

# Preparation, characterization and coagulation behaviour of polyferric magnesium silicate (PFMSi) coagulant

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## ABSTRACT

A composite coagulant polyferric magnesium silicate (PFMSi) was synthesized by co-polymerization. The structure and morphology of PFMSi were characterized by X-ray diffraction, Fourier transform infrared spectra and scanning electron microscope microphotographs; meanwhile, the coagulation efficiency was evaluated under different ratios of Fe/Si, Mg/Si, basicity ([OH]/[M] ratio), and dosage. The results suggested that the PFMSi coagulant shows an amorphous phase structure, and new chemical compounds had been formed; simultaneously, the different preparation conditions had major effects on coagulation performance. Additionally, the raw water collected from Pearl River was used as a treated water sample to verify the coagulation efficiency of PFMSi. Overall, it is suggested that PFMSi is an efficient coagulant in the removal of turbidity, UV<sub>254</sub> and total organic carbon, and it shows a markedly better coagulation performance than polymeric aluminium and non-modified coagulant. The study of coagulation kinetics and zeta potential showed that adsorption-bridging was the main mechanism for the introduction of silicon.

**Key words** | adsorption-bridging, coagulation performance, efficiency, polyferric magnesium silicate

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## INTRODUCTION

Coagulation process plays an important role in water or wastewater treatment facilities (Moussas & Zouboulis 2008). When coagulant is added to water, the suspended solids and colloidal particles undergo a process of destabilization, collision, aggregation, and sedimentation, and are finally removed (Jiang & Lloyd 2002). More importantly, part of the natural organic matter, even some toxic and hazardous pollutants, can be removed (Cheng & Chi 2002; Cheng *et al.* 2008; Mikola *et al.* 2013; Yang *et al.* 2013).

The coagulants could be classified into inorganic and organic coagulants (Sun *et al.* 2012), and the former is more used in treatment facilities. Nowadays, the major types of inorganic coagulants are the metal salts. The common coagulants of metal salts are based on aluminium and iron, i.e., AlCl<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeCl<sub>3</sub> and FeSO<sub>4</sub>, etc., which can be hydrolyzed in water to form positively charged irons and complexes. The inorganic polymer coagulants such as polyferric sulphate (PFS) and polyaluminum chloride (PAC) are pre-hydrolyzed coagulants, their coagulant performance being improved by the OH bridges and large number of inorganic macromolecular compounds with a high positive charge. However, given the unsatisfactory

humic substances removal efficiency and the residual color for conventional coagulants, the composite coagulant has become the research focus in recent years.

The composite coagulant is prepared by combining a metal or inorganic ion, and the aim is to overcome the problems of the individual coagulants, such as small flocs, the neurotoxic effects associated with high residual Al concentration and the high residual color associated with high residual Fe concentration, etc. Previous study also confirmed that flocculating activity and floc properties are significantly improved by introducing various ions in PFS to produce a new type of composite coagulant (Sun *et al.* 2010; Zhu *et al.* 2011).

The iron-based composite coagulants possess the advantages of non-toxic, larger flocs and superior coagulation performance (Jiang & Graham 1998). On the other hand, magnesium salts are regarded as an efficient class of coagulant in the removal of color. Additionally, a number of researchers have revealed that enhanced removal of impurities or pollutants has been observed in the presence of magnesium. For instance, a good coagulation performance could be achieved if enough magnesium ions are

present in the system of lime treatment (Liao & Randtke 1986; Folkman & Wachs 1973). More importantly, the magnesium can be removed from the precipitated sludge and recycled through the process (Gao *et al.* 2007), indicating a great reduction in chemical costs.

Moreover inorganic polymeric coagulants, which possess the advantage of higher efficiency than the conventional coagulants, but still much lower efficiency compared to organic polymeric coagulants, have started to be used in treatment facilities (Tang & Shi 2002). As another type of inorganic polymer coagulant, the polysilicate complex coagulant based on polysilicic acid (PS) and metal salts has been developed since the 1990s (Hasegawa *et al.* 1991). This is a complex of a positively charged metal coagulant and a negatively charged PS flocculant (Fu *et al.* 2009). The combining of PS with metal ions can increase the molecular weight of the coagulants and thereby, promote the aggregation capacity. On the other hand, the amount of residual metal ions is greatly reduced. (Ohno *et al.* 2004; Fu *et al.* 2006). There are two conventional methods to prepare metal-polysilicate complex coagulants, i.e., co-polymerization and composite-polymerization (Li *et al.* 2013a, 2013b). The former, by hydrolyzing after mixing, is relatively more simple and maneuverable than the latter by mixing after hydroxylation (Xu *et al.* 2009). Moreover, the coagulant prepared by the first method is more effective. For example, the polyferric silicate sulphate prepared by co-polymerization exhibited better performance in removal of turbidity,  $UV_{254}$  and phosphate than the composite-polymerization ones (Moussas & Zouboulis 2008). Therefore, the co-polymerization method was selected to prepare the coagulant. Although there are a number of researches focusing on using metal salts and PS to prepare the coagulants, the combination of magnesium, iron and PS is really rare, there has been no report of the synthesis of composite coagulant polyferric magnesium silicate (PFMSi) by co-polymerization.

In this paper, a relatively novel coagulant, PFMSi, was prepared by the method of co-polymerization. In order to investigate the coagulation mechanism, the characterization of the products was studied. The structure and morphology analysis were achieved by obtaining X-ray diffraction (XRD),

Fourier transform infrared (FT-IR) spectra and scanning electron microscopy (SEM) microphotographs. Moreover, the destabilization ability of the coagulants and the coagulation kinetics were evaluated by the zeta potential values and the ratio R curves respectively. Finally, coagulation experiments were carried out to determine the effects of molar ratios of Fe/Si, Mg/Si,  $[OH]/[M]$  and coagulant dosage on the coagulation performance in terms of removal of turbidity (NTU),  $UV_{254}$  ( $cm^{-1}$ ) and total organic carbon (TOC) (mg/L). Meanwhile, the conventional polymerized and non-polymerized coagulants were also used to make a comparison. For the aforementioned indexes, 1 NTU is defined as 1 mg  $SiO_2$  in 1 liter water,  $UV_{254}$  represents the absorbance of some organic matter in water irradiated by ultra violet with A wavelength of 254 nm, TOC can be defined as the content of total carbon of resolvable and suspended organic matter in water.

## MATERIALS AND METHODS

All reagents, i.e., concentrated sulfuric acid (98 wt%),  $FeSO_4 \cdot 7H_2O$ ,  $MgSO_4 \cdot 7H_2O$ ,  $NaClO_3$ ,  $NaHCO_3$ ,  $NaOH$ ,  $Fe_2(SO_4)_3$ , polymeric aluminium (PAC) and Ferron<sup>TM</sup> were analytically pure chemicals except for the water glass (industrial grade,  $\omega(SiO_2) = 26\%$ ,  $\rho = (1.36-1.41) \times 10^3$  kg/m<sup>3</sup>, modulus = 3.1-3.4). Deionized water with conductivity lower than 0.5  $\mu S/cm$  was used to prepare all the solutions.

The raw water used in this study was collected from the Pearl River in Guangzhou. Table 1 summarizes the physico-chemical parameters of the raw water and the water treated by PFMSi.

### Preparation of PFMSi

With rapid stirring using an electric stirring apparatus, water glass diluted with deionized water was introduced into sulfuric acid ( $H_2SO_4$ , 20 wt%), then the fresh PS was obtained after 1 h of polymerization.  $FeSO_4 \cdot 7H_2O$  and  $MgSO_4 \cdot 7H_2O$  were firstly dissolved in deionized water to obtain sulfate solution, and in order to keep a strong acid condition, sulfuric acid ( $H_2SO_4$ , 98 wt%) was added. Then the sulfate solution was mixed with fresh PS, which was stirred with

**Table 1** | Characteristics of raw water and the water treated by PFMSi

	Turbidity (NTU)	Temperature (°C)	N-NH <sub>3</sub> (mg/L)	TOC (mg/L)	$UV_{254}$ ( $cm^{-1}$ )	Zeta-potential (mv)	pH
Raw water	42.5	22.5	0.63	5.05	0.045	-17.8	7.58
Treated water	0.51	-	-	2.93	0.018	-8.3 to -6.2	7.04-7.27

an electric stirrer, and a small amount of NaClO<sub>3</sub> was added subsequently to ensure that all the Fe<sup>2+</sup> was oxidized to Fe<sup>3+</sup>. Finally, a certain amount of NaHCO<sub>3</sub> solution was added to increase the degree of polymerization, and the product of PFMSi was obtained after 3 h of stirring.

To obtain a more efficient coagulant, the factors, Fe/Si (the molar ratio of Fe and Si), Mg/Si (the molar ratio of Mg and silicon) and OH/M (the basicity) were studied.

### Characterization of PFMSi coagulant

The liquid products were freeze-dried for 48 h by a vacuum freeze drier (Virtis, USA) and then placed into a desiccator to cool for another 2 h. The solid PFMSi was ground using a mortar and pestle for further characterization studies.

The crystal characteristics of solid PFMSi were analyzed by Empyrean X-ray diffractometer (PANalytical B.V., The Netherlands) with Cu K radiation in the range of 5–65 ° 2θ at a scan rate of 1 °/min. The surface morphology of the coagulants was observed and analyzed by SEM microphotographs using a Merlin scanning microscope (Zeiss Company, Germany). Samples of PFMSi were characterized by FT-IR spectroscopy for the determination of structure characteristics using a CCR-1 Spectrophotometer (Thermo-Nicolet, USA) and the spectra were recorded in the range of 4,000–400 cm<sup>-1</sup>.

In this study, Fe–Ferron™ complexation timed spectrophotometry was used to measure the Fe(III) species distribution with a UV-5800 spectrophotometer (MET-TASH, China); the selective wavelength is 600 nm. In general, the Fe(III) species that reacted rapidly with Ferron™ was considered to be Fe(III) monomeric species (Fe<sub>a</sub>), over the next 2 h and later, the reacted Fe(III) species were considered to be polymeric species (Fe<sub>b</sub>) as well as colloidal and precipitated species (Fe<sub>c</sub>) respectively (Song *et al.* 1997).

### Coagulation experiments

The PFMS coagulant used was diluted with deionized water to a concentration of 2 g/L, as Fe.

The jar test was carried out in 1.0 L Plexiglas® beakers using a six paddle stirrer (ZR4–6, China). The same batch of raw water was dosed with PFMSi coagulants of 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, 10 mg/L, 12 mg/L, as Fe, respectively. The experimental conditions were the following: the fast stirring time was set to 2 min at a speed of 200 rpm to allow the particles to be destabilized. At this point, a sample was collected for zeta potential measurement. Then a

flocculation period (10 min at 50 rpm) and final sedimentation (30 min) followed. After sedimentation, a water sample was taken 3 cm below the surface for further analysis.

Zeta potential measurements were performed on a Nano-zs90 analyzer (Malvern, UK). Turbidity was measured with a 2100Q turbidimeter (HACH Company, USA). UV<sub>254</sub> was measured using a standard method by a UV-5800 spectrophotometer (METTASH, China) at a wavelength of 254 nm with a 1 cm quartz cell. The water samples were first filtered through a 0.45 μm membrane filter to remove turbidity to avoid interfering with the measurement, and the TOC measurement was carried out using a Liqui TOC analyzer (Elementar, Germany). Besides, the pH value was measured with a PHS-3C meter (Rex Company, China).

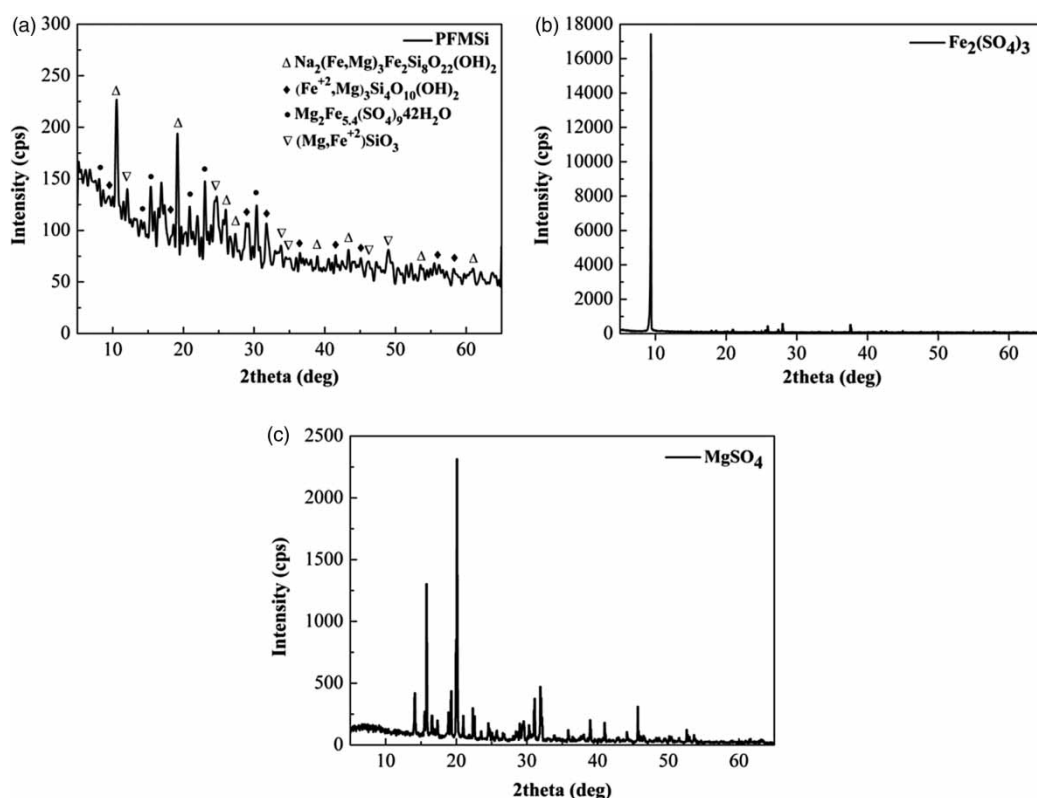
### Coagulation kinetics

An intelligent photometric dispersion analyzer (i-PDA100, EcoNovel Company, South Korea) was used to monitor the kinetics of coagulation and the extent of aggregation. The i-PDA instrument measures the ratio R, also called flocculation index (FI), defined by the dimensionless value of  $R = \sqrt{(nL/A)} * C$ , where n is the particle number concentration, L is the optical path length of the fluorescent cell, A is the effective cross area of the light beam and C is the scattering cross section of the particles, which is directly related to the mean concentration and size of flocs. In that case, the R values can be effectively utilized to describe the aggregation process of the particles. In addition, the coagulation process consisted of 2 minutes of fast stirring (200 rpm) and 10 minutes of slow stirring (50 rpm) for floc formation.

## RESULTS AND DISCUSSION

### Structure and morphological analysis

Figure 1 shows the XRD patterns of solid PFMSi, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and MgSO<sub>4</sub> samples. It can be seen that the diffractive peaks of the composite coagulant (PFMSi) are different from Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and MgSO<sub>4</sub>; no standard crystals, such as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and MgSO<sub>4</sub>, can be observed, which is consistent with similar studies (Moussas & Zouboulis 2008; Fu *et al.* 2009). And some kinds of compounds containing Fe, Mg and Si are found in the XRD pattern, such as Na<sub>2</sub>(Fe,Mg)<sub>3</sub>Fe<sub>2</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>, (Fe<sup>+2</sup>,Mg)<sub>3</sub>Si<sub>4</sub>O<sub>19</sub>(OH)<sub>2</sub>, Mg<sub>2</sub>Fe<sub>5,4</sub>(SO<sub>4</sub>)<sub>9</sub>42H<sub>2</sub>O and (Mg,Fe<sup>+2</sup>)SiO<sub>3</sub>. Therefore, it can be concluded that such materials as Fe<sup>3+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and PS have been incorporated with the polymerization,



**Figure 1** | X-ray diffractometer scan of PFMSi (a),  $\text{Fe}_2(\text{SO}_4)_3$  (b) and  $\text{MgSO}_4$  (c).

i.e., PFMSi is a polymer compound of Si, Fe, Mg and many other ions, instead of a simple mixture of raw materials (Li *et al.* 2013a, 2013b).

Figure 2 presents SEM micro-photographs of PFMSi,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$ . As presented in Figure 2(a), PFMSi exhibits a corrugated morphology, indicating that an amorphous phase exists, which corresponds to the result of XRD. However, an obvious crystal structure can be observed in the SEM micro-photographs of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$ , which are shown in Figure 2(b) and 2(c). Additionally, for the PFMSi coagulant, it is noticed that the protuberant edges are situated unevenly on the surface and create a series of pleated ditches of different width and depth. In view of that, the surface energy and absorption area of the coagulants are increased, leading to better performance. In addition, the energy spectrum graph of the PFMSi coagulant is shown in Figure 3; it can be observed that the PFMSi coagulant contains the elements of Fe, Mg and Si, which are the main components of the PFMSi coagulant.

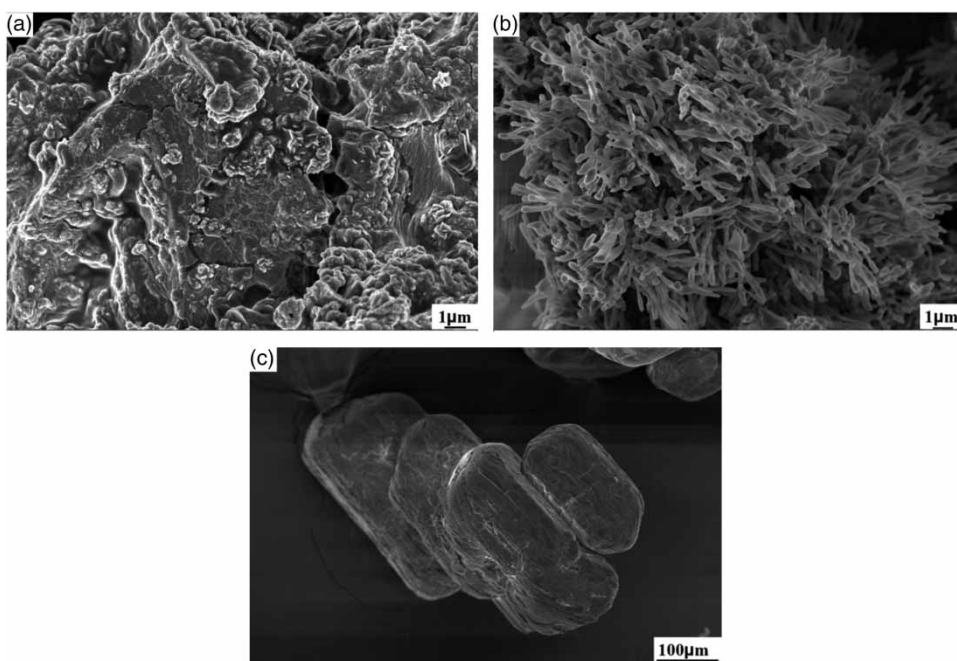
The FT-IR spectroscopy plays a vital role in the study of materials' chemical properties, components, stereo structure and so on. Figure 4 shows the infra-red absorption spectra of PFMSi,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$ . The absorption peak at

$3,383\text{ cm}^{-1}$  (for PFMSi) appears by the stretching vibration of hydroxyl groups, which exist in a free state or contiguous with metal ions, indicating that the reactions between metal ions and PS are carried out. Moreover, the absorption peak at  $1,631\text{ cm}^{-1}$  (for PFMSi) is a variable-angle vibration of absorbed water, coordinated water and crystal water. In particular, the peaks at  $987$ ,  $596$  and  $460\text{ cm}^{-1}$  (for PFMSi) are related to the Si-O-Fe, Si-O-Si and Fe-O bonds, respectively. Additionally, the peak at around  $515\text{ cm}^{-1}$  (for PFMSi) might be assigned to the Si-OH-Mg and Mg-O bonds stretching and bending vibrations (Wei *et al.* 2015). Overall, the results of FT-IR analysis indicate that new chemical species were formed.

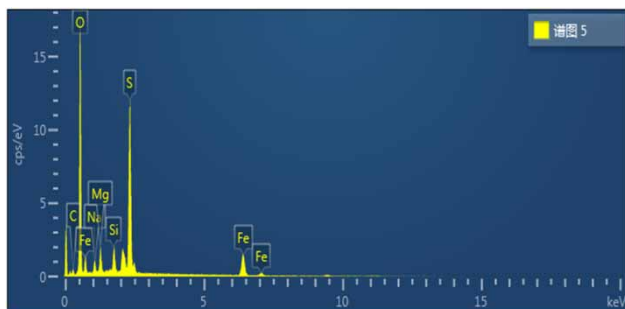
### Fe species distribution

The effect of different basicity on the Fe species distribution is shown in Figure 5. It shows that with the increase in basicity, the monomeric species ( $\text{Fe}_a$ ) content decreases, while the colloidal and precipitated species ( $\text{Fe}_c$ ) content increases. The highest Fe(III) polymeric species ( $\text{Fe}_b$ ) content is achieved at a basicity of 0.4. The introduction of a base in the synthesis process leads to formation of a series of polymeric species, colloidal and precipitated species, which correspond to the





**Figure 2** | SEM micro-photographs of PFMSi (a),  $\text{Fe}_2(\text{SO}_4)_3$  (b) and  $\text{MgSO}_4$  (c).



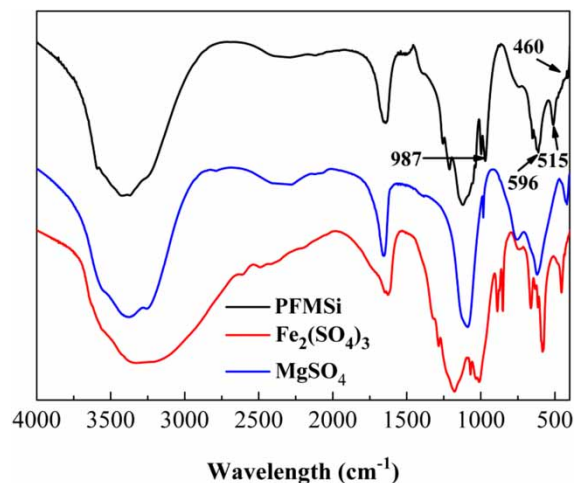
**Figure 3** | Energy spectrum graphs of PFMSi.

transformation of Fe(III) species. In general,  $\text{Fe}_b$  (Fe(III) polymeric species) is considered to be the most effective species in the coagulation process (Zouboulis & Moussas 2007). A certain amount of basicity in the synthesis process could improve the degree of polymerization, and enhance the coagulation performance.

### Coagulation performance of PFMSi

#### Effects of PFMSi dosage and Fe/Si molar ratio

In order to investigate the effects of PFMSi dosage and Fe/Si molar ratio on the coagulant performance, a series of coagulation experiments were conducted at the pre-determined factor level. The parameters, residual turbidity and removal



**Figure 4** | FT-IR spectra of PFMSi,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$ .

of humic acid (expressed as  $\text{UV}_{254}$  absorbance), are measured to evaluate the coagulation efficiency of PFMSi in treating the raw water.

The coagulation performance of PFMSi coagulants with different Fe/Si molar ratios are presented in Figure 6; the change of zeta potential is also studied simultaneously. It is shown that with the increasing coagulant dosage, the removal efficiencies of turbidity and  $\text{UV}_{254}$  increase accordingly. Figure 6(a) shows that the turbidity changes slightly with the dosage of 8–10 mg/L, which means a

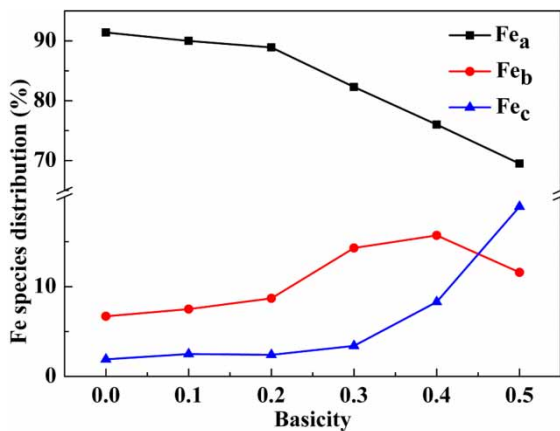


Figure 5 | Fe species distribution with different basicity.

re-stabilization state of coagulation. Meanwhile, the coagulation efficiency decreases slightly with the increasing molar ratio of Fe/Si. The reason might be the fact that the higher concentration of silicon enhances the polymerization degree, leading to the formation of large polymers with high molecular weight, which increases the surface and facilitates the adsorption of organic matter (Moussas & Zouboulis 2008). Therefore, the function of adsorption-bridging is improved, leading to better coagulation performance.

It is known that the charge neutralization is generally considered to be the coagulation mechanism of hydrolyzing metal salts; however, Figure 6(c) shows that the optimal values of turbidity removal efficiencies are not always close to the isoelectric point, indicating a function of adsorption-bridging (Sun *et al.* 2010). Additionally, the zeta potential exhibits a rising trend with increasing Fe/Si molar ratio and coagulant dosage. This can be attributed to the fact that the higher Fe/Si molar ratio causes the result of stronger ionic strength, which enhances the function of charge-neutralization, leading to higher zeta potential values.

### Effects of PFMSi dosage and Mg/Si molar ratio

Figure 7 shows the coagulation performance of PFMSi with different Mg/Si molar ratios. As is seen from Figure 7(a) and 7(b), they exhibits similar trends to that of Fe/Si, the removal efficiencies of turbidity, UV<sub>254</sub> and zeta potential increase with the increasing coagulant dosage, whereas the removal efficiency of UV<sub>254</sub> decreases slightly with the increasing molar ratio of Mg/Si.

However, differently from PFMSi with various Fe/Si molar ratios except for 2 mg/L PFMSi, the removal efficiency of turbidity exhibits no significant difference with the increasing ratio of Mg/Si, while the removal of UV<sub>254</sub>

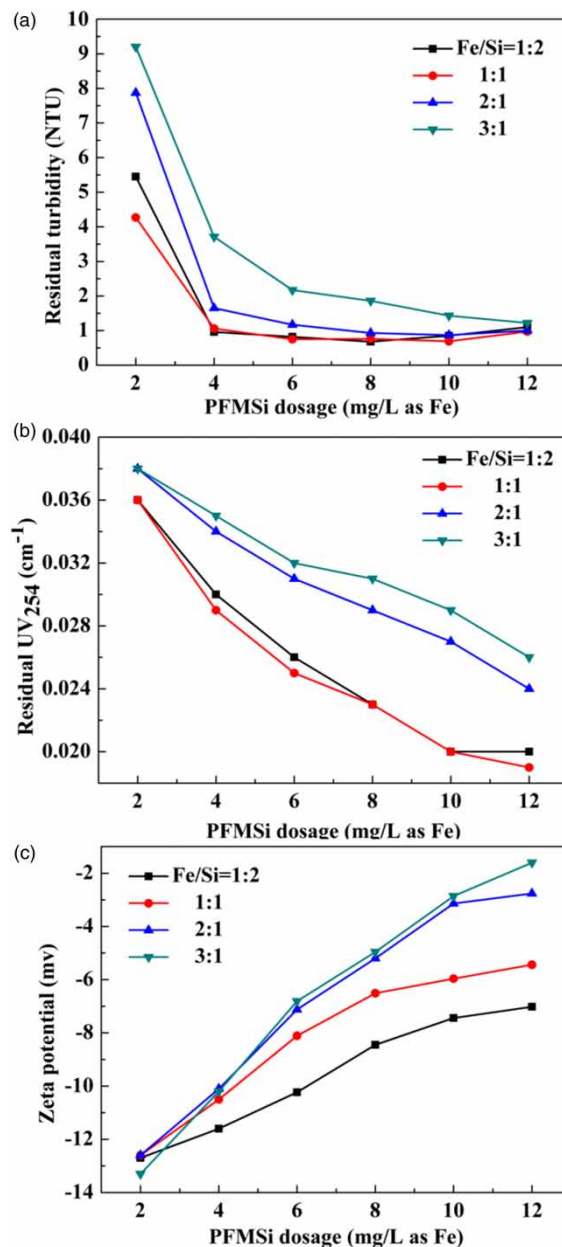
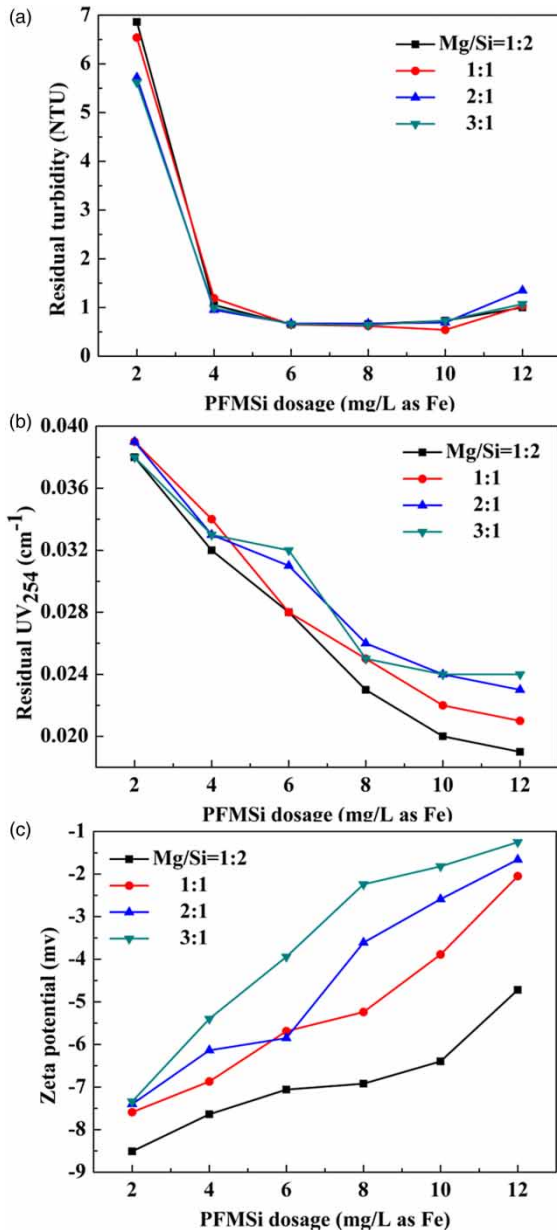


Figure 6 | The change of turbidity, UV<sub>254</sub> and zeta potential of raw water treated by PFMSi with different Fe/Si molar ratio.

presents a similar trend to that of the Fe/Si molar ratio. The reason might be that the magnesium ions and hydrolysis products of PFMSi possess the strong ability to adsorb suspended solids and colloidal particles, which reflects the high removal rate of turbidity at low dosage.

It is worth mentioning that in spite of the higher zeta potential values due to the higher molar ratio of Fe/Si or Mg/Si, the removal efficiencies of turbidity, UV<sub>254</sub> decrease slightly with the increasing Mg/Si molar ratio, further confirming that the introduction of Fe or Mg could improve



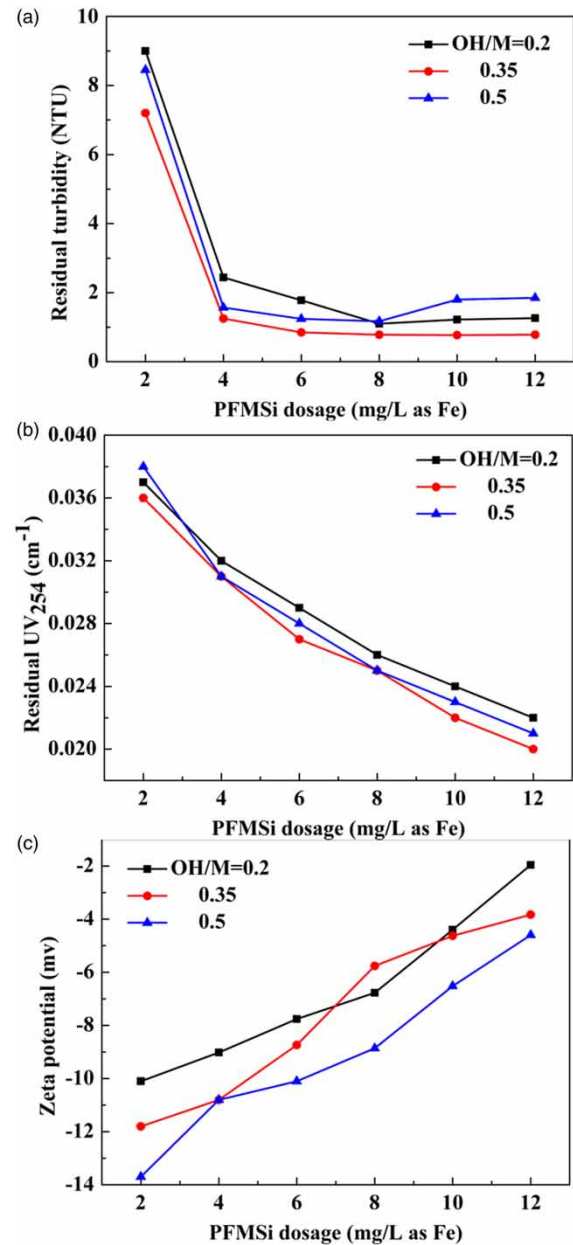
**Figure 7** | The change of turbidity, UV<sub>254</sub> and zeta potential of raw water treated by PFMSi with different Mg/Si molar ratios.

the process of charge-neutralization; nevertheless, adsorption-bridging still dominates the whole coagulation process.

#### Effects of PFMSi dosage and $r$ ( $[\text{OH}]/[\text{M}]$ molar ratio, $M$ represents the metal ions)

In general,  $r$  ( $[\text{OH}]/[\text{M}]$  molar ratio) is a significant parameter in the process of coagulant preparation (Wang & Tang 2001). In order to improve the degree of polymerization, the base is introduced in the synthesis process. The base used in this

study is  $\text{NaHCO}_3$ , which has better properties than a strong base such as  $\text{NaOH}$ . Three different  $r$  levels are discussed for getting the appropriate  $[\text{OH}]/[\text{M}]$  molar ratio, which are presented in Figure 8. As is shown, the level of  $r = 0.35$  exhibits the best coagulation performance, no matter in the respect of removal of turbidity or UV<sub>254</sub>. The reason may be that the polymerization degree of  $r = 0.2$  is lower than others, so the adsorption-bridging function is not sufficient. For the higher level of  $r = 0.5$ , more Fe(III) ions would react with the OH groups to produce the iron hydroxide



**Figure 8** | The change of turbidity, UV<sub>254</sub> and zeta potential of raw water treated by PFMSi with different OH/M molar ratio.

precipitate, leading to the worse coagulation efficiency (Zhu *et al.* 2012); simultaneously, the percentage of polymeric species in the PFMSi coagulant with  $r = 0.5$  is lower than that with  $r = 0.35$ , which can be seen in Figure 5, thus leading to the result of a worse coagulation performance.

The study of the zeta potential verifies that from another perspective, as it decreases gradually with the increasing of  $r$  at the same coagulant dosage. The higher  $r$  values increase the process of adsorption-bridging, while weakening the charge-neutralization process, thereby the zeta potential decreases, as is shown in Figure 8(c).

### Comparison of coagulation efficiency

Figure 9 displays the coagulation efficiency comparison of three coagulants, i.e. PFMSi (the molar ratio of Fe/Mg/Si is 1.0,  $r = 0.35$ ), PAC (polymeric aluminium), FMS (the compound of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$ , the molar ratio of Fe/Mg is 1.0). As it shows, the PFMSi coagulant exhibits a significantly better coagulation performance in terms of turbidity,  $\text{UV}_{254}$  absorbance and total organic carbon than the other conventional coagulants. What's more, with the increasing dosage of coagulants, the zeta potential values increase accordingly

for all the coagulants, which means the process of charge-neutralization occurs and the pH values of water treated by different coagulants all meet the demands. Additionally, the zeta potential of raw water treated by PFMSi rises relatively more slowly than others (Figure 9(d)), indicating that the process of adsorption-bridging is more prominent.

According to the coagulation performance and zeta potential values, the introduction of silicon has a great effect on the efficiency of the coagulant, i.e. increasing the proportion of polymeric species, and relatively low M/Si (M represents the metal) leads to a higher degree of polymerization. This can be explained by the fact that PS contains a series of silica species, such as dimeric ( $\text{Si}_2\text{O}_3(\text{OH})_4^-$ ), trimeric ( $\text{Si}_3\text{O}_5(\text{OH})_5^-$ ), tetrameric ( $\text{Si}_4\text{O}_8(\text{OH})_4^-$ ) and the polymeric species (Dietzel 2000; Wang & Tang 2001). For example, a composite coagulant poly-zinc-silicate-sulfate (PZSS) was prepared by introducing PS to zinc salt, and the PZSS showed better coagulation performance than that of conventional ferric and aluminum coagulants in oily wastewater (Zeng & Park 2009). The poly-magnesium-silicate-chloride prepared by combining magnesium chloride and PS presented more efficient coagulation performance in dyeing wastewater treatment than conventional magnesium chloride (Wei *et al.* 2015).

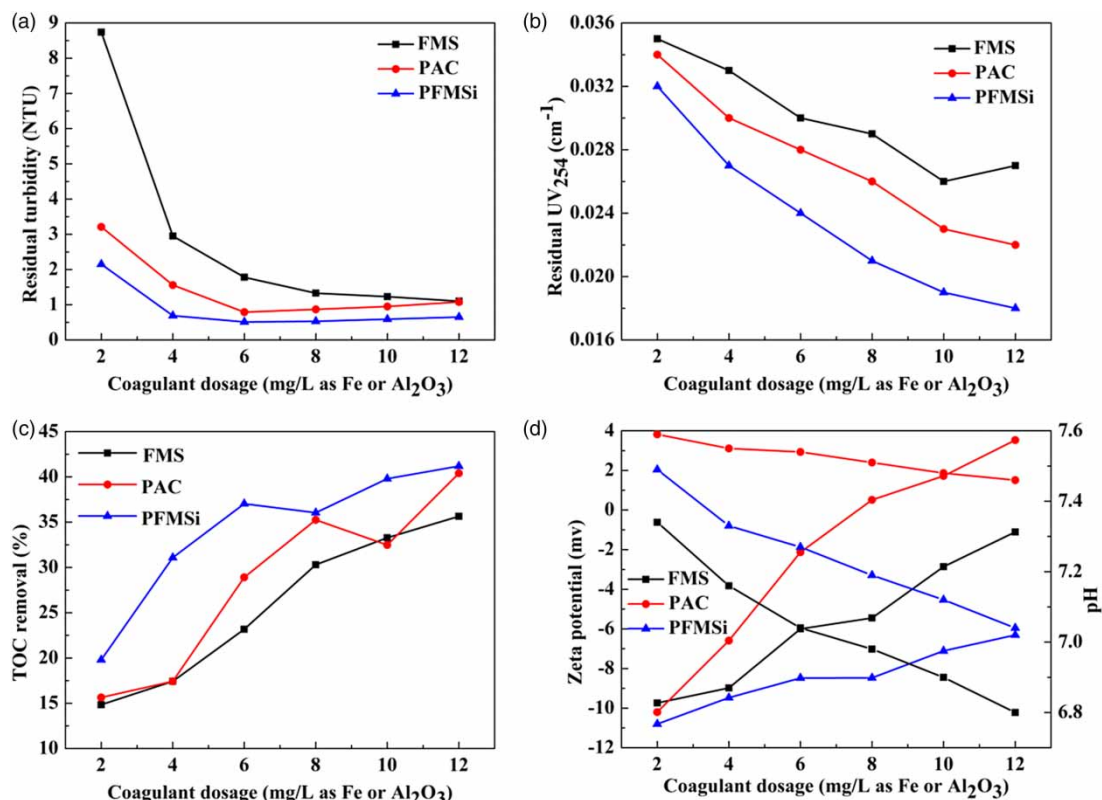


Figure 9 | Comparative of coagulation performance of PFMSi, PAC and FMS.



Therefore, the introduction of silicon increases the polymeric species and molecular weight of the coagulant, and the major mechanism is adsorption-bridging. In that case, the flocs produced are bigger and take less time to precipitate. In contrast, conventional coagulants are predominant in the mechanism of charge-neutralization, while the other two abilities are relatively weaker. As seen from Figure 9(a), when the coagulant dosage is 6 mg/L as Fe, the residual turbidity decreases to about 0.5 NTU using PFMSi, slightly higher than the standard of tap water. This means that it can reduce the load of filtration to a great extent when used in practical projects. Moreover, Figure 9(b) shows that PFMSi exhibits absolute superiority in the respect of UV<sub>254</sub> removal. Meanwhile, the PFMSi coagulant exhibited a better performance than others in the removal of TOC, which can be observed in Figure 9(c).

### Study of coagulation kinetics using i-PDA100

The coagulation kinetic of three different coagulants is demonstrated in Figure 10; two kinds of conventional coagulant (FMS and PAC) are used for comparison. The kaolin suspension was prepared by dispersing kaolin in tap water, and the mass concentration was 50 mg/L. The optimal coagulant dosage of each coagulant was used in the coagulation process.

As shown in Figure 10, all the coagulants exhibit a similar trend. With the addition of coagulants, the FI R increases rapidly, indicating that the growth and formation of flocs, and then reaches the steady phase. It is evident that the PFMSi shows quicker formation of flocs, as the linear growth phase is shorter than FMS and PAC in duration. For the conventional coagulants FMS and PAC, the formation of flocs is relatively retarded and the produced flocs are smaller, as the R values are lower.

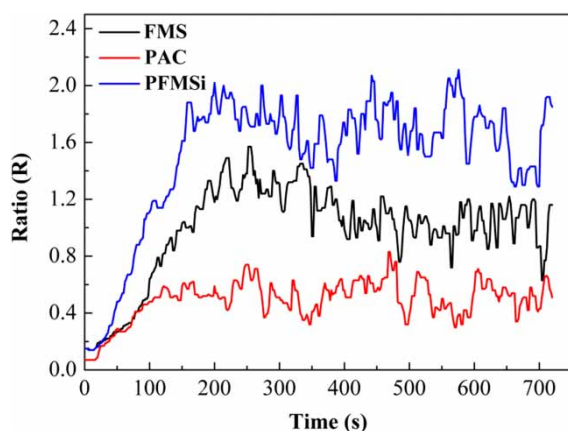


Figure 10 | Comparative FI of PFMSi, FMS and PAC.

In general, for conventional metal salt coagulants with low molecular weight, the predominant mechanism of particle destabilization and floc formation is charge-neutralization. When introducing the silicon to metal salts under appropriate conditions, hydrated irons and polynuclear hydroxyl complexes are formed, which bond with PS to subsequently form new structures of chains or networks. In that case, the molecular weight of the coagulant is greatly increased, meaning that the presence of PS facilitates the formation of flocs through the adsorption-bridging mechanism, and the coagulation process is enhanced simultaneously.

### CONCLUSIONS

XRD and FT-IR results suggest that PFMSi coagulant consists of new chemical species, containing the metals Fe and Mg and the nonmetal Si. According to the morphology, the solid PFMSi presents an amorphous phase. The Fe(III) species of PFMSi coagulant is analyzed by Fe–Ferron™ complexation timed spectrophotometry, and the results show that the higher basicity is conducive to the formation of Fe<sub>b</sub> and Fe<sub>c</sub>. Fe<sub>b</sub> plays the most important role in the coagulation process, the optimal *r* is 0.4. The factors of Fe/Si, Mg/Si and [OH]/[M] greatly influence the coagulation performance, which is reflected in the removal of turbidity and UV<sub>254</sub>. The results indicate that a higher percentage of Si and appropriate basicities can improve the polymerization degree and increase molecular weight, and Mg<sup>2+</sup> and hydrolysis products that contain magnesium possess the strong ability to adsorb suspended solids and colloidal particles. Coagulation experiments show that the PFMSi coagulant works better than conventional coagulants of PAC and FMS, regardless of the removal of turbidity or the removal of organic matter. The zeta potential values suggest that the adsorption-bridging function of PFMSi coagulant is more prominent than in conventional coagulants. I-PDA analysis reveals that the introduction of silicon leads to the formation of large polymers with high molecular weight, thereby the flocs are bigger in size than the flocs produced by conventional coagulants, which reflects on the R curves, indicating the existence of adsorption-bridging process.

### ACKNOWLEDGEMENTS

The research was financially supported by grants from National Nature Science Foundation of China (21677052), Major Science and Technology Program for the Industry-Academia-Research Collaborative Innovation (201605122301117, 201604010043),

Guangdong Province Science and Technology Project (2016B090918104, 2013B090200016, 2015B020215007, 2015B020235009, 2016B020240005), State Key Laboratory of Pulp and Paper Engineering (2016C03), Joint fund of Guangdong Province (U1401235), and Zhanjiang of Guangdong Energy Co. (ZY-KJ-YX-2016X085F).

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