Research progress on wastewater treatment methods and technologies in paper industry

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Abstract. The pulp and paper industry has polluted a large amount of water, and it has the traits of high concentration and wide coverage, which can be said to be one of the most serious polluting sectors in China. With the rapid development of the paper industry, the treatment of its wastewater has also attracted the attention of many departments. The treatment of industrial wastes from the paper industry has always been concerned by researchers, and it has many treatment methods which has its own advantages and disadvantages. This paper discusses different common methods and combination techniques and their application in treatment of industrial wastes from the paper industry.

1. Introduction
The paper industry is one of the important pillar industries of China's national economy[1-2]. Its production process requires a large amount of water resources and a large amount of wastewater. Therefore, the treatment of paper industry wastewater has become a hot and difficult research issue in the scientific community. The total displacement of China's paper industry ranks among the top three in the industrial sector. Papermaking wastewater cannot be mixed with conventional urban sewage due to its high chemical oxygen demand (COD), high total suspended solids content (SS), poor biodegradability, and a wide variety of organic pollutants. The water quality of papermaking wastewater is characterized by large alkalinity, large chroma, high content of difficult-to-degrade substances, large oxygen consumption, and serious damage to the ecological environment. The chemical additives used in the pulping, bleaching, washing, and papermaking processes in the papermaking process will be discharged along with the water. The papermaking wastewater is complex and toxic, and there are about 89 organic pollutants in the papermaking wastewater[3]. Biodegradability is also worse than other sewage.
2. Paper industry introduction and main situation

2.1 Introduction to the paper industry
Wastewater from the paper industry is largely discharged and has complex components, particularly organic materials that are difficult to degrade, such as lignin, hemicellulose, and monosaccharides. It is prone to serious environmental pollution, is a high concentration of organic wastewater, and is very difficult to handle. Paper industry wastewater has the characteristics of poor biodegradability, high toxicity, heavy odor, and more foam[4]. Moreover, the discharge of wastewater is large, the composition of wastewater is complex, the toxic content of wastewater is high, and the level of industrial governance is relatively backward.

2.2 The main situation of the paper industry
Along with the rapid development of the paper industry, the problem of wastewater pollution has become increasingly prominent. Coupled with the declining water resources in China, it is urgent to find a suitable wastewater treatment process. At present, China's paper industry is in a period of rapid development, both in terms of pollutant emissions and wastewater discharge. Contaminants are mainly derived from chemical residues, dissolved organic matter, and partially lost fibers added during the production process. The papermaking wastewater also contains some toxic and harmful substances. The development of new pulp and paper wastewater treatment processes, improving the treatment effect, reducing the cost of treatment, and improving the ecological environment have become the focus of continuous research by environmental protection departments and papermaking departments at home and abroad[4].

3. Paper industry wastewater quality

3.1 cooking waste liquid
The cooking waste liquid includes an alkaline pulping black liquor and an acid pulping red liquor, and belongs to an ultra-high concentration organic wastewater. Alkaline pulping (currently used in most paper mills in China) produces brownish black, the main components are lignin and carbohydrate degradation products, pigments, pentose, residual alkalis and other dissolved substances[5].

3.2 middle section wastewater
The middle-stage wastewater is the wastewater produced by washing and bleaching the pulp after the pulp black liquor is extracted. This part of the water is lighter in color than the cooking wastewater, and the CODc and BOD5 are smaller, but the composition of the wastewater is complicated[5].

3.3 white water
White water is the waste water produced by the paper machine papermaking section, which mainly contains fine fibers, fillers and rubber compounds. This section of wastewater has a low pollution load and is easier to handle. At present, most paper mills use white water for reuse or partial reuse, which greatly reduces wastewater discharge[5].

4. Common methods and combination techniques for wastewater treatment in paper industry

4.1 Common methods for wastewater treatment in paper industry
At present, there are many kinds of techniques for treating wastewater in the paper industry. The traditional treatment methods mainly include physical treatment, physical and chemical methods, chemical treatment and biological treatment[5]. Common methods of physical treatment include mechanical filtration, precipitation and air flotation; common methods of physical chemical methods include coagulation, adsorption and membrane analysis; common methods of chemical treatment include advanced chemical oxidation, wet oxidation, and supercritical water. Oxidation method and
electrochemical oxidation method; biological treatment methods commonly used are activated sludge method, biofilm method, anaerobic biological treatment method, biological filter method and artificial wetland method. With the development of technology, a series of technologies such as advanced oxidation technology, membrane separation technology, photocatalytic technology, and microbial flocculant are widely used[6]. However, this series of technologies has certain limitations on the treatment effect of sewage, and the problems of secondary pollution and high treatment cost are also serious. Therefore, the development of a new and efficient green environment-friendly wastewater treatment technology has become an important task in the research community[7].

4.2 Paper industry wastewater treatment combined technology

4.2.1 Physical chemical method combined with biological treatment. The physical and chemical methods in the paper industry wastewater mainly use coagulation and precipitation methods[8]. The membrane separation technology applied is mainly ultrafiltration and reverse osmosis[9], which is a liquid membrane separation method based on the pressure difference. The disadvantage of using this method is that the cost is high. The conventional pretreatment method uses a coagulant to coagulate and precipitate. Recently developed magnetic coagulation technology, the magnet acts as a flocculant to adsorb the chemical substances in the papermaking waste liquid that cause the COD value to increase, and then the super-conductive high-gradient magnetic separation treatment, the treated wastewater can be reused not only in the paper mill, The treatment cost is also 6-10 times lower than the traditional activated sludge process[10]. Some scholars[11] use the "magnetization + two-stage reaction precipitation" process to deeply treat the secondary effluent of a waste paper pulping and papermaking enterprise in Jiangsu Province, and the effluent quality meets the "Pulp and Paper Industry Water Pollutant Emission Standard" (GB3544(1) 2008) “Special Emission Limits for Water Pollutants”.

The biological treatment method in the paper industry wastewater can be combined with the aerobic method by the anaerobic method. The advantage of activated sludge treatment is that it is low in cost, easy to manage, and has good treatment effect. It is the most commonly used aerobic treatment method. The shortage is that a large amount of sludge needs to be treated separately, and the effect of treated water on sludge expansion is greatly affected. Oxidation ditch technology is also a kind of activated sludge process, and it is widely used in papermaking wastewater treatment in China[12-14]. Compared with activated sludge, the biofilm method can prevent sludge from expanding, but it is prone to biofilm clogging and has high cost and is not suitable for treating high SS wastewater. Compared with aerobic treatment, anaerobic treatment has less energy consumption, less sludge production, less nutrient salt, simple and flexible equipment, convenient sludge storage, and biogas production for plant power generation[15].

Zhang Zunju et al[16] used a slanting net-coagulation-anaerobic/aerobic-ozone-aeration biological filter deep treatment combined process to treat high-concentration pulping and papermaking wastewater, and the effluent reached the new national wastewater discharge standard (GB3544-2008) The effluent water quality is stable, and the high-efficiency anaerobic treatment and ozone-aeration biological filter advanced treatment system are the key to the stable treatment of high-concentration papermaking wastewater. Therefore, coagulation, sedimentation, anaerobic biological method and aerobic biological method can be used, and the advantages are low cost and good effect. If you are pursuing better water quality, you can add advanced treatment technology after this combined technology to re-coagulate and precipitate the effluent using the combined technology.

4.2.2 Combination of physical and chemical methods, chemical treatment methods and biological treatment methods. First, the pretreatment is carried out by coagulation sedimentation. Of course, the coagulation flotation method can also be used, but the latter is relatively expensive. Then, the chemical treatment method is used, and the usual methods include advanced chemical oxidation method, wet air oxidation method, supercritical water oxidation method, and the like. Fenton
oxidation (Fenton) has many advantages as an advanced oxidation technology, such as Fenton's wide range of reagents, low cost, easy operation, and high safety[17]. Supercritical water oxidation technology is a highly promising advanced oxidation technology without secondary pollution. Its reaction is fast and efficient, and it has a strong advantage in the treatment of wastewater and waste containing toxic and difficult to degrade organic matter. The treated wastewater and the heat generated by the treatment process can be recycled and reused in the pulping and papermaking process, which can save resources and achieve comprehensive utilization of energy, and is beneficial to energy saving and emission reduction in the pulp and paper production process. The supercritical water oxidation technology has developed rapidly, the SCWO process conditions have been continuously optimized, and new reactor materials have been continuously developed, enabling new reactors to emerge. However, equipment corrosion problems and salt deposition problems have not been substantially solved, and the supercritical water oxidation technology is effectively used to deal with the treatment of papermaking wastewater[7]. Wet Air Oxidation (WAO) is a wastewater treatment method that uses air or oxygen as an oxidant to oxidize organic matter into water vapor and carbon dioxide in the liquid phase to remove organic matter at high temperatures and pressures, but due to investment and operating costs. Problems such as too high, harsh reaction conditions, and some limitations in large-scale promotion[18].

The constructed wetland treatment system has the characteristics of high treatment efficiency and low operating cost, and has certain advantages as deep treatment after secondary treatment of wastewater. The existing operating experience of the constructed wetland system of papermaking enterprises shows that the well-operated constructed wetland system, through physicochemical flocculation and secondary biochemical treatment, controls the water quality of the wastewater entering the system below CODCr 500mg/L, and can reach new through different residence time. National standard regulations for wastewater discharge requirements[5]. Therefore, the coagulation, sedimentation/air flotation, chemical oxidation method and the combined wetland method/biofilter combination technology are feasible, can meet the emission requirements, and have good effects.

5. summary
In recent years, sewage discharge standards have been continuously improved, and many domestic papermaking enterprises have adopted safe and reliable methods to treat papermaking wastewater. However, the composition of the paper industry wastewater is relatively complicated, and the treatment is relatively difficult. It is difficult to meet the discharge standard using only a single method. This requires the combination of physical methods, chemical methods and biological methods in the actual paper industry wastewater treatment process, taking full account of the advantages and disadvantages of various treatment methods. The combined technology can adopt the process of screen recovery + first-level physical treatment + secondary biochemical treatment + three-level deep treatment. The primary physical and chemical treatment methods are mainly divided into two types; one is coagulation and precipitation, and the other is plasma flotation. The secondary biochemical treatment methods mainly include the following: (1) activated sludge method; (2) advanced oxidation method; (3) biofilm method. The three-stage advanced treatment methods mainly include: (1) coagulation + precipitation + filtration; (2) artificial wetland method; (3) biological filter method. We should choose the best combination treatment solution to achieve the unity of practicality and economy, and to achieve sustainable development.

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