

A Review: Pharmaceutical Wastewater Treatment Technology and Research in China

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Abstract—The origin and character of pharmaceutical wastewater were summarized in this paper. And some popular disposal technologies used in wastewater treatment of pharmacies were introduced, such as physicochemical disposal process, bio-chemical disposal process and process of deeply oxidation at elevated temperature. All kinds of waste categories, respectively, described the similarities and differences in their approach. It contained the sources of this waste water, the most suitable method and cost. Several mainstream in articles on this treatment method, for a detailed discussion of the process of adaptation to their overall costs and technical bottlenecks were summarized. Meanwhile, operating parameters, residence time, reaction temperature, catalyst, secondary pollution and other technical details are within the scope of the discussion. At last, it gives a prospect of the market of pharmaceutical wastewater in our institutions.

Keywords- pharmaceutical wastewater; advanced oxidation; disposal costs; bio-treatment; photo-catalytic degradation.

I. INTRODUCTION

Pharmacy industry is a high-tech, high investment, high efficiency which recognized as a most promising international industry [1]. At present, China has more than 4,000 pharmaceutical enterprises [2]. It can produce about 1500 kinds of chemical raw materials, chemical preparations as well as more than 4,000 species, and the total output of about 1.935 million tons in 2009 [3]. The pharmaceutical industrial output value reached 1.04 trillion yuan. However, along with pharmacy industry continues to develop, it leads to environmental problems [4]. Currently, it is one of 12 national environmental planning key governance sectors [5]. Some statistics said that pharmacy industry output accounted for 1.7% of GDP while the country's total water emissions accounted for 2% of sewage discharge [6]. Pharmaceutical wastewater has a composition of complex and it contained many kinds of organic pollutants in high concentrations, COD, BOD₅, NH₃-N and high levels of suspended solids, color depth, toxicity and other features [7]. According to incomplete statistics, Chinese pharmaceutical exhaust emissions per year (standard state) are about 1 billion cubic meters, which contains about 100,000 tons of harmful substances [8]. Wastewater discharge is about 500,000 cubic meters per day, and waste and emissions of about 100,000 tons per year with the most polluted pharmacy chemical

synthesis [9]. This paper focuses on the details of these treatment methods and pharmaceutical wastewater [10].

II. CHARACTERISTICS OF PHARMACY WASTEWATER

According to distinguish between pharmaceutical products, this waste is divided into bio-pharmaceutical, chemical, pharmaceutical and herbal production waste water [11].

A. Properties of Bio-pharmaceutical Waste

Bio-pharmaceutical wastewater containing mainly mycelium, residual nutrients, metabolites and organic solvents. The current process is mainly used for the production of bio-pharmaceutical antibiotics. A high concentration of organic matter in the wastewater, COD is up to 5000-20000mg/L, BOD₅ is up to 2000-10000mg/L, SS concentration can reach 5000-23000 mg/L while TN reach 600-1000mg/L. China currently has more than 300 producers of antibiotics. It can produce more than 70 varieties, yields of 20%-30% of the world. And for each 1t products, high concentrations of wastewater discharge reached 150-850m³, thus causing serious environmental pollution. Common bio-pharmaceutical waste physical chemical properties as shown in the following TABLE I.

TABLE I. COMMON BIO-PHARMACEUTICAL WASTE PHYSICO-CHEMICAL PROPERTIES

Item	Concentration	Item	Concentration
COD (mg/L)	2000-10000	SS(mg/L)	200-500
Chromaticity	500-1000	BOD ₅ (mg/L)	1000-2500
Temp. (°C)	25-80	TP (mg/L)	50-250
pH	4-8	TN (mg/L)	500-1500

B. Composition and Properties of Chemical and Pharmaceutical Waste

The main production processes of pharmacy are chemical and pharmaceutical chemistry. Due to its materials complex, multi-step reaction, resulting in low conversion rate and the raw product with suffering serious losses. Such a wide variety of wastewater containing toxic and hazardous chemicals, such as steroids, nitro compounds, anilines, piperazine and fluorine, mercury, chromium copper, and organic solvents which contain ethanol, benzene, chloroform, petroleum ether and other organic compounds, metals and waste acid and other pollutants, it can cause serious trace pollution problems. However, because synthesized pharmaceutical

industry is more complex, a pharmaceutical company's product range is often not the one, so the wastewater pollutants contained in the synthesis of pharmaceutical companies the situation is more complicated. According to statistics show that domestic surveillance, COD concentration range of chemical synthetic pharmaceutical companies in 432-32140mg/L; BOD₅ concentration is range of 300-8000mg/L; SS concentration is range of 80-2318 mg/L; NH₃-N concentration range in 4.8-1764 mg/L. Common chemical and pharmaceutical wastewater properties as shown in the following TABLE II.

TABLE II. COMMON CHEMICAL AND PHARMACEUTICAL WASTEWATER PROPERTIES

Item	Concentration	Item	Concentration
COD (mg/L)	1000-10000	SS (mg/L)	200-500
Chromaticity	500-1000	BOD ₅ (mg/L)	500-2500
Temp. (° C)	25-80	TP (mg/L)	50-250
pH	1-6	TN (mg/L)	500-1500
SO ₄ ²⁻ (mg/L)	5000-25000	Chlorobenzenes (mg/L)	500-3000
Zn ²⁺ (mg/L)	1000-5000	Aniline (mg/L)	500-1000
Salts (mg/L)	10000-25000	Antibiotic(μg/L)	1-100

C. Chinese Traditional Pharmaceutical Waste

Chinese traditional medicine and folk medicine are our medical science features and advantages. As of 2014, these industrial output value is of 577.2 billion yuan accounting for 27% of the entire pharmaceutical industrial output value. Chinese traditional medicine production has many processes with washing, cooking drugs, purification separation, evaporation and concentration processes for producing wastewater to be discharged. It comprises a washing wastewater, the separation of water, evaporation condensate, loss of liquid water. Currently, these wastewater are mainly a variety of traditional Chinese medicine decoction natural biological organic matter, such as organic acids, anthraquinone, lignin, alkaloids, tannins, tannins, proteins, carbohydrates, starch. Its water quality volatile, additional water may also contain alcohol used in preparing medicine and other organic solvents. Common Chinese traditional pharmaceutical wastewater properties as shown in the following TABLE III.

TABLE III. COMMON CHINESE TRADITIONAL PHARMACEUTICAL WASTEWATER PROPERTIES

Item	Concentration	Item	Concentration
COD(mg/L)	1000-10000	SS(mg/L)	200-500
Chromaticity	500-1000 times	BOD ₅ (mg/L)	500-2500
Temperature	25-80° C	TP(mg/L)	50-250
pH	1-6	TN(mg/L)	500-1500
Cyclic	Trace	Phenol	Trace
Heterocyclic	Trace	Unsaturated fatty-acids	Trace
Organochlorine	Trace	Antibiotic (μg/L)	1-100

III. PHARMACY WASTE PHY-CHEMISTRY TREATMENT

A. Coagulation and Sedimentation

Current research for pharmaceutical wastewater treatment technology domestic and abroad are often based on high concentrations of the most representative, most pollutant of bio-fermentation pharmacy, bio-chemical, pharmaceutical and other produce. Biodegradable organic waste is the main object, commonly used mainly for processing physic-chemical, biological method and high-temperature oxidation depth. Physic-chemical treatment is

not only as a pre-biological treatment processes, and sometimes also is a post-treatment process alone or pharmaceutical wastewater treatment processes. At the same time, integrated pharmaceutical wastewater treatment currently used methods are mainly materialized following: coagulation and sedimentation, flotation, adsorption, chemical oxidation (Fenton reagents, wet oxidation, etc.), electrolysis (Fe-C micro-electrolysis) and so on.

Materialized in economical methods of coagulating sedimentation method is preferred. Coagulant to the water, wastewater colloidal particles can lose stability, cohesion and large particles sink. This method is usually treated by coagulation, not only can effectively reduce the concentration of pollutants, and biodegradability of wastewater can be improved.

B. Flotation

Flotation using highly dispersed tiny bubbles as a carrier to adhere to the wastewater pollutants. With less dense than water, it realized the water and float to the solid-liquid or liquid-liquid separation. Flotation applicable pretreatment high suspended solids content of wastewater, with less investment, low energy consumption, simple process, and easy maintenance.

C. Adsorption Method

Adsorption method is the use of porous solids from wastewater in one or several pollutants, to recover or remove contaminants, so that waste water is purified approach. In the pharmaceutical wastewater treatment, commonly soot or carbon adsorption wastewater pretreatment production medicine, lincomycin, such as paracetamol, significant reduction in COD, while removing waste water color and odor.

D. Fe-C Method of Micro-electric Field

Production in Fe-C is as a pre-processing step pharmacy wastewater. In the process flow, after pretreatment of wastewater biodegradability greatly improved, the effect is obvious. Plus the use of inexpensive Fe²⁺ catalyst such wastewater treatment, COD removal can reach the second part of the industry's highest pollutant emission concentration, and this method over other many methods is economic and stable.

E. Fenton Method

Pretreatment pharmaceutical wastewater using Fenton's reagent, COD removal rate is about 40-50%. A pharmaceutical factory in Wuhan of pharmaceutical wastewater treatment using this method. And the decolonization rate achieved 100%. The COD removal efficiency is of 92.3% in results. Comprehensive comparison of all of the above approach is as follows in TABLE IV.

TABLE IV. COMPARISON OF SEVERAL PHYSICAL-CHEMICAL TREATMENT METHOD

Treatments	Efficiency	Processing	Costs
Coagulation sedimentation	50-80%	Pretreatment	Low
Adsorption	70-85%	Pretreatment	Low
Fe-C	80%	Pretreatment	Low
	60-75%	Secondary processing	Low
Fenton	60-95%	Secondary processing	Low
Photo-catalytic	85-99%	Advanced treatment	High

IV. BIOLOGICAL TREATMENT

A. Aerobic Biological Treatment Technology

There are aerobic biological treatment process microbial treatment, anaerobic treatment and anaerobic-aerobic combined treatment process. Common aerobic biological wastewater treatment facilities have conventional activated sludge method. It contained high load activated sludge, oxidation ditch, SBR, CASS, CAST, ICEAS, UNITANK, DAT-IAT, MSBR, BAF, etc. In terms of process technology evolution, domestic pharmaceutical wastewater aerobics biological treatment is first used for aerobic activated sludge process represented; the mid-1990s, SBR, ICEAS, CASS technology has made relatively good results; and for the 21st century, three oxidation Ditch, UNITANK and MSBR pharmaceutical wastewater treatment and other new technology has made continuous exploration and applications. It was often used for the easily-biological wastewater and the ratio of BOD₅/COD was more suitable to be more appropriate.

B. Anaerobic Process

At present, domestic pharmacy treatment of high concentration organic wastewater, anaerobic fermentation is basically approach. Compared with the aerobic treatment, anaerobic treatment of high concentration organic wastewater typically has the following advantages: high organic loading; sludge production is low, easily biological sludge dewatering; fewer nutrients needed; without aeration, low energy consumption; can produce biogas energy recovery; suitable for a wider range of temperature; long active anaerobic sludge retention time. It was often used in the non-biological wastewater.

C. Combination Process

Anaerobic and aerobic treatment methods have advantages and disadvantages, the combination of two processes together, and their respective advantages to get promoted, get inadequate remedy. Common combination process route micro electrolysis-anaerobic hydrolysis acidification process-SBR series, pretreatment-UBF-contact oxidation-BAF treatment processes, hydrolysis acidification-UASB-SBR processes are often process route. It was also often used in non-biological wastewater. Compare the pros and cons of these three processes are as follows in TABLE V.

TABLE V. ANAEROBIC, AEROBIC AND COMBINED PROCESS OF THE PROS AND CONS.

Treatments	Aerobic	Anaerobic	Combined
Adaptation Temp.	Adapt high Temp.	Room Temp.	Adapt high Temp.
Pressure	Atmospheric	Atmospheric	Atmospheric
Removal	Thoroughly	Not Completely	Thoroughly
Residence	Few hours	Few hours	Soon
Secondary Pollution	Little	No	No
Costs	Low	Low	High

V. HIGH-TEMPERATURE OXIDATION

A. Wet Air Oxidation (WAO)

High-temperature oxidation treatment technologies include: Wet Air Oxidation (WAO), supercritical water

oxidation technology (SCWO) and incineration. WAO is at a high temperature (150-350°C) and high pressure (0.5-20 MPa.G) under air or pure oxygen as the oxidant for the oxidative decomposition of organic pollutants and chemical processes of inorganic or small organic molecules. Operation in the waste liquid and mixed by the high-pressure pressurized air into the air warmed by the heat exchanger after the oxidation reactor, the reaction product obtained after the heat exchanger into the cooling tower heat exchanger heated with continued cooling, and then divided by the sort of gas-liquid separator and liquid, and then sent to the subsequent processing. COD removal is generally wet oxidation of 60% -96%, the water cannot be discharged directly WAO treatment, most wet oxidation system used in conjunction with biological treatment systems.

B. Super-critical Water Oxidation Technology (SCWO)

SCWO The principle is: the water temperature and the pressure was increased to the critical point ($T_c=374^\circ\text{C}$, $p_c=22.1\text{ MPa.G}$) above, the water becomes supercritical water, hydrogen water, no longer exists; After supercritical water leads to oxygen and supercritical water can dissolve excellent, oxidation of organic matter can be carried out in a uniform oxygen-rich phase. Meanwhile, a high reaction temperature (400-600°C) also accelerate the reaction rate, organic matter in the waste water can achieve high destruction efficiency within a few seconds, and the reaction is fully and completely; Make organic matter into CO₂, N₂, H₂ and H₂O, Cl chloride ions into a metal salt, and the nitro group was converted into N₂, S is converted to sulfate. This method is somewhat similar to the simple combustion process similar to emit a lot of heat in the oxidation process, once the operating normally, reaction heat can not only meet the heating needs of the wastewater, but also generate a lot of heat for the production.

SCWO for organic matter removal rate is about 99.99%. Therefore, it compared with the traditional approach, with high efficiency, energy saving, no secondary pollution and other significant advantages, is a promising high concentration organic wastewater treatment technology.

C. Incineration

Incineration of waste is to be treated with an excess of oxidizing air in the incinerator combustion reaction, so that the pollutants contained in the wastewater at a high temperature oxidative decomposition is destroyed, is an integrated and high-temperature treatment of deep oxidation processes. Incineration can greatly reduce the volume of waste water, the elimination of many of these harmful substances, while the recovery of heat. Thus, for some temporary recovery value method and other methods cannot solve or handle combustible waste is not complete, it is a valid burning. This method enables the complete oxidation of waste into harmless substances, COD removal efficiency of 99.5%. Therefore, suitable for handling high organic content or higher calorific value of waste is widely regarded. Through the organic content of the waste water is less, it may be added to the auxiliary fuel.

Seen from TABLE VI, supercritical water oxidation and incineration highest COD removal, almost completely removed, and the water after the wet air oxidation process cannot meet emissions standards, the need to follow-up treatment; from an investment point of view, partial incineration investment large, and wet air oxidation technology minimum; operating cost analysis from the point of view, at least supercritical water oxidation, and the largest incineration.

TABLE VI. MERITS OF THE THREE KINDS OF HIGH-TEMPERATURE PROCESSING METHOD.

Treatments	SCWO	WAO	Incineration
Adaptation Temp	>400	150~350	1200~2000
Pressure	30MPa.G	2-20MPa.G	Atmospheric
Removal rate	≥99.99%	70~90%	99.99%
Catalysts	No	Yes	No
Processing time	≤60s	15~20min	≥100min
Subsequent process	Colorless nontoxic	Colorless nontoxic	NOx
Spontaneous Costs	Yes 65 Yuan/t	No 100 Yuan/t	No 15000 Yuan/t
Initial Investment	650 M Rmb	500 M Rmb	1000 M Rmb

VI. CONCLUSIONS

It extensively carried out high-tech applications in the study of pharmaceutical wastewater treat, its rapid development for the chemical industry and the pharmaceutical industry for high concentration organic wastewater provides a broad application prospects. It can focus on high-temperature, combination treatment technology, deeply oxidation technology to high COD concentration, complex composition, and poor biodegradability of pharmaceutical wastewater as a focus of upgrading industrial restructuring. Play burned advantages waste treatment, in the original engineering experience to develop new technology and high added value with intellectual property, promote the development of domestic pharmaceutical wastewater treatment and disposal. At last, it is a widely optimistic about the growth of new technologies and potential markets.

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