Study on environmental nanomaterials in food industry wastewater

Bei Liu1,*, Qian Wang2, Yongli Zhang3 and Xin Chen4

1Foshan Environmental Protection Investment Co. LTD, Foshan 528000, China
2Foshan Shuiye Group Co. LTD, Foshan 528000, China
3School of Chemical and Environmental Engineering, Hanshan Normal University, Chaozhou 521041, China
4School of Environment and Chemical Engineering, Foshan University, Foshan 528000, China

*Corresponding author e-mail: 670511263@qq.com

Abstract. In recent years, with the rapid development of the food industry, the accompanying food wastewater pollution has become increasingly serious, which has become one of the most important sources of industrial wastewater and even water pollution in China. However, the traditional food wastewater treatment technology has gradually been unable to meet the needs of social development, and the development of cheap, convenient, and efficient food wastewater treatment technology has become a current research hotspot. Nanomaterials are capable of absorbing or degrading pollutants more than conventional materials. The innovation of water supply treatment technology has brought good opportunities. Due to its adjustable chemical form, it can realize the regulation of various excellent properties such as hydrophobicity, low dimension, photothermal conversion capacity, catalytic activity, and adsorption capacity, etc., which is very suitable for the removal of major pollutants in food industrial wastewater. The excellent adsorption properties and optical properties of different materials have realized the efficient removal of major pollutants from food industrial wastewater.

1. Introduction

Low water use efficiency and a large discharge of sewage are the main reasons for the shortage of water resources in China. To ensure the healthy and sustainable development of China's economy and society, it is undoubtedly an urgent task for us to tap the potential of the treatment and reuse of food industrial wastewater and exploit food industrial wastewater as water resources [1]. However, traditional water treatment technology has been unable to meet the needs of the development of human society. To better solve the problem of water pollution, the development of cheap, convenient, and efficient water treatment technology has become a research hotspot. In recent years, the rapid development of nanotechnology has attracted extensive attention from environmental researchers, and a variety of water treatment methods based on nanotechnology have been published. Nanomaterials are capable of absorbing or degrading pollutants more than conventional materials. The innovation of water supply treatment technology has brought good opportunities. According to the needs of the development of the
post-industrial era and the actual situation of the development of China's food industry, the application of nanotechnology in the treatment of pollutants in food industrial wastewater has far-reaching significance for the development of advanced water treatment technology and the guarantee of social sustainable development.

2. Sources, characteristics, and characteristics of wastewater from the food industry

At present, persulfate has a good treatment effect on refractory organic wastewater, so it has become a research hotspot in the field of water treatment. There are many kinds of researches on the activation of persulfate, mainly by light energy, heat energy, transition metal, alkali and other methods to achieve the activation of persulfate. However, all of the above methods have their own disadvantages, such as high energy consumption and harsh technical conditions for energy-excited persulfate technology [2]. The toxicity of transition metals introduced in transition metal activation technology may cause secondary pollution. Alkali activation technology requires a strong alkali environment and requires high requirements for instruments and equipment. All these factors hinder the wide application of persulfate technology in organic wastewater treatment.

2.1. Sources of wastewater from the food industry

The wastewater of food industry mainly comes from three production sections [3], including: (1) The raw material cleaning section: a large amount of sand and soil debris, skin, leaves, meat, scales, hairs, feathers, as well as heavy metals, natural pigments and oils extracted from the equipment and raw materials in the raw materials will enter the wastewater; (2) Production section: the raw materials that are not completely processed or cannot be used will enter the wastewater so that the wastewater contains a large number of organic substances; (3) Forming section: To increase the color, aroma, and taste of food and extend the shelf life of food, various food additives are added, including pigment, etc., part of which will be lost and run into the wastewater, making the chemical composition of the wastewater extremely complex.

2.2. Characteristics of wastewater from the food industry

The pollutants in the wastewater of food industry mainly include solid objects floating in the wastewater, such as vegetable leaves, ground meat, peel, bird feathers, etc.; Oil, protein, colloidal substance and starch suspended in water; Microorganisms such as pathogenic bacteria dispersed in water; Pigment substances, metal ions and sugars dissolved in water; And the entrainment of sand and other organic materials in the raw materials [4].

If the food industrial wastewater is discharged into the water without treatment, a large number of high nutrient substances such as oils and fats will cause serious eutrophication in the water body, and rapidly consume dissolved oxygen in the water body, leading to severe hypoxia in the water body and causing the death of fish and aquatic organisms. The suspended solids in the wastewater will sink to the bottom of the river and decompose under anaerobic conditions, worsening the water quality and producing a foul odor, and seriously polluting the environment. Besides, the wastewater contained in animal waste may contain pathogenic bacteria and insect eggs will lead to the spread of disease, harm to the health of humans and animals. Various kinds of soft drinks and food processing process of bright color, often use a lot of colorful pigment, and even some illegal additives, can produce large amounts of wastewater contaminated with pigment, the dye will greatly reduce the light transmittance of water, photosynthesis, which affect aquatic organisms and the composition such as metal, aromatic can cause toxic to aquatic organisms. Some raw materials polluted by heavy metals will lose heavy metals and discharge them into sewage in the process of processing. In the process of food processing, the equipment and pipes used are made of metal. Long-term friction and contact between food and metal elements will lead to the mixing of trace metal elements into food and the loss of metal elements into wastewater. Besides, the packaging materials, food storage materials, and containers in the food industry mostly contain trace amounts of heavy metals, which will be discharged along with sewage in the
production and processing process, causing pollution. If untreated wastewater is directly used in farmland irrigation, it will affect the quality of agricultural products and cause groundwater pollution. Low water use efficiency and a large discharge of sewage are the main reasons for the shortage of water resources in China. Therefore, it is an urgent task to exploit food industrial wastewater as water resources to ensure the sustainable and healthy development of China's economy and society and tap the potential of its treatment and reuse.

2.3. Characteristics of wastewater from the food industry
The characteristics of wastewater from the food industry are mainly reflected in six aspects [5], including the followings. These are shown in Table 1.

| No. | Aspects                                                      | Characteristics                                                                 |
|-----|--------------------------------------------------------------|-------------------------------------------------------------------------------|
| 1   | The size of wastewater discharge varies.                    | The scale of the food industry in China ranges from households to large factories, and there is a wide variety of products to be processed, with great differences in raw materials, processes, and processing capacity. Meanwhile, there are also great differences in wastewater discharge. |
| 2   | There are a variety of pollutants in wastewater.            | Food processing is seasonal, and the water quality and amount of wastewater change with the seasons. The type of wastewater changes according to the change of raw materials; |
| 3   | The content of organic matter in the wastewater of the food industry | It is relatively high, and there are many biodegradable components. For the general food industry, most of its raw materials come from organic matter in nature, and the wastewater produced also takes organic matter as the main component, such as natural pigment. Also, it may include heavy metals and oils leached from raw materials; |
| 4   | Composition of wastewater.                                  | It contains a variety of microorganisms, including pathogenic microorganisms, which make the wastewater easy to rot and smell; |
| 5   | Concentration of wastewater.                                | The concentration of wastewater is generally large, and its scope is 200-20000 mg/L. |
| 6   | Concentration of nitrogen and phosphorus.                   | High content of nitrogen and phosphorus in wastewater, and its scope is 50-5000 mg/L. |

3. Application of new environmental protection materials in food industrial wastewater

3.1. Treatment of grease
Oils from the food industry wastewater can exist in two forms, including floating on the surface of the water as oil layers and suspended and dispersed in the water as oil droplets [6]. At present, the main method of grease removal in sewage treatment plants is to use grease traps. Grease traps can effectively remove floating grease, with a removal rate of over 90%. However, grease traps have poor ability to remove oil droplets suspended in wastewater, so it is of great significance to develop a new and convenient method for oil suspension. In the review of grease removal methods in industrial wastewater treatment, the adsorption method was first proposed as a new technology for oil pollution removal. The role of adsorption in the treatment of oily wastewater has changed greatly. Among them, organic clay has multiple functions in the process of oil removal, which can be used for pretreatment of the membrane separation process as well as a secondary treatment after gravity separator. In recent studies, active clays and other mineral adsorbents are successful in treating wastewater from olive oil plants. In addition to absorbing oil, they also absorb other organic compounds, such as polyphenols. At present, a variety of lipid adsorbents have been reported, including activated carbon, rubber powder, fungal biomass, walnut shell, and chitosan powder and flakes, etc. As some materials themselves do not have a high affinity for
oil, pretreatment is required to improve oil absorption, such as surface modification using cationic surfactants or silica nanoparticles. The application effect and prospect of adsorption technology in oil pollution control have been proved by the existing reports, and the development of new and efficient oil adsorbents will further promote the treatment of oil wastewater.

3.2. Treatment of microorganisms

Microorganisms are another common and harmful pollutant in the food industry wastewater, and most food processing industries produce wastewater containing microbial contamination [7]. In the aspect of microbial control, with the widespread use and even abuse of antibiotics in the world, antibiotic resistance of many pathogens is constantly emerging. The rise of antibiotic resistance in pathogenic bacteria is one of the major challenges threatening our healthy lives. Therefore, it is urgent to develop new antibacterial schemes and new materials.

At present, many nanometers based microbiological control technologies are based on physical/chemical adsorption to improve the selectivity and efficiency of bacterial separation by incorporating functional groups (such as amino) or magnetic components. On the other hand, microbicides based on nanomaterials are also widely used in microbial control. To improve microbial killing efficiency, different bactericidal modes can be combined to act on microorganisms together. It is of great significance to load iron oxide nanoparticles on nanomaterials to improve the magnetic separation performance of bacteria, and to improve the photothermal transformation antibacterial agents of nanomaterials to efficiently capture, separate, and kill bacteria in food industrial wastewater. By compounding, nanomaterials are endowed with the function of non-specific binding to microbial cells and used as bacterial capture agents and photothermal agents in the bacterial treatment of food industrial wastewater, which avoids the use of antibiotics and provides a new idea for the development of efficient microbial removal technology in wastewater.

3.3. Removal of pigment

The sources of organic dyes in food industrial wastewater mainly include food colorants, raw material pigments, and illegally added industrial dyes [8]. Food colorant is a kind of additive that can be used to enhance or improve the color and luster of food. It can enhance the taste of food and at the same time play a certain role in increasing appetite. It is widely used in the food industry. Colorants are divided into natural pigments and synthetic pigments. The most commonly used ones are synthetic pigments. There are 11 kinds of synthetic pigments allowed in the national standard, including quinolone yellow, sunset yellow, citron yellow, azo red, amaranth red, erythrina red, carmine red, indigo blue, bright blue, new red and seductive red. Other synthetic pigments are not allowed as food additives. The foods allowed to be added include soft drinks, candies, cold drinks, fruit juices, and prepared wines, but generally no more than 1/10000; Artificial pigments are not allowed to be added to fish and its processed products, meat, and its processed products, condiments such as fermented bean curd, vinegar and soy sauce, dairy products and fruit and its products, biscuits, pastries, and baby food. Industrial dyes are widely used in textiles, wood products, fur products, and ceramic products, etc.

In recent years, with the rapid development of China's food industry, China's food structure has also produced a huge change. Under the temptation of interests, some illegal elements will be toxic and harmful non-edible substances added to the food. To improve the sensory properties of food, and even illegally seek high profits, food colorants and illegal additives have been overused in the food industry to a certain extent, and have been eliminated along with industrial wastewater, and have become one of the main ingredients in the food industry wastewater. Therefore, removing it from industrial wastewater is a very important project. The photocatalytic degradation of organic dyes by nanomaterials was investigated through an advanced oxidation process. On this basis, this method is applied to the degradation and removal of pigment pollution in food industrial wastewater, to lay a theoretical foundation and provide a new idea for the development of new and efficient technology for the removal of organic pigment in food industrial wastewater.
3.4. Removal of heavy metals

The accumulation of heavy metals in water will cause serious harm to the aquatic ecosystem composed of the water body, aquatic plants, and aquatic animals, and may affect human health through the accumulation of food chain to the human body [9]. Food processing will also cause heavy metal pollution, including the phenomenon that some raw materials polluted by heavy metals will be drained of heavy metals and discharged into sewage in the processing process. In the process of food processing, the equipment and pipes used are made of metal. Long-term friction and contact between food and metal will lead to the mixing of trace metal elements into food and the loss of metal elements into wastewater. Besides, the packaging materials and food storage materials and containers in the food industry mostly contain trace amounts of heavy metals, which will be discharged along with sewage in the production and processing process, causing pollution. If untreated wastewater is directly used in farmland irrigation, it will affect the quality of agricultural products and cause groundwater pollution. It is difficult to remove heavy metals from a complex substrate of food wastewater. Among the existing heavy metal control technologies, adsorption has become the best choice for removing heavy metals due to its simple process and environmental friendliness. Traditional heavy metal adsorbents include activated carbon, clay, activated alumina, and zeolite, but due to their weak affinity for heavy metal ions, these adsorbents show limited heavy metal removal ability. To improve the removal capacity of heavy metals and reduce the cost, researchers have developed a variety of heavy metal adsorbents based on nanomaterials. Among them, superparamagnetic iron oxide nanoparticles have been widely used in various fields as substrates due to their low cost, convenience in regeneration and separation, and show a broad prospect.

However, the report is based on iron-based magnetic adsorbent preparation technology mostly complex, adsorption ability is limited, the most important thing is that the selectivity of heavy metals is poorer, adsorption of substrate selectivity, so in dealing with the food system, a complex matrix due to the effect of nonspecific adsorption of the adsorbent and lead to serious erosion and food ingredients greatly limit the practical application value of these sorbents. Selective adsorption may be one of the most economical methods for the removal or recovery of heavy metals, according to reports. Selective adsorbents can adsorb certain heavy metal ions with little or no adsorption to other substances. Therefore, the heavy metal ions in the extruded food matrix of the selective adsorbent show a certain potential. In the chemical industry, the need for selective separation of metal ions in selective systems has promoted the development of new adsorbents.

3.5. Removal of volatile organic compounds

Distillation is an ancient but very effective wastewater treatment method [10]. It can be used to remove any volatile substances, but it cannot be separated to remove volatile pollutants and requires a lot of energy. In the recent cutting-edge scientific and technological work, the use of solar energy to generate water vapor has a wide range of application prospects and has been widely reported to be used in desalination and purification of seawater. The core of this emerging technology mainly lies in solar absorbing materials. So far, a large number of metal particles, carbon materials, plasma, and other absorbents have been reported. The ideal absorber should have the following properties: (1). Efficient absorption of solar energy; (2). certain hydrophobicity is required to ensure that the absorbent floats on the water surface for interface heating; (3). It has a porous network structure for the transport of water vapor. Aerogels are characterized by low density, large surface area, high porosity, and low thermal conductivity, which meet some requirements of ideal light absorbers. After modification and design, the obtained porous hydrophobic aerogels have been successfully applied to the generation of solar hot steam. Considering the similar principle of distillation, solar thermal steam generation technology is expected to be applied to the purification of wastewater from the food industry. Nanomaterials not only have good oil removal ability but also theoretically meet the requirements of ideal solar absorbent. The solar-thermal conversion capacity of nanomaterials was studied, and the water purification capacity was evaluated. The model equipment for producing pure water from solar heat was built, which provided new technical means and ideas for the treatment of industrial wastewater.
4. Conclusion
Nanomaterials have excellent chemical and optical activities and have a good prospect in food industrial wastewater treatment.

(1) Preparation of nanometer bactericide with specific adsorption to microorganisms. To be suitable for the removal of both Kelan-positive and Gram-negative microorganisms, chitosan can be used as a microbial cross-linking agent to functionalize nanomaterials, and it has no specific adsorption-separation effect on microbial adsorption. In specific application systems, the use of expensive microbial antibodies to replace chitosan in the synthesis of antibacterial agents may be an effective measure to improve the selection of antibacterial agents.

(2) Load and fix the nanometer photo catalyst. It has the advantages of easy control under operating conditions, simple process equipment, strong oxidation capacity, and low treatment cost. To solve the problem that the catalyst is difficult to be recovered due to its small particle size and promote its industrial development and utilization, the reasonable catalyst loading technology can be used to load the catalyst, which lays a foundation for the practical application of nano catalyster.

(3) Improve the food industry wastewater treatment technology based on solar hot steam generation. It is a promising wastewater treatment technology with the characteristics of energy-saving and environmental protection. To promote the development of this technology, it is necessary to further optimize the solar absorbers from the aspects of substrate influence, service life, and recycling, to establish a perfect solar thermal steam-generating wastewater treatment technology.

Acknowledgments
This work was supported by Special Fund for Public Welfare Research and Capacity Building of Guangdong Province in 2015 (2015A020208019); Environmental Pollution Catalytic Treatment Engineering Technology Research Center of Foshan, 2017 Foshan Science and Technology Project (2017GA10159); 2017 Guangdong Science and Technology Project, Engineering Technology Research Center of Guangdong Water Pollution Control (2017g60162).

References
[1] Rodriguez-Vidal F J, Garcia-Valverde M, Ortega-Azabache B, et al. Characterization of urban and industrial wastewaters using excitation-emission matrix (EEM) fluorescence: Searching for specific fingerprints, Journal of Environmental Management, 2020, 263: 110396.
[2] Barrios M E, Blanco Fernandez M D, Cammarata R V, et al. Viral tools for detection of fecal contamination and microbial source tracking in wastewater from food industries and domestic sewage, Journal of Virological Methods, 2018, 262: 79-88.
[3] Campos-Manas M C, Plaza-Bolanos P, Martinez-Piernas A B, et al. Determination of pesticide levels in wastewater from an agro-food industry: Target, suspect and transformation product analysis, Chemosphere, 2019, 232: 152-163.
[4] Duran A, Monteagudo J M, Sanmartin I, et al. Homogeneous sonophotolysis of food processing industry wastewater: Study of synergistic effects, mineralization and toxicity removal, Ultrasonics Sonochemistry, 2013, 20 (2): 785-791.
[5] Hafez A, Khedr M, Gadallah H. Wastewater treatment and water reuse of food processing industries. Part II: Techno-economic study of a membrane separation technique, Desalination, 2007, 214 (1-3): 261-272.
[6] Xu Q, Du M, Liu X, et al. Calcium peroxide eliminates grease inhibition and promotes short-chain fatty acids production during anaerobic fermentation of food waste, Bioresource Technology, 2020, 316: 123947.
[7] Torres S, Verón H, Contreras L, et al. An overview of plant-autochthonous microorganisms and fermented vegetable foods, Food Science and Human Wellness, 2020, 9 (2): 112-123.
[8] Pereira T, Barroso S, Mendes S, et al. Optimization of phycobiliprotein pigments extraction from red algae Gracilaria gracilis for substitution of synthetic food colorants, Food Chemistry, 2020,
321: 126688.

[9] Landin-Sandoval V J, Mendoza-Castillo D I, Bonilla-Petriciolet A, et al. Valorization of agri-food industry wastes to prepare adsorbents for heavy metal removal from water, Journal of Environmental Chemical Engineering, 2020, 8(5): 104067.

[10] Chowdhury B, Lin L, Dhar B R, et al. Enhanced biomethane recovery from fat, oil, and grease through co-digestion with food waste and addition of conductive materials, Chemosphere, 2019, 236: 124362.