

A NEW WATER TREATMENT AGENT PREPARED from a “WASTE ACID FILTER CAKE”

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Abstract: A new type of inorganic water treatment agent of poly-Ti-Fe (M-PTF) was prepared mainly using a kind of “Waste acid filter cake” (WAFC) and was characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The removal of chemical oxygen demand (COD_{Cr}) by M-PTF in treating different wastewaters was studied, compared with that of polyaluminum chloride (PAC). The results indicated that M-PTF consisted of much more co-polymerized crystalline and amorphous materials, and appeared to be some sort of net structure (having large surface area) composed of some irregular structures and crystalline-like structures. M-PTF displayed higher COD_{Cr} removal than PAC, and gave suitable broader both pH and dosage ranges than PAC in removing COD_{Cr}. The coagulation performance of M-PTF depended on its special micro-characteristics which gave better “catching ability” for organic matters.

Keywords: water treatment agent, “waste acid filter cake”, COD_{Cr} removal, wastewater

1. Introduction

Rapid accumulation of solid wastes has become a worldwide problem due to the quick development of economy and people's living standard. China, experiencing rapid development, has become one of the countries which were seriously polluted by solid wastes. The solid waste in China was over 6 billion tons currently and increased rapidly at annual growth of 10% which was larger than 2.5% abroad [1]. Therefore, the disposal of solid wastes has become more and more important in the near future. However, as well known, most of solid wastes discharged in one point maybe have their values in other points, so, resource disposing becomes one of the main treating methods, 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 [2-5].

China is not only one of the countries having the largest storage capacity of titanium in the world [6], but also one of the largest consumers. Two methods are mainly used to produce TiO₂: Sulfate method and Chloride method. The latter is usually utilized abroad, and the former is widely used in China. But, lots of wastes and byproducts are generated [7] in the former method, for instance, a sort of WAFC (containing elements of Ti, Fe, Al, Si, etc; w(TiO₂)=70–73%, and w(Fe₂O₃)=7–9%) will be generated from the waste acid coming from the washing process [8,9]. Fe and Si are often important components for producing inorganic coagulants, while Ti is often used in preparation of water purifying agents as a new element [10-14]. 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”.

PAC showing excellent coagulation behavior has been widely used around the world for several decades [15,16], especially in China. However, PAC did not perform excellent removal of organic matters. So, in this work, a new type of inorganic water treatment agent of poly-Ti-Fe (M-PTF) was prepared mainly using WAFC, and was characterized by X-ray Diffraction (XRD)

and Scanning Electron Microscopy (SEM). The elimination of organic matters by M-PTF in treating a simulated dyeing wastewater and sewage was studied, compared with that of PAC. The work will provide a new way for resource disposing of solid waste of WAFC.

2. Material and methods

2.1. Preparation of M-PTF

M-PTF was prepared mainly using a WAFC. Firstly, a little water was added to 10 g WAFC (Fig.1a) at room temperature to make some ivory-white slurry under slow stirring. 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 a two-fold dilution to obtain a diluent. Then the diluent was filtrated to obtain a filtrate. And then NaOH solution (17 mmol/L, industrial grade) was added slowly into the filtrate under rapid stirring to obtain a semi-polymerized product with pH 0.5, followed by a heating of 10–20 min at 40 °C, 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.

Liquid M-PTF was dried at 70 °C in oven for more than 24 h to make solid M-PTF (Fig.1b) with $w(\text{TiO}_2)=12.98\%$ and $w(\text{Fe}_2\text{O}_3)=0.45\%$, respectively.

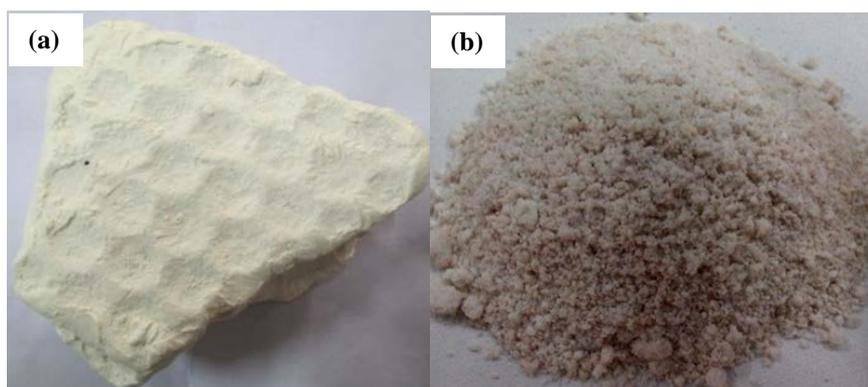


Fig.1 Pictures of (a) “Waste acid filter cake” (WAFC) and (b) solid M-PTF product

2.2. Microscopic characteristics of M-PTF

2.2.1. Crystal characteristics by XRD spectra

The crystal characteristics of solid M-PTF was analyzed by D8 ADVANCE XRD (German BRUKER-AXS Ltd) under the following conditions: Diffraction slit from left to right of 1 mm, Nickel monochromator (0.6 mm), LynxEye array detector, Voltage 40 kV, Current 40 mA, Linear range of scintillation counter 2×10^6 cps, The minimum step length 0.0001 °, Angle reproducibility 0.0001 °, Angular resolution 0.02 °, and Scanning speed 2 θ of 5 °/min.

2.2.2. surface morphology by SEM

SEM (Hitachi S-2500, Japan) was used to study the surface morphology of M-PTF at 10 K time magnification.

2.3. Coagulation behaviour of M-PTF

M-PTF and PAC were used as coagulants. A simulated dyeing wastewater and sewage were selected as water samples. The preparation of the simulated dyeing wastewater was as follows: 0.1 g solid dispersion brown dye and 1 g solid NaCl were mixed in 1 L tap water under 10 min rapid string to make the water sample. The real sewage was taken from a sewer located on the campus at University of Jinan. The water qualities were shown in [Table 1](#).

Table 1 Qualities of tested wastewater

Wastewater samples	Turbidity /NTU	pH	Temperature /°C	COD _{Cr} /(mg/L)	Color /CU
Simulated dyeing wastewater	305-306	7.87-7.92	18-23	120.23-146.88	2.11-2.16
Sewage	74.6-182	8.16-8.45	15-18	620.16-654.20	1.12-1.14

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 hydrolysis flocs was allowed to settle 15 min and then the supernatant were taken out from a position of 2–3 cm below the surface after sedimentation for the analysis of COD_{Cr} with HACH DR1010 COD Rapid Detector (USA, HACH) . All tests were performed in three runs. The results represented the averages of the tests.

Influence of dosage. Dosage ranged between 0.5 and 3 mmol/L for the simulated dyeing wastewater and between 2 and 4.5 mmol/L for the sewage (as Ti or Al amount in water samples).

Influence of pH value. The pH of raw water samples were adjusted to 3–13 using NaOH or HCl solutions, respectively. Dosages were selected as 2 and 3 mmol/L for the simulated dyeing wastewater and sewage, respectively.

3. Results and discussion

3.1. Micro-characteristics of M-PTF

3.1.1. Crystal characteristics

To study the crystal properties of coagulants, XRD spectra of M-PTF was analyzed, as shown in [Fig.2](#).

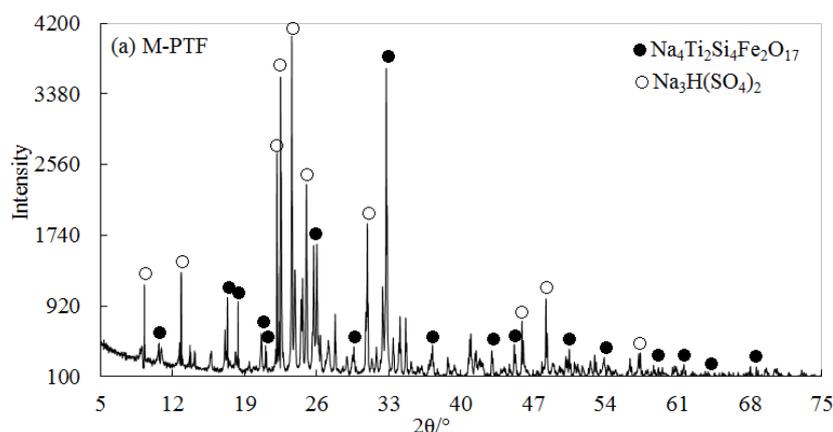


Fig.2 XRD spectra of M-PTF

Generally, a series of sharp characteristic diffractive peaks of crystal materials can be observed at certain 2θ in XRD spectra, but amorphous substances which are often composed of one or two diffuse peaks, a wider halo or diffuse distribution of rings will not be detected by XRD method [17]. Much more small peaks having the characteristics of polycrystalline phase appeared in M-PTF at different diffraction angles than that in PAC [18], indicating that much more crystalline of metal copolymers were formed in M-PTF. $\text{Na}_3\text{H}(\text{SO}_4)_2$ and $\text{Na}_4\text{Ti}_2\text{Si}_4\text{Fe}_2\text{O}_{17}$ which was composed of Na, Fe, Ti, O, Si and other elements were detected in M-PTF. But, no crystals of oxides or salts of Fe, Ti and other metal elements could be detected, such as $\text{Fe}_2(\text{SO}_4)_3$, Fe_2O_3 , $\text{Fe}(\text{OH})_3$, Fe_3O_4 , TiO_2 , TiOSO_4 or $\text{Ti}(\text{OH})_4$ and so on. This suggested that M-PTF consisted of much more co-polymers of crystalline and amorphous substances probably due to the copolymerization of Fe, Ti and many other ions [19], instead of a simple mixture of polymer products of one metal alone.

3.1.2. Surface morphology

To visually study the surface features of M-PTF, the SEM pictures of M-PTF was photographed compared with that of PAC, as shown in Fig.3.

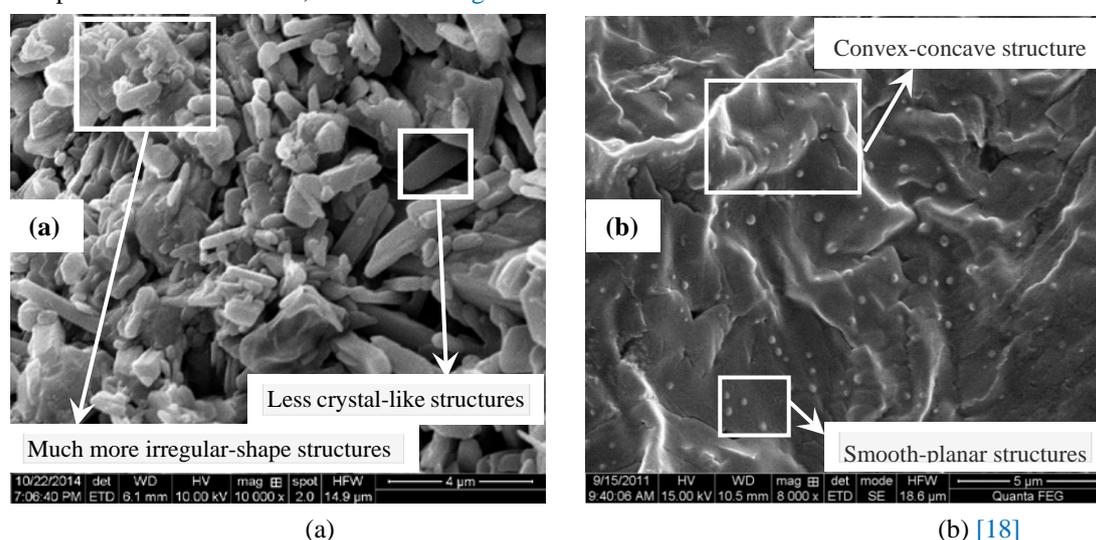


Fig.3 Surface morphology of (a) M-PTF ($\times 10000$) compared with that of (b) PAC ($\times 8000$) [18]

As seen in Fig.3(a), the surface morphology of M-PTF appeared to be some sort of network structure which was built up by a variety of structures having large surface area and mainly consisted of some irregular and crystalline-like structures, in which the dominant structure was irregular type having various and smaller size of gap structure. The characteristics of M-PTF surface morphology were consistent with the analysis from Fig.2, that is, the fact that M-PTF was a complex polymer copolymerized by Fe, Ti and many other ions was reflected by the properties of its surface structure. While PAC (Fig.3b) [18] was composed of a sort of irregular mountain appearance of convex-concave structure, in which there are some sudden changes from convex to concave structures and some morphology presented a large area of smooth plane, thus leading to smaller surface area of PAC than that of M-PTF. In addition, there were some smooth elliptical structures distributed unevenly on the surface of PAC.

3.2. Removal of COD_{Cr} by M-PTF

3.2.1. Influence of dosage

Fig.4 displays the impact of M-PTF dosage on COD_{Cr} removal with final Ti or Al concentration from 0.5 to 3 mmol/L and 2 to 4.5 mmol/L in treating simulated dyeing wastewater and sewage, respectively, compared with that by PAC.

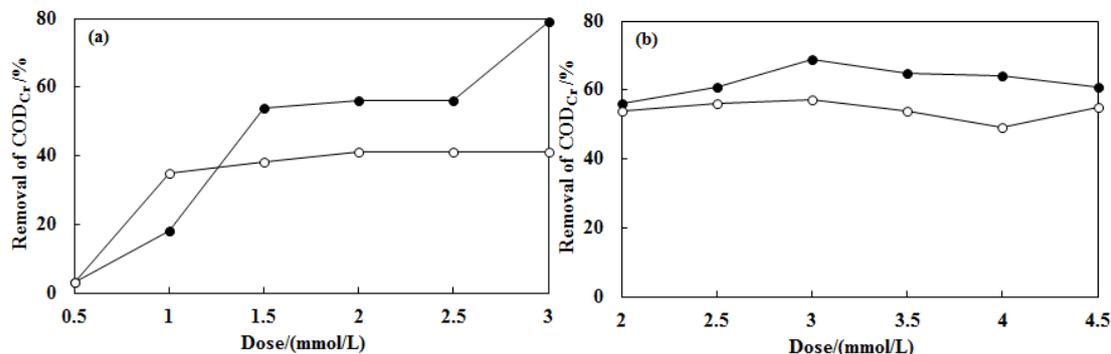


Fig.4 Influence of dosage on removal of COD_{Cr} by M-PTF and PAC in treating (a) simulated dyeing wastewater and (b) sewage. M-PTF (●) and PAC (○). The error bars for all the data points represent the standard error of the mean of three experiments

As shown in Fig.4, M-PTF gave higher COD_{Cr} removal than PAC for the two types of wastewaters. For the simulated dyeing wastewater (Fig.4a), when dosage was lower than 1.5 mmol/L, M-PTF gave lower COD_{Cr} removal than PAC. And COD_{Cr} removal by M-PTF increased continuously with the increasing of dosage, in which M-PTF gave around 54% COD_{Cr} removal at dosage 1.5 mmol/L, more 14% than PAC. The greatest COD_{Cr} removal by M-PTF achieved about 80% at dosage 3 mmol/L, more 40% than PAC at the same dosage. While PAC posed the greatest COD_{Cr} removal (35%) at dosage 3 mmol/L, and then almost unchanged with the increasing of dosages.

For the sewage (Fig.4b), the removal of COD_{Cr} by M-PTF increased firstly with increasing of dosage, and then was followed by a decrease, in which M-PTF gave the greatest COD_{Cr} removal (around 70%) at dosage 2.5 mmol/L, more 20% than PAC. PAC only posed the greatest COD_{Cr} removal of 53% at dosage 3 mmol/L.

In addition, dosage posed less impact on COD_{Cr} removal by M-PTF than that by PAC.

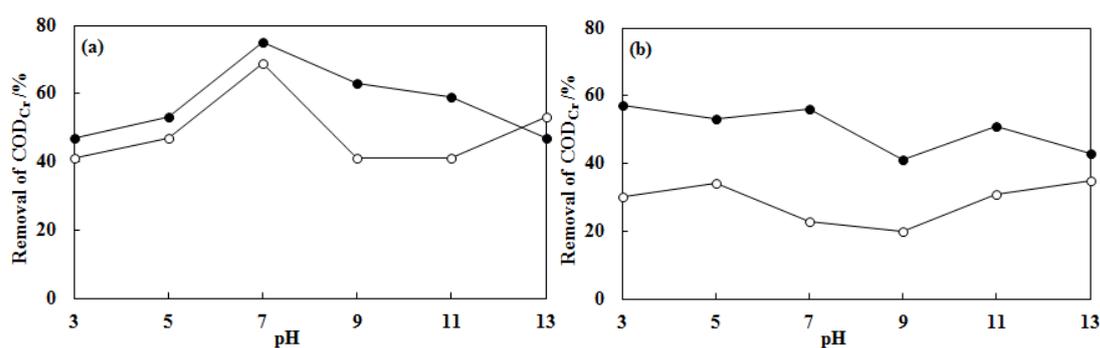


Fig.5 Influence of pH on removal of COD_{Cr} by M-PTF and PAC in treating (a) simulated dyeing wastewater and (b) sewage. Dosage was 2mmol/L for the simulated dyeing wastewater and 3 mmol/L for the sewage, respectively. M-PTF (●) and PAC (○). The error bars for all the data points represent the standard error of the mean of three experiments

3.2.2. Influence of pH

Fig.5 displays the comparison of COD_{Cr} removal between M-PTF and PAC at pH from 3 to 13 in

treating simulated dyeing wastewater and sewage, respectively.

The influence of pH of the tested wastewaters on COD_{Cr} removal by M-PTF was almost the same to or a little different from that by PAC (Fig.5). For the simulated dyeing wastewater (Fig.5a), the suitable pH of M-PTF almost was the same to that of PAC (in neutral range), but, the impact of pH on COD_{Cr} removal by the former was smaller than that by the latter. While for the sewage (Fig.5b), the suitable pH of M-PTF (pH of 3, 7 and 11) was slightly different from that of PAC (pH of 3, 11–13).

M-PTF almost gave higher COD_{Cr} removal than PAC for the two types of wastewaters over the tested pH range. For the simulated dyeing wastewater (Fig.5a), M-PTF achieved COD_{Cr} removal of 63% at pH 9, more 22% than PAC. For the sewage (Fig.5b), the removal of COD_{Cr} by M-PTF achieved about 53、56 and 51% at pH 5、7 and 11, respectively, more 29、33 and 20% than PAC, respectively. It can be inferred from Fig.5, M-PTF almost had the optimum pH conditions for removing organic matters over the tested pH values in treating sewage, so organic matters can be effectively removed if choosing different pH conditions in treating different actual wastewaters. While PAC gave the lowest removal of COD_{Cr} under neutral conditions, which giving great restriction for its application in treating real wastewaters.

It can be indicated from Fig.4 and Fig.5, M-PTF can be adapted to a greater range of dosage at the same pH values and a wider pH range at the same dosages than PAC, which makes M-PTF have much more application significance in treating complex wastewater samples for organic matters removal.

M-PTF performed the characteristics of removing organic matters (above-mentioned) maybe due to the following reasons. (1) M-PTF is a multi-component copolymer (high degree of crosslinking) mainly composed of a variety of metals and anions, and much more crystalline and amorphous substances were formed, thus leading to rough surface morphology (Fig.3) which makes the organic pollutants can be easily grabbed by the complex surface structures. (2) M-PTF hydrolyzes immediately after it is added into water samples, and then migrated onto the surface of impurities to perform adsorption/destabilization. In general, inorganic coagulant of Al or Fe hydrolyzes to form metal complexes within a very short period of time. For instance, formation of $\text{Al}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})^{2+}$ only needs 10^{-10} s, followed by a formation of hydrated hydroxyl complexes in 0.01 s, while the time for adsorption/destabilization (about 0.01–1 s) is much longer than that for hydrolysis. M-PTF is a coagulant mainly copolymerized by two metals of titanium and iron. So, although there is no much specific hydrolysis data for M-PTF, its hydrolysis time on the order of magnitude will be similar to that of Al or Fe. The composition of M-PTF was much more complex than that of PAC, so leading to much more complex hydrolysis products formed by the former than that of the latter. M-PTF can be hydrolyzed to be some mononuclear and polynuclear hydrolyzate of multi-metals, including hydrolysis gels or solids, while PAC only gave some mononuclear and polynuclear of hydrolyzate of single metal. In addition, the hydrolysis products of M-PTF posed much more positive charges and probably gave better adsorption function than that of PAC. So, M-PTF can exert fully the neutralization/adsorption performance for organic matters. (3) M-PTF probably produced different amount of hydrolyzate of different types under different pH conditions due to the complex hydrolysis process, which probably made M-PTF have different amount of various types of surface structures at different pH conditions. In addition, the hydrolyzate of M-PTF probably carried different positive charges at different pH ranges. So, the hydrolyzate of M-PTF probably exerted different function of neutralization/adsorption, bridging and sweeping performance, leading to its more flexible adapted dosage and pH ranges in treating different wastewaters than PAC.

4. Conclusion

M-PTF gave some sort of network surface morphology which had large surface area and was composed of both irregular and crystalline-like structures, in which the dominant structure was irregular type having various and smaller size of gap structure. M-PTF consisted of much more copolymers of crystalline and amorphous substances, instead of a simple mixture of polymer products of one metal alone.

M-PTF posed higher COD_{Cr} removal than PAC for different wastewaters at the tested pH and dosage ranges. M-PTF gave more around 40% (the simulated dyeing wastewater with dosage of 3 mmol/L) and 20% (sewage with dosage of 2.5 mmol/L) COD_{Cr} removal than PAC. The influence of pH of the tested wastewaters on COD_{Cr} removal by M-PTF was almost the same to or a little different from that by PAC. M-PTF gave more about 22% (simulated dyeing wastewater with pH of 9) and 33% (sewage with pH of 7) COD_{Cr} removal than PAC. M-PTF can be adapted to a greater range of dosage and a wider pH range than PAC.

M-PTF giving the better removing rate of organic matters mainly depended on the complex micro-characteristics and the characteristics of hydrolysis products deduced.

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