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Application of Nanotechnology in Wastewater Treatment

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ABSTRACT

Because the current social water pollution is serious, and the conventional method cannot effectively manage all types of water pollution, and its single effect cannot be satisfactory, we must seek new and effective treatment. The paper is a comprehensive review of the best practices of the conventional wastewater treatment method with reference to the experiments and research results of nanotechnology in sewage treatment. Comparison of nanotechnology can be compared with conventional methods to make the particles have a special function, and some special performance just in the sewage treatment medium to a good effect: the depth of the catalytic method can be effective in the decomposition of many types of organic pollutants such as halogenated hydrocarbons Class, chlorinated phenols, cyanide, various organic acids and can handle metal particles; adsorption method for the water heavy metal pollution treatment costs less, simple and widely used, nanofiltration membrane can replace the adsorption and electrochemical methods, Pulping and precipitation are one of the most effective methods for the treatment of colloidal wastewater. It can effectively reduce the turbidity and chroma of waste water, remove a variety of macromolecular organic matter and some heavy metal ions (Mercury and lead); organic / inorganic composite nanoparticles with its excellent inorganic materials, light, electricity, magnetic and other properties, organic materials, excellent processing performance, biocompatibility, for many difficult to deal with water pollution control, which has a corresponding method, can be simple and effective to solve the problem. The application of nanotechnology in water treatment has shown a broad prospect, but needs further research and improvement.

KEYWORDS: Sewage treatment; nanotechnology; photocatalysis; nano flocculation; nanofiltration

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1. Introduction

With the ever-changing life, more and more sewage discharge has become the most interesting topic. The growing shortage of water resources and water pollution have plagued China's economic and social development, and it has become an important factor restricting the sustainable development of social economy. Is there a simple and effective way to deal with sewage is the most talked about today One of the topics. Now there are many or more problems such as coagulation sedimentation method, oxidation method, electroplating method, flocculation method and so on. Therefore, it is hoped that there will be a simpler and more economical water treatment method.

Application of nanotechnology to deal with sewage can achieve some unexpected results. Nanotechnology is a hot topic in today's society, and the special properties of nanomaterials can solve many problems that cannot be solved by conventional methods. In the aspect of sewage treatment, nanotechnology has shown a high degree of superiority over conventional methods. Nanotechnology has a good effect on organic waste, especially organic matter such as chlorides, which cannot be used in conventional methods. Nano-technology without secondary pollution characteristics is the people's favorite. It can be seen that nanotechnology is a very promising technology.

2. Current Situation of Water Pollution in China

2.1. Water pollution situation

Due to the socio-economic development, the increasing demand for clean water, the rational use of existing water sources, the protection of existing water sources from pollution, the management of life and industrial waste water and the recycling of sewage are not only imperative for our country, World issues. China's per capita water resources is only the world's per capita possession of 1/4 (about 2700m3), spatial and temporal distribution is very uneven Moreover, China is in the industrialization and urbanization of the rapid development period, the development and utilization of natural resources , Pollutant emissions increased, water pollution situation is very grim. The water quality of the river flowing through the city is more than three types of standards and is not suitable for domestic water up to 78%, while more than 50% of urban groundwater is polluted to varying degrees.

Years of groundwater monitoring [1] evaluation results show that the current groundwater resources are more polluted, the national 2/3 urban groundwater quality generally decreased, the local lot of water quality deterioration, more than 300 cities due to groundwater pollution caused by water supply tension. 97% of the city's groundwater is polluted to varying degrees in the 195 cities of the country, and 40% of the urban water pollution is increasing: 16 of the 17 provincial capitals in the north are increasing, with three of the 14 provincial capitals in the south increased pollution trends. The main components of groundwater pollution are nitrogen (NO3-, NO2-, NH4 +), phenol, cyanide, heavy metal and total hardness and organic pollution index COD, the relevant departments in some areas of groundwater detected 133 kinds of organic pollutants.

2.2. Hazards of various types of water pollution

Water soluble organic pollutants on human health hazards began in the 20th century, 60 years, foreign discovery of chlorine disinfection on the human body hazards, followed by epidemiological survey, long-term residents of different drinking water to track and animal experiments. It has been proved that artificial synthetic chemicals discharged into water bodies have caused great harm to human health. It is reported that 80% to 90% of human cancers are associated with environmental factors, and 80% of the carcinogenic chemicals found are organic pollutants.

Nitrate in groundwater is not harmful to the human body, but the content is too high will corrupt the water taste, and even cause diarrhea, so that intestinal dysfunction. The key to nitrate is that it can produce nitrite in the human body by nitrate reductase, and nitrite can pose a threat to human health. Nitrite into the human blood, the blood can be transmitted from the blood function of hemoglobin to form methemoglobin, thus affecting the blood oxygen transport capacity, so that tissue due to hypoxia and poisoning, severe cases can lead to respiratory and circulatory failure [2]. When the nitrate content of drinking water to 90 - 140mg / L, can lead to infant methemoglobinemia, commonly known as 'blue baby disease', when the blood heme content of 70%, which lead to suffocation [3] The

The United States HHComley as early as 1954 reported in the mountains in the drinking water in the high concentration of nitrate nitrogen caused by infantile methemoglobinemia cases, Sweden in the Cristian area of 35 cases of cancer patients, the cause of the analysis shows that more than half of them Of the cases are due to the high nitrate content of groundwater caused by [4] In addition, the water nitrate and nitrite in a variety of nitrogen-containing organic compounds (amine, amide, urea and cyanamide) will form a role with Chemical stability of the highly carcinogenic, teratogenic, mutagenic substances nitrosamines and nitroso amides, they will induce the production of intestinal, brain, nervous system, bone, skin, thyroid and other tumor diseases [5].

Heavy metals are an important contaminant that is potentially harmful. The threat of heavy metal pollution is that it cannot be decomposed by microorganisms. In contrast, organisms can enrich heavy metals and convert certain heavy metals into more toxic metal-organic compounds. The toxicity of most heavy metal ions increases with concentration and the time of action.

3. Conventional sewage treatment

Although today's efforts to promote cleaner production, green chemicals, but to fully achieve clean production will be a long process and therefore the end of the treatment is still very necessary, that is, industrial wastewater and urban sewage must be treated to discharge. The current methods of sewage treatment are: sedimentation, flocculation [6], filtration [7], adsorption [8] and biological treatment [9], but these methods inevitably bring a pollution, but also the cost of regeneration or processing Cycle and other shortcomings. Although domestic sewage can be effectively treated with traditional biological treatments, hundreds of highly toxic compounds cannot be treated with biological methods [10], and new and appropriate treatments must be sought.

Conventional water treatment processes mainly remove suspended solids, colloidal impurities and bacteria from water sources. For the dissolved organic pollutants in water, the conventional process is not ideal. Domestic and foreign experimental studies and actual production results show that [11], contaminated water by conventional treatment can only remove 20% -30% of organic matter, and because of the presence of dissolved organic matter is not conducive to damage the stability of colloids and conventional process The removal efficiency of raw water turbidity also decreased significantly (only 50% -60%). Moreover, due to the conventional process on the water chloride can not only be removed, but because of the role of flocculant in the process of chlorination in the effluent after the increase in halogen, and give priority to control the number of pollutants and toxic pollutants have increased significantly Hazardous substances increased by 50% -60% before treatment [12]. As a result, conventional processes are no longer compatible with existing water and water quality standards and new water treatment technologies must be developed.

4. Application of nanometer technology in sewage treatment

4.1. Overview of nanotechnology

Nanotechnology (Nano-ST) is the 20th century, the late 80s has just emerged and is emerging new technology, it is studied by the size of 0.1-100nm material composition between the movement of the system and the interaction and possible practical application Technical issues of science and technology. Mainly include: (1) nano-system physics; (2) nano-chemistry; (3) nano-materials science; (4) nano-biology; (5) nanoelectronics; (6) nano-processing; (7) nano-mechanics [13].

Nano-materials is an important foundation for the development of nanotechnology, nanotechnology is the most important research object. Since 1861, with the establishment of colloidal chemistry, people began to study the so-called colloidal system of diameter 1 nm - 100 nm, but the real intention of the nanoparticles as a research object began in the 20th century, 60 years. In the broadest sense, nanomaterials are those in which at least one dimension is in the nanoscale range or as a basic unit in the three-dimensional space, that is, the nanomaterial is a system in which the material is assembled in a nanometer structure in a certain way, or the nanostructures are arranged in a certain The dispersion system formed in the matrix, including nano-ultrafine particles, nanometer bulk materials and nanocomposites. The basic unit of nanomaterials can be divided into three categories in dimension: (1) zero dimension, which means that the three dimensions of space are in nanometer scale, such as nano-scale particles and atomic clusters; (2) one-dimensional, in nanometer scale, such as nanosilts, nanorods and nano-bamboo; (3) two-dimensional. Refers to the three-dimensional space in a dimension at the nano-scale, such as ultra-thin film, multilayer, super-character and so on. The types of materials that make up the nanomaterials can be divided into metal nanomaterials, semiconductor nanomaterials, nanometer ceramic materials, organic-inorganic nanocomposites and nanometer mesoporous solid and mesoporous composites.

Throughout the history of the development of nano-materials, can be divided into two stages, the first stage is limited to synthetic nanoparticle powder or synthetic block and other single materials and single-phase materials; the first stage is focused on various types of nanocomposites And the nanostructures of nano-array, mesoporous assembly system and thin film mosaic system were introduced into the second stage. The research of nanomaterials also extends from the initial nanoparticles and the films and blocks formed by them to nanosized, nanorods, nanobulks, microporous and mesoporous materials [14].

4.2. Application of nanotechnology in sewage treatment

Today, the application of nanotechnology in wastewater treatment mainly has the following applications: deep oxidation technology, flocculation method, nanofiltration membrane method, and organic / inorganic composite nanoparticles.

4.2.1 Deep oxidation technology

Advanced oxidation technology based on ultraviolet radiation and photocatalytic oxidation mechanism is also called deep oxidation technology. The most common is the photocatalytic oxidation technology. It is a waste water treatment technology which has been studied in recent years. It uses efficient photocatalyst to produce activity in the reaction. Strong free radicals, with the role of organic compounds, so that oxidative degradation of pollutants, and ultimately produce non-toxic harmless H2O, CO2. It has been proved that photocatalytic oxidation can effectively treat halogenated hydrocarbons, chlorinated phenols, cyanide, various organic acids and metal particles, the key lies in the photooxidation catalyst. At present, TiO2 is considered to be the most effective photooxidation catalyst [15]. Based on the huge specific surface area, surface free energy and strong absorption of ultraviolet rays, the adsorption of organic matter in waste water, under the ultraviolet light, in the reaction to produce a strong oxidation capacity of the radical (- OH), photocatalytic oxidation Rapid degradation of organic matter, efficient treatment of wastewater, and to avoid secondary pollution [16]. In 1976, it was found that TiO2 photocatalytic oxidation could completely dechlorination of polychlorinated biphenyls: nano-TiO2 photocatalytic oxidation bleaching wastewater could degrade chlorinated aromatic compounds such as chlorophenols [17], which could make the pulping wastewater The use of chlorine dioxide bleach bleach pulp can form a highly toxic chlorinated diphenyl and dioxin, with TiO2, O2, UV treatment of such waste water, such a highly toxic carcinogenic organic matter has a rapid degradation [18].

TiO2 redox is strong, in the larger pH range stable and inexpensive, non-toxic. But its absorption spectrum only a small part of the solar spectrum, at the same time, its light quantum efficiency has yet to be improved, the researchers from a variety of ways to nano-TiO2, modified research. The modified nano-Ti02 can significantly improve its photocatalytic activity and extend the range of light absorption wavelength while maintaining the advantages of pure nano-TiO2. At present, for the modification of TiO2, there are main surface photo-sensitization, surface precious metal precipitation, ion doping, composite semiconductor and surface reduction treatment, where the ion doping has a simple method, good modification effect and the rate of catalytic reaction, and thus much attention [19].

Hundreds of organic contaminants have so far been found to be treated by photocatalysis. Nano-TiO2 photocatalytic oxidation degradation rate is fast, no selectivity degradation, oxidation reaction conditions are mild, no secondary pollution, almost all of the waste water can be used. High efficiency photocatalyst, nano-particle loading and metal doping, photoelectric combination of catalytic methods and solar technology research and development, so that nano-TiO2 photocatalytic oxidation technology used in the field of water treatment has a good prospect. But at present the technology is mostly in the experimental stage, the development of its industrial water treatment process, people are waiting to see.

4.2.2 Nanofiltration technology

Membrane separation technology has been rapidly developing in the last 40 years since the 1960s for seawater desalination. So far, various membrane technologies such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED) and pervaporation (PV), have been widely used in chemical, paper, oil, food, medicine, nuclear and other industrial wastewater treatment.

For water heavy metal pollution, there are many ways to remove, which adsorption method to less cost, simple and widely used. While carbon nanotubes and coal-based micro-carbon fibers have distinct characteristics and potentials that are distinct from traditional adsorbents. It is possible to use as a highly effective adsorbent in water pollution and environmental protection, such as adsorption of heavy metal ions, trace metal ion analysis and so on. Carbon nanotubes and coal-based micro-carbon fiber structure and surface properties can be modified by chemical oxidation. The study reveals that the relationship between the structure and surface properties of nano / microcorite materials and their adsorption properties has important academic and potential application value.

Nanofiltration is a membrane process between reverse osmosis and ultrafiltration, which is named according to the size of the residual molecules separated by the membrane and the size of the membrane pore size of about 1 to several nanometers [20]. It is the same as the reverse osmosis and super-process, is a pressure-driven membrane process. Nanofiltration is suitable for the separation of molecular weight of more than 200g / mol, the molecular size of about 1nm dissolved components. Nanofiltration membrane is a polyamide series composite membrane, the network structure is looser than the reverse osmosis membrane, so with ion selectivity, part of the inorganic salt can be dialyzed through the nanofiltration membrane, making the nanofiltration osmotic pressure than reverse osmosis low. In order to ensure a certain amount of membrane flux under the premise of nanofiltration required operating pressure is much lower than the reverse osmosis, can save power and reduce the cost of water treatment.

The nanofiltration membrane is mainly composed of sulfonated poly (SPS), sulfonated polyether alum (SPES), cellulose acetate (CA), polyamide (PA), polyvinyl alcohol (PVA) or compound Filter. The nanofiltration membrane containing the charged group is called a charged nanofiltration membrane, which can be divided into a negative charge film, a positive electrode film and a bipolar film according to the charge of the charged group, wherein the positive electrode film is easily present in the water Is not widely used, and the negatively charged film is often made of a polymer material containing a sulfonic acid group (-S03H) or a shuttle acid group (-COOH) or a negative group on a polymer film, Selective separation of polyvalent anions, the positive ion separation effect is not good; bipolar membrane is a new type of nanofiltration membrane, can be positive and negative ions were positive and negative layers were interception [21].

Composite nanofiltration membrane is a hotspot in membrane separation technology. Guiver et al. [2] Preparation of sulfonated polyphenylene ether composite nanofiltration membrane [23]; Galtseva et al. Preparation of cellulose acetate sulphate nanofiltration membrane [24] Kim and other polyacrylamide as the membrane material, the composite membrane of the cortex through the cross-linking agent and polyvinyl alcohol to form vinegar cross-linking, preparation of nanofiltration membrane [25]. Compared with the polymer materials, inorganic materials with high temperature and chemical solvents and other characteristics, inorganic nanofiltration membrane research has also been people's attention. Guizard et al. Deposited polyphosphates and polysiloxanes on the inorganic microfiltration membrane to prepare inorganic nanofiltration membranes [26]. Lin et al. [5] made inorganic nanofiltration membranes with surface pore size of 0.61.5 nm by vapor deposition [27], have greatly improved the film retention performance.

The nanofiltration membrane can replace the adsorption and electrochemical methods to deal with a large amount of contaminants in the pulp and paper industry wastewater, remove the dark matter and the chloride produced from the pulp bleaching process. It has been reported that UF / NF membrane treatment of kraft paper production wastewater has a very good effect [28] with nanofiltration membrane has been a good deal with the organic compounds containing sulfate-containing wastewater, the use of membrane flux than the ultrafiltration Film 3 times higher, but also remove more than 90% COD. Compared with the OF membrane ratio, the organic matter in the waste water is less harmful to the nanofiltration membrane. Nanofiltration membranes are also used in fiber processing to bleach wastewater treatment to control contaminants. The emergence of nanofiltration membrane technology to improve the membrane separation process, the application of wastewater treatment in the rapid growth. It is foreseeable that with the further research and development of nanofiltration membrane technology and technology, it will greatly promote the management and recycling of pulp and paper industry wastewater.

4.2.3 Nano flocculation technology

Flocculation and sedimentation is one of the effective methods of wastewater treatment, which can effectively reduce the turbidity and chroma of waste water, remove a variety of high molecular organic matter and some heavy metal ions (mercury and lead), improve the sludge dewatering performance [29], Its technical key is to study and select efficient flocculants.

Flocculation is one of the main means to remove colloidal substances and strengthen solid-liquid separation. Because of its simple operation, good adaptability and low cost, China's major water plants use flocculation as the main purification technology of drinking water without exception. Factors affecting the flocculation flocculant species, flocculant dosage, pH, stirring strength, raw water quality, flocculant and coagulant dosage sequence. The so-called enhanced flocculation is to improve the conventional flocculation effect taken by a series of strengthening measures, that is, to determine the best conditions for flocculation, play the best flocculation effect, usually including three aspects: flocculant (including coagulant) performance Improve the flocculation process to strengthen, such as optimizing the flocculation and agitation strength, shorten the reaction time of the process to determine the best reaction pH and so on.

The addition of nano-technology for the flocculation and sedimentation technology into a new vitality of nano-flocculant instead of the traditional flocculant, the use of nano-particles of strong adsorption capacity, through the adsorption bridge, roll sweep and other flocculation, can remove some of the traditional Flocculation method is difficult to remove the pollutants, and the precipitate is easy to dehydrate: a company to nano-materials for sewage purification agent / flocculant and disinfectant, the formation of these nano-composite multi-efficient ultra-efficient water treatment agent, not only pollution control effect Good, but also shorten the process, reducing the cost of pharmaceuticals. Through the experiment of dispersing nano-Si02 in water, nano-Si02 as a coagulant to strengthen flocculation to remove water in several typical dissolved organic HA, SDS and p-chlorophenol experiments and its turbidity removal experiment, can be obtained the following conclusions [30]:

(1) The nano-Si02 dispersion dispersed with inorganic dispersant has a particle size d of less than 30 nm in the dispersion after the dispersion of nano-Si02 dispersion at a pH of 7 for at least 10 minutes. The dispersant used is an inorganic salt dispersant, Processing to bring secondary pollution.

(2) Nano-Si02 on high molecular substances such as HA, SDS and kaolin particles have good adsorption, and small molecules such as p-chlorophenol adsorption is very weak.

(3) The coagulation effect of high molecular weight HA and nano Si02 is obvious, especially at pH 7, when the dosage is low (1 - 10mg / L), there is obvious coagulation effect. At this time, Bridge-based. But with the increase of nano-Si02 dosage, the removal of HA has a hindrance.

(4) The best removal of HA occurs between pH 5 and 6, and flocculation is mainly neutralized by the addition of Si02 coagulation and only aluminum sulfate as flocculant. With the increase of Si02 dosage, the pH range is wide, and the better removal rate is: pH = 5-9 The dosage of aluminum sulfate is 20-40mg / L. Si02 dosage is 1- 10mg / L. The optimum point appears at pH 7, the dosage of Si02 is 1mg / L, the dosage of aluminum sulfate is 20 mg / L, and the ηmax is 73.6%. At this time, the flocculation is dominated by adsorption bridge.

(5) The temperature is too high (greater than or equal to 35 'C) or the end (less than or equal to 7 ℃) is not conducive to the removal of Si02 on HA, but the removal of turbidity is still better effect.

4.2.4 Organic, inorganic composite nanoparticles

Organic / inorganic composite nanoparticles have attracted much attention because of their excellent properties such as light, electricity and magnetic properties, excellent processing properties and biocompatibility of organic materials. In recent years, organic / inorganic composite nanoparticles with special functional properties have become a hotspot in nanoscience and technology [31]. For many kinds of difficult to deal with water pollution control, it has a corresponding method, can be simple and effective to solve the problem.

Nano-iron particles with high activity, just control the anaerobic, at room temperature, oscillation conditions, without the need to control the pH value and nitrate in 30min within the rapid and complete response, the effect is much better than ordinary zero iron. The nano-iron prepared in the laboratory has a good effect on the actual groundwater denitrification: the removal rate of nitrate nitrogen in nanometer iron can reach 99% in 16min [32].

The use of nanometer zero-valent iron [33] for environmental pollution is a new pollution control technology. Nano-scale iron powder with traditional materials do not have some of the new features. The nano-particles have a small diameter and the percentage of surface atoms in the total atoms increases abruptly. At the same time, the surface area and surface energy of the nanoparticles increase rapidly. Such as particles having an average particle size of 10 to 100 nm, and a specific surface area of up to 10 to 70 m2 / g. 10nm zero-valent iron specific surface area of 33.5 m2 / g. In contrast, the specific surface area of iron powder is only 0.9 m2 / g, the difference between the two as much as 37 times [34] as much. This makes the nanomaterials have excellent surface adsorption and high chemical reactivity. Nano-scale zero-valent iron can handle a variety of pollutants [35], for halogenated alkanes, halogenated aromatic hydrocarbons, PCBs, pentachlorophenol, organochlorine pesticides, pesticides, dyes, heavy metal ions, nitric acid Salt, chromate, arsenate and perchlorate and other pollutants have a reduction and transformation. Nano-iron in the process of dealing with pollutants in the environment, the biggest advantage is that the particle surface area, high reactivity, the rate of degradation of pollutants is very fast. Especially in the case of low pollutant concentration, the removal rate of pollutants from nanometer iron is much higher than that of ordinary iron powder.

In recent years, nanoscale hydrated iron oxide (HFO) has been widely concerned because of its excellent adsorption of arsenic, scientists around the mechanism of its adsorption of arsenic and industrial applications for a wide range of research prospects. At present, the resin-based hydrated iron oxide based on Donnan membrane effect developed by the State Key Laboratory of Pollution Control and Resource Research in Nankai University, China is the most advanced research [36]. Nano-metal aluminum powder [Al0 (OH)] to the activated carbon fiber mat as a carrier, the preparation of a new composite water purification material, the test of its many kinds of heavy metal ions with adsorption. Indicating that the kind of particles in the treatment of heavy metal ions pollution has research value.

5. Conclusions

Nanotechnology in the application of wastewater treatment research, but also need to carry out a lot of work, summed up mainly in the following areas:

（1） The current research on the mechanism of nano-photocatalyst oxidation is still very shallow, most of the literature is concerned about the phenomenon and results of this reaction, not from the depth of the reaction mechanism to reveal its essence. It is necessary to further study the photocatalytic oxidation degradation of organic pollutants and their intermediates in wastewater, and fully study the mechanism of photocatalytic reaction, and promote the industrial application of this technology for the theory and experimental data.

(2) The development of cheap and high performance NF membrane is the key to nanofiltration technology in wastewater treatment and other applications. There are a lot of technical problems to be solved in the preparation, characterization and separation mechanism of membrane. For the papermaking wastewater treatment of this complex system, we must use a variety of technical methods in order to receive better results.

(3) For a variety of organic / inorganic composite nanoparticles of the excellent nature of the study, there are still a lot of one-sided use, need to be in the future for a long time to further increase investment and research to make it more practical.

(4) Nanotechnology also has a potential negative effect, so far the negative effect of its application has been almost no special research. As with the nanotechnology itself, the biological effects of nanoscale substances on the human body will also be a long-term subject.

The application of nanotechnology in water treatment has shown a broad prospect. It is foreseeable that nanotechnology will play an important role in solving global water shortages and water pollution problems with the deepening of research and the improvement of practical level.

References

1. Zhang Kunmin. Study on removal of nitrate from groundwater by nanometer iron-based metal composites [J]. China Science and Technology, 1998 (3): 41-45.
2. Super M, Heese H, MsvKenxit D, et al. An epidemiologic study of well-water nitrates in a group of South West African Namibian infants [J]. Water Research, 1981 (15): 153-161
3. Kostraba J. N., Gay E. C., Reviewrs M., et al. Nitrate levels in community drinking waters and risk of IDDM [J]. Diabetes Care. 1992 (15): 57-62
4. Grahan L, Roger P, Patricia M, et al. Non-Hodgkin's Lymphoma and nitrate in drinking water: a study in Yorkshire, United Kingdom [J]. Epidemiology Community Health. 1999 (53): 31-37
5. Dorsch M. M., Scargg R., Mcmichael A. E. A. Congential malformation and maternal drinking water supply in rural South Australia [J]. A case-control study. Am. J. Epidemiol 1984 (4): 119-124
6. Ma Xiaoou, Liu Yanfei. Sewage treatment scheme [J]. Industrial Water Treatment 1999, 19 (4): 8-10.
7. Yu Yongli, Su Yongbo. Modernized sewage treatment [J]. Industrial Water Treatment [J] .2000, 20 (1): 39-40.
8. Flotation Wu Yingjuan, Xie Wenbiao. Adsorption method for industrial wastewater treatment [J]. Industrial water treatment [J] .1998, l8 (6): 19-21.

9. Chen Yuancai, Xiao Jin. The status of biodegradation [J]. Environmental Science, 2000, 21 (2): 94-97.
10. Cheng Cangcang, Xiao Zhonghai et al. Photocatalytic Degradation of Dyeing Wastewater by TiO-2 Thin Films Supported on Stainless Steel [J]. Environmental Pollution and Control, 2001 (5): 241-242.
11. Zhang Bin. Application of nano-SiO2 enhanced flocculation treatment of water-soluble organic pollutants, [D]. School of Civil Engineering, Hunan University, 2003, 6.
12. Fang Yun, Yang Chengyu, Chen Mingqing, Jiang Huiliang. Nanotechnology and nano-materials (I) [J]. Daily Chemical Industry, 2003, 33 (2).
13. LUO Ming-liang, PU Chun-sheng, LU Feng-ji, GUO Zhong. Application and prospect of nanotechnology and materials in environmental protection [J]. New Materials for Chemical Engineering, 2001 (7) 27-30.
14. Liu Renlong, Zhang Yunhuai, Zhang Binghuai. TiO2 photocatalytic oxidation of the influencing factors [N]. Journal of Chongqing University,
15. LIU Ren-long, ZHANG Bing-huai, ZHANG Yun-huai. Effects of calcination temperature on photocatalytic oxidation of TiO2 thin films [J]. Journal of Chongqing University,
16. Li Hui, et al. Nano-TiO, photocatalytic oxidation technology in papermaking wastewater treatment applications [J]. China Paper, 2003 (8): 45-49.
17. Tinucc L, Borgarello E, et al. Treatment of industrial wastewaters by photocatatytic oxidation on TiO2 [J]. Photo-catalytic purification and treatment of water and Elsevier Science Publishers Amsterdam, 1993 (6): 79-85
18. BAO Zhi-cheng, ZHANG Zhi-jun, et al. Photolysis of chlorinated dibenzo-p-dioxins catalyzed by TiO2 catalyzed [J]. Environmental Chemistry, 1996 (1): 45-61.
19. DING Ming-jie, QIN Ming-li, CHEN Si-shun. Study on the Treatment of Papermaking Wastewater by Nanotechnology [N]. Journal of China Pulp and Paper Society, 2007, No. 03.
20. Membr. Sei. Application of charged membrane in water softening [J]. Soltaniehm, Mousavim, 1999 (1): 53-56
21. Chung, YC., Son, D.H., Ahn, D.H., Nitrogen and organics removal from industrial wastewater using natural [J]. Zeolitemedia. Water. Sci. Tech. 2000 (5): 127-134.
22. Guiver M D, Tam C M. Preparation and membrane application of functional group polysulfones [C]. In: 1NPUC Int. Symp. MACROMOL,, 1992: 473
23. Hamxa A, Chowdhury G, Matuura T, et al. Characterization of a novel charged thin-film composite nonafiltration [C]. Abstracts Posters. In: ICOM '93, Heideberg, 1993
24. Galtseva O V, Grishin E P, Nosoval 11, et al. Cellous acetate sulfate for preparing NF membrane [P]. RU 2047622, 1995-11-10
25. Kim H T, Park J K, Lee K H. Preparation, characterization, and performance of poly (acrylamidocaproic acid) partially neutralized with calcium for use in nanofiltration [J]. J. Appl. Polymers SEI, 1996, 60: 1811
26. Guizard C, Larbot A, Cot L. A new generation of membranes based on organic-inorganic polymers [C]. Proc. Conf. Inog. Membranes. Montpellier, 1990: 55
27. Lin C, Flowers D F, Lin K T. Characterization and performance evaluation of modified commercial ceramic membrane [C]. 5th Ann Meeting North Membrane Soc., Lexington, 1992: 17
28. Voigt I, et al. Integrated cleaning of color wastewater by ceramic NF membranes [J]. Separation and Purification Technology, 2001, 25 (1/3): 5, 09
29. Membrane Science and Technology, 1999 (1): 19-20. [J]. Membrane Science and Technology, 1999 (1): 19-20.
30. Zhang Bin. Nano-Si02 enhanced flocculation treatment of water-soluble organic pollutants in the application of [D]. Hunan University School of Civil Engineering .2003, 6.
31. Jiang Lizhong. Design, Synthesis and Application of Organic-inorganic Composite Nanoparticles [M]. Beijing University of Chemical Technology .2007 (1) 1, 26.
32. Zhang W X, Wang C B. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs [J]. Environ Sci Technol, 1997, 31 (7): 2154-2157
33. A. F Wan Nei-xiu, A.. Myers, Zhang Lin, Han Hongli, translation. Urban sewage treatment methods [M]. Water supply and drainage, 2001, 2 (21).
34. Zhang W X, Wang C B, Lien H. Treatment of chlorinated organic contaminants with nanoscale bimetallic particles [J]. Catalysis Today, 1998, (40): 387-395
35. Zhang Q, Supported nano-iron copper binary metal synthesis and modification and repair of groundwater organic chlorine pollutants in the basic research [D]. Nankai University Environmental Science .2006, 10.
36. Pan Bingcai, Zhang Qingjian, Chen Xinqing, Zhang Weiming, Pan Bingjun, Zhang Quanxing. Study on the preparation of resin-based hydrated iron oxide based on Donnan membrane effect and its adsorption on arsenic [J]. Chinese Journal of Science,
37. Liu Guanghui. Nano-metal aluminum powder hydrolysis method of preparation of water purification materials and micro-polluted wastewater treatment in the application [D]. Jilin University .2008, 5.