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The role of magnetic MOFs nanoparticles in enhanced iron coagulation of aquatic dissolved organic matter

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Abstract

Dissolved organic matter (DOM) is not only a vector for the migration of aquatic environmental pollutants, but is also key to the control of water pollution. Economic and effective DOM removal through coagulation is essential in water treatment processes. This work investigated the role of carboxylated magnetic metal organic frameworks (MMOFs) nanoparticles in polymeric iron-based coagulation for the removal of aquatic DOM using a MMOFs-doped polyferric iron-based coagulant (MMOF-PIC). Analytical methodologies and tools used in this research included scanning electron microscopy (SEM), zeta potential, molecular weight cut off (MWCO), vibrating sample magnetometer (VSM) measurement, excitation emission matrix spectroscopy (EEMs), and X-ray photoelectron spectroscopy (XPS). The results showed that MMOF-PIC had the potential to change the structure of the polyferric iron-based coagulant (PIC) and charge, as determined by a porous surface morphology, a higher medium polymeric species distribution, and a more positive zeta potential. The MMOFs consequently enhanced PIC action on the removal of UV254 exposed DOM species with molecular weight < 30 kDa, including aromatic C=C based compounds, org-N as primary amines and amide/peptide bound species, water containing microbial metabolites and protein-like materials. The coagulation of DOM was enhanced by improving charge neutralization, adsorption-bridging and sweep-flocculation in the presence of MMOFs nanoparticles. This was due to hydrogen bonds, π–π bonds and covalent bonds resulting from actions of nanoparticles and pollutants. These results indicate that magnetic MOF nanoparticles can improve PIC coagulation for DOM, enhancing future removal of target pollutants.

Keywords: water; dissolved organic matter; polymeric-iron coagulation; nanomaterials; magnetic metal organic frameworks
1. INTRODUCTION

Dissolved organic matter (DOM) is considered as a product of a variety of biological metabolic processes of animals and plants. These typically consist of fulvic and humic acids, a range of organic acids, carbohydrates, carboxylic acids, amino acids, hydrocarbons, and other substances (Ravichandran, 2004; Jiang et al., 2017b; Zhu et al., 2017; Hua et al., 2018; Li et al., 2019b). High levels of DOM can lead to eutrophication in aquatic systems (Dodds and Smith 2016; Zhang et al. 2016) and in addition DOM is a major precursor of toxic carbonaceous and nitrogenous disinfection byproducts in treated drinking water and wastewater (Hua and Reckhow, 2007; Jiang et al., 2017a; Bian et al., 2018a; Han and Zhang, 2018; Li et al., 2019a; Li et al., 2019c).

Coagulation is an economic and effective process using coagulants which include alum (potassium aluminium sulfate), polyaluminum chloride (PAC), and aluminum chlorohydrate (ACH), as well as a number of other commercially produced chemical mixtures. They are used to remove these compounds through a water treatment process involving hydrolysis of metal salts (Rebhun and Lurie, 1993; Jiang and Graham, 1998). The mechanism of coagulation is electrical neutralization, adsorption-bridging, and sweep-floc formation (Wang et al., 2011a; Wang et al., 2019). However, coagulation cannot easily remove all components of the organic matter in water at low concentrations such as the low molecular weight components of DOM, with strong hydrophilicity (Bose and Reckhow, 2007; Matilainen et al., 2010; Wang et al., 2012). Because the coagulation process is widely used, it is of value to establish an effective coagulation system to comprehensively treat all DOM components.

Good coagulation is determined by the use of the most appropriate coagulants and the physicochemical characteristics of the water. Polyaluminium-based and iron-based coagulants are most widely used, and their coagulation performance depends on the specific coagulant type, dose, and water quality (such as pH value, total
organic concentration, and different molecular fractions) (Edzwald, 1993; Matilainen et al., 2010). Among them, the coagulant type is a key factor. Improving coagulation efficiency is often achieved through modification of conventional coagulant systems to form a new type of coagulant. The most extensively applied approach introduces new external substances to supplement the original coagulant system. For example, adding some inorganic components (such as calcium (Sudoh et al., 2015), magnesium (Wei et al., 2015), phosphorus (Zheng et al., 2011), zinc (Zhu et al., 2016), silicon (Zouboulis and Moussas, 2008)) or organic substances (such as polyacrylamide (PAM) (Ma et al., 2017a; Ma et al., 2017b; Zhu et al., 2018), polydimethyldiallylammonium chloride (PDMDAAC) (Wang et al., 2011b)) to polyferric and polyaluminum salts (such as polyferric sulfate (Moussas and Zouboulis, 2012) and PAC (Gao et al., 2005)), have been identified as being effective in improving coagulation compared to the original products. Recently, the introduction of magnetic nanoparticles into the coagulation process has increased interest in enhancing performance. For example, magnetic nanoparticles ($Fe_3O_4$ or gamma-$Fe_2O_3$) are added to metal salt coagulants (such as PAC (Zhang et al., 2017), polyferric sulfate (Jiang et al., 2010)) or organic flocculants (such as PAM (Zhou et al., 2017; Ma et al., 2019) and chitosan (Liu et al., 2018; Xiong et al., 2019)) to remove turbidity, total phosphorus, potentially toxic elements and algae. The results show that magnetic nanoparticles can accelerate the precipitation rate of colloidal particles. Magnetic nanoparticles can also enhance adsorption, charge neutralization, and bring out the adsorption-bridging ability of the coagulant. However, research has also shown that magnetic nanoparticles sometimes only play a role in accelerating precipitation during coagulation, while not significantly improving the removal of a DOM (Wan et al., 2011; Jiang, 2015b). Therefore, to obtain better removal of DOM, the magnetic nanoparticles need to be functionalized. Limited examples include amino-functionalized magnetic nanoparticles which are known to enhance removal of proteins, polysaccharides and humic acid (Ren et al., 2016). In fact, functionalized magnetic nanoparticles have a higher affinity for DOM and can assist in obtaining
better coagulation efficiency. For example, those magnetic nanoparticles modified by cyclooctetrin have a better adsorption for amino acids, phenylalanine and tyrosine (Kakhki, 2015). Compared with traditional doped components, these cyclooctetrin-modified nanoparticles have a unique superparamagnetism, volume effect, quantum size, and quantum confinement effect, which means they have a higher reactivity and adsorption performance for pollutant removal (Qu et al., 2013; Xu and Hu, 2015; Santhosh et al., 2016). However, it is still not clear how these magnetic nanoparticles affect coagulation.

Selection of magnetic nanoparticles with an easily controlled structure and high adsorption capacity will be of greater value in the design of pollutant removal systems. Metal-organic frameworks (MOFs) are characterized by an ease of functionalization and structure modification, and an enhanced adsorption and functional group-modified MOFs have been shown to be more selective for organic pollutants (Khan et al., 2013; Hasan and Jhung, 2015). Functional group-modified MOFs couple with magnetic nanoparticles (denoted as MMOFs), which gives them better removal properties (Ryu et al., 2010; Bian et al., 2018b), such as relatively easy physical separation, dispersion and reuse. At present, MMOFs nanoparticles are widely used in environmental fields, such as the treatment of contamination by potentially toxic elements and dye wastewater (Huang et al., 2018), but they are less frequently applied in the removal of aquatic DOM. The typical adsorption mechanisms involved using nanomaterials include hydrogen, π-π, and covalent bonds, which are effective for a wide range of organic carbon/nitrogen compounds. Bonding properties of MOFs (such as CuCl/MIL-100 (Cr) and NH₂-MIL-101 (Al)) have made it possible for them to interact with nitrogen-containing organic compounds (such as nitrogen compounds in fuel oil, nitrophenol, and pyridine) through π-π and hydrogen bonding (Ahmed and Jhung, 2014; Liu et al., 2014). It is of interest to determine the effectiveness of these nanoparticles on aquatic dissolved organic matter during coagulation, considering the fact that MMOFs have greater adsorption.
Polyferric iron-based coagulant (PIC) can form larger scale flocs than the traditional aluminum-based coagulant, which is better for adsorption for DOM. Therefore, we investigated the influence of MMOFs in aquatic DOM removal during polymeric iron-based coagulation. In the presence of MMOFs, we investigated the physico-chemical properties of a PIC, such as structure, charge and magnetic properties. The influence of MMOFs in PIC coagulation for DOM was examined by measuring the removal of turbidity, specific ultraviolet absorption at 254 nm and dissolved organic carbon (DOC). The DOM was divided into molecular weight fractions, fluorescence fractions, and C/N-based components and then systematically analyzed using molecular weight cut off (MWCO), fluorescence excitation emission matrix spectroscopy (EEMs), and X-ray photoelectron spectroscopy (XPS).

2. MATERIALS AND METHODS

2.1 Materials

Water samples were collected from a number of different locations representing a range of different aquatic systems including an artificial ornamental lake and a local domestic pond on the campus of Hunan University of Science & Technology, the water from the downstream and upstream of Xiangjiang River of Xiangtan City, Hunan Province, China, effluent from a local wastewater treatment plant (WWTP), and water from a tributary of the Xiangjiang River. The samples were used immediately for the measurement of key water characteristics, which included turbidity, pH, UV254, and DOC.

The PIC and magnetic nanoparticles were synthesized at the laboratories of Hunan University of Science and Technology from basic chemical reagents. Sodium chlorate, ascorbic acid, and potassium bromide, were
purchased from Kemiou Chemical Reagent Co. (Tianjin, China). Ferric chloride hexahydrate (FeCl₃·6H₂O) was purchased from Taishan Chemical Plant Co. (Taishan, China), and ethanol and N,N,-dimethyl formamide (DMF) was purchased from Guangdong Guanghua Polytron Technologies Inc. (Shantou, China). Chemicals tetraethyl orthosilicate (TEOS), zirconium tetrachloride (ZrCl₄), 1, 2, 4, 5-benzenetetracarboxylic acid (BTEC) were purchased from Aladdin (Shanghai, China), chemicals (hydrochloric acid (HCl), while concentrated sulfuric acid (H₂SO₄) came from Zhuzhou Xingkong Chemical Co. (Zhuzhou, China). Ferrous sulfate, sodium salt trihydrate, 1,10-Phenanthroline monohydrate, acetic acid, ammonium hydroxide, Ferron, and sodium acetate anhydrous came from Sinopharm Chemical Reagent Co. (Shanghai, China), and sodium carbonate anhydrous came from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). All solutions were prepared with LBY-20 ultrapure water (Chongqing Owen Science and Technology Co., Ltd., China). The glassware and other labware were acid-washed, rinsed thoroughly with ultra-pure water, and dried prior to use.

2.2 Preparation of magnetic nanoparticles and PIC

The PIC was prepared using a simple procedure: 55.60 g of FeSO₄·7H₂O was acidified by 5.40 mL of concentrated sulfuric acid, followed by a slow stirring in a beaker until a homogeneous liquid mixture was obtained; secondly 10 mL of 3 M sodium chlorate solution was added into the reaction vessel; followed by 20 mL of ultra-pure water and stirred slowly for 30 min at 40 °C. Finally, Na₂CO₃ was added into the reaction system according to the predetermined molar ratio of -OH to Fe of 0.16. Finally, the PIC was aged for at least 24 h at room temperature prior to usage.

Magnetic Fe₃O₄ nanoparticles (nano-Fe₃O₄) were prepared through a solvothermal reduction by the following procedure: 0.54 g of FeCl₃·6H₂O and 1.50 g of C₂H₃NaO₂ were dissolved in 20 mL of ethylene glycol, which was stirred at room temperature for 30 min until a homogeneous solution was achieved. The solution was
subsequently transferred to a polytetrafluoroethylene (PTFE)-lined autoclave to maintain reactions at 200 °C for 10 h. The solid products were separated under an external magnetic field at room temperature and then washed three times with ultra-pure water and ethanol. After vacuum drying for 24 h at 60 °C, the nano-Fe$_3$O$_4$ was produced. The nano-Fe$_3$O$_4$ was further modified by a silica core shell through the Stober method using the following procedure: 1.0 g of Nano-Fe$_3$O$_4$ and 320 mL of ethanol were dispersed in 80 mL of ultra-pure water. The solution then underwent ultrasonic dispersion for 30 min, prior to the addition of ammonia hydroxide solution (5 mL). After mechanical stirring for 15 min, 20 mL of TEOS was slowly added 5 mL at a time every three hours, which maintained a reaction while being stirred under nitrogen for 12 h at 25 °C. Finally, the product was collected with an external magnetic field and washed three times with ethanol and water. After vacuum drying for 24 h at 60 °C, the modified nanoparticles (MNPs) were obtained.

The MOFs (UiO-66-2COOH) was prepared by using the hydrothermal method: 2.30 g of 10 mM ZrCl$_4$ and 4.30 g of 17 mM of BTEC were dissolved in 50.40 mL of ultra-pure water and stirred at room temperature for 30 min until a homogeneous solution was obtained. Subsequently, the solution was treated by a reflux heating for 24 h at 100 °C. When it was cooled to room temperature, white gel was washed repeatedly with ultra-pure water for removal of the excess acids and then redispersed in ultra-pure water for 16 h to undergo reflux heating at 100 °C. Then, the product was centrifuged and washed three times with ethanol and water. After vacuum drying for 24 h at 70 °C, the MOFs were obtained. Using the same method, in the presence of 4.60 g of MNPs, black MMOFs were obtained. Using the same method with MOFs, MMOFs were prepared with the details as shown in Supplementary Materials Text S1.

2.3 Jar test
In nano-PIC coagulation, the nanoparticles and PIC were pre-mixed (denoted as nano-PIC) for over 24 h before coagulation, which produced three types of nano-PIC coagulation including MOF-PIC, metal nanoparticle-polyferric iron-based coagulant (MNP-PIC), and MMOF-PIC coagulation. The nano-PIC could be adjusted through the mass ratio of components (such as MOFs, MNPs, MMOFs) to PIC or to each other and were denoted as $R$ such as $R_{m\text{MNPs}/m\text{MOFs}}$, $R_{m\text{MOFs}/m\text{Fe}}$, and $R_{m\text{MMOFs}/m\text{Fe}}$, as well as the molar ratio of $-\text{OH}$ to Fe such as $R_{m\text{OH}/m\text{Fe}}$. PIC dose was calculated using the Fe component.

The PIC coagulation and nano-PIC coagulation experiments were performed using a ZR4-6 program-controlled jar test apparatus (Zhongrun Water Industry Technology Development Co. Ltd., China) at room temperature. One liter of collected water sample was transferred into a beaker and the initial pH of the sample was adjusted to the set value using 0.50 M HCl and 0.50 M NaOH. After the addition of the appropriate coagulant dose, the sample was rapidly mixed at the set agitation speed (rpm) of 210 rpm for 2 min, followed by a slow mixing phase at 70 rpm for 15 min, and then a 30 min settling time. The supernatant sample was extracted from the beaker 2 cm below the water surface for analysis of water characteristics. The coagulant dose was calculated based on the effective iron content.

### 2.4 Analytical methods

The turbidity and DOC were measured using a Turbidity NTU Hach turbidimeter Model Q 2100 and an Elementar Vario MICRO Cube (Elementar Analysensysteme GmbH, Germany), respectively. The UV254 was measured on a TU-1901 UV-visible spectrophotometer (Purkinje General Instrument Co., Ltd., Beijing, China). Iron content was determined by 1, 10-Phenantroline spectrophotometry (National Standard of China, GB/T 23834.6-2009). Except for the turbidity, water quality parameters were analyzed after the samples were filtered.
through a membrane (pore size = 0.45 µm). When the DOM in water was dominated by larger molecular and hydrophobic organic matter, SUVA (m⁻³mg⁻¹L), as the ratio of UV254 (cm⁻³) to DOC (mg/L) percentage, presented a higher value. Conversely, lower values indicated more hydrophobic organic matter in the water (Edzwald, 1993; Matilainen et al., 2010).

The species distribution of PIC and nano-PIC was measured and compared using timed complexation spectroscopy known as the Ferron method (Baozhen and Hongxiao, 1989). Three types of iron hydrolysis species were tested in this study, including monomeric, medium size polymeric, and colloidal species, denoted as Fe (a), Fe (b), and Fe (c), respectively. Those species reacting with a Ferron reagent within 1 min were considered to be the monomeric species. Those species reacting to the Ferron reagent until the absorbance finally ended in a plateau were considered to be medium size polymeric species. Fe (c) values were calculated by subtracting Fe (a) and Fe (b) from the known total Fe content. Flocs were freeze dried to remove water (Creatrust CFTD-12S vacuum freeze dryer, Qingdao Creatrust Co. Lt, China). The XPS was recorded on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo-Scientific Co., Waltham, MA, USA) and was used to analyze the elemental composition of coagulants and flocs. The SEM images of coagulants and nanoparticles were obtained on a JEOL JSM-6380LV electron microscope instrument. Their TEM images were also collected using a FEI Tecnai G2 F20 transmission electron microscope. The Zeta potential values of PIC, nano-PIC and jar test samples were tested using an NS90 Malvern Zetasizer (Malvern Instruments, Malvern, UK).

The excitation-emission matrix spectroscopy (EEMs) of DOM in water samples filtered using a 0.45 µm membrane filter was tested using an FL4600 fluorescence spectrophotometer (Hitachi High Technologies, Tokyo, Japan). The excitation wavelengths and emission wavelengths were fixed from 200 nm to 400 nm in 2
nm steps, and from 200 to 500 nm in 3 nm steps, respectively. The fluorescence intensity of an ultra-pure water as a blank sample was subtracted from each jar test samples. The Rayleigh and Raman scatter were removed following the procedure reported in (Bahram et al., 2006). We used fluorescence region integration (FRI) developed by Chen, et al. (Chen et al., 2003) who divided these EEMs regions into five parts including aromatic protein-like materials denoted as I, aromatic protein-like materials denoted as II, fulvic acid-like materials denoted as III, soluble microbial metabolites denoted as IV, and humic substance-like material denoted as V. The study did not give more information about subclassification of I and II although they represent the same category. The protein-like materials contain many fluorescence fractions such as Tryptophan-like material, Tyrosine-like material and Phenylalanin-like material, which are distributed in different fluorescence regions. It tends to represent Tyrosine-like material while II to Tryptophan-like material (Zhu et al., 2017).

The integral volume of each of the above fluorescence regions is calculated as $\phi$, which reflects the relative content of organic matter in the integral region. Their reduction rates are determined by the subtraction of each part between that before coagulation and that after coagulation. The integral volume value is expressed as follows.

$$\phi_{i,n} = \alpha \int_{ex} ^ {em} I d\lambda_{ex} d\lambda_{em}$$  

(1)

Where $\phi_{i,n}$ (au.nm$^2$) is standard integral volume of $i^{th}$ fluorescence region; $\lambda_{ex}$ is the excitation wavelength (nm); $\lambda_{em}$ is the emission wavelength (nm); $I$ is fluorescence intensity at fixed $\lambda_{ex}$ and $\lambda_{em}$, and $\alpha_i$ is the ratio of the integral volume of all regions and the integral volume for the $i^{th}$ region.
The raw water and samples after coagulation were fractionated using a 0.45 μm pore size filter membrane and different molecular weight cut-off of 30 kDa, 10 kDa, and 3 kDa of ultrafiltration membranes on an MSC 300 ultrafiltration cup of 300 mL (Shanghai Mosu Science Equipment Co., Ltd., China) under a nitrogen pressure of 0.1 MPa with a magnetic stirring speed of 100 r/min. After water samples permeated the membrane, the filtrates were collected for quality measurement including UV254 and DOC. In each size range, the removal percentages of DOC and UV254 were calculated as follows:

\[
C_{DOM} (MW < 0.45 \mu m) \% = \frac{C_{0.45 \mu m}}{C_{raw}} \times 100 \%
\]

(2)

\[
C_{DOM} (0.45 \mu m > MW > 30 kDa) \% = \frac{C_{0.45 \mu m} - C_{30kDa}}{C_{raw}} \times 100\%
\]

(3)

\[
C_{DOM} (MW = 30-10 kDa) \% = \frac{C_{30kDa} - C_{10kDa}}{C_{raw}} \times 100\%
\]

(4)

\[
C_{DOM} (MW = 10-3 kDa) \% = \frac{C_{10kDa} - C_{3kDa}}{C_{raw}} \times 100\%
\]

(5)

\[
C_{DOM} (MW < 3kDa) \% = \frac{C_{3kDa}}{C_{raw}} \times 100\%
\]

(6)

Where \( C_{DOM} (MW \text{ range}) \% \) is the percentages of reduced raw concentration \( (C_{raw}) \) of DOM in the MW size range. \( C_{0.45 \mu m}, C_{30kDa}, C_{10kDa} \) and \( C_{3kDa} \) are the concentrations of molecular weight fractionations of filtered DOM using membranes (pore size = 0.45 μm, 30kDa, 10 kDa and 3 kDa).

3. RESULTS and DISCUSSION

3.1 Influence of nanoparticles in structure of PIC
The results of the SEM and TEM analyses of nanoparticles are shown in Fig. 1(a–f). The surface morphology of MOFs showed irregular, rough shapes as shown in Fig. 1(a) and (d). Nano-Fe$_3$O$_4$ nanoparticles took a spherical shape with a diameter of about 300-400 nm. After being coated in an approximately 10-nm wide silica shell, the nano-Fe$_3$O$_4$ nanoparticle shape did not change as shown in Fig. 1(b) and (e). This core-shell layer prevented nanoparticles from being destroyed by outside ambient conditions. The morphology of the MMOFs nanoparticles was in the form of MOFs covering the surface of nano-Fe$_3$O$_4$ as shown in Fig. 1(c) and (f). When combining MOFs and MMOFs with PIC, the PIC surface morphology changed as shown in Fig. 1(g)–(i). The PIC had an irregular square-like shape with a surface that was very smooth, as shown in Fig. 1(g). MOF-PIC and MMOF-PIC were different. In the MOF-PIC surface, irregular MOFs cover the PIC surface, similar to coral cluster structures, as shown in Fig. 1(h). However, the surface of an MMOF-PIC was an irregular mesh structure with a few cavities as shown in Fig. 1(i). From a morphological point of view, there is no good evidence to directly prove the correlation between them, but coagulants with different morphological features are likely to produce different coagulation results. Mesh structure with irregular holes in common metal-based coagulants are less frequently reported because their surfaces are often present in a branched structures, chain-net structures, irregular squares, and smooth surfaces (Moussas and Zouboulis, 2008; Zouboulis et al., 2008; Zeng and Park, 2009; Zhu et al., 2011; Li et al., 2013). Better adsorption depends on a porous surface, which means the morphology of a nanoparticle MMOF-doped PIC would be more conducive to adsorption.

Fig. 1

Nano-Fe$_3$O$_4$, MNPs and MMOFs had magnetic characteristics, which were identified by their magnetization curves as shown in Fig. 2(a). The original magnetization of nano-Fe$_3$O$_4$ was 74.99 emu/g. Due to the core-shell effect, their magnetization intensity decreased to 69.38 emu/g and 38.35 emu/g for MNPs and MMOFs,
respectively. Introducing these nanoparticles into PIC produced those flocs with magnetic properties, which were observed by measuring their elemental components and magnetization using XPS and VSM analysis. As shown in Fig. 2(b), two significant Fe 2p peaks at 710.1 eV and 725 eV corresponded to the characteristic peaks of nano-Fe₃O₄ (Yamashita and Hayes, 2008). Consequently, the flocs showed a significant magnetization effect in magnetic iron that could be easily separated by a magnet under an external magnetic field. Their magnetization was controlled by $R_{\text{mMMOFs/mFe}}$. Increased $R_{\text{mMMOFs/mFe}}$ could enhance its magnetization. The floc generation value produced at $R_{\text{mMMOFs/mFe}}$ of 0.3 as shown in Fig. 2(c) was significantly higher than that at 0.2. These results indicated that the magnetic nanoparticles dispersed in PIC still maintain their magnetic properties.

Fig. 2

3.2 Influence of nanoparticles on species and charge properties of PIC

The coagulation efficiency always depends on those species characteristics and charge properties of hydrolysates of metal salt coagulants (HongxiaoTang, 2006). When MNPs, MOFs and MMOFs were introduced into PIC, the species distribution, corresponding to Fe (a), Fe (b) and Fe (c) changed as did the charge properties of PIC. The change in PIC charge properties indicated that MMOFs had the most significant influence as shown in Fig. 3. For example, as illustrated in Fig. 3(a), the original percentage distribution of Fe (a), Fe (b) and Fe (c) in PIC were 41.98%, 24.18% and 33.84%, respectively; however, after introducing MNPs into PIC, the distributions of Fe (a) and Fe (b) increased by 3.84% and 2.91%, respectively, and that of Fe (c) decreased by 6.75%. After introducing MOFs into the PIC, these proportion distributions increased by 5.29% Fe (a) and 3.53% Fe (b). However, for Fe (c) an 8.82% decrease was observed. After introducing MMOFs into the PIC, the distributions of Fe (a) and Fe (b) increased by 2.06% and 8.79%, respectively. This time, the distribution of Fe
(c) decreased by 10.85%, which indicated that the presence of nanoparticles reduced the distribution of Fe (c) species while increasing the distribution Fe (a) and Fe (b) species. The MMOFs were the most significant factor in reducing Fe (c) distribution when increasing the Fe (b) distribution. When using other nanoparticles, the authors also found that they could increase the distribution of Fe (b) in PIC as shown in Fig. 3(b) and (c). The decrease in the level of Fe (c) had to be balanced out by an increase in the sum of the other species distribution. Species distribution has always played an important role in the control of pollution removal by coagulation. For example, the medium polymeric species of an aluminum-based coagulant has proven to be more effective for dissolved organic carbon (DOC) and UV$_{254}$ (Yang et al., 2013; Feng et al., 2015; Ni et al., 2015; Sadrnourmohamadi and Gerczyca, 2015; Tang et al., 2015); additionally, for an iron-based coagulant, the medium polymeric species are also the most effective coagulation species for DOC removal (Duan and Gregory, 2003; Matilainen et al., 2010). Therefore, increased medium polymeric species would improve the PIC coagulation for the removal of DOM. In addition, the positive potential value of PIC could be increased when those nanoparticles were added to PIC, as shown in Fig. 3(d). As illustrated in Fig. 3(d), the original potential value of PIC was 10.95 mV, but after adding nanoparticles, including MNPs, MOFs and MMOFs, those values increased to 11.10 mV, 11.70 mV, and 12.25 mV. Among them, MMOFs were the most effective nanoparticles to increase the positive potential value of PIC. The increased potential value was also beneficial to the development of charge neutralization.

The pH-induction of MMOF-PIC coagulation produces a better adsorption-bridging role, which is often expected to be generated at relatively higher values, whereas charge neutralization as the primary coagulation mechanism often occurs at lower values (Chang et al., 1993; Wen, 2002; Zhu et al., 2018). As shown in Fig. 3(e), the zeta potential in the coagulation with MMOF-PIC was higher than that with PIC when the pH value was less
than or equal to 7, and charge neutralization was the main coagulation mechanism; when the pH value was increased to a higher value (e.g., 8), those zeta potential values in coagulation with MMOF-PIC were lower than that with only PIC. The main reason for the occurrence of lower value would be that at a higher pH value, MMOF-PIC showed a stronger adsorption ability than PIC which was possibly due to a specific chemical binding that could reduce more negatively charge substances.

Fig. 3

3.3 Enhanced PIC coagulation of DOM by nanoparticles

The effect of coagulation on DOM with MMOF-PIC (5 mg/L and 10 mg/L) at different $R_{\text{mNPs/mMOFs}}$ ranged from 2:1 to 1:6, as shown in Fig. 4. Fig. 4(a)-(c) showed that the MMOFs enhanced the performance of PIC coagulation for turbidity, UV254 and DOC. For example, with $R_{\text{mNPs/mMOFs}}$ at 2:1 to 1:6, MMOFs-PIC produced a higher removal efficiency of turbidity than PIC (see Fig. 4a). With PIC at 5 mg/L, the enhanced removal efficiency of DOC only achieved a $R_{\text{mNPs/mMOFs}}$ of 2:1; however, increasing the PIC concentration to 10 mg/L, DOC removal could be obtained within a wider range from 2:1 to 1:6 as shown in Fig. (4b). Fig. 4(c) shows the coagulation results for UV254 to be different for DOC. Using PIC at 5 mg/L, the UV254 removal efficiency could be increased at a $R_{\text{mNPs/mMOFs}}$ of 2:1 to 1:2. Increasing the PIC dose to 10 mg/L could enhance the removal efficiency, but it also limited the range of $R_{\text{mNPs/mMOFs}}$ within 2:1 to 1:1. Therefore, obtaining the increased DOC and UV254 removal efficiency by MMOF-PIC had different requirements for $R_{\text{mNPs/mMOFs}}$; however, the MMOF-PIC requirements for turbidity removal seemed insignificant when it came to DOC and UV254 removal.

Fig. 4
A significance influence from the presence of magnetic nanoparticles in PIC coagulation for DOM was observed again using a response surface methodology analysis, which identified the correlation between various factors and DOC removal efficiency. Three significant factors and horizontal ranges were determined by our preliminary single factor experiments, corresponding to $R_{mMNPs/mMOFs}$ (denoted as $X_1$, ranging from 0.5, 1 and 2), $R_{mMOFs/mFe}$ (denoted as $X_2$, ranging from 0.2, 0.3 and 0.4), and $R_{nOH/nFe}$ (denoted as $X_3$, ranging from 0.04, 0.10 and 0.16). Box-Behnken and response surface methodologies (Aslan and Cebeci, 2007; Ferreira et al., 2007) were used and were also able to find an optimum condition for DOC removal: $R_{mMNPs/mMOFs}$ of 2, $R_{mMOFs/mFe}$ of 0.2, and a $R_{nOH/nFe}$ of 0.16. The BOX-Behnken experimental protocol and results are shown in Supplementary Materials Table S1. The results of analysis of variance (ANOVA) (Xu et al., 2019) for the response surface quadratic model with Design Expert 8.0.6 software is shown in Supplementary Materials Table S2 and an evaluation of coefficient factors is shown in Supplementary Materials Table S3. The square of the correlation coefficient between the predicted DOC removal efficiency and the measured values was up to 0.86. The F-test value of the model was 4.66, and the Prob > F value was 0.0274 (< 0.05). These results showed that the model was significant. $X_1$ and $X_2$ were those variables related to MMOFs or MOFs, which were also the significant items in the model. This once again demonstrated that MMOFs had a significant positive influence in PIC coagulation for DOM.

The results of DOM removal by MMOF-PIC at various dose ranges from 4 mg/L to 26 mg/L is shown in Fig. S1. In Fig. S1(a), MMOF-PIC were able to increase turbidity removal with its increased dose in the range of 4 mg/L to 16 mg/L. At 8 mg/L of MMOF-PIC, the turbidity removal efficiency reached 91.09%. At 16 mg/L of MMOF-PIC, the residual turbidity reached the minimum 0.65 NTU, corresponding to a removal efficiency of 95.16%. When further increasing the dose of MMOF-PIC, the turbidity removal efficiency became worse,
which was attributed to the dose effect of MMOF-PIC. As shown in Fig. S1(b), the removal efficiency of UV254 by MMOF-PIC increased with the increase of its dose. At 16 mg/L, the removal efficiency of UV254 reached the maximum removal efficiency of 49.09%, but further increasing MMOF-PIC dose decreased its value. Lower turbidity removal would lead to a poorer result for UV254 removal. In the range of 4 mg/L to 22 mg/L of MMOF-PIC, the removal efficiency of DOC increased with the increase of the MMOF-PIC dose. At 22 mg/L of MMOF-PIC, the maximum removal efficiency was achieved at 52.29%. The optimum dose for MMOF-PIC coagulation for UV254 and DOC was different, showing the effect of MMOF-PIC coagulation for UV254 and DOC depended on its dose. In addition, the UV254 removal was different from the DOC: those removal efficiencies with a turbidity of over 90% could be achieved with MMOF-PIC at 8 mg/L to 22 mg/L. In this range, the removal efficiency of UV254 increased first and then decreased, while DOC increased gradually until the dose was over 22 mg/L. This may be attributed to the fact that DOC and UV254 represent different types of organic molecules, leading to different dose requirements. However, throughout the whole dose effect study, an appropriate amount was required for the best removal efficiency of DOC, UV254, and turbidity. Lower or excessive dose was likely to lead to a poorer coagulation, which indicated that the adsorption-bridging mechanism was playing a role in coagulation for DOM removal (Subramanian et al., 1999; Jiang, 2001; Sadri Moghaddam et al., 2011).

3.4 Removal of molecular weight fractions

The size of pollutants effectively removed by coagulation/filtration is considered to be between 1 nm and 10 μm (Xu and Long, 2000). This DOM contains different molecular weight fractions, while those smaller molecular organic compounds are often difficult to treat by coagulation. Coagulation of these molecular weight fractions were used to examine the effect of MMOFs doped PIC. The results are shown in Fig. 5. The raw water included
different molecular weight UV254 fractions characterized by a MW > 30 kDa (35.71%), MW = 30-10 kDa (1.79%), MW = 10-3 kDa (16.06%) and MW < 3 kDa (46.43%). As shown in Fig. 5(a), PIC removed the UV254, which was different from the nanoparticle-doped PIC: PIC could almost completely remove organic matter of MW > 30 kDa, while in the presence of nanoparticles, there were lower residual materials (about 3.57%); MOF-PIC could not completely remove the fractions with MW between 30 kDa and 10 kDa, but MNP-PIC and MMOF-PIC could completely remove them, indicating that magnetic nanoparticles were effective for PIC removal of this type of organics. These organics with a MW between 10 kDa and 3 kDa were removed more efficiently in the presence of nanoparticles. The removal efficiency of fractions of MW < 3 kDa and 0.45 μm increased in an ascending order: PIC < MOF-PIC < MNP-PIC < MMOF-PIC. MMOFs were, therefore, most effective for assisting PIC in removing these small molecular compounds. Raw water included different molecular weight DOC fractions characterized by MW > 30 kDa (35.35%), MW = 30-10 kDa (19.12%), MW = 10-3 kDa (8.63%), and MW < 3 kDa (36.90%). The DOC fractions in the range of MW = 30-10 kDa and MW < 3 kDa had higher content than those UV254 fractions. As shown in Fig. 5(b), PIC, MOF-PIC, MNP-PIC, and MMOF-PIC removed MW > 30 kDa organics, which increased in ascending order. However, the results were reversed when removing the fractions between 10 kDa and 30 kDa. The removal efficiency of these DOC fractions with MW < 10 kDa was similar. Lower concentration DOC fractions were missed due to instrument interference in this study. UV254 is the absorbance of natural waters at UV wavelengths 254 nm, which is caused primarily by aromatic DOM moieties, while DOC consists of a wider range of organic matter fractions, which is a measure of the total DOM in a sample (Karanfil et al., 2005). Therefore, in the coagulation, characteristics of UV254 removal differed from that of DOC removal. Overall, in the presence of nanoparticles, PIC was more effective for aromatic compounds, especially UV254 organic
compounds with MW < 3 kDa and 30 -10 kDa. MMOF-PIC had a good effect in removing DOC with MW > 30 kDa.

Fig. 5

3.5 Dependence on water characteristics

Water characteristics, pH and DOM fractions, are both important factors affecting coagulation performance. We aimed to evaluate their influence in MMOF-PIC coagulation for DOM. The pH effect on DOM removal with MMOF-PIC is shown in Fig. S2.

As illustrated in Fig. S2, an increase of pH, resulted in the increased efficiency of turbidity removal. When analysed between pH = 4-6, the turbidity and UV254 removal efficiencies were not found (Fig. S2 (a) and (b)). At pH = 7-12, they increased gradually. At pH = 9 and 10, the turbidity removal efficiency was 90.65% and 93.03%, respectively. The removal efficiency of UV254 reached a maximum of 52.73% at pH = 9. In the range of pH = 4-9, with the increase of pH value, the removal efficiency of DOC gradually increased (see Fig. S2 (b), and when pH = 9, it reached the maximum (51.31%). Any further increase of the pH value would lead to the loss of effective components of the coagulant system and the possibility of colloidal restabilization, producing a decreased removal efficiency for DOC and turbidity.

In the MMOF-PIC coagulation, the zeta potential of a jar test sample gradually increased with the increase of MMOF-PIC under a fixed pH 9, as shown in Fig. S2 (c), which indicated that MMOF-PIC was a positively charged polymer. As a result, it could reduce the pH value of water after coagulation (see Fig. S2 (a)). Therefore, at a low pH value, the MMOF-PIC increased the positive zeta potential value. Generally, under a relatively high
dose and pH value, the hydrolysate Fe(OH)_3 of polyferric salts has a significant effect on the removal of pollutants through adsorption-bridging and the sweep-floc mechanism, while at low pH and dose, the hydrolysate of polyferric salts has a higher positive charge density; thus, the main mechanism for coagulation is charge neutralization, chelation or complexation of ferric salts with water organics (Edzwald and Tobiaszon, 1999; Komatsu et al., 2005; Hussain et al., 2013). Through a reduction of negative charge from the suspension, a maximum NOM removal was achieved within a zeta potential window between $-10\ \text{mV}$ and $+5\ \text{mV}$ (Matilainen et al., 2010). If the positive potential is too high, the electrostatic repulsion will lead to a deteriorated coagulation. Therefore, with excess coagulants at a lower pH, the higher positive potential value produced was not conducive to the removal of pollutants. The poorer coagulation at pH=4-6 would be attributed to the occurrence of the higher potential value. Thus, an appropriate dose was likely to bring a better coagulation. The MOF-PIC with a higher positive charge than PIC might require a smaller dose. At a higher pH value, the higher zeta potential value was reduced towards zero potential, which meant the adsorption-bridging between the organics and coagulant as well as sweep-floc became the predominate mechanisms for the adsorption of DOM. When the MMOF-PIC produced a lower zeta potential value than the PIC at higher pH, the MMOF-PIC were more active, which indicated that they were possibly adsorbing more negatively charged pollutants.

Even though we adjusted coagulant dose and the initial pH of the water, the DOC removal efficiency was always lower than 60%. The MMOF-PIC had a better range of application to water samples containing DOM fractions, making it easier to treat. Thus, we examined the effect of MMOF-PIC coagulation for six kinds of surface water. Details of water characteristics and the best results with an applicable PIC dose according to DOC removal are shown in Table S4. The results of turbidity, UV254 and DOC removal as well as influence of PIC dose on the removal of DOC at three DOC concentrations are shown in Fig. S3. Table S4 highlighted that the
turbidity of secondary effluent water, tributaries of the Xiangjiang River, and the upstream water of the Xiangjiang River were tested using Nephelometri testing units (NTUs) at 5.15 NTU, 7.52 NTU, and 8.28 NTU, respectively. Pond water and artificial lake water contained relatively higher DOC values, corresponding to 11.18 mg/L and 4.51 mg/L, respectively. However, pond and lake water also had lower SUVA values, indicating that they possibly contained more hydrophilic substances. At an approximate pH of 7.5, the results as shown in Fig. S3 indicated a better treatment of turbidity and DOC in pond and artificial lake water. With the dose of 10 mg/L to 26 mg/L, MMOF-PIC could treat pond water samples better than other water samples, and the turbidity of pond water after treatment was as low as 0.29 NTU. Low turbidity water needed lower dose (10 mg/L) to achieve the optimum removal efficiency, whereas a higher turbidity needed a higher dose (18 mg/L). Removal efficiencies were different for DOC and UV254. UV254 removal efficiency was less dependent on their initial value. For example, the treatment efficiency of a downstream river (UV254) at 0.03 cm$^{-1}$ was 43.33%, while for treatment of upstream water at 0.03 cm$^{-1}$ it was 55.17%. In addition, Xiangjiang River tributary included a lower UV254 value (0.06 cm$^{-1}$) but its treatment result was higher than that of pond water with a high UV254 value (0.08 cm$^{-1}$). The UV254 removal was possibly related to the source of water. The removal of DOC was different from the reduction in UV254 because high concentration DOC could be more easily treated. For example, the removal efficiency of pond water DOC at a concentration of 11.18 mg/L was up to 78.44%. Other DOC concentration effects were also examined as shown in Fig. 6d. With the increase of DOC concentration from 2.67 mg/L to 11.18 mg/L, the removal efficiencies of DOC in the coagulant dose range of 14 mg/L to 26 mg/L all increased.

3.6 EEMs characterization of DOM fractions
The results of this study indicated that MMOF-PIC coagulation for DOM was dependent on water characteristics. The results showed that in the coagulation of DOC, pond and artificial lake water were easier to treat, and coagulation focused on UV254 could be applied to a wider range of water sources. These differences may be related to variation in the nature of the DOM in the source waters. In this study, EEMs were used to analyze the differences in DOM components from different source waters and during the coagulation process.

As shown in Fig. 6, EEMs shows the component distribution and water treatment efficiency of six different water samples (downstream river water, secondary effluent water of WWTP, tributary water, upstream river water, pond water and artificial lake water) at optimum conditions. Fluorescence intensities of all water samples observed throughout the EEM data collection process were reduced after coagulation. MMOF-PIC has a good coagulation effect on DOC removal from pond and artificial lake water. In these waters, the DOM percentages were 25.00% –30.00% for I and II, 10.00% –15.00% for III, 20.00% –30.00% for IV, and less than 5.00%–7.00% for V. In other waters, the DOM percentages were 7.00% –23.00% for I, 20.00%– 25.00% for II, 19.00% –22.00% for III, 20.00%–30.00% for IV, and 10.00% –20.00% for V. As seen from the results, I and II had a similar proportion of DOM for pond water and artificial lake water, which was higher than I and II in the other water samples, with similar IV, and lower III and V. Thus pond water and artificial lake water had a similar composition. The DOC concentration also affected coagulation: Artificial lake water contained a lower DOC concentration; therefore, better coagulation occurred in pond water with a higher DOC concentration. The coagulation process for other waters was dependent on DOM’s composition and concentration. For example, for treatment of the downstream Xiangjiang River water and the pond water at the same pH (8.02), the coagulation of the former was far inferior to the coagulation for the latter. The results of coagulation for all water samples indicated that the removal efficiency of UV254 was different from that of DOC, which would be related to the composition of DOM components. All of them contained higher II and IV components. For the treatment of
DOM from pond and artificial lake water, the removal efficiencies of I, II, III, IV and V were 66.76%–66.98%, 41.67%–65.63%, 36.61%–39.23%, 58.27%–69.83%, and 47.41%–55.15%, respectively. However, for the treatment of other waters, the DOM removal efficiencies were 8.31%–36.84%, 11.16%–27.69%, 21.90%–43.18%, 11.55%–32.10%, and 35.36%–51.86%, respectively. The removal efficiencies of I, II and IV in pond water and artificial lake water were obviously higher than for the other waters, but the removal efficiencies of III and V in other waters were not always lower than the other associated waters such as for the tributary for the case of III and the upstream river water for the case of V.

Table S5 presents the correlation between DOM components and water treatment efficiency obtained by measuring the square correlation coefficients ($R^2$) between fluorescent components removal efficiency (I%, II%, III%, IV% and V%) denoted as FCR, the percentage proportion of the fluorescent component (%) in raw water denoted as FCPr and water treatment efficiency (DOC%, UV254%) denoted as WTE. The results show that FCR (I%, II%, IV%) produced a relatively good correlation between FCPr (I%, II%, III%) and DOC% as well as UV254%. The $R^2$ of FCR (I%) with DOC% and UV254% reached 0.61 and 0.60, and with FCPr (I%, II%, III% and V%), reached 0.92, 0.65, 0.76 and 0.91, respectively. The $R^2$ of FCR (II%) with DOC% and UV254% reached 0.88 and 0.92, respectively, and with FCPr (I%, II%, III% and V%) reached 0.42, 0.60, 0.93 and 0.50 respectively. The $R^2$ of FCR (IV%) with DOC% and UV254% reached 0.82 and 0.80, and with FCPr (I%, II%, III% and V%) reached 0.49, 0.53, 0.92 and 0.54, respectively. From the above results, the $R^2$ of FCR (II%, IV%, I%) with UV254% and DOC% decreased in turn, and the $R^2$ values of FCR (II%) with DOC% and UV254% were more than 0.86; thus, it was feasible to evaluate the water treatment efficiency using this FCR. The $R^2$ of FCR (II%) and FCPr (II%) was 0.60, and those of FCR (IV%) with FCPr (II% and V%) were 0.53 and 0.54.
respectively, suggesting that for treatment of DOM containing higher II and V proportions, it would achieve better coagulation. The $R^2$ values of FCR (II% and IV%) with FCPr (III%) showed a very high negative correlation with $R^2$ up to 0.93 and 0.92, respectively, indicating that the smaller the FCPr (III%) was, the better coagulation results. The $R^2$ values of FCR (II% and IV%) with FCPr (III%) also showed positive correlation values of FCR (I%) with UV254% and DOC % with $R^2$ up to 0.61 and 0.60, and with FCPr (I%) up to 0.91, and also gave a negative correlation of FCR (I% with V%) with $R^2$ up to 0.91. These results showed the higher FCPr (I%), the lower FCPr (V%), and better coagulation results. According to the above analysis, the coagulation effect of DOM might be better for those waters with low FCPr (V% and III%) as well as high FCPr (I%, II% and IV%); thus, II and IV would be the most important indicators for evaluating the coagulation results. Overall, the MMOFs doped PIC had a stronger affinity for proteins and soluble microbial metabolites.

3.7 XPS characterization of C/N-based components

The primary mechanisms of coagulation for DOM consist of charge neutralization, adsorption bridging and sweep-flocculation. The findings of this study demonstrated that nanoparticles were able to enhance them through chemical bonds such as $\pi-\pi$, covalent and hydrogen bond interaction. This was confirmed by measuring the XPS spectra of coagulant and flocs as shown in Fig. 7, corresponding to a statistical analysis of component distribution as shown in Table S6.

Fig. 7(a) and (b) showed that the composition of the coagulants and flocs was of carbon (C), nitrogen (N), oxygen (O), sulfur (S), zirconium (Zr), and iron (Fe). Original PIC and MMOF-PIC did not contain nitrogen, but their flocs had significant N 1s peaks, and MMOF-PIC produced an intensity higher than PIC as shown in Fig. 7(a-c). These results implied that improved removal occurred for N-containing compounds during
MMOF-PIC coagulation. In addition, PIC and MMOF-PIC produced different results in the removal of carbon-based compounds. Those MMOF nanoparticles as porous carbon-based polymers were introduced into PIC to increase C 1s peak intensity and peak position shifting, as demonstrated in Fig. 7(d); moreover, those results in flocs also occurred (see Fig. 7(e) and (f). A statistical analysis of area percentage of four components (O-C=O, C=O, aliphatic C-C, aromatic C=C) in flocs is listed in Table S6. MMOF-PIC produced a higher value in the level of aromatic C=C, which rose to 56.32%, but this also showed a slight reduction in the distribution levels of O-C=O, C=O, and aliphatic C-C. These results implied that MMOFs could help PIC to have a better coagulation for those aromatic C=C based compounds. The π-π bond has been identified as having an important role in adsorption for C=C bond-contained compounds onto the surface of those nanoparticles containing benzene rings (Chen et al., 2002; Chen and Mitra, 2008; Jiang, 2015a). This may explain the observation that the MMOF-PIC with benzene rings were most effective for removal of aromatic compounds-contained UV254.

Fig. 7

The distributions of three other components (aromatic/pyridine organic nitrogen, amide/peptide bond organic nitrogen and primary amine organic nitrogen) in flocs were different (see Fig. 7(g) and (h) and Table S6). The percentages of primary amine organic N and amide/peptide bond organic N increased with MMOF-PIC. Covalent bonds have a linking role between the functional groups in organic compounds and nanoparticles such as –COOH, –OH, –NH₂ (Pan et al., 2008; Jiang, 2015a). The –NH₂ or –COOH group in DOM possibly connected with –COOH, –OH and other functional groups of MMOFs thus enabling PIC to better remove the nitrogen compounds. In the presence of chemical groups such as –COOH, –OH, and –NH₂ in organic molecules or in nanoparticles, hydrogen bonding becomes an important adsorption force (Vermisoglou et al., 2007; Yang et al., 2008; Jiang, 2015a). For example, these chemical groups in organic molecules can be used as hydrogen
donors while the benzene rings on the surface of nanoparticles can be used as hydrogen acceptors (Yang et al., 2008; Jiang, 2015a). The chemical groups in MMOFs nanoparticles, such as –COOH and –OH, could be used as the hydrogen donors, while those included in benzene rings could also be used as hydrogen acceptors. They could form the hydrogen bonds between these chemical groups and others such as –COOH, –OH, –NH₂ and the benzene rings in DOM, thus enhancing the PIC coagulation.

These results indicated that the introduction of magnetic nanoparticles, MMOFs, into PIC could improve its mechanisms of coagulation for DOM through chemical bonding through π-π, covalent and hydrogen bond interactions. As a result, the aromatic C=C, primary amine organic N and amide/peptide bond organic N compounds can be better removed. A simple framework diagram can be used to describe coagulation mechanism of PIC in the presence of nanoparticles, is shown in Fig. S4.

4. CONCLUSIONS

The study showed that magnetic MOFs nanoparticles could help PIC improve coagulation for DOM, and played significant roles in: (1) improving the positive charge properties, thus enhancing charge neutralization of PIC; (2) enhancing the medium species distribution, which would be favored for improved aquatic DOM treatment; (3) enhancing UV254 treatment of the <30 kDa, compounds (aromatic C=C, N-containing (primary amine org-N, amide/peptide bond org-N), and for water containing higher content of microbial metabolites and protein-like materials; (4) the formation of π-π, covalent and hydrogen bond, resulting from the interaction between the magnetic nanoparticles and pollutants, possibly contributed to the enhancement of DOM adsorption. The potential of the future work on the selective modification of magnetic nanoparticles in coagulation systems for further removal of aquatic DOM was also highlighted.
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References


3-D fluorescence: characterization of natural organic matter in natural water and water purification systems. J.
Fluoresc. 27, 2069-2094.


coagulation for dissolved organic nitrogen using polymeric zinc-iron-phosphate coagulant. Water Res. 100,
201-210.


Zouboulis, A., Moussas, P., 2008. Polyferric silicate sulphate (PFSiS): Preparation, characterisation and
coagulation behaviour. Desalination 224, 307-316.

Zouboulis, A., Moussas, P., Vasilakou, F., 2008. Polyferric sulphate: preparation, characterisation and
Figure Caption list

Fig. 1. Transmission electron microscope (TEM) images are shown in (a) metal organic frameworks (MOFs), (b) modified nanoparticles (MNPs) and (c) magnetic metal organic frameworks (MMOFs). The scanning electron microscope (SEM) images are shown in (d) MOFs, (e) MNPs, (f) MMOFs, (g) a polyferric iron-based coagulant (PIC), (h) a MOF-PIC and (i) a MMOF-PIC.

Fig. 2. (a) Vibrating sample magnetometer (VSM) magnetization curves of magnetic nanoparticles, (b) X-ray photo spectrometer (XPS) results of flocs based on counts per second and binding energy (eV), and (c) VSM curves based on the $R_{m\text{MMOF}/m\text{Fe}}$ results of floc tests in MMOF-PIC coagulation. The $R_{m\text{MMOF}/m\text{Fe}}$ is defined as the mass ratio of MMOFs to Fe in the MMOF-PIC.

Fig. 3 Influence of MMOFs nanoparticles in species distributions (%) in PIC and their zeta potential values (mV). (a) species distributions (%) in PIC and nano-PIC, (b) species distributions (%) in PIC and nano-PIC with varying $R_{m\text{MNPs}/m\text{MOFs}}$, (c) species distributions (%) in PIC and nano-PIC with varying $R_{m\text{MMOFs}/m\text{Fe}}$, (d) zeta potential values with varying pH values at a coagulant dose of 18 mg/L, and (e) effect of pH on zeta potential of jar test sample and the zeta potential value of raw water at $-5.73$ mV.

Fig. 4 Effect of MMOFs nanoparticles with varying $R_{m\text{MNPs}/m\text{MOFs}}$ on PIC coagulation for (a) turbidity (b) DOC and (c) UV254. Water samples were collected from artificial lake with a pH of around 8.4, a turbidity at 14.78 NTU, a UV254 at 0.05 cm$^{-1}$, and a DOC at 5.40 mg/L.

Fig. 5 Removal of molecular weight fractions with nano-PIC: (a) UV254 removal, and (b) DOC removal. Water samples were collected from an artificial lake with a pH of around 8.29, a turbidity at 13.43 NTU, a UV254 at 0.056 cm$^{-1}$, and DOC at 4.56 mg/L. The nano-PIC dose used in this test was 22 mg/L. Removal rates represent the removed percentages, while those (>30 kDa, 30-10 kDa, 10-3 kDa and < 3kDa) represent the residual concentration percentages in samples.
Fig. 6 Variations of DOM fluorescence fractions before and after coagulation divided into EEM data, fraction distribution percentages (%), and fractions removed percentages (%). The Roman numeral colors represent five categories or EEM data: I. aromatic protein-like materials, II. aromatic protein-like materials, III. fulvic acid-like materials, IV. soluble microbial metabolites, and V. humic substance-like materials.

Fig. 7 XPS survey scans, C 1s and N 1s of flocs, PIC and MMOF-PIC: (a) survey scans of PIC and flocs, (b) survey scans of MMOF-PIC and flocs, (c) N 1s scans of flocs, (d) C 1s scans of PIC and MMOF-PIC, (e) C 1s scan of PIC-producing flocs, (f) C 1s scan of (MMOF-PIC)-producing flocs, (g) N 1s scan of PIC-producing flocs, and (h) N 1s scan of (MMOF-PIC)-producing flocs.
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MMOFs nanoparticles were prepared through the hydrothermal method: 4.6 g of MNPs, 2.3 g of ZrCl₄ and 4.3 g of BTEC were ultrasonically dispersed into 50.4 mL of ultra-pure water in a three neck flask using a KQ5200DB ultrasonic bath (Kunshan Ultrasonic Instrument Co., Kunshan, China) at room temperature for 30 mins until a homogeneous solution was obtained. Subsequently, the solution was treated by reflux heating under nitrogen for 24 hours at 100 °C. When it was cooled to room temperature, black gel was washed repeatedly with ultra-pure water for removal of the excess acids, and redispersed in ultra-pure water for reflux heating of 16 hours at 100 °C. Then, the product was centrifuged and washed three times with ethanol and water. After vacuum drying for 24 hours at 70 °C, the MMOF was obtained.
**Table S1** BOX-Behnken experimental protocol and results

<table>
<thead>
<tr>
<th>No.</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$X_3$</th>
<th>DOC (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.3</td>
<td>0.1</td>
<td>49.69</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.3</td>
<td>0.04</td>
<td>38.96</td>
</tr>
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<td>1</td>
<td>0.4</td>
<td>0.04</td>
<td>54.33</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
<td>47.63</td>
</tr>
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<td>1</td>
<td>0.3</td>
<td>0.1</td>
<td>49.69</td>
</tr>
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<td>0.3</td>
<td>0.04</td>
<td>47.11</td>
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<td>1</td>
<td>0.3</td>
<td>0.1</td>
<td>49.69</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>0.3</td>
<td>0.16</td>
<td>38.98</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>0.4</td>
<td>0.1</td>
<td>44.51</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.3</td>
<td>0.16</td>
<td>56</td>
</tr>
<tr>
<td>11</td>
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<td>0.3</td>
<td>0.1</td>
<td>49.69</td>
</tr>
<tr>
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<td>0.16</td>
<td>51.29</td>
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<td>0.3</td>
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<td>49.69</td>
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<td>45.77</td>
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<td>0.1</td>
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<tr>
<td>16</td>
<td>2</td>
<td>0.2</td>
<td>0.1</td>
<td>59.55</td>
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Table S2 Analysis of ANOVA for response surface quadratic model

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<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
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</thead>
<tbody>
<tr>
<td>Model</td>
<td>403.13</td>
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<td>44.79</td>
<td>4.66</td>
<td>0.0274</td>
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<td>$X_1$</td>
<td>190.71</td>
<td>1</td>
<td>190.71</td>
<td>19.83</td>
<td>0.0030</td>
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<td>$X_2$</td>
<td>67.00</td>
<td>1</td>
<td>67.00</td>
<td>6.97</td>
<td>0.0334</td>
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<td>$X_3$</td>
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<td>5.82</td>
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<td>$X_1X_2$</td>
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<td>42.57</td>
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<td>$X_1X_3$</td>
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<td>0.1203</td>
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<tr>
<td>$X_2X_3$</td>
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<td>1</td>
<td>33.93</td>
<td>3.53</td>
<td>0.1024</td>
</tr>
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<td>$X_1^2$</td>
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<td>80.96</td>
<td>8.42</td>
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<td>12.91</td>
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<td>0.3410</td>
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<td>Residual</td>
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<td>Lack of Fit</td>
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<td>22.44</td>
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<td>Pure Error</td>
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<td>4</td>
<td>0.000</td>
<td></td>
<td></td>
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<td>Cor Total</td>
<td>470.44</td>
<td>16</td>
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</table>
### Table S3 Estimate of coefficient factors

<table>
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<tr>
<th>Coefficient Factor</th>
<th>Standard Estimate</th>
<th>95% CI df</th>
<th>95% CI Error</th>
<th>Low</th>
<th>High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>51.88</td>
<td>1</td>
<td>1.54</td>
<td>48.24</td>
<td>55.52</td>
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<tr>
<td>$X_1$</td>
<td>4.88</td>
<td>1</td>
<td>1.1</td>
<td>2.29</td>
<td>7.47</td>
<td>1.06</td>
</tr>
<tr>
<td>$X_2$</td>
<td>-2.97</td>
<td>1</td>
<td>1.12</td>
<td>-5.63</td>
<td>-0.31</td>
<td>1.05</td>
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<tr>
<td>$X_3$</td>
<td>0.87</td>
<td>1</td>
<td>1.12</td>
<td>-1.78</td>
<td>3.53</td>
<td>1.05</td>
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<tr>
<td>$X_1 \times X_2$</td>
<td>-3.18</td>
<td>1</td>
<td>1.51</td>
<td>-6.74</td>
<td>0.39</td>
<td>1.05</td>
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<tr>
<td>$X_1 \times X_3$</td>
<td>2.67</td>
<td>1</td>
<td>1.51</td>
<td>-0.9</td>
<td>6.24</td>
<td>1.05</td>
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<tr>
<td>$X_2 \times X_3$</td>
<td>-2.91</td>
<td>1</td>
<td>1.55</td>
<td>-6.58</td>
<td>0.75</td>
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<tr>
<td>$X_1^2$</td>
<td>-5.08</td>
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<td>-9.21</td>
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<td>$X_2^2$</td>
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<td>1.51</td>
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<td>$X_3^2$</td>
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<td>1.51</td>
<td>-5.12</td>
<td>2.03</td>
<td>1.01</td>
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</table>

Note: According to these results, the removal efficiency of DOC can be expressed by $X_1$, $X_2$ and $X_3$ as follows:

$$\text{DOC removed (\%) = 51.88 + 4.88X_1 + 2.97X_2 + 0.87X_1X_3 + 2.67X_1X_3 + 2.91X_2X_3 - 5.08X_1^2 + 1.75X_2^2 - 1.54X_3^2.}$$
<table>
<thead>
<tr>
<th>No.</th>
<th>Water samples</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>UV254 (cm⁻¹)</th>
<th>DOC (mg/L)</th>
<th>SUVA (m⁻¹mg⁻¹L)</th>
<th>UV25 (%)</th>
<th>DOC (%)</th>
<th>Residual turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>River downstream</td>
<td>8.0</td>
<td>15.73</td>
<td>0.03</td>
<td>1.60</td>
<td>1.9</td>
<td>43.33</td>
<td>25.50</td>
<td>1.34</td>
</tr>
<tr>
<td>2</td>
<td>Effluent from WWTP</td>
<td>7.3</td>
<td>5.15</td>
<td>0.05</td>
<td>2.42</td>
<td>2.1</td>
<td>53.19</td>
<td>29.46</td>
<td>1.34</td>
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<tr>
<td>3</td>
<td>Tributary water</td>
<td>7.4</td>
<td>7.52</td>
<td>0.06</td>
<td>2.91</td>
<td>2.1</td>
<td>53.13</td>
<td>25.62</td>
<td>1.14</td>
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<tr>
<td>4</td>
<td>River upstream water</td>
<td>7.8</td>
<td>8.28</td>
<td>0.03</td>
<td>1.70</td>
<td>1.8</td>
<td>55.17</td>
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<td>0.73</td>
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<td>Pond water</td>
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<td>18.35</td>
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<td>11.18</td>
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<td>68.29</td>
<td>78.44</td>
<td>0.29</td>
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<td>6</td>
<td>Artificial lake water</td>
<td>7.3</td>
<td>13.92</td>
<td>0.04</td>
<td>4.51</td>
<td>0.9</td>
<td>57.89</td>
<td>42.50</td>
<td>0.54</td>
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</table>
Table S5 Correlation coefficients among FCR (%), FCPr (%) and WTE (%)

<table>
<thead>
<tr>
<th>FCR (%)</th>
<th>FCP (%)</th>
<th>WTE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I%</td>
<td>II%</td>
</tr>
<tr>
<td>I%</td>
<td>0.92</td>
<td>0.65</td>
</tr>
<tr>
<td>II%</td>
<td>0.42</td>
<td>0.60</td>
</tr>
<tr>
<td>III%</td>
<td>0.03 *</td>
<td>0.05 *</td>
</tr>
<tr>
<td>IV%</td>
<td>0.49</td>
<td>0.53</td>
</tr>
<tr>
<td>V%</td>
<td>0.06</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Note: * indicates the negative correlation. FCR (%) represents fluorescent components removal efficiencies (I%, II%, III%, IV% and V%); FCPr (%) represents fluorescent component percentage (%) in raw water; WTE stands for water treatment efficiency (DOC%, UV254%).
### Table S6 C 1s and N 1s scans of floc samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>Peak position</th>
<th>Area</th>
<th>Percentage (%)</th>
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<tbody>
<tr>
<td>C 1s scan of PIC-producing flocs</td>
<td>O-C=O</td>
<td>288.08</td>
<td>11400.32</td>
<td>16.00</td>
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<tr>
<td></td>
<td>C=O</td>
<td>286.22</td>
<td>8204.10</td>
<td>11.51</td>
</tr>
<tr>
<td></td>
<td>Aliphatic C-C</td>
<td>285.35</td>
<td>26636.47</td>
<td>37.37</td>
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<tr>
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<td>Aromatic C=C</td>
<td>284.56</td>
<td>25028.20</td>
<td>35.12</td>
</tr>
<tr>
<td>C 1s scan of (MMOF-PIC)-producing flocs</td>
<td>O-C=O</td>
<td>288.27</td>
<td>7996.52</td>
<td>11.56</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>287.19</td>
<td>5775.29</td>
<td>8.35</td>
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<td>Aliphatic C-C</td>
<td>286.12</td>
<td>16432.05</td>
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<td>Aromatic C=C</td>
<td>284.62</td>
<td>38944.28</td>
<td>56.32</td>
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<tr>
<td>N 1s scan of PIC-producing flocs</td>
<td>Primary amine org-N</td>
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<td>305.09</td>
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<td>399.93</td>
<td>2650.10</td>
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<td>Aromatic/pyridinic org-N</td>
<td>397.94</td>
<td>211.50</td>
<td>3.49</td>
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</table>
Fig. S1 MMOFs-PIC dosage influence in coagulation efficiencies. Water samples were collected from artificial lake with pH around 8.42, turbidity at 13.43 NTU, a UV254 at 0.055 cm$^{-1}$ and DOC at 3.52 mg/L.
Fig. S2 (a) pH effect on turbidity removal, (b) pH effect on UV254 and DOC removal, and (c) dosage effect on zeta potential value. Water sample was collected from artificial lake with pH around 8.4, a turbidity at 12.22 NTU, a UV254 at 0.055 cm$^{-1}$ and DOC at 3.6 mg/L. The zeta potential value of raw water was $-5.73$ mV.
Fig. S3 MMOF-PIC dose effects on removal of (a) turbidity, (b) UV254, and (c) DOC, with (d) showing the initial DOC concentration influence on DOC removal (%). Water samples were collected from six locations.
Fig. S4 A simple scheme for MMOF-enhanced PIC coagulation for DOM