EDITORIAL

Developing Magnetic Material for Remediation of Aquatic Nitrogen Pollution in Water Facilities

Guocheng Zhu*  Junming Chen
Hunan Provincial Key Laboratory of Shale Gas Resource Utilization, Hunan University of Science and Technology, Xiangtan, Hunan, 411201, China

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Natural organic matters (NOM) affect water environmental security and have posed a potential threat to human health, and thus they have long been considered as a key index to evaluate water treatment performance. Dissolved organic nitrogen is one of the NOM, which produces some disinfection byproducts having more toxic than those carbon-based materials. Coagulation is a key unit of drinking water purification and has received wide attention. However, conventional flocculation technology on removal of DON is so poor that we have to seek more effective technologies [1,2]. Compared with activated carbon, biological aerated filter and sand filtration, the coagulation efficiency of removing DON is relatively low [3]. The combined use of conventional flocculant and organic polymer can improve treatment efficiency to a certain extent [4,5], and enhanced coagulation can also improve the DON removal rate, but their DON removal performance is still not dreamful [6]. For example, the removal efficiency of DON by conventional water treatment process in China is not good [7]. A drinking water plant in the south of China found that the removal rate of DON in the conventional sewage treatment process (coagulation sedimentation + bio-filter + disinfection) is only 27% [2]; It is reported that among the 28 drinking water plants in the United States, the average removal rate of DON is only 20% [1]. The current flocculation method can only be used to remove particulate matter in raw water, and the effect on removal of those DON with low content, low molecular weight and strong hydrophilicity is not good [8], which still needs to be coupled with relevant processes [3,9,10]. For example,

*Corresponding Author:
Guocheng Zhu,
Hunan Provincial Key Laboratory of Shale Gas Resource Utilization, Hunan University of Science and Technology, Xiangtan, Hunan, 411201, China;
Email: zhuguoc@hnust.edu.cn

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coagulation potassium permanganate \[^{11}\], coagulation ultrafiltration / microfiltration \[^{9}\], coagulation adsorption \[^{10}\], ozone coagulation \[^{12}\]. These combined processes can improve DON removal rate, but will increase operational process complexity and economic cost. The reason for the poor flocculation is that flocculation usually has a good effect on removal of macromolecules and hydrophobic organics. However, most of the components contained in DON are hydrophilic organics (studies have shown that the proportion of hydrophilic components of DON in the effluent of wastewater treatment plant is as high as 80\% \[^{13}\]). At present, there is a lack of systematic research on flocculation to remove DON. Although some achievements have been made, there is still a big gap between the preparation technology of flocculant and the goal of efficient removal of DON in water.

Magnetic flocculants are often prepared by hybriding nano Fe\(_2\)O\(_4\) or \(\gamma\)-Fe\(_2\)O\(_3\) with metal salt flocculants (such as polyaluminium chloride \[^{14}\], polyferric sulfate \[^{15}\]) or organic flocculants (such as polyacrylamide (PAM) \[^{16}\], chitosan \[^{17}\]). These magnetic flocculants can remove water turbidity, total phosphorus, heavy metals, and algae. However, the effect of those magnetic flocculants prepared using current methods on removing DON is still not ideal. Often, after flocculation, under the action of magnetic field, the flocculation sedimentation speed is fast, but the DON removal efficiency is not improved. Too high dosage will also lead to poor flocculation result. The main reason for the poor magnetic flocculation effect may be that the adsorption performance of magnetic nanoparticles is closely related to the microstructure of magnetic nanoparticles (such as particle size, specific surface area, surface functional groups), environmental conditions (such as temperature, pH value, ion type and strength) \[^{18,19}\]. Magnetic nanoparticles (MNPs) modified by cyclodextrin have good adsorption effects on amino acids, phenylalanine and tyrosine \[^{20}\]. For treatment of secondary effluent of industrial wastewater, some studies show that the use of Fe\(_2\)O\(_3\) mainly has the effect of accelerating separation, but the adsorption effect is not good. However, with the synergistic flocculation of amino functionalized Fe\(_2\)O\(_3\) it has a good effect on removing water protein, polysaccharide and humic acid, which can meet the water quality discharge standard and reduce the dosage of flocculant \[^{21}\]. The above results show that functional nanoparticle materials are of great significance to improve the adsorption and flocculation performance. Therefore, the functional modification of magnetic nanoparticles plays an important role.

The surface modification of magnetic nanoparticles is diverse, and a variety of modifiers can be introduced into the surface. Although different groups will be introduced into Fe\(_2\)O\(_4\) modified by organic substances such as chitosan and polyacrylamide, the effect of chitosan and polyacrylamide on the removal of DON is not good. After compounding with magnetic nanoparticles, the effect of improving the removal of DON is also limited. Therefore, how to increase the site-specific selection and adsorption capacity is an important problem to improve the pollutant removal efficiency of magnetic nanoparticles and magnetic flocculant. The removal of micro pollutants in water has always been a difficult problem in some water treatment methods \[^{22}\], such as flocculation and activated carbon adsorption. It is found that some porous materials have good removal effect on such pollutants after modification, such as porous materials β-Cyclodextrin \[^{22}\], porous aluminum Pillared Bentonite \[^{23}\] (good adsorption of DON in water). The adsorption effect of these materials is closely related to the structure of adsorption materials. Compared with these porous materials, metal organic frameworks (MOFs) materials have the advantages in specific surface area, porosity and convenience in synthesis \[^{24}\].

The surface modification of magnetic nanoparticles is diverse, and a variety of modifiers can be introduced into its surface. Although Fe\(_2\)O\(_4\) modified by organic compounds such as chitosan and polyacrylamide will introduce different groups, the removal effect of chitosan and polyacrylamide on DON is not ideal. After being coupled with magnetic nanoparticles, the effect of improving DON is also limited. Therefore, how to improve site selection and adsorption capacity of magnetic nanoparticles is a key point. In some water treatment methods, the removal of trace pollutants in water has always been a difficult problem \[^{22}\], such as flocculation and activated carbon adsorption. It is found that the modified porous materials have a good removal effect on such pollutants, such as porous materials β- Cyclodextrin \[^{22}\], porous aluminum Pillared Bentonite \[^{23}\] (good adsorption of DON). The adsorption effect of these materials is closely related to the structure of adsorbents. Compared with these porous materials, metal organic frameworks (MOFs) materials have advantages in specific surface area, porosity and convenient synthesis \[^{24}\].

The MOFs have the advantages of easy functional modification, easy structure adjustment and various adsorption mechanism, and the functional group modified MOFs have higher selectivity, and can obtain better properties after compounding with other functional materials \[^{25}\]. At present, the research on MOFs for drinking water treatment has been reported \[^{26}\]. Combining the magnetism of magnetic nanoparticles with the porous structure of MOFs can obtain easily separated, easily dispersed and
reusable magnetic MOFs composites \cite{27}. It can not only retain the structure and properties of MOFs materials, but also increase the magnetism of nanoparticles. Through the regulation of synthesis conditions, magnetic MOFs materials for specific applications have been applied in the field of water treatment \cite{28}. At present, magnetic MOFs are widely studied in the removal of gas pollutants, but there are relatively few studies on the removal of water pollutants. Therefore, application of MOFs in the field of water environment analysis and remediation needs to be further developed \cite{25}. MOF has advantages of easy functional modification, easy structural adjustment and varied adsorption mechanism. Functional groups modified MOF has higher selectivity and can obtain better properties after hybriding with other functional materials \cite{25}. Application of MOF in drinking water treatment has been reported \cite{26}. Combining magnetic nanoparticles with MOFs forms magnetic MOFs composites are easier to make MOFs disperse and reusable \cite{27}. It can not only maintain the structure and properties of MOFs materials, but also improve the magnetism of the materials. Through adjusting the synthesis conditions, magnetic MOFs materials have been applied in specific field of water treatment \cite{28}. At present, magnetic MOF has been widely studied in the removal of gas pollutants, but less used in the removal of water pollutants. Therefore, the application of MOF in the field of water environment analysis and remediation needs to be further developed \cite{25}.

The results show that MOFs can interact with nitrogen-containing organic compounds through π - π bonds and hydrogen bonds. For example, MOF can adsorb nitrogen-containing compounds through π - π bonds: CuC/MIL-100 (CR) adsorbs nitrogen-containing compounds in fuel \cite{29}; MOF adsorbs nitrogen-containing organic compounds through hydrogen bonding \cite{30}, such as nitrophenol adsorbed by NH₂-MIL-101 (Al) (see Figure 1). Although there are different environments and types of organic nitrogen compounds, the removal of DON by MOFs modified nanoparticles hybridized coagulant would be a promising method.

![Image](image_url)

Figure 1. Adsorption mechanism diagram of nitrophenol onto NH₂-MIL-101(Al) \cite{30}.

References


