

HYDROLYSIS CHARACTERISTICS of POLY-Ti-Fe (M-PTF) COAGULANT from a SOLID WASTE and its CONTRIBUTION to COAGULATION EFFECT

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Abstract

A new Poly-Ti-Fe (M-PTF) coagulant was prepared from a waste, and surface morphology, microscopic image and UV absorption before and after hydrolysis were investigated, respectively. Coagulation behavior of M-PTF in treating sewage was studied, compared with that of Poly Aluminum Chloride (PAC). The results indicated the micro-characteristics of the Hydrolysis Products of M-PTF (HPM) gave great difference (HPM carrying more positive charges gave various rough surface morphologies and appeared to be light and floating with larger water content) from that of M-PTF consisted of strong acid weak alkaline salts or acid salts. M-PTF had relatively weaker charge neutralization and stronger adsorption/bridging/sweeping in removing turbidity and color, but charge neutralization, adsorption/bridging and sweeping played important role in its removing organic matters, which may be one of the reasons that M-PTF had lower required dosage for COD_{Cr} removal than that for turbidity and color removal over the given pH and dosage ranges..

Keywords: Ti; Coagulant; “Waste Acid Silter Cake”; Hydrolysis; Micro-characteristics; Coagulation performance

1. Introduction

Rapid accumulation of solid wastes has become a worldwide problem due to large development of economy and great improvement of people's living standard. China, as one of rapid development countries, has been seriously polluted by solid wastes which were over 6 billion tons currently and increased rapidly at annual growth of 10% [1]. Therefore, how to dispose solid wastes is so important now. As well known, most solid wastes still have their value in other fields, so, resource disposing is one of hot topics, in which preparation of various inorganic and organic coagulants using various solid wastes has become a promising focus in the field of water and wastewater treatment [2-7].

“Waste Acid Filter Cake” (WAFC) is a kind of solid waste generated from the production of “titanium white”. Titanium dioxide (TiO_2) is one of important compounds of titanium element, and is also the main component of “titanium white” which is considered to be the best white pigment widely used in paints, plastics, paper, printing ink, and so on [8,9]. China is not only one of the countries with the largest storage capacity of titanium in the world [10], but also one of the largest consumers. Sulfate process one of methods to produce TiO_2 widely used in China, in which lots of wastes and byproducts are often generated [11], for instance, a sort of WAFC (containing elements of Ti, Fe, Al, Si, etc) [12] coming from a waste acid generated from washing process. Fe and Si are often important components in producing inorganic coagulants, and Ti is a new element used in preparation of water purifying agents recently. Moreover, Fe, Si and Ti are all non-toxic. Therefore, the

preparation of M-PTF using WAFC has its theoretical and practical basis, according with the aim of “waste control by waste”.

A kind of coagulant containing titanium is a relatively new water treatment agent studied in recent years, most of which were mainly about preparation (using titanium tetrachloride or titanium sulfate as raw materials), removing efficiency for pollutants, flocs features and so on [13-15]. However, studies on preparation and hydrolysis of coagulant containing Ti using WAFC were rarely studied. As well known, Al-based and Fe-based coagulants hydrolyzed quickly to be some complex hydrolysis products after added to water samples, some actions (such as charge neutralization/destabilization, bridging, and sweeping) occurred between the hydrolysis products and pollutants negatively charged in water samples, and then some flocs formed and precipitated, thus achieving the purpose of pollutant elimination after solid-liquid separation. However, flocs sedimentation, pollutants removal, and water content of sludge are all related to the characteristics of hydrolysis products of coagulants.

Additionally, PAC showing excellent coagulation behavior has been widely used for several decades around the world [16,17], especially in China. However, lots of studies reported in the literature said PAC did not perform excellent removal of organic matters [18,19]. Moreover, the flocs formed by PAC in treating wastewater does not precipitate quickly, leading to a large volume of wet sludge, further causing obvious burden for subsequent concentrating and dewatering [20]. So, PAC was used to be a reference sample in this work.

So, to overcome some weakness of PAC in treating waters, such as low removal efficiency of organic matters, slow precipitation of flocs, and high water content of sludge, M-PTF coagulant was prepared mainly using WAFC. And surface morphology, actual microscopic images and UV absorption characteristics of M-PTF before and after hydrolysis were probed by SEM, fluorescence microscopy and UV spectrophotometer, respectively, and effect of hydrolysis process of M-PTF on coagulation performance was analyzed in detail. Last, coagulation performance of M-PTF in treating sewage was studied using Jar tests, compared with that of PAC. The purpose of this work is to provide some basic data for the further study on upgrade preparation, coagulation mechanism analysis, chemical sludge reduction, and practical application of M-PTF in treating various water samples, and is also to offer some possibility of a new way for resource disposing of solid waste of WAFC.

2. Material and Methods

Solid PAC ($w(\text{Al}_2\text{O}_3)=29\%$) was purchased from Henan province in China with the basicity from 60 to 99%.

2.1. Preparation of M-PTF coagulant

2.1.1. Preparation of liquid M-PTF

Firstly, 10 mL tap water was added to 10 g of WAFC ($w(\text{TiO}_2) = 70\text{--}73\%$, $w(\text{Fe}_2\text{O}_3) = 7\text{--}9\%$, Jinan Yuxing, China) to make some ivory-white slurry under slow stirring at room temperature. H_2SO_4 solution (75–85% (w/w), industrial grade) was introduced rapidly into the slurry under slow stirring and 100 °C for 1 h to obtain a leaching solution, and then was followed by 2 times dilution to obtain a diluent. Then the diluent was filtrated to obtain a filtrate. Secondly, NaOH solution (17 mol/L, industrial grade) was added slowly to the filtrate under rapid stirring to obtain a semi-polymerized product with pH 0.5, and was followed by a heating of 10~20 min at 40 °C (Fu and Su, DOI: 10.1007/s12649-016-9723-x; Su, 2015), and then was

polymerized for 24 h to obtain a yellow-green liquid product of M-PTF with TiO_2 of 1 mmol/L and density of 1.359 kg/L, respectively.

2.1.2. Preparation of solid M-PTF

Liquid M-PTF was dried at 70 °C in oven for 26 h to make solid M-PTF with $w(\text{TiO}_2)$ of 12.98% and $w(\text{Fe}_2\text{O}_3)$ of 0.45%, respectively.

2.2. Micro-characteristics of M-PTF before and after hydrolysis

The following dosage was as Ti amount in water samples.

2.2.1. Surface morphology

SEM (Hitachi S-2500, Japan) was used to study the surface morphology of M-PTF before and after hydrolysis, in which solid M-PTF in Section 2.1.2 and solid HPM (hydrolysis products of M-PTF) was used as samples, respectively.

Solid HPM was prepared as follows. The pH of 1000 mL distilled water (The qualities were shown in Table 1) was adjusted to 12 by NaOH solution (17 mmol/L, industrial grade) (there is no production of HPM flocs when pH is lower than 12). And Jar test was conducted to form flocs of HPM.

The dosage of liquid M-PTF was selected as 3 mmol/L in Jar test according to coagulation tests conducted previously. Jar test procedure performed using a six-unit multiple stirrer system (ZR4-6 flocculator, zhongrun, China) consisted of a rapid mixing at 200 r/min for 1 min after coagulant addition, and followed by a 10-min and a 5-min mixing periods at 60 r/min and 40 r/min, respectively. Then the flocs (HPM) was allowed to settle 15 min and was taken out to be dried at 70 °C in oven for 26 h to make powder HPM, and then was analyzed by SEM under voltage of 40 kV, compared with that of solid M-PTF.

2.2.2. Microscopic image

ECLIPSE 80i Fluorescence Microscope (Japan, Nikon) was used to study the actual microscopic image of flocs formed during Jar test by M-PTF in distilled water with pH 12 (HPM flocs), compared to that formed during Jar test by M-PTF in real sewage (Practical flocs). The real sewage was taken from a sewer located on the campus on University of Jinan, and the qualities were also summarized in Table 1.

Table 1 Qualities of water samples

Water samples	Turbidity (NTU)	pH	Temperature (°C)	COD _{Cr} (mg/L)	Color (CU)
Distilled water	0.05	5.8	23	0	0
Sewage	95.3–112.5	8.16–8.29	25	554.88–612.53	0.603–0.712

1000 mL distilled water and 1000 mL sewage were used as the tested waters for Jar tests to produce HPM flocs (in distilled water) and Practical flocs (in real sewage), respectively.

Jar test procedure was the same as Section 2.2.1. The dosage of liquid M-PTF was 3 mmol/L. HPM flocs and Practical flocs were carefully taken out and introduced onto the object plates, and then were photographed under 40 magnification times with Fluorescence Microscope, in which the same conditions were exactly taken in order to minimize the impact of human factors on the results to a large extent.

2.2.3. PH value

Liquid M-PTF in Section 2.1.1 was taken out and diluted for different dilution times of 20, 60, 150, 400 and 800 using distilled water, respectively, and then the pH values of the diluents were measured with PB-10 pH meter (Germany, Sartorius).

2.2.4. UV absorption

The diluents at different dilution times of 20, 60, 150, 400 and 800 in Section 2.2.3 were conducted full scan from wavelength 200 nm to 430 nm with T6 UV/VIS spectrophotometer (PUXI, Beijing) to analyze the changes of UV absorption of M-PTF when diluted to different levels.

2.2.5. Zeta potential

The Zeta potentials of liquid M-PTF diluted 20, 60, 150, 400 and 800 times were measured (Li, 2012) five times by a 300HS potential and nano-particle size analyzer (Malvern, UK) at temperature 25 °C.

The pH of liquid M-PTF diluted 150 times was adjusted to different values, and then their Zeta potentials were measured three times and the results represented the averages.

2.3. Coagulation behaviour of M-PTF

M-PTF and PAC were used as coagulants. The sewage in Section 2.2.2 was used as water samples.

Jar test procedure was the same as Section 2.2.1.

Influence of dosage. Dosage ranged between 2 and 4.5 mmol/L (as Ti or Al amount in water samples).

Influence of pH value. The water samples were adjusted to 3–13 using NaOH or HCl solutions, respectively. Dosage level was selected to be 2 mmol/L.

100 mL supernatant in Jar tests were withdrawn from a position of 2–3 cm below the surface after sedimentation for the analysis of turbidity and color with 2100AN Turbidity Meter (USA, HACH) and COD_{Cr} with HACH DR1010 COD Rapid Detector (USA, HACH), respectively.

All tests were performed in three runs. The results represented the averages of the tests.

3. Results and Discussion

3.1. Changes of micro-characteristics of M-PTF before and after hydrolysis

Generally, lots of metal ions are to be hydrolyzed and produce various hydrolysis products after added to water solutions with different pH values. Titanium (“biophile metal”) whose activity is between Mg and Al, has “average electron binding energy” of -7.37 eV. Fe³⁺ is characterized by having larger ratio of charge and diameter, stronger positive electricity field, and a little larger “average electron binding energy” (-8.72 eV) [21]. For metal atoms, the more negative the “average electron binding energy” is, the greater the attraction to external electrons has, and the larger the hydrolysis constant is. So, it can be inferred that iron will be hydrolyzed a little more easily than titanium after diluted, but they probably gave similar hydrolysis process. As well known, graded hydrolysis occurs after iron ion is added to water solutions, for instance, Fe³⁺ will hydrolyze to form dimers, trimers, and a large number of polynuclear substances connected by hydroxyl bridges. So, titanium will also hydrolyze to form polynuclear substances (having different amount of nucleus numbers) connected by different amount of hydroxyl bridges. Generally, titanium will often be hydrolyzed to various

substances (such as $[\text{Ti}(\text{H}_2\text{O})_6]^{4+}$ or $[\text{TiO}]^{2+}$, $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_6]^{4+}$, etc) (Zhao, 2014) at lower pH side. The preparation of M-PTF in this work involved two stages (leaching with acid and polymerization with alkali), in which complex cross-copolymerization maybe occurred, probably forming some complex polymers mainly containing some polynuclear polymers of iron or titanium connected by hydroxyl bridges; in addition, some other substances involving silicon, sodium, SO_4^{2-} , etc, also were co-polymerized in M-PTF. So, HPM should belong to a multicomponent system. In fact, dilution of M-PTF was also a hydrolysis process, so there will be different changes in species, structure, component and amount, and charge density of the polymers of titanium and iron after M-PTF was diluted to different dilution times, thus resulting in different changes in M-PTF's surface morphology, flocs appearance, acidity or alkalinity, intensity of absorption peak, and so on. So, the changes of micro-characteristics during hydrolysis process of M-PTF were studied in the following parts.

3.1.1. Surface morphology

Fig.1 displays the comparison of surface morphology between M-PTF (Fig.1a) at 10 K magnification times and HPM (hydrolysis products of M-PTF) in distilled water (Fig.1b) at 5 K magnification times, respectively. Though HPM was obtained under alkaline conditions in this test, the changing trend of the characteristics of surface morphology during hydrolysis process can be reflected to some extent. Fig.1 showed that the surface morphology of HPM (Fig.1b) was obviously different from that of M-PTF (Fig.1a).

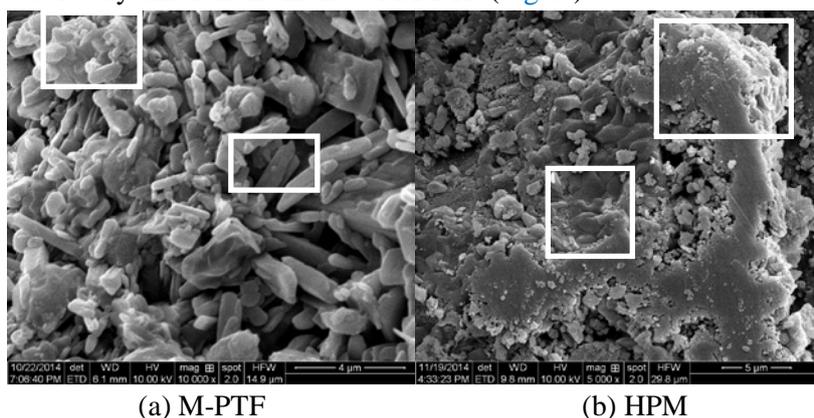


Fig.1 Surface morphology of (a) M-PTF under 10 K magnification times and (b) HPM under 5 K magnification times

The surface morphology of HPM was much more complex and diverse than that of M-PTF, in which the structure, size and composition of HPM became more and more various, uneven, and rough. While M-PTF appeared to be some sort of net structure (having large surface area) which was composed of a variety of different morphologies.

From another point of view, M-PTF consisted of a kind of mixed structures involving some irregular structures and crystalline-like structures. The dominant type was irregular structures which were characterized by having various gap-like structures with smaller size. The smaller amount of crystalline structures was characterized by ditch-like structures with larger size.

The surface structure of HPM (Fig.1b) was mainly composed of ups-and-downs planar structures, soft blocky structures (having rough surface, bigger size, and larger surface area), and smaller size of crumb structures giving smooth surface. So, it can be inferred that the hydrolysis process of M-PTF was quite complex, and almost had great impact on species, structure, composition and size of HPM, in which various HPM were formed, such as polynuclear copolymers of different molecular weight, gels and solid products, etc. Moreover,

under different pH conditions, it can be inferred the proportion of different HPM was also different, thus resulting in different percentage of different morphology in the total surface structures of HPM.

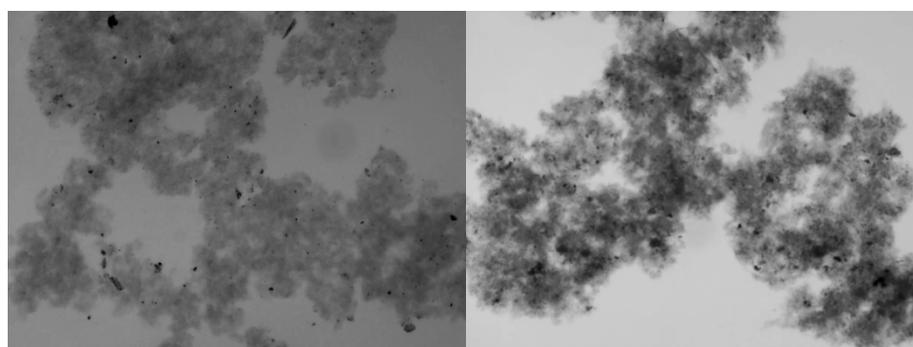
Great difference of the surface morphology between M-PTF (Fig.1a) and HPM (Fig.1b) indicated that complex hydrolysis strengthened the ability of HPM of catching pollutants: much more various structures of HPM probably increased appropriate "catching points" for different pollutants, and different amount of various structures which were formed under different pH conditions also strengthened removal efficiency of different pollutants.

3.1.2. Microscopic images

Actual microscopic image of the flocs formed by M-PTF in distilled water with pH 12 (HPM flocs) was studied with Fluorescence Microscope, in comparison with that of the flocs formed by M-PTF in treating sewage (Practical flocs), as shown in Fig.2.

The image of Practical flocs (Fig.2b) was quite different from that of HPM flocs (Fig.2a). These two images appeared to be some soft and fluffy catkins-like or cotton-like structures which were tightly connected with each other, without small flocs scattered, but there almost had no core particles in HPM flocs (almost in floating status) and there were lots of core particles overlaid with each other in Practical flocs.

In addition, Practical flocs had clearer boundary than HPM flocs. Practical flocs were obviously thicker and heavier than HPM flocs, because the latter (Fig.2a) were simply generated by M-PTF itself, while the former (Fig.2b) were the combination between HPM and pollutants. HPM flocs were more transparent than Practical flocs, indicating that water content of the former (Fig.2a) was greater than that of the latter (Fig.2b), which was one of the reasons for which the latter (Fig.2b) was easily and quickly separated from water to form precipitates.



(a) ^a HPM flocs

(b) ^b Practical flocs

Fig.2 Microscopic images of (a) ^aHPM flocs and (b) ^bPractical flocs ($\times 40$), dosage=3 mmol/L

^a HPM flocs: refers to the flocs formed by HPM in distilled water with pH 12;

^b Practical flocs: refers to the flocs formed by M-PTF in sewage treatment

The sort of catkins-like structures in HPM flocs obviously has strong adsorption, bridging and sweeping performance for impurities. Although HPM flocs was generated at higher pH side (no flocs was formed at pH lower than 12), there is some referential value in analyzing the performance of actual HPM having high degree of polymerization in treating real wastewaters.

3.1.3. PH values

Fig.3 displays the pH changes of M-PTF at different dilution times.

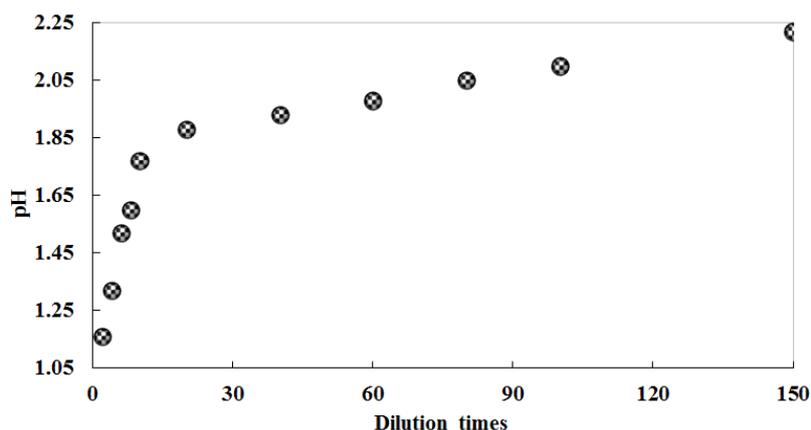


Fig.3 Influence of dilution times on pH value of M-PTF

As seen in Fig.3, the acidity of M-PTF decreased sharply with the increasing of dilution times when dilution times was lower than 20, and then followed by a slow decrease with the increasing of dilution times. This indicated that the hydrolysis products of the salt components in M-PTF showed to be acidic, that is, M-PTF maybe was composed of strong acid weak alkaline salts or acid salts. Some weakly acidic electrolyte were formed from the reaction between the weak acid ions (ionized out from the strong acid weak alkaline salts or acid salts during the hydrolysis of M-PTF) and H^+ (ionized out from water), meanwhile, a certain amount of OH^- was released, thus resulting in a slight increasing of the alkalinity of M-PTF. When dilution times was smaller (<20), the hydrolysis process of M-PTF was not yet finished, so, much more OH^- was released than the previous dilution times, thus leading to a rapid increase of pH values. When dilution times was larger than 20, M-PTF almost finished its hydrolysis process, so, pH tended to be stable. The results in Fig.3 also indicated that the changes of species, structure, and component ratio of different HPM were very different before and after M-PTF was diluted 20 dilution times, which was consistent with the changes in UV absorption in Fig.4.

3.1.4. UV absorbance

Fig.4 displays the changes of UV absorbance of M-PTF with wavelength from 190–430 nm at different dilution times.

As previously analyzed at the beginning of Section 3.1, there will be some changes in micro-characteristics (such as species, structure, component and amount, and charge density of polymers of titanium and iron, and so on) before and after hydrolysis of M-PTF, thus resulting in intensity weakening or disappearing of some absorption peaks. Generally, metal ions in low polymers are easily to be hydrolyzed, but metal ions in middle or high polymers are the opposite, which makes metal polymers with different polymerization degrees have different changes in intensities of some characteristic UV absorption peaks. Therefore, some changes in types, structures, and component contents of HPM (hydrolysis products of M-PTF) can be qualitatively analyzed to some extent according to the various changes of UV absorption peaks during hydrolysis process.

As displayed in Fig.4, with the increasing of dilution times, there were the following main two changes in UV absorption characteristics of M-PTF.

a. Increasing dilution times led to an occurrence of blue shift in M-PTF absorption peaks on the whole, mainly because some auxochrome groups (such as $-OH$, etc.) having lone pairs of electrons gradually entered into some positions (such as meta positions having no impact

on UV absorption) of HPM during hydrolysis process, thus leading to further development of three-dimensional structures, further increase of larger spatial size, and further increase of molecular weight. It also indicated that the components of M-PTF having absorption at lower wavelength maybe was composed of middle or high polymers, compared with low polymers at higher wavelength range.

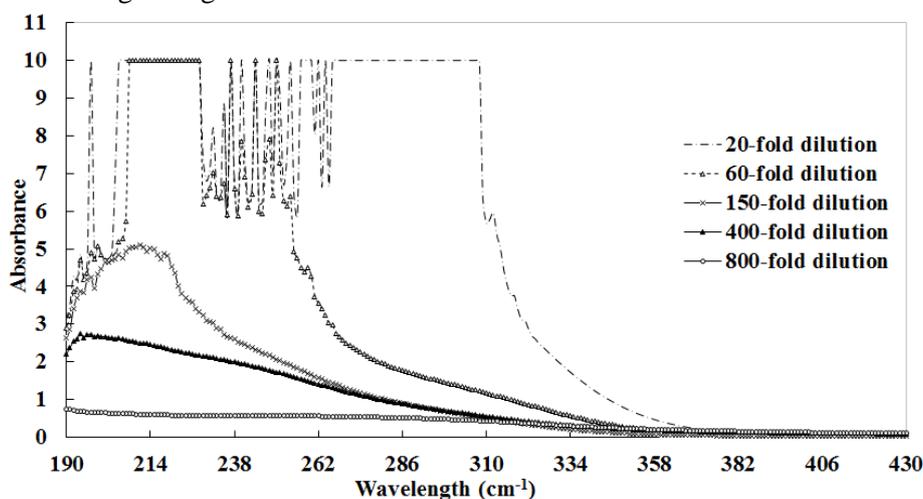


Fig.4 Influence of dilution times on UV absorbance of M-PTF

b. The number and intensity of the absorption peaks decreased on the whole with the increasing of dilution times, especially some peaks almost disappeared after M-PTF was diluted to a certain times. This indicated that various HPM having different absorption wavelengths tended to be converted into single type with the increasing of dilution times, probably becoming the same type or the same products at last.

So, it can be inferred from Fig.4, there was complex changes HPM during hydrolysis, in which the composition, structure and percentage of various types varied largely in different hydrolysis extent. This work can provide some theoretical support for qualitative analysis of coagulation mechanism of M-PTF in different application situations, and also provide some theoretical basis for both directional selection of certain pollutants removal and analysis on removing mechanism.

3.1.5. Zeta potential

Fig.5 shows the changes of Zeta potential of M-PTF with the increasing of dilution times and pH values.

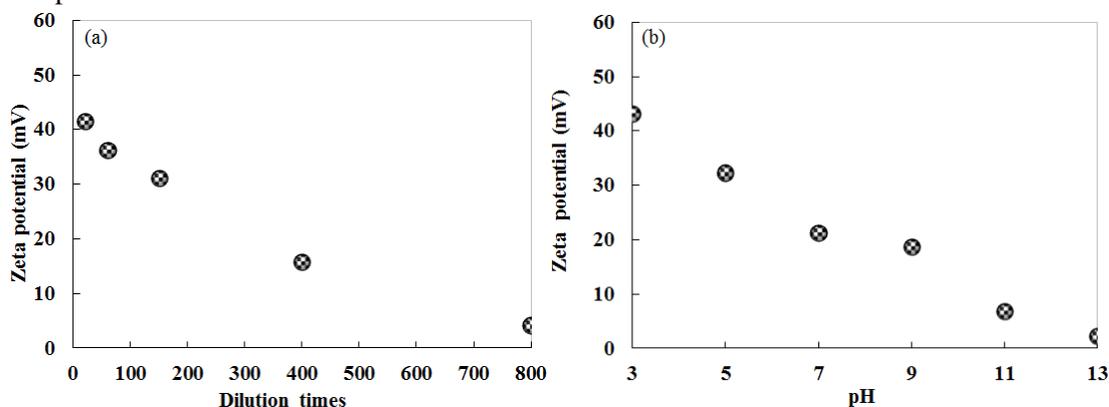


Fig.5 Influence of dilution times and pH on Zeta potentials of M-PTF

As seen from Fig.5, the Zeta potentials of M-PTF were much larger than the isoelectric

point (net charge equivalent to 0 mV) at different tested both dilution times and pH values, in which the Zeta potential decreased with the increasing of dilution times and with the increasing of pH. M-PTF reached the highest Zeta potentials at dilution times of 20 and pH 3, and tended to be the value equivalent to the isoelectric point at dilution times of 800 and pH 13, respectively, which suggested that the neutralization ability of M-PTF for pollutants negatively charged was stronger at smaller dilutions times and lower pH side than larger dilutions times and higher pH side, respectively.

3.2. Coagulation behavior of M-PTF.

Influence of dosage and pH on coagulation behavior of M-PTF was conducted, compared with that of PAC, as shown in Fig.6 and Fig.7.

3.2.1. Influence of dosage

Fig.6 presents the removal of turbidity, COD_{Cr} and color in treating sewage with final Ti or Al level ranged from 2–4.5 mmol/L.

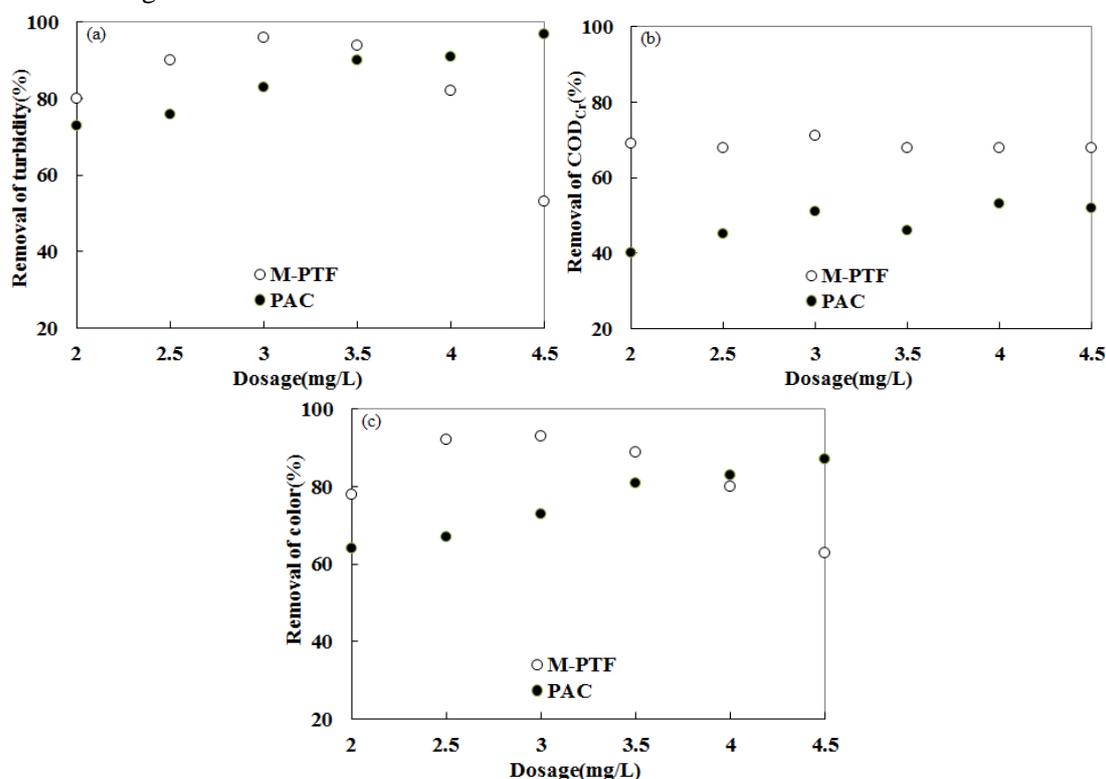


Fig.6 Removal of (a) turbidity, (b) COD_{Cr} and (c) color by M-PTF (○) and PAC (●) in treating sewage at different dosages

As indicated in Fig.6, dosage had different impact on pollutants removal by M-PTF from that by PAC. M-PTF almost had better removal rate for various pollutants than PAC, and PAC only gave higher removal rate of turbidity and color than M-PTF at higher dosages. The removal of turbidity and color by M-PTF was increased firstly and followed by decrease with the increasing of dosage, while PAC almost showed continuous increasing removal of pollutants with the increasing of dosage, suggesting that the required dosage of PAC was far greater than that of M-PTF when reaching the same removal efficiency of pollutants.

Additionally, M-PTF had lower required dosage (optimal dosage) for COD_{Cr} (2 mmol/L) removal than that for turbidity (3 mmol/L) and color (2.5 mmol/L) removal, and M-PTF gave

higher 14% (3 mmol/L), 29% (2 mmol/L), and 25% (2.5 mmol/L) removal of turbidity, COD_{Cr} and color than PAC, respectively.

3.2.2. Influence of pH

Fig.7 presents the comparison of turbidity, COD_{Cr} and color removal between M-PTF and PAC with pH from 3–13 in treating sewage at dosage 2 mmol/L.

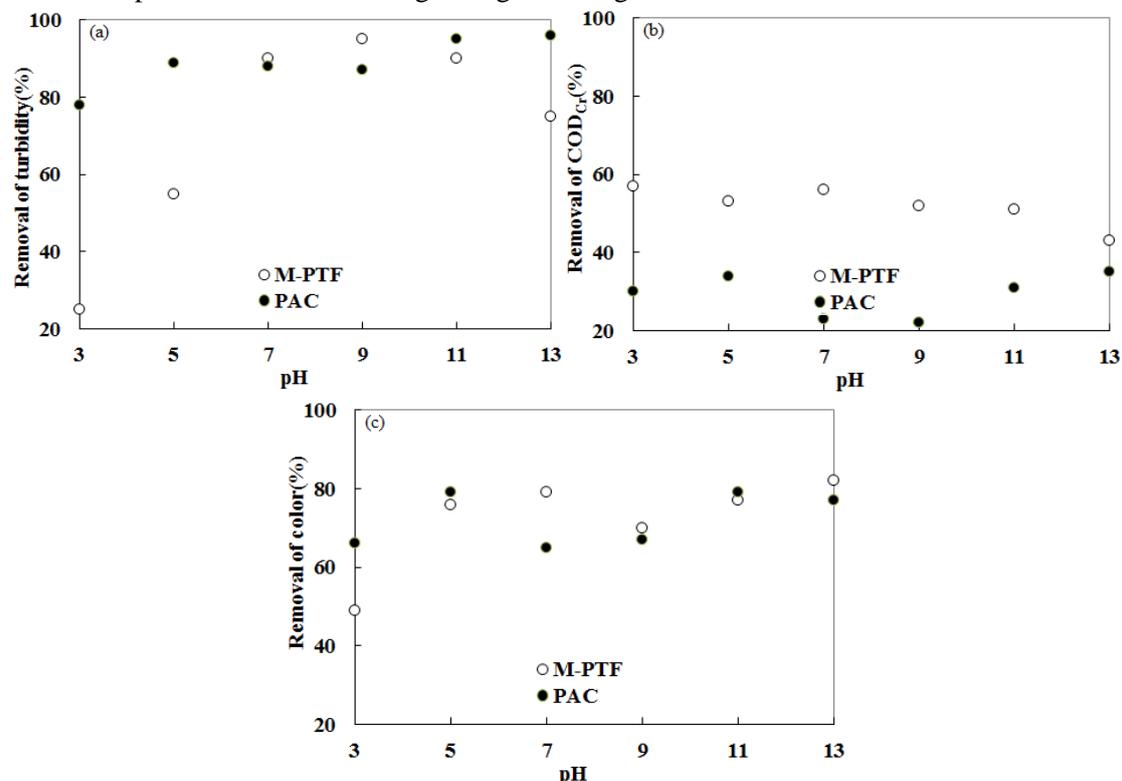


Fig.7 Removal of (a) turbidity, (b) COD_{Cr} and (c) color by M-PTF (○) and PAC (●) in treating sewage at different pH, dosage=2 mmol/L

Fig.7 showed that pH had different impact on pollutants removal by M-PTF from that by PAC. M-PTF had higher turbidity and color removal (Fig.7a and Fig.7c) under nearly neutral and alkaline conditions. But, M-PTF almost gave higher COD_{Cr} removal (Fig.7b) over the entire pH values, and far higher COD_{Cr} removal than PAC. For instance, COD_{Cr} removal by M-PTF was up to 58, 56 and 51% at pH 3, 7 and 11, higher 27, 33 and 20% than that by PAC, respectively. So, it can be inferred that M-PTF resulted in suitable pH values for removing organic matters over the entire pH ranges, so, different pH ranges can be selected to effectively remove organic matters in treating different actual wastewaters. However, as also seen in Fig.7, PAC almost gave the lowest removal of turbidity, COD_{Cr} and color under near neutral conditions, which largely restricted its application in treating real wastewaters.

As also shown from Fig.6 and Fig.7, both dosage and pH gave smaller impact on organic matters removal by M-PTF than that by PAC; moreover, M-PTF almost resulted in higher removal of organic matters than PAC at given dosage and pH ranges. This suggested that M-PTF had a wider suitable dosage range than PAC at the same pH values; similarly, M-PTF also posed a wider suitable pH range than PAC at the same dosages. The flexible adaptation ranges of dosage and pH made M-PTF have much more actual application significance in removing organic matters in treating complex wastewaters.

M-PTF gave the above-mentioned performance of eliminating pollutants can be mainly explained by the following reasons.

a. In general, inorganic coagulants (such as Al-based or Fe-based) hydrolyzed to form metal complexes within a very short period of time, and then migrated onto the surface of impurities to perform adsorption/destabilization. Although there is no much specific hydrolysis data for M-PTF, the hydrolysis process of M-PTF will be similar to that of Al-based or Fe-based coagulants. The hydrolysis process of M-PTF under weak alkaline conditions (Fig.6) was slightly different from that of strong alkaline conditions (Fig.1b and Fig.2b), which probably made the composition of HPM formed in Fig.6 was of some difference, thus leading to that the amount of each type structures on the surface was of some difference. However, as inferred from Fig.1 that HPM appeared to be a big surface area structures (characterized by having various rough surface morphologies), and gap-like structures (characterized by having various size and shape) no matter whether M-PTF was in acidic or in alkaline conditions; moreover, the sort of catkins-like flocs of HPM obviously can exert fully strong adsorption, bridging and sweeping performance (Fig.2a); additionally, as a complexed co-polymer of two cations of Ti and Fe, M-PTF will hydrolyze to form much more different complicated hydrolysis products carrying more positively charged (Fig.5) than PAC which is only composed of one metal of aluminum, so, M-PTF gave full multi-type driving forces (including Electrostatic attraction, Hydrogen bonds, Coordinate bonds and Van der Waals forces) for removing pollutants, exerted superior charge-neutralization, bridging and sweeping function, and so on, so M-PTF had lower required dosage than PAC when reaching the same removal efficiency of pollutants, and gave better removal rate for various pollutants.

b. For coagulation, the process of dosage changing is equivalent to the process of dilution times changing, so, there will be complex changes in species, structure, component and amount, and charge density of the hydrolysis products of M-PTF (Fig.1–Fig.5). Dosage changing from less to more is equivalent to an decreasing of dilution times (decreasing of dilution degree), in which HPM changed from single type to various types (Fig.4) and the total charges carried by HPM changed from less to more (Fig.5). As seen in Fig.6, by calculation, dilution times was equivalent to variation from 500 (low dosage) to 140 (high dosage) during coagulation, in which the types of HPM increased (Fig.4), the surface morphology of HPM having much more complex and diverse structures increased (Fig.1), the total charges carried by HPM increased (Fig.5), and the size and chain length of HPM decreased, so, it can be inferred that the ability of charge neutralization was relatively weaker and adsorption/bridging/sweeping was relatively stronger in removing turbidity and color by M-PTF. While for organic matters, charge neutralization, adsorption/bridging and sweeping all played important roles, moreover, charge neutralization, adsorption/bridging or sweeping can also be replenished by one of those when each action was weakened at some cases, which may be one of the reasons for which M-PTF had lower required dosage for COD_{Cr} removal than that for turbidity and color removal (Fig.6).

c. The total charges carried by HPM decreased (Fig.5) and the size and chain length increased with the decreasing of acidity. M-PTF having higher turbidity and color removal (Fig.7a and Fig.7c) at nearly neutral and alkaline conditions further indicated that the ability of charge neutralization of M-PTF was relatively weaker and adsorption/bridging/sweeping was relatively stronger in removing turbidity and color. Meanwhile, M-PTF almost having higher COD_{Cr} removal (Fig.7b) over the entire pH values further suggested that charge neutralization, adsorption/bridging and sweeping all exerted important action in removing organic matters. According to the results from Fig.1 to Fig.7,

the proportion of charge neutralization, adsorption/bridging and sweeping of M-PTF in removing organic matters may be adjusted based on different water conditions, thus making M-PTF have more flexible dosage and pH ranges than PAC.

Of course, the hydrolysis process of M-PTF in real water samples is much more complex than that in distilled water, and the components and surface structures of HPM may be far more complex in the former than that in the latter, but it also has some reference value for the actual hydrolysis process of M-PTF in treating real wastewaters.

4. Conclusion

The micro-characteristics of M-PTF was very different from that of HPM which carried more positive charges, had more various, uneven and rough surface morphology, gave lighter and more floating actual image with larger water content. M-PTF maybe consisted of strong acid weak alkaline salts or acid salts. Diluting M-PTF resulted in blue shift, intensity weakening or disappearing of some UV absorption peaks.

The required dosage of M-PTF was far lower than that of PAC when reaching the same removal efficiency of pollutants, and M-PTF gave higher 14% (3 mmol/L), 29% (2 mmol/L), and 25% (2.5 mmol/L) removal of turbidity, COD_{Cr} and color than PAC, respectively.

For M-PTF, the ability of charge neutralization was relatively weaker and adsorption/bridging/sweeping was relatively stronger in removing turbidity and color, while charge neutralization, adsorption/bridging and sweeping all played important roles in removing organic matters, which may be one of the reasons for which M-PTF had lower required dosage for COD_{Cr} removal than that for turbidity and color removal over the entire pH and dosage ranges.

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