

# Preparation of composite coagulant of PFM-PDMAAC and its coagulation performance in treatment of landfill leachate

Simin Li, Yongkang Lv and Zhanmeng Liu

## ABSTRACT

A novel inorganic–organic composite coagulant, poly-ferric-magnesium (PFM) polydimethyldiallylammonium chloride (PDMDAAC), was prepared using  $\text{FeSO}_4$ ,  $\text{MgSO}_4$  and PDMDAAC as raw materials and was introduced to treat landfill leachate. The coagulation performance of the new reagent was evaluated and compared with those of other coagulants. The new reagent was characterized in terms of the analysis of ferron-timed spectroscopy, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The coagulation mechanism was investigated by measuring the  $\zeta$ -potential reduction and chemical oxygen demand removal at different dosages. Coagulation experiments revealed that the new reagent exhibited better coagulation performance compared with the simple PFM and the PFM + PDMDAAC. Ferron-timed spectroscopy showed that the new reagent exhibited increased effective polymer species concentration. XRD and FTIR spectroscopy showed that the new reagent was not a simple mechanical mixing of PFM and PDMDAAC, but a composite system with inorganic–organic complex interpenetration networks. The predominant coagulation mechanism of the new reagent was charge neutralization at low dosages, as well as adsorption bridging and co-precipitation netting at high dosages, when treating landfill leachate.

**Key words** | coagulation, composite coagulant, landfill leachate, PFM-PDMAAC

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## INTRODUCTION

In recent years, the yield of municipal solid waste has rapidly increased with urbanization and economic development in China. Sanitary landfill is the most common technique for the management of municipal solid waste due to its low cost and simple operation. One of the greatest environmental problems associated with solid waste disposal in landfills is leachate generation (Bilgili *et al.* 2007). Landfill leachate is a very heavily polluted wastewater and is characterized by high concentrations of toxic and carcinogenic chemicals, which should be safely collected and efficiently treated in order to eliminate the potential for pollution of ground water and surface water. In practice, its disposal continues to be a thorny problem and is one of the most necessary tasks in refuse landfill management

(Tatsi & Zouboulis 2002). Biological degradation is the most prevalent technology used for the treatment of landfill leachate and is often used as a preferred process due its low cost (Jiang *et al.* 2005; Ying *et al.* 2008). However, biological degradation alone cannot treat landfill leachate efficiently, and the effluent does not always meet the national discharge standards (Zouboulis *et al.* 2004; He *et al.* 2009). In addition, during operation of landfills, the chemical oxygen demand (COD) value and ammonium nitrogen concentration increase and the biodegradability of organic pollutants decreases, which would lead to the biological technology used on its own being unsuitable for effectively treating landfill leachate (Kjeldse *et al.* 2002). Therefore, biodegradation is usually used in

combination with other technologies for the treatment of landfill leachate (Kargi & Pamukoglu 2004).

Coagulation is a core environmental protection technology that has a wide range of applications in wastewater treatment projects. When combined with other appropriate technologies, coagulation is a viable option for the treatment of various types of wastewater including landfill leachate. For example, this method has been used in the pre or post treatment of landfill leachate to enhance the biodegradability of the leachate or to remove residual recalcitrant matter (Amokrane *et al.* 1997; Aziz *et al.* 2007). Increasing the performance of the coagulation stage seems to be a key factor in enhancing the overall leachate treatment efficiency (Ntampou *et al.* 2006).

Coagulation efficiency is fundamentally determined by the individual properties of the coagulant used (Tatsi *et al.* 2003). Inorganic polymeric coagulants (IPFs), including poly-ferric sulfate (PFS), poly-ferric chloride and poly-aluminum chloride, are widely applied as reagents in water or wastewater facilities (Ghafar *et al.* 2009). Currently, many studies are being conducted to improve IPFs by introducing other components for coagulation. Magnesium salts have been shown to remove impurities or contaminants, and thus act as an effective alternative coagulant for wastewater treatments (Semerjian & Ayoub 2003). Some researchers have evaluated magnesium as an additive in some novel type of IPFs for some wastewater treatment and reported that the improved IPFs had better coagulation performance than other coagulants (Patel & Suresh 2006; Sang *et al.* 2008; Li *et al.* 2009). Despite the improved coagulation efficiency of newer IPFs, they still do not enable satisfactory removal of certain contaminants from some types of wastewater. The increasing demand for organic matter removal from wastewater has encouraged numerous researchers to focus on the application of organic polymeric coagulants (Ahmada *et al.* 2008; Lee *et al.* 2011). Polydimethyldiallyl-ammonium chloride (PDMDAAC) has long been applied as a primary coagulant or flocculant aid in water and wastewater treatment. Compared with metal coagulants, its superior performance is manifested in a wider working pH range and the lower dosage required, although its high cost limits its application in practical projects. Therefore, in order to overcome the aforementioned difficulties and achieve better coagulation efficiency, researchers recently focused on the preparation of composite inorganic–organic coagulants by combining a metal coagulant with an organic polymer so as to fully utilize

their superior properties and overcome the defects of the individual components (Wei *et al.* 2009a, b; Chen *et al.* 2010).

In this study, a novel inorganic–organic composite flocculants, poly-ferric-magnesium (PFM) PDMDAAC was prepared and used to treat landfill leachate. The purpose of this work was to optimize the preparation technology and evaluate the coagulation performance in treating landfill leachate based on a comparison with other coagulants. The new reagent was subsequently characterized in terms of ferron-timed spectroscopy, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The destabilization mechanism was determined by measuring the  $\zeta$  potential of the flocs produced *in situ*.

## EXPERIMENTAL PROCEDURES

### Preparation of PFM-PDMAAC coagulant

The PFM used in this study was prepared in our laboratory. The preparation of PFM products with four Mg/Fe molar ratios, i.e. 1/5, 1/4, 1/3 and 1/2 were initially accomplished, using one r OH/(Fe + Mg) molar ratio (0.3). The procedure for the preparation of the PFM coagulant was recently described (Liu *et al.* 2013).

The PFM-PDMAAC composite coagulants with different PDMDAAC/PFM weight ratios were prepared by adding a measured amount of PDADMAC into the PFM solution and stirring thoroughly until it was completely mixed with the solution. The composite coagulants were subsequently allowed to age for 24 h at room temperature.

All reagents used for the preparation of PFM products were analytically pure chemicals and all solutions used for synthesis of the coagulant were prepared with deionized water. PDMDAAC (40% (w/w) aqueous solution) was provided by Shang Hai Botai Chemical Co., Shanghai, China. Its intrinsic viscosity was 1.5 dL/g, which is proportional to the molecular weight of PDMDAAC.

### Landfill leachate

Maiyuan sanitary landfill was established in 1997, in Nanchang, the capital of Jiangxi Province, People's Republic of China. Now, the total area of the landfill is 10<sup>7</sup> ha and about

2,200 t of municipal solid waste is disposed of every day. About 800 m<sup>3</sup>/day landfill leachate is generated in the landfill. The leachate treatment plant was established at the first stage of construction of the landfill and began operation in order to decrease or eliminate pollution to the surrounding environment. The leachate generated in the landfill was collected into an equalization storage pond with 50,000 m<sup>3</sup> capacity. Twenty liter bulk leachate samples were collected from the equalization storage pond, transported to the laboratory in acid pretreated polyethylene bottles and then stored at 4 °C until analysis for chemical composition. The characteristics of raw leachate were as follows: COD 7,800–10,000 mg/L; biological oxygen demand<sub>5</sub> (BOD<sub>5</sub>) 1,500–2,100 mg/L; pH 7.5–8.1; ammonia nitrogen 820–1,200 mg/L; total nitrogen 1,200–1,600 mg/L; total phosphate 12.4–46.6 mg/L and suspended solids 300–800 mg/L. Dilution of 600–800 times with water was required to produce a near colorless sample.

### Coagulation test

Coagulation experiments were conducted by jar test in a six-gang stirrer. Briefly, 1,000 mL of wastewater were added with the chosen amount of coagulant, after which the test was conducted by rapid mixing of the solution for 1 min at 300 rpm followed by 15 min of slow mixing at 70 rpm. After the mixed samples had settled without any agitation for 30 min, samples were taken from 2.0 cm below the surface of the test wastewater for analysis. The coagulation temperature was 20 ± 2 °C in all experiments. To analyze the structure of the coagulants, the coagulant samples were freeze dried. Each coagulation test was run in triplicate and the result reported in this paper was the arithmetic average result of the three tests.

### Analysis methods

COD, BOD<sub>5</sub> and color were measured according to the Standard Methods for the Examination of Water and Wastewater established by the China Environmental Protection Agency. Distilled water served as a reference, UV<sub>254</sub> values were read using an ultraviolet spectrophotometer (model UV-2450). The pH was measured by using a pH meter (model PHS-3C). The chemical reagents used in this study were all analytical grade. All samples were analyzed at room temperature and the results were based on triplicate analysis.

### Measurement of the degree of iron polymerization

The degree of iron polymerization was measured by the ferron-timed spectroscopy method using an ultraviolet spectrophotometer (UV-2450). Different species of iron are usually classified into three categories, namely Fe<sub>a</sub> (oligomers), Fe<sub>b</sub> (polymers) and Fe<sub>c</sub> (precipitated species), based on the different reaction times of iron species with the ferron reagent (8-hydroxy-7-iodoquinoline-5-sulfonic acid). Ferron reagent can immediately form complexes (within 1 min) with single ferric ions, as well as with monomeric and dimeric species. It can more slowly form complexes with medium- and high-molecular-weight iron polymers (within 180 min), and the precipitated ferric species do not react with the ferron reagent. These complexes can absorb light at a maximum wavelength of 600 nm. Therefore, the absorbance at 600 nm was measured at predetermined time intervals (1 or 180 min), and each absorbance corresponded to the respective ferric species concentration (Fe<sub>a</sub> or Fe<sub>b</sub>). The concentration of precipitated iron species, i.e. as Fe<sub>c</sub>, was calculated by subtracting the two other Fe species from the total iron concentration. Because the method was originally developed for the determination of the species of pure iron salts solutions, it is necessary to investigate whether the presence of PDMDAAC will have any effect on the method. According to previous studies, the ferron reagent cannot react with PDMDAAC (Gao *et al.* 2005). Therefore, the data obtained by the ferron method only denoted the distribution of Fe(III) hydrolysis species.

### Structure analysis of PFM

PFM, PDMDAAC and PFM-PDMDAAC coagulants were analyzed by FTIR spectroscopy using a FTIR spectrophotometer (model Tensor27). Briefly, small aliquots were taken from the freeze-dried coagulants and mixed with KBr (5% of the mixture), which resulted in formation of a pellet that was suitable for FTIR analysis. FTIR spectroscopy showed that the spectra were in the range 4,000–400 cm<sup>-1</sup>. The PFM and PFM-PDMDAAC coagulants were analyzed by XRD using an X-ray diffractometer (model D/Max-RC) to determine the crystalline phases in the solid coagulants with Cu-Kα radiation in the 2θ range of 5.00–79.98 ° at a scan rate of 4 °/min.

## RESULT AND DISCUSSION

### Evaluation of the coagulation performances of PFM-PDMAAC products

#### Effects of the Mg/Fe molar ratios

The PFM products with different Fe/Mg molar ratios would produce different forms of polymer during the preparation and then further influence the coagulation performance of the PFM-PDMAAC. To find the optimum Fe/Mg molar ratio, the initial PDMAAC/PFM weight ratio was kept constant at 0.07, while varying the Fe/Mg molar ratio. Coagulation experiments of the new reagents prepared with different Fe/Mg molar ratios were performed under the same conditions and the results are shown in Figure 1.

For different Mg/Fe molar ratios the trend of the COD removal rates was similar with dosage and the COD removal first increased then slowly decreased. Comparing the coagulation performance of PFM products prepared at different Mg/Fe molar ratios, it was found that Mg/Fe molar ratio was a significant parameter influencing the COD removal. When the Mg/Fe molar ratio changed from 1/5 to 1/4, the COD removals at the same dosage clearly increased in the whole range of dosage. When the Mg/Fe

molar ratio changed from 1/4 to 1/3, the removal rate remained relatively steady. However, when the Mg/Fe molar ratio changed from 1/3 to 1/2, the coagulation performance deteriorated and a decline in COD removal was observed. Generally, the best coagulation efficiencies appear at the Mg/Fe molar ratios from 1/4 to 1/3. It is evident from the Figure 1 that the COD removal rates of PFM-PDMAAC products prepared with Mg/Fe molar ratio of 1/4 and 1/3 were higher than those with other two Mg/Fe molar ratios. The flocculating constituents formed by iron salts are thinner and denser and thus have good settling performances. Magnesium salts have been shown to remove impurities or contaminants with a good adsorption capacity, and thus act as an effective alternative coagulant for water and wastewater treatments. The new reagent with an appropriate Mg/Fe molar ratio can both overcome the inadequacies of individual iron and magnesium salts, and utilize their advantages.

#### The effects of PDMAAC/PFM weight ratios

Previous publications (Gao *et al.* 2005; Wei *et al.* 2009a, b; Chen *et al.* 2010) had indicated that appropriate organic/inorganic weight ratio is necessary in order to gain the better coagulation performances when preparing inorganic-organic

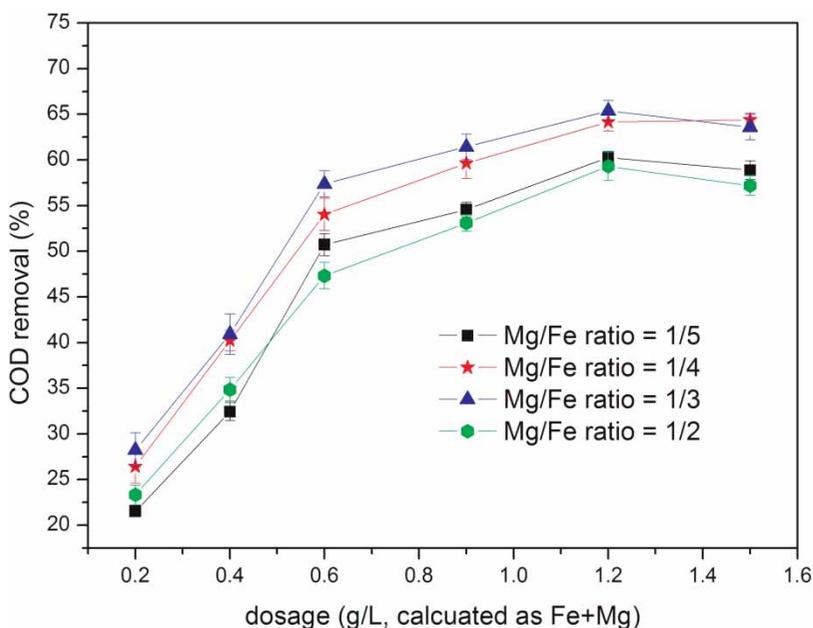


Figure 1 | Effects of the Mg/Fe molar ratios on the COD removal.

composite coagulants. Certainly, appropriate PDMDAAC/PFM weight ratio would improve the coagulation performance of the new reagent. To find the optimum PDMDAAC/PFM weight ratio, the Mg/Fe molar ratio was kept constant at 1/3, while varying the PDMDAAC/PFM weight ratio. Coagulation experiments using the new reagents prepared with different PDMDAAC/PFM weight ratios were performed under the same conditions and the results are shown in Figure 2.

As shown in Figure 2, the coagulation performance improved with the increase of the PDMDAAC/PFM ratio, suggesting that the presence of PDMDAAC enhanced the coagulation efficiency, as it facilitated the destabilization of the colloid impurities through the charge neutralization mechanism and the formation of large and better settleable flocs through the adsorption/bridge formation mechanism. When the PDMDAAC/PFM weight ratio increased from 0.04 to 0.10, the COD removals at the same dosage clearly increased in the whole range of dosage. However, when the PDMDAAC/PFM ratio increased from 0.10 to 0.15, minimal enhancement of COD removal was observed. An increase in PDMDAAC/PFM weight ratio may be uneconomical since PDMDAAC is more expensive than PFM. Thus, high PDMDAAC/PFM weight ratio would not facilitate the application of the new reagent in practical engineering.

Consequently, we suggest that the optimum PDMDAAC/PFM weight ratio is 0.10 when treating the landfill leachate. At the PDMDAAC/PFM weight ratio of 0.10, the dosage from 1.2 to 1.5 g/L would be adequate in the experimental set up and could be properly adjusted according to the wastewater quality in practical engineering.

### Comparison with other coagulants

The traditional method of applying organic-inorganic coagulants is to add two kinds of reagents into the wastewater separately and the organic coagulant is often added some time after the metal coagulant. As part of our study, three coagulants – PFM, PFM-PDMDAAC and PFM + PDMDAAC – used to treat landfill leachate and the results were shown in Figure 3; in the PFM + PDMDAAC treatment, PFM was added at the start of rapid mixing period and followed by PDMDAAC after 1 min, then the rapid mixing continued for an additional 1 min in the coagulation process. The Mg/Fe molar ratio was 1/3 in all three coagulants and the PDMDAAC/PFM weight ratio was 0.10 in both PFM-PDMDAAC and PFM + PDMDAAC.

As shown in Figure 3, the coagulation performance of PFM-PDMDAAC was better than that of the PFM +

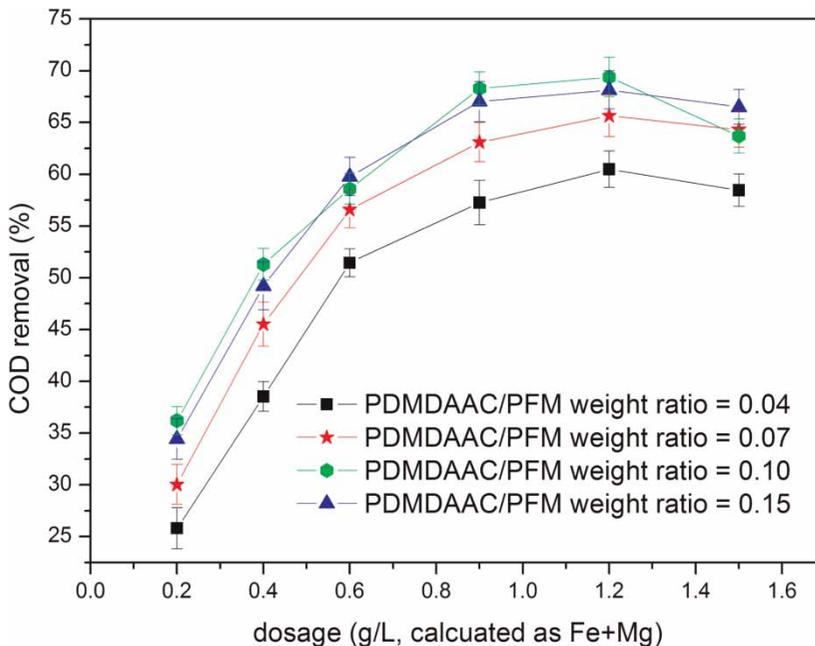


Figure 2 | Effects of PDMDAAC/PFM weight ratio on COD removal.

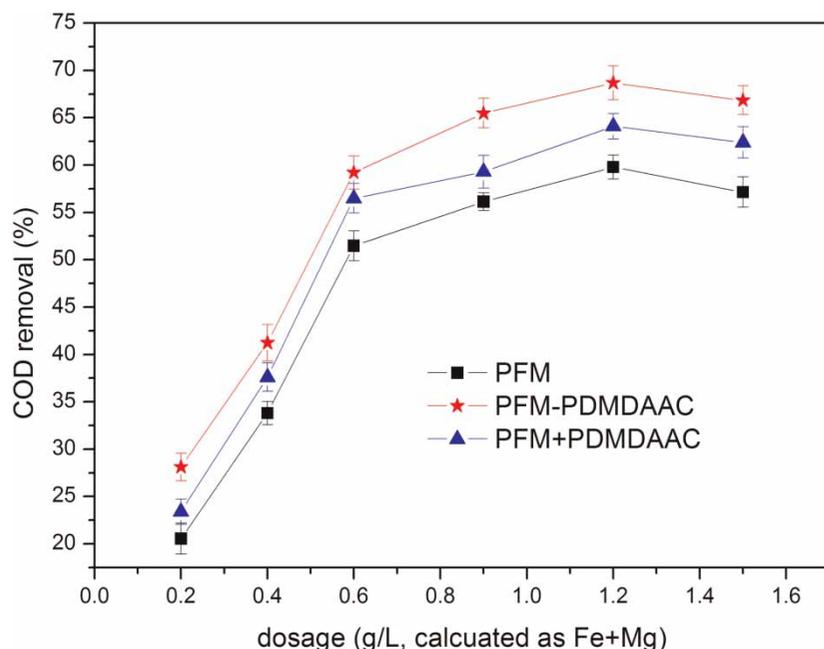


Figure 3 | COD removals with changes in the dosage of different coagulants.

PDMDAAC at the same dosage, which demonstrated that the optimized composite coagulant was more efficient compared with the simple sequential addition of the same reagents. This also verified that the new reagent can give full play to the respective advantages of the PFM and PDMDAAC and produce a clear synergistic effect on the coagulation performance. Another shortcoming of the PFM + PDMDAAC is that two reagent addition systems are required in the coagulation process. However, the new PFM-PDMDAAC reagent can be added to the wastewater to be treated in one step. Nevertheless, the PFM + PDMDAAC exhibited better coagulation performance than PFM.

### Removal efficiencies of BOD<sub>5</sub>, UV<sub>254</sub> and color

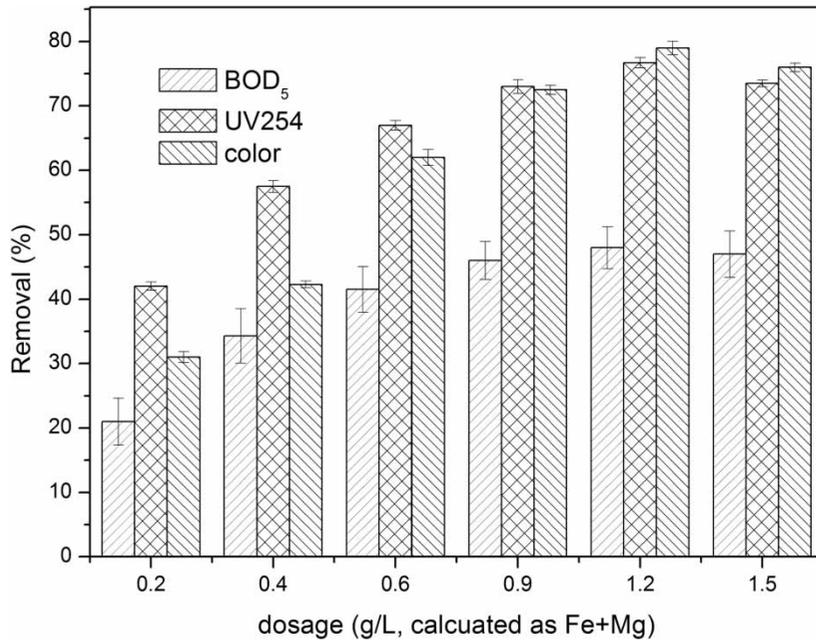
The organic matter in the landfill leachate is not only measured as COD, but also BOD<sub>5</sub>, UV<sub>254</sub> and color. PFM-PDMDAAC was prepared with a PDMDAAC/PFM weight ratio of 0.10 and Mg/Fe molar ratio of 1/3 and was used to treat landfill leachate at different dosages and the BOD<sub>5</sub>, UV<sub>254</sub> and color of the treated supernatants were determined.

It can be seen from Figure 4 that the removal of BOD<sub>5</sub>, UV<sub>254</sub> and color all increased at first and then slowly declined with the dosage, with the peak removals 48%, 76.7% and

79%, respectively, at the dosage of 1.2 g/L. Good coagulation performances could be obtained at a wide range of dosage from 0.9 to 1.5 g/L, with the removal of BOD<sub>5</sub>, UV<sub>254</sub> and color reaching up to 46%, 73% and 72%, respectively. The experimental phenomena here were similar to those in COD removal efficiencies with different dosage. Doubtless, a wide optimum range of dosage would facilitate the required coagulation efficiencies as it is not easy to control the appropriate dose at engineering sites. In addition, the BOD<sub>5</sub>/COD value variations of the leachate after coagulation were investigated. Before coagulation, the BOD<sub>5</sub>/COD value was 0.28. After coagulation, obvious improvements in the biodegradability characteristics of the landfill leachate were observed. The BOD<sub>5</sub>/COD value was found to increase greatly and reached up to 0.45 in the optimum dosage range of 0.9–1.5 g/L. This efficiently improved the feasibility and efficiency of later biological degradation.

### Fe(III) species distribution

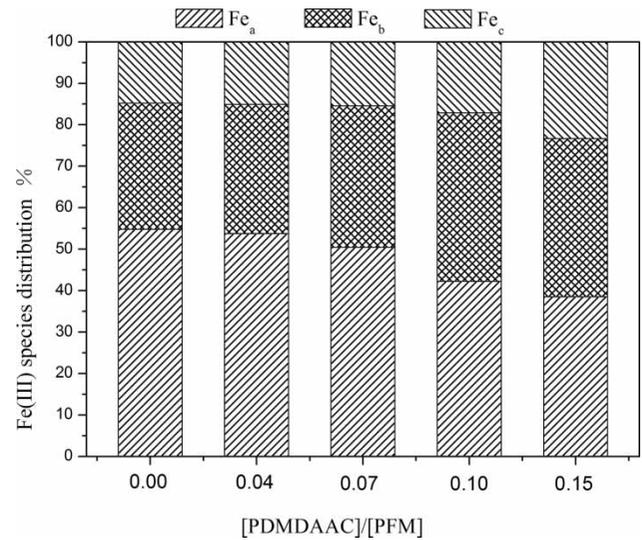
Fe(III) species distribution has a great effect on the coagulation performances. Fe<sub>a</sub> and Fe<sub>b</sub> are commonly thought to induce better coagulation efficiency than Fe<sub>c</sub>, and that Fe<sub>b</sub> is universally acknowledged as the most efficient species for coagulation



**Figure 4** | Removal of BOD<sub>5</sub>, UV<sub>254</sub> and color with changes in dosage of PFM-PDMAAC.

(Zouboulis *et al.* 2008). Different Fe(III) species (i.e. Fe<sub>a</sub>, Fe<sub>b</sub> and Fe<sub>c</sub>) would mutually transform during the preparation of the PFM products and these transformations were predominantly determined by the OH<sup>-</sup> ions concentration in the coagulant. Because the pH of the PDMAAC is higher than that of the PFM, the chemical equilibrium between OH<sup>-</sup> ions and H<sup>+</sup> ions in the PMF would be disturbed and the mutual transformations among the different Fe(III) species in PMF would reach a new balance after the introduction of the PDMAAC. The presence of PDMAAC itself would also influence the mutual transformation among different Fe(III) species in the solution. The Fe(III) species distribution of PFM-PDMAAC products with different PDMAAC/PFM weight ratio was investigated and the results are shown in Figure 5.

As shown in Figure 5, the addition of PDMAAC typically influenced the Fe(III) species distribution of the new reagents. The proportion of Fe<sub>b</sub> species first increased with PDMAAC/PFM weight ratio from 0.00 (i.e. no addition of PDMAAC) to 0.10, reaches a maximum at PDMAAC/PFM weight ratio = 0.10, and then decreases at PDMAAC/PFM weight ratio >0.1. The proportion of Fe<sub>a</sub> continuously decreased when increasing the PDMAAC/PFM weight ratio, and correspondingly, the proportion of Fe<sub>c</sub> continuously increased. Fe<sub>a</sub> and Fe<sub>b</sub> were commonly thought to be the



**Figure 5** | Fe(III) species distribution with change in different PDMAAC/PFM weight ratio.

efficient Fe(III) species, and Fe<sub>b</sub> has been universally acknowledged as the most efficient species for coagulation. Increasing PDMAAC/PFM weight ratio would result in Fe<sub>a</sub> gradually transforming into Fe<sub>b</sub>, and Fe<sub>b</sub> gradually transforming into Fe<sub>c</sub>. According to our analysis, it was concluded that an appropriate PDMAAC/PFM weight ratio would improve the polymerization of the new reagent. This is in agreement with

the conclusion provided in a study conducted by Wei to evaluate the Fe(III) species distribution of poly-ferric-PDMDAAC (Wei *et al.* 2009a, b).

However, when the PDMDAAC/PFM weight ratio was too large, a large amount of Fe<sub>b</sub> would transform into Fe<sub>c</sub>, and then result in reduction of the Fe<sub>b</sub> content because of the continual iron hydrolysis in the solution. Therefore, an appropriate PDMDAAC/PFM weight ratio is necessary in the preparation of the new reagent.

## Structure analysis

### XRD analysis

The XRD spectra of PFM and the new reagent are shown in Figure 6. It is evident that there was a distinct difference between PFM and PFM-PDMDAAC. The spectra of PFM presented semi-amorphous shapes, some crystal shapes and some

amorphous shapes. Significantly, the presence of PDMDAAC altered the XRD pattern. The new reagent was amorphous with rather obscure traces of crystal shapes. This finding demonstrated that the new reagent was a novel polymer that is different from the PFM. When compared with the respective PFM pattern, the new reagent had a broad intense shoulder at around  $18^{\circ}2\theta$ , which was ascribed to the amorphous nature of PDMDAAC. The lack of characteristic peaks in the reagent suggested that there were no adsorbing chemical compounds. During preparation of the new reagent, PDMDAAC dispersedly interweaved into PFM, forming a composite system with inorganic–organic complex interpenetration networks. This conclusion is similar to that in a study conducted by Gong *et al.* (2004) to analyze the XRD spectra of PFS-PDMDAAC: the inorganic–organic composite coagulant of PFS-PDMDAAC was not a simple mechanical mixing of PFS and PDMDAAC, but a formation of a composite system with inorganic–organic complex interpenetration networks. Based

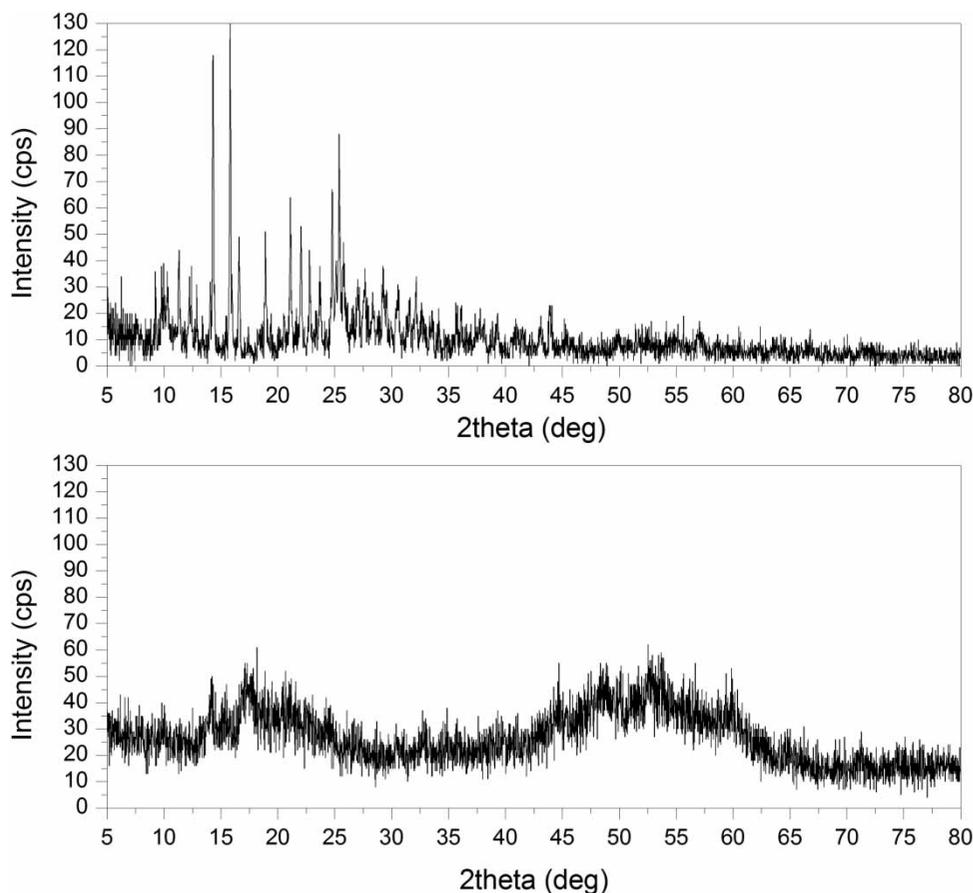


Figure 6 | XRD patterns of PFM and PFM-PDMDAAC.

on the above analysis, some reactions between the PFM and PDMDAAC took place, which resulted in the formation of new substances with better coagulation performance.

### FTIR spectroscopy

FTIR spectra of PFM, PDMDAAC and PFM-PDMAAC are shown in Figure 7. The spectrum of the new reagent was similar to that of PFM but not the complete combination of PFM and PDMDAAC spectra. The new reagent exhibited a characteristic peak at around  $1,398\text{ cm}^{-1}$ , which can be attributed to the  $-\text{CH}_2-$  adsorption from PDMDAAC. However, an obvious blue shift occurred in this adsorption peak compared with the PDMDAAC spectrum. Observing the spectra of PFM and the new reagent, it can be seen that the characteristics peak at around  $2,375\text{ cm}^{-1}$

attributed to sulfate radical adsorption nearly disappeared in the spectrum of the new reagent. In addition, some peaks appeared around  $1,075$  and  $998\text{ cm}^{-1}$  in the spectrum of the new reagent, which were hardly observable in the PFM spectrum and totally absent from the PDMDAAC spectrum. According to these experimental findings, it could be suggested that some new chemical compound formed when the PDMDAAC was introduced into the PFM. It also indirectly demonstrated that the new reagent was not a simple mechanical mixing of PFM and PDMDAAC, and some reactions occurred between the PFM and PDMDAAC.

### Coagulation mechanism

It is commonly believed that there are four reaction mechanisms involved in coagulation: compression twin electrical

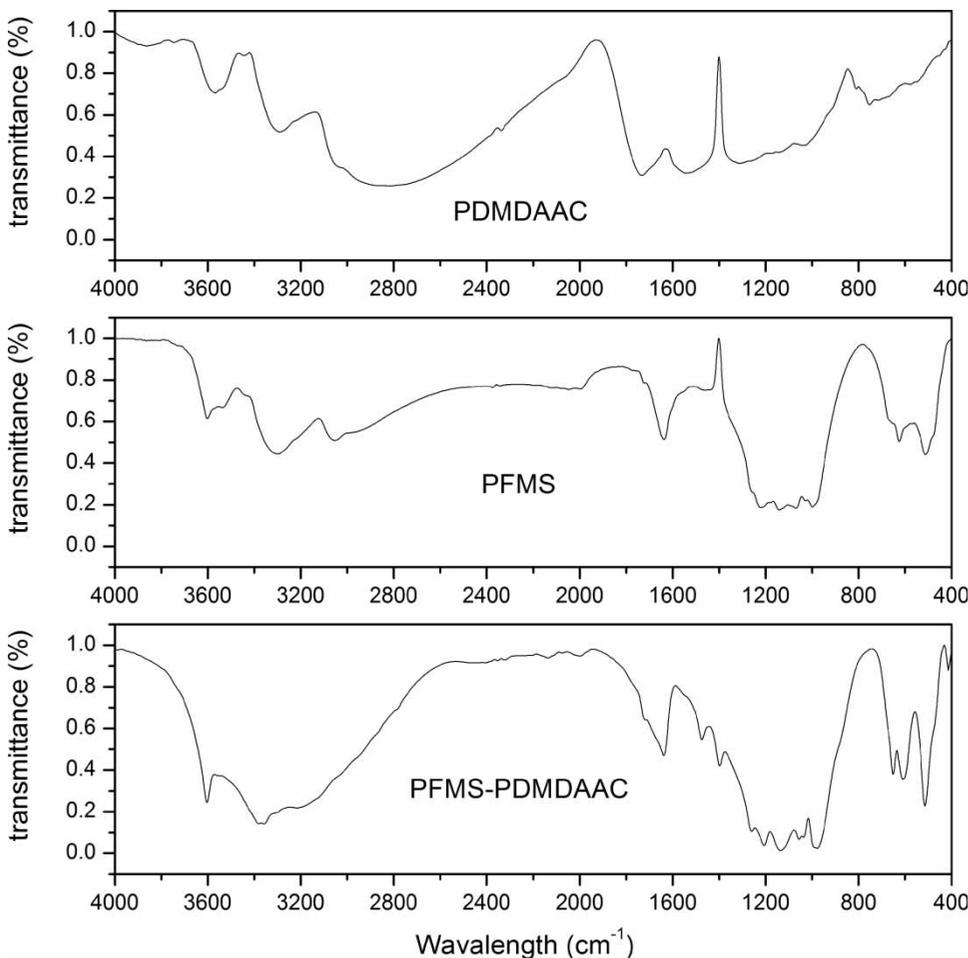


Figure 7 | FTIR spectra of PFM, PDMDAAC and PFM-PDMAAC.

layer, charge neutralization, adsorption bridging and co-precipitation netting. During coagulation of the new reagent, charge neutralization and adsorption bridging initially occurred when it was introduced into the wastewater. Charge neutralization occurred due to the contact of various species of iron and magnesium with the negatively charged colloidal particles, and simultaneously, adsorption bridging also played a role due to contact of high-molecular-weight and linear structure cationic organic matter with pollutants in wastewater. In the coagulation process, the destabilization of colloidal impurities is dependent on the characteristics and amount of colloidal impurities in the wastewater and the dosage of the coagulant. If the colloidal impurities in wastewater have a certain size and possess the ability to self-aggregate, large flocs easily form with the added coagulant and good sedimentation results. However,

if the colloidal impurities are relatively small or do not form large flocs, the coagulant dosage must be continuously increased. When increasing the dosage to a certain amount, the colloidal impurities, various species of iron and magnesium, and the cationic linear structure of PDMAAC adhere to each other and form much larger flocs. During the precipitation of these flocs, the partially stabilized particles are netted and removed. At this time, the coagulation may be driven by a combination of adsorption bridging and co-precipitation netting. To determine the coagulation mechanism of the new reagent, the COD removal and  $\zeta$  potential of landfill leachate at different dosages were measured, and the results were shown in Figure 8.

The COD removal rate initially increased to the peak value and then remained relatively steady with the

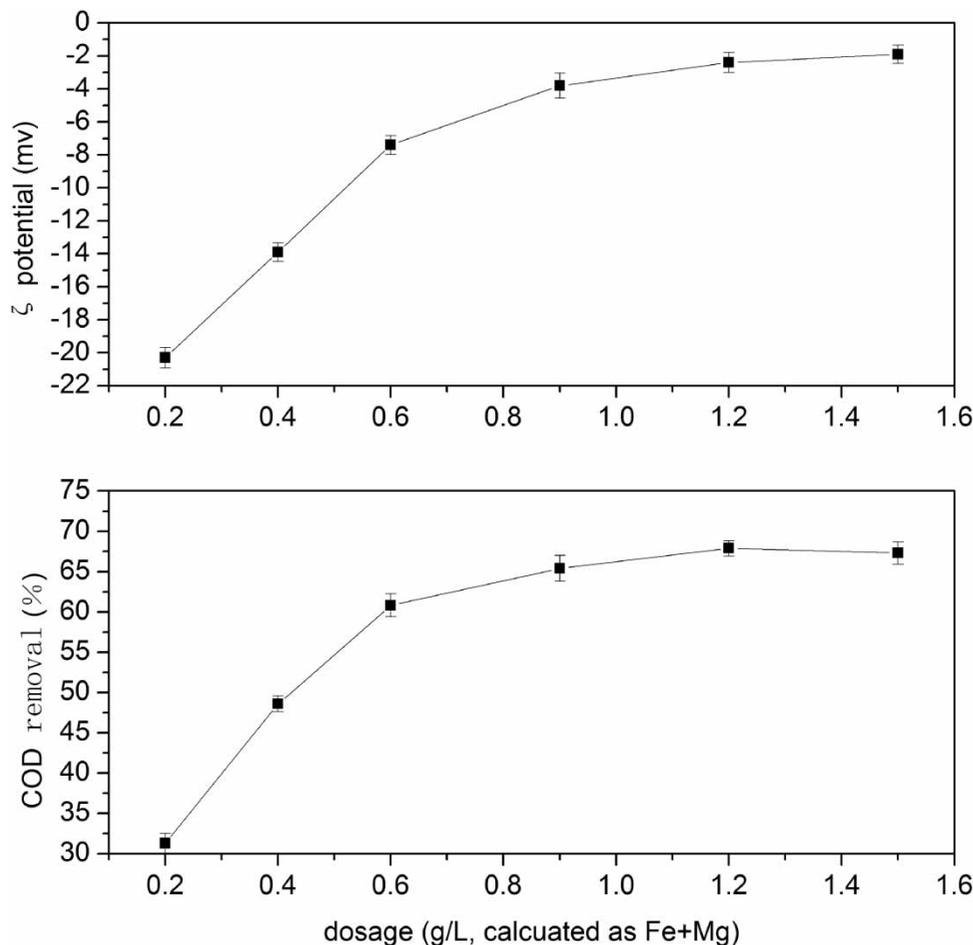


Figure 8 | Variation in the relationship of  $\zeta$  potential and the COD removal with dosage.

dosage and the  $\zeta$  potential of colloidal impurities in the effluent of landfill leachate gradually rose and gradually moved from negative to positive. At low dose ( $<0.6\text{--}0.8\text{ g/L}$ ), both the COD removal and the  $\zeta$  potential of colloidal impurities increased with increasing dosage, and the  $\zeta$  potential nearly correlated with the coagulant dosage. Accordingly, it is suggested that the coagulation efficiency primarily depended on the self-aggregation that occurs after the neutralization of the surface negative charges of colloidal impurities by the positive charge of the coagulant (Pefferkorn 2006). The PDMDAAC component in the new reagent has positive charges, a high-molecular-weight and linear structure, which indicates that it may conduct by charge neutralization and adsorption bridging during the coagulation process. However, adsorption bridging should play an auxiliary role as PDMDAAC is only the assistant component in the new reagent. On the whole, the new reagent primarily conducted by the charge neutralization when treating landfill leachate at low dosage. At high dosage ( $>0.6\text{--}0.8\text{ g/L}$ ), the COD removal remained optimal within a wide range of dosage and the  $\zeta$  potential gradually increased but the rising rate was obviously lower than that at the low dosage. This showed that the negative charges could be reduced by the added reagent. However, as shown in Figure 8, the  $\zeta$  potential of the effluent was not close to zero when the high COD removal rate was achieved, which indicates that the negative charges were not completely neutralized by the added reagent. If the charge neutralization is the path for coagulation, the  $\zeta$  potential should be highly correlated with the coagulant dosage and the  $\zeta$  potential should be close to zero when a high COD removal rate was achieved. Therefore, charge neutralization could not play a key role under such conditions. At the pH of experiment, there was a trend of formation of various hydrolysis species of iron and magnesium with inorganic–organic complex interpenetration networks as well as flocculent amorphous precipitates of  $\text{Fe}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$  with few charges in the coagulation system. The increasing amplitude of the  $\zeta$  potential of the colloidal impurities was small within a wide range of dosage because of the reduced charge. The colloidal impurities were attached into the inorganic–organic complex interpenetration networks and netted onto the precipitate, and subsequently removed by

co-precipitation. Certainly, the coagulation efficiency was primarily driven by adsorption bridging and co-precipitation netting.

## CONCLUSION

PFM-PDMDAAC prepared using a PDMDAAC/PFM weight ratio at 0.07 and Mg/Fe molar ratio of 1/3 exhibited superior COD removal over other prepared samples as well as PFM and PFM + PDMDAAC when treating landfill leachate. The  $\text{BOD}_5$ ,  $\text{UV}_{254}$  and color could also be efficiently removed at a wide optimum range of dosage and clear improvement in the biodegradability characteristics was observed. The new reagent displayed the synergistic effect of the PFM and PDMDAAC and the coagulation efficiency was increased after synthesis. The species distribution of the PFM-PDMDAAC products characterized by the ferron-timed spectroscopy method showed that an appropriate PDMDAAC/PFM weight ratio can improve the polymerization degree of PFM and then increase the proportion of  $\text{Fe}_b$ . XRD and FTIR spectroscopy showed that the new reagent was not a simple mechanical mixing of PFM and PDMDAAC. PDMDAAC dispersedly interweaved into the PFM, forming a composite system with inorganic–organic complex interpenetration networks. Some reactions between the PFM and PDMDAAC occurred and some new chemical compounds formed. These properties are the main reasons for the better coagulation efficiency of the new reagent than other coagulants. When treating landfill leachate, the coagulation mechanism of new reagent was primarily charge neutralization at low dosages as well as adsorption bridging and co-precipitation netting at high dosages.

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