C . It was discovered when a foreign academic group used Fenton's reagent to treat trichlorophenol. When the temperature is lower than 60°C , the temperature has a positive effect on the reaction, and when the temperature is higher than 60°C , it is not conducive to the progress of the reaction. Studies have shown that there is an optimal reaction temperature for Fenton reaction, which generally needs to be determined through experiments. (Tian 2013.)

The dosage of H_2O_2 is an important factor affecting the Fenton reaction. Within a certain range, when the concentration of H_2O_2 is relatively low, the larger the amount, the more $\cdot\text{OH}$ produced. The better the oxidation effect, and the greater the organic matter removal rate. However, the high concentration of H_2O_2 will accelerate the decomposition of itself, and will consume $\cdot\text{OH}$, so that the oxidation effect is reduced. (Tian 2013.)

Like the effect of the dosage of hydrogen peroxide on the reaction, in the case of low concentration, the oxidation effect increases with the increase of the dosage of Fe^{2+} , and at the same time, the excessive concentration of Fe^{2+} . On the contrary, it will reduce the removal effect of organic matter. The removal rate of organic matter in wastewater showed a change that first increased and then decreased, the reason why removal rate of organic matter first increased and then decreased is: when the concentration of Fe^{2+} is low, the concentration increases to promote the formation of $\cdot\text{OH}$, and the generated $\cdot\text{OH}$ can effectively react with organic matter; but when the concentration of Fe^{2+} is too high, excess Fe^{2+} reacts with $\cdot\text{OH}$ to make $\cdot\text{OH}$ the utilization rate is reduced. Therefore, the dosage should less. (Tian 2013.)

5.3 Nanofiltration Membrane Method

The membrane separation method uses synthetic membranes or natural membranes to use chemical head differences or external energy as power to separate and purify the substances in the wastewater to purify the wastewater. Among them nanofiltration as an emerging technology has the advantages of wide application range, stability, high efficiency, and low energy consumption. It has a good interception effect

on divalent salts and macromolecular organics in wastewater. Hydrazine hydrate wastewater contains a large amount of organic matter and high concentration of NaCl. Nanofiltration can achieve the separation of organic pollutants and salts, without losing NaCl, but also effectively removing organic matter, ammonia nitrogen and other pollutants. (Tang 2020.)

Shen Dongfang and others used nanofiltration membranes to treat hydrazine hydrate high-salt organic wastewater. The removal rates of COD and ammonia nitrogen can reach 67.3% and 52.9%, respectively. Washing the membrane with clean water can restore the membrane flux. Tang Li adopted wet method to prepare PPSU membrane for hydrazine hydrate wastewater treatment, combined with activated carbon adsorption pre-treatment and ozone catalytic oxidation advanced treatment, so that the COD removal rate of hydrazine hydrate wastewater can reach more than 80%. (Tang 2020.)

Membrane treatment of hydrazine hydrate high-salt organic wastewater can achieve the purpose of simultaneous desalination and COD removal, but there are various problems in practical engineering, for example, membrane pressure difference, membrane flux, membrane fouling and membrane cleaning. In particular, the membrane conditions of sewage should be considered. Membrane separation technology should seek and develop special membrane materials to reduce membrane fouling, increase membrane flux and membrane regeneration times after cleaning, improve effluent quality, reduce operating costs, and enable membrane separation technology to be more widely used. The researcher's use of nanofiltration membranes to treat hydrazine hydrate wastewater has practical application significance, laying the foundation for the reuse of NaCl in the production of ion-exchange membrane caustic soda. (Tang 2020.)

5.3.1 Materials about Nanofiltration membrane

Nanofiltration membrane materials can be divided into two categories, inorganic membrane materials and organic polymer membrane materials. Organic polymer membrane materials include five types, cellulose, polysulfone, polyamide, polyelectrolyte, and aromatic ester. Inorganic membrane materials include silicon dioxide, titanium dioxide, aluminium oxide and zirconium oxide and other materials. At present, most of the commercial nanofiltration membranes are prepared by interfacial polymerization, that is, by condensation polymerization of highly active aqueous monomers and organic monomers. The main membrane materials of the interfacial polymerization method are aromatic polyamides, poly piperazine-amide. When making the nanofiltration membrane there are commonly two-phase monomer substances, the water-phase monomer substances include aromatic polyamines and aliphatic polyamines,

such as m-phenylenediamine (MPD), piperazine (PIP), p-phenylenediamine (PDM). Organic phase Monomer substances mainly include polybasic acid chlorides, such as trimesoyl chloride (TMC) and isophthaloyl dichloride. (Zhang 2015.)

5.3.2 Preparation method of nanofiltration membrane--- Charging method

The charging method for preparing nanofiltration membranes is usually combined with the blending method and the composite method, and it is one of the important methods for preparing nanofiltration membranes. The nanofiltration membrane prepared by the charging method can be divided into two types: surface charged membrane and overall charged membrane. The nanofiltration membrane prepared by the charging method has obvious advantages: it improves the compactness, acid and alkali resistance and pollution resistance of the membrane and improves the hydrophilicity and water flux of the nanofiltration membrane. In the preparation process, by adjusting the degree of looseness of the membrane surface, the chargeability of the membrane surface and the charge quantity of the membrane surface, ions of different valences can be separated to adapt to different application systems. The existing commercial nanofiltration membrane series include chloromethylated/quaternized polysulfone membranes, sulfonated polysulfone membranes, chloromethylated polysulfone membranes, UTE series membranes, polyanion and polycation membranes. The charged properties and the amount of charge of the membrane are determined by the control of the ion exchange capacity (I.E.C value) and the membrane potential value. (Childress & Elimelech 2000, 3710-3716.)

Surface chemical treatment to prepare the nanofiltration membrane, for the surface chemical treatment method, firstly, prepare the nanofiltration membrane, and then modify the surface of the membrane. The main process of preparation is, first, prepare a nanofiltration membrane with reactive groups, and then treat the surface of the nanofiltration membrane with a charged reagent, so that the surface of the membrane is charged, and the surface pore size of the membrane is reduced. (Childress & Elimelech 2000, 3710-3716.)

Adsorption method to prepare the nanofiltration membrane, first add the charged material to the base film soaking solution, and then under certain conditions, such as heat, light, radiation, ionic body, as the medium environment, make the base film and the surface of the charged material exchange the film. For example, using a PES or PSf ultrafiltration membrane as the base membrane, the base membrane is

soaked in a sodium polystyrene sulfonate solution, and then grafted with light to prepare a nanofiltration membrane. The main disadvantages of the nanofiltration membrane prepared by the adsorption method including these aspects, poor tolerance of the membrane, short membrane service life, and few industrial applications. (Childress & Elimelech 2000, 3710-3716.)

5.3.3 The existing major problems in the application of nanofiltration--Membrane fouling

Membrane fouling is one of the common problems faced in the application of membrane separation technology. Due to the interaction between nano-scale pores and the charging effect, the problem of membrane fouling of nanofiltration membranes is more serious than that of other types of membranes. The membrane pollution of complex nanofiltration membranes is mainly divided into organic pollution, inorganic pollution, colloidal particulate pollution, and biological pollution. The corresponding pollutants mainly include organic solutes, inorganic solutes, colloids and biosolids. In practical applications, the phenomenon of nanofiltration membrane fouling is often caused by multiple types of membrane fouling occurring at the same time. (Van der Bruggen et al 2008.)

When the concentration of the solute components at the feed liquid end is oversaturated, fouling and silica pollution are likely to occur on the membrane surface. This phenomenon usually occurs in the latter part of the membrane process. The deposition of metal oxides and colloids occurs in the early stage of membrane filtration when the permeation flux is high. At present, the formation mechanism of organic pollution is not very clear. It is generally believed that this process still has something to be done with the specific types of pollutants and molecular characteristics. The specific location of organic pollution is still unpredictable. It may occur in the front or the end of the membrane module. The specific causes and mechanisms need to be further studied.

The rapid biological fouling is related to the deposition of particulate matter at the initial stage of filtration, while the slow biological fouling will gradually appear in each section of the membrane module with the extension of the filtration time. To reduce and eliminate membrane pollution, it is necessary to identify the types of pollutants. Usually, when the types of pollutants are known, corresponding membrane pollution control strategies can be formulated. The results of research and practical applications show that the choice is based on the quality of raw water treated reasonable and effective pre-treatment process (coagulation, adsorption, pre-oxidation, pre-filtration). Select the appropriate type of nanofiltration

tion membrane (non-contaminated material/membrane surface modification, appropriate membrane surface charge, chlorine tolerance, porosity rate, hydrophobicity, surface roughness), reasonable membrane module configuration design and operation mode, optimized process design, suitable and efficient membrane cleaning cycle and method (hydraulic flushing, backwashing, pulsed backwashing,). It can effectively prevent and reduce membrane pollution, extend the service life of membranes, and improve water production efficiency. (Waite et al 2005.)

6 DISCUSSION

In the hydrazine production process, considering environmental protection, product quality and cost, the urea method will eventually be eliminated, and the hydrogen peroxide method has the most advantages. Only by eliminating outdated production technology as soon as possible and adopting advanced technology to improve the overall level of production equipment can suit the law of development in the world today. Meanwhile, due to the increasing demand for hydrazine hydrate, the position of hydrazine hydrate is becoming more irreplaceable. To reduce the wastewater during the production of hydrazine hydrate, chemical substances containing less nitrogen and phosphorus can be used as raw material in the synthesis of hydrazine hydrate.

About the wastewater treatment, compared with the evaporation and distillation method and the nanofiltration membrane method. Fenton oxidation method has more advantages and Fenton oxidation method oxidizes organic matter thoroughly. It can be used as an independent treatment unit or combined with other treatment processes. For example, as a pre-treatment process, it can improve the biochemical properties of wastewater, and the product is not harmful to the environment and has no secondary pollution. Otherwise, the reaction of Fenton oxidation method is convenient and easy to control, the speed is fast, and the efficiency is high. However, if use nanofiltration membrane method, there will have lots of problem to be done, such as material selection of nanofiltration membrane and cleaning of nanofiltration membrane, so compared with the Fenton oxidation method there are still many technical problems to be solved.

7 CONCLUSION

Although the world science and technology has developed rapidly, but in the production of hydrazine hydrate and wastewater treatment there are many problems worthy to be discussed. Taking nanofiltration membrane method as an example, on one hand, in terms of material and preparation, need to further improve organic membrane pollution resistance and easy cleaning performance, extend the service life of membrane, improve the reagent resistance, heat resistance and oxidation resistance of membrane, reduce the cost of the membrane. In terms of nanofiltration membrane technology, producer and the researchers should develop membrane components and perfect operating systems that can give full play to membrane performance, explore membrane cleaning skills in various application fields, and further expand the application fields of nanofiltration membrane. China's current technology, membrane technology, is still in the laboratory stage. China should increase the intensity of the membrane technology research, break the foreign monopoly and reduce the enterprise production with membrane. On membrane fouling of membrane pollution, the problem of membrane fouling can be started from the development of new materials and optimizing the use of NF technology to reduce pollution and prolong the service life of nanofiltration membranes.

Most of the hydrated hydrazine wastewater is derived from the chlorine industry. This wastewater has a high salt content, which contains a poisonous organic matter. This feature also makes it difficult to deal with, but there is a certain recycling value about the hydrated hydrazine wastewater. Therefore, the research direction of hydrated hydrazine high salt organic wastewater is to reduce organics and ammonia nitrogen content, purify concentrated brine, and reuse to chlorine ionic membrane electrolysis. The world's researchers carry out many experimental research and engineering practice applications on the harmless treatment and resource utilization of hydrated hydrazine wastewater, providing a theoretical basis and technical reference for achieving zero-emitting cyclic emissions from chlorine-alkali chemical hydrate.

In the production of hydrazine hydrate, there are four methods, the Raschig method, the urea method, the ketazine method, and the hydrogen peroxide method. With the development of science and technology and the rise of environmental protection concepts, those methods that consume much energy and produce more pollutants should be eliminated and improved. About the wastewater treatment, although there are various methods now, but not every method can achieve the best treatment effect, and some

methods still need further development. Taking the nanofiltration membrane method as an example, about the membrane production and cleaning there are still many unsolved problems.

In recent years, with the continuous development of science and technology, the living standards of human beings have been continuously improved. However, the ensuing environmental problems have also continuously attracted people's attention. The excessive emission of carbon dioxide has caused global warming and energy depletion caused by over-exploitation of fossil raw materials have become the problems that human must deal. The development of clean energy, and the rational development and utilization of resources to achieve sustainable development have become the theme of the current era.

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