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Volume and mass reduction of sludge formed by polymerized-organic-Al-Zn-Fe (POAZF) coagulant in treating sewage

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ABSTRACT

A coagulant of polymerized-organic-Al-Zn-Fe (POAZF) was prepared. The volume and mass reduction sludge of POAZF, poly-Al-Zn-Fe (PAZF), and polyaluminum chloride (PAC) were investigated with fluorescence microscope, Field Emission Scanning Electron Microscopy and Jar test. The results indicated that the volume reduction of wet sludge of POAZF ranged from 33.3 to 38.5%, 19.5 to 46.2%, and 26.7 to 61.5% (compared with PAZF), and from 42.9 to 52.4%, 21.5 to 51.4%, and 63.3 to 74.1% (compared with PAC) at dosages of 62, 186, and 372 mg L^{-1}, respectively. Dry sludge reduction of POAZF was from 18.4 to 38% (compared with PAZF) and from 23.2 to 40.6% (compared with PAC) at the same coagulation performance with dosage of 62–122 mg L^{-1}, respectively. POAZF having different amount of similar hydrolysis species from PAZF and having different hydrolysis species and species composition from PAC may be the microscopic reason that the dry sludge of POAZF posed the following surface characteristics. The surface morphology of the dry sludge of POAZF consists of some sort of ball-like or coral-like loose floc structures and bulk crystal-like structures, which is the reason that POAZF has lower dosage than PAZF and PAC when achieving the same coagulation effect and is also the reason that POAZF has large mass reduction of dry sludge.

Keywords: POAZF; Coagulation; Flocs settling; Wet and dry sludge; Reduction

1. Introduction

In recent years, the flow of sewage increased dramatically due to the rapid development of urbanization in China, and the amount of wastewater discharged was estimated to reach 66 billion tons per year [1,2]. Meanwhile, environmental requirement proposed by Chinese government became increasingly stringent due to the potential environmental risk of water body, which resulted in significant increase in treating capacity of sewage. By 2012, sewage treatment capacity in China was upto 138 million m^3 per day [3,4]. With the increasing of amount and treatment scale of sewage, sludge production has certainly increased rapidly [5–7]. The treatment and ultimate disposal of sludge is very expensive and usually accounts for 25–50% of the total operating cost of a conventional wastewater treatment plant, sometimes even up to 65% [2,8–12]. The total production of sludge in moisture content of 80% is nearly upto 30 million tons in China [13], while sludge treatment and

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disposal has not received enough attention for many years. Currently, only about twenty-five percent of sludge has been treated or disposed in harmless methods [3,14]; so, some cities almost appear to be flooded by sludge, which brings about serious risks to the environment. Therefore, sludge disposal has become one of the restricting elements for economic development in China.

Sludge reduction, as a method of sludge treatment from the starting point, is a relatively new concept proposed in the 1990s [8,15–17]. Currently, a number of studies on volume or mass reduction technologies of sludge have been widely conducted [18–24], most of which mainly involved reduction of biological sludge [5,12,23,25–31]. However, investigation on how to reduce chemical sludge from the starting point has been rarely reported. Only recently, researchers paid some attention to the field of metal oxide nanoparticles for sludge reducing and dewatering, such as titanium oxide, silver oxide, zinc oxide, and aluminum oxide [32–34], and also to some studies on magnetic nanomaterials [35]. But, the operation cost of the methods mentioned above in reducing chemical sludge is very high. So, investigation on reducing volume or mass of chemical sludge based on conventional coagulation unit still has great significance in developing countries in which the development of quality coagulants are still more important in the field of sludge reduction.

In addition, solid waste has become a global pollution problem due to the sustainable development of agriculture and industry, as well as the great improvement of people's living standard brought by modernization. China has become one of the countries seriously polluted by solid waste because China is one of the regions which have rapid economy development in the world. The amount of solid waste in China was over six billion tons currently and increased rapidly at annual growth of 10% which is largely greater than that of 2.5% abroad [36,37]. Therefore, the future of solid waste disposal will become one of the most important things. Meanwhile, most of solid waste still has their use value in other areas, so resource utilization becomes one of the main disposal methods, in which preparation of various inorganic and organic coagulants using different types of solid waste has been a promising focus in the field of water and waste water treatment [38–41].

In this work, resource disposing of solid waste was combined with sludge reduction. First, a polymerized-organic-Al-Zn-Fe (POAZF) coagulant was prepared by utilizing a galvanized aluminum slag as a raw main material and polyacrylamide (PAM) as an organic modifier. And then, the microscopic characteristics of the sludge of POAZF in treating sewage, reduction of its wet and dry sludge were analyzed in detail, in comparison with those of poly-Al-Zn-Fe (PAZF) and polyaluminum chloride (PAC). The work is to achieve a purpose of chemical sludge reduction, apart from improving the coagulation performance. This paper is to provide some sort of theoretical basis and fundamental data for chemical sludge reduction using coagulant prepared by solid waste.

2. Materials and methods

2.1. Preparation of coagulants

2.1.1. Preparation of PAZF

The preparation of PAZF is the same as the method which was published in the previous paper [39].

2.1.2. Preparation of liquid POAZF

A color-free filtrate was obtained by the method published in the previous paper [39].

PAM solution (1% (w/w), analytical grade) was poured into a color-free filtrate mentioned in the previous publication [39] under vigorous stirring to obtain a mixed solution. After stirring for 5 min, NaOH solution (5% (w/w), analytical grade) was introduced slowly into the mixed solution at 30–70℃ under stirring to obtain a final solution with pH from 2.0 to 3.0 (PB-10 pH meter, Germany), and was followed by 5–72 h of polymerization to obtain a light brown liquid product of POAZF. The liquid POAZF shows the following properties: w(Al) of 2.43%, w(Zn) of 1.15%, w(Fe) of 0.26%, and density of 1.09 kg L^{-1}.

Solid PAC ($w(Al_2O_3) = 29\%$) was obtained from Jinan Yuantuo Chemical in Shandong Province in China.

2.2. Jar test for coagulation effect

2.2.1. Tested water

The tested water was a sewage which was actual wastewater taken from a sewer located on the campus in University of Jinan. The qualities of the water sample were as follows: Turbidity = 159 NTU, pH = 7.4–7.69, Temperature = 17–21℃, COD_{Cr} = 386 mg L^{-1}.

2.2.2. Jar test

POAZF, PAZF, and PAC were used as coagulants in the following tests, and dosage ranged from 62 to 372 mg L^{-1} (as Al amount in water samples).

The jar test procedure was as follows. Coagulants were introduced rapidly into the water sample (1 L) which was in the cups on the six-unit multiple stirrer system (ZR4-6 Flocculator, Zhongrun, China). Firstly, a rapid mixing stage was conducted at 200 r min^{-1} for 1 min, followed by a slow mixing stage of 10 min at 50 r min^{-1}. Secondly, the treated wastewater was allowed to settle for 15 min, and then 100 mL supernatant sample was withdrawn from a position of 2 cm below the surface for the analysis of turbidity and COD_{Cr} with 2100AN Turbidity Meter (USA, HACH) and HACH DR1010 COD Rapid Detector (USA, HACH).

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

2.3. Volume and mass reduction of sludge

2.3.1. Settling performance of flocs and volume reduction of wet sludge

2.3.1.1. Image of flocs. The flocs formed by POAZF, PAZF, and PAC in Section 2.2.2 (with dosage of 186 mg L^{-1}) was carefully taken out and introduced onto the object plate and was photographed under 100 magnification times with ECLIPSE 80i FM (Japan, Nikon), in which the same conditions were exactly taken in order to minimize the impact of human factors on the image appearance.

2.3.1.2. Settling performance of flocs and volume reduction of wet sludge. Wet sludge in this work refers to sum of the flocs containing some water. The flocs after flocculation of 10 min (in Section 2.2.2) by POAZF, PAZF, and PAC was introduced rapidly and carefully into 100 mL measuring cylinder. And then the settling performance (sedimentation speed of flocs) of flocs formed by POAZF at dosages of 62, 186, and 372 mg L^{-1} and settling time of 5–30 min were observed, in comparison with that of PAZF and PAC, in which the volume change of wet sludge settled was recorded from 5 to 30 min.

Fig. 3 gives the influence of settling time (5–30 min) and dosage (62, 186, and 372 mg L^{-1}) on the volume of wet sludge formed by POAZF, PAZF, and PAC in which the dotted line refers to the polynomial regression trend line corresponding to the settling curve of flocs. As mentioned above, the volume of wet sludge here refers to the sum of flocs containing some water after settling different times in a measuring cylinder of 100 mL.

2.3.2. Surface morphology and amount of dry sludge

2.3.2.1. Surface morphology of dry sludge. The surface morphology of dry sludge formed by POAZF, PAZF, or PAC was investigated with SUPRA™ 55 FESEM (Germany, Zeiss). The flocs (dosage of 186 mg L^{-1}) after sedimentation was dried at 60–70℃ in oven for 48 h and was made into powder samples for the analysis of surface morphology under the following conditions: Schottky Field emission electron source, Accelerating voltage 2–3 kV, In-lens SE detector, Electron beam booster.

2.3.2.2. Amount of dry sludge. The flocs of POAZF, PAZF, or PAC (dosage of 186 mg L^{-1}) after sedimentation was introduced into weighing bottle (60 × 30) and dried at 60–70℃ in oven for 48 h, and the mass of dry sludge was analyzed.

3. Results and discussion

3.1. Coagulation performance of coagulants

Fig. 1 presents the comparison of turbidity and COD_{Cr} removal among POAZF, PAZF, and PAC with final Al concentration ranged from 62 to 420 mg L^{-1} in the tested water samples.

As indicated in Fig. 1, the optimal dosage of POAZF, PAZF, and PAC was 186, 186, and 248 mg L^{-1} for the removal of turbidity and COD_{Cr}, respectively. POAZF and PAZF gave much higher coagulation behavior than PAC, in which POAZF gave slightly higher coagulation performance than PAZF. Compared with PAC, POAZF and PAZF had much advantage in removing organic matters. As seen in Fig. 1(b), POAZF and PAZF achieved more 16.1 and 9.6% COD_{Cr} removal than PAC at the optimal dosage of 186 mg L^{-1}, and more 11.1 and 3% COD_{Cr} removal than PAC at the lowest experimental dosage of 62 mg L^{-1}, respectively.

3.2. Settling performance of flocs and volume reduction of wet sludge

3.2.1. Image of flocs

To study the settling performance of wet sludge formed by POAZF, appearance of flocs of POAZF in treating sewage was photographed and analyzed firstly, in comparison with those of PAZF and PAC, as shown in Fig. 2.

As seen in Fig. 2, most of POAZF and PAZF flocs appeared to be a sort of strip-like structures. POAZF presented a tighter connection between the flocs and between the floccules in flocs, greater massive degree of flocs, and larger floc size than PAZF significantly. While the floc image formed by PAC mainly consisted of some sort of round clump-like structures

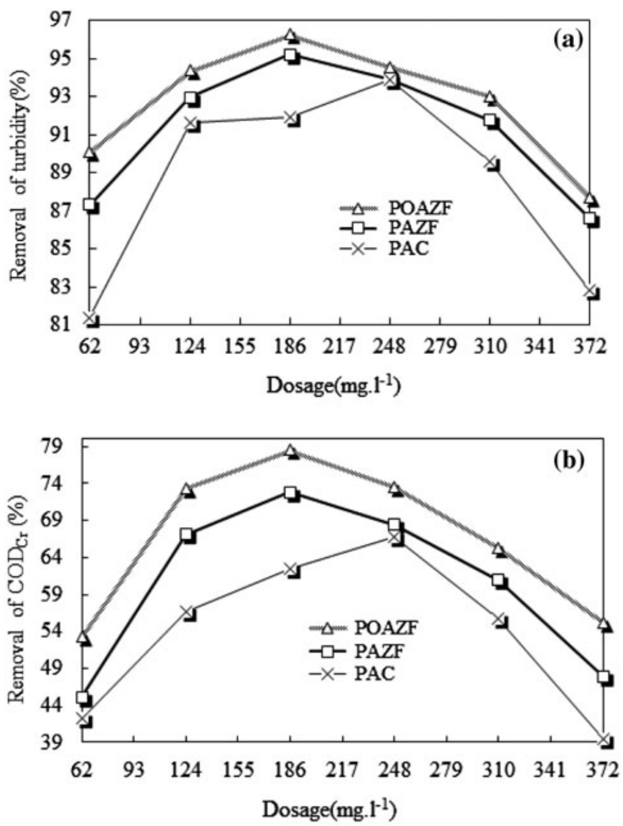

Fig. 1. Influence of dosage on removal of (a) turbidity and (b) COD_{Cr} by POAZF, PAZF and PAC in treating sewage.

distributed loosely with some small strip-like structures scattered around.

3.2.2. *Settling performances of flocs, and prediction of volume reduction of wet sludge*

Fig. 3 gives the influence of settling time (5–30 min) and dosage (62, 186, and 372 mg L^{-1}) on the volume of wet sludge formed by POAZF, PAZF, and PAC, in which the dotted line refers to the polynomial regression trend line corresponding to the sedimentation curve of flocs. As mentioned above, the volume of wet sludge here refers to the sum of flocs containing some water after settling different times in a measuring cylinder of 100 mL.

As indicated in Fig. 3, the settling performance of flocs of POAZF was far superior to that of PAZF and PAC at the three dosages tested.

At lower (Fig. 3(a)), medium (Fig. 3(b)) and higher dosage (Fig. 3(c)), the flocs of POAZF almost settled completely at 15, 25, and 20 min, respectively, in comparison with that of PAZF and PAC at 25, 25, and 30 min, and at 25, 30, and 30 min, respectively. Therefore, the complete settling time of POAZF at dosage of 62, 186, and 372 mg L^{-1} was shorter 40, 0 and 33.3% than that of PAZF, and shorter 40, 16.7 and 33.3% than that of PAC, respectively. The volume of wet sludge after complete settlement at dosage of 62, 186, and 372 mg L^{-1} was as follows: POAZF of 8, 21, and 11 mL, PAZF of 12, 32, and 15 mL, and PAC of 14, 32, and 30 mL; that is, the volume reduction of wet sludge formed by POAZF at dosage of 62, 186, and 372 mg L^{-1} was less 33.3, 34.4, and 26.7% (Defined as volume reduction ratio of wet sludge (VRRWS)) than that of PAZF, and less 42.8, 34.4, and 63.3% than that of PAC. Fig. 3 also shows that the settling times are different for different dosages. The reasons are as follows: the amount of pollutants combined with coagulants is different at different dosages, and the compactness of flocs produced is also different. In addition, the amount, volume, and compactness of hydrolysis products formed by coagulants after adding to water samples are also different at different dosages, thus leading to that the volume or the amount of flocs are different at different dosages. On the other hand, lower dosage, medium dosage, and higher dosage were selected in this section according to the dosage range shown in Fig. 1, and the extra amount of medium (186 mg L^{-1}) or higher dosage (372 mg L^{-1}) was much greater than that of lower dosage (62 mg L^{-1}) in this work, so the amount of flocs formed by the higher dosages (186 or 372 mg L^{-1}) was much higher than that by the lower dosage (62 mg L^{-1}), so it may be took a little longer time to settle for the flocs formed by the higher dosages (186 or 372 mg L^{-1}).

In addition, as also seen from Fig. 3, within the experimental settling time, the VRRWS range of POAZF was as follows: 33.3–38.5% (62 mg L^{-1}), 19.5–46.2% (186 mg L^{-1}), and 26.7–61.5% (372 mg L^{-1}) compared with that of PAZF, and 42.9–52.4% (62 mg L^{-1}), 21.5–51.4% (186 mg L^{-1}) , and 63.3–74.1% (372 mg L^{-1}) compared with that of PAC, respectively.

Generally, larger VRRWS of POAZF can be determined by its micro-characteristics which could be further expressed by its image of flocs to some extent (Fig. 2); so, larger VRRWS of POAZF will be related closely with its floc appearance. Though the images in Fig. 2 were photographed at dosage of 186 mg L^{-1}, according to the larger floc size, tighter connection between the flocs and between the floccules in flocs formed by POAZF than that by PAZF and PAC, it can be inferred that POAZF will give lower water content and larger density than PAZF or PAC at the same volume of wet sludge, which may be the basic reason for which the volume of wet sludge formed by POAZF decreased a lot compared with that by PAZF and PAC.

In order to predict VRRWS of POAZF at different settling times and different dosages, the fitting data

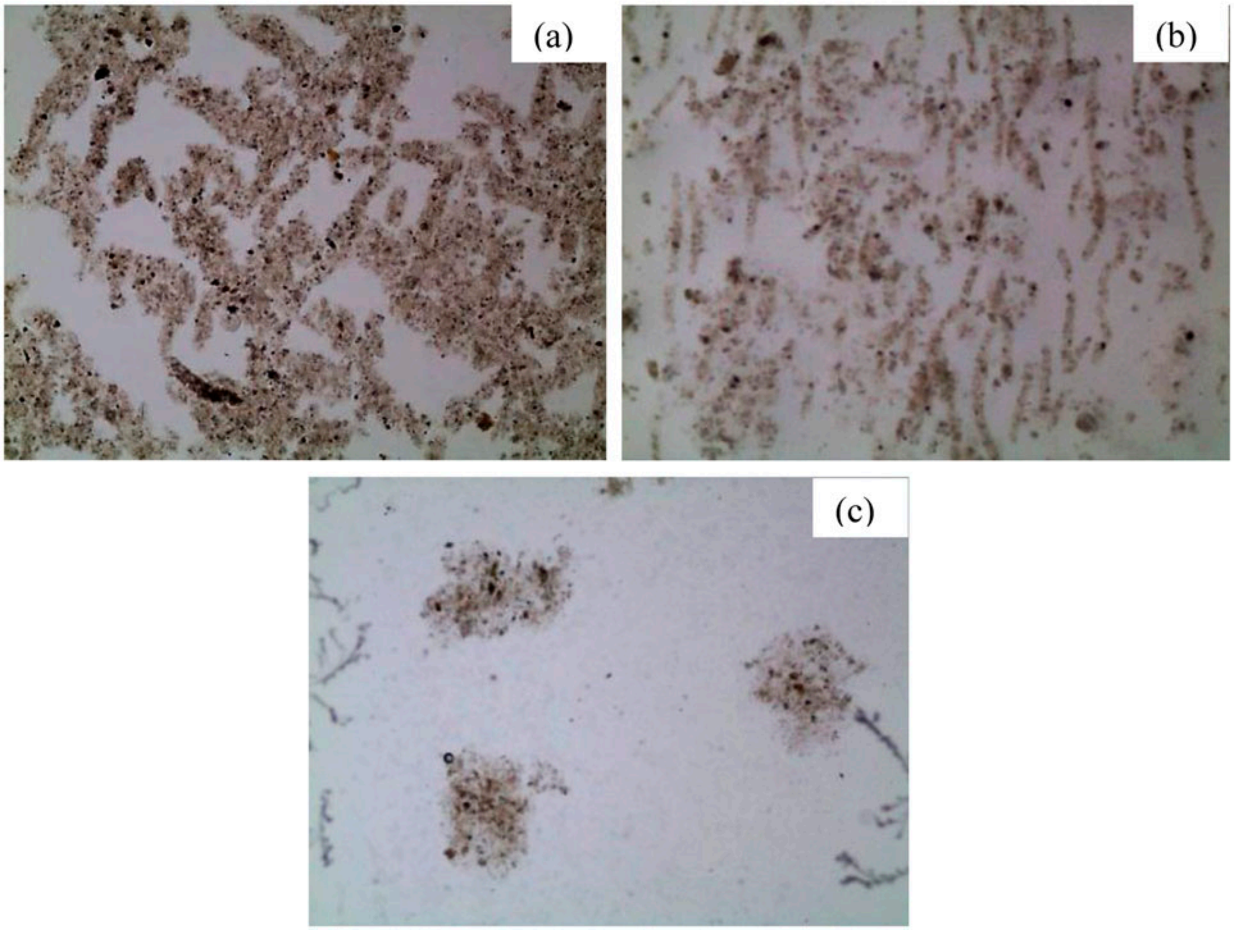

Fig. 2. Image of flocs formed by (a) POAZF, (b) PAZF, and (c) PAC in treating sewage (magnifies 100 diameters). Dosage = 186 mg L^{-1}.

was calculated from some polynomials which were obtained by fitting process using the experimental data, so the settling curve of flocs formed by POAZF was drawn using the fitting data, in comparison with that of PAZF and PAC. For instance, the polynomial fitting curve of POAZF at dosage of 62, 186, and 372 mg L^{-1} was as follows: $y = -4E\text{-}05x^4 + 0.0028x^3 - 0.054x^2 + 0.2028x + 10$ ($R = 0.9889$), $y = 0.0004x^4 - 0.0354x^3 + 1.1689x^2 - 17.478x + 124.33$ ($R = 1$), and $y = -0.0015x^3 + 0.1049x^2 - 2.4384x + 29.667$ ($R = 0.99967$) (y: volume of wet sludge in measuring cylinder; x: settling time; R^2: judging coefficient which reflected the fitting precision between the estimating value based on fitting curve and experimental data, and the greater the R^2, the reliability of the fitting curve). And then the change of VRRWS of POAZF with dosage at different settling times (0–35 min) was calculated according to the polynomial fitting curve, compared to that of PAZF or PAC, respectively, and then compared to the actual experimental data at settling times from 5 to 30 min. The results were graphed in Fig. 4.

As indicated in Fig. 4, the fitting precision of VRRWS achieved by POAZF between the experimental data and fitting data was higher than that by PAZF at higher dosage of 372 mg L^{-1}, with the error range of POAZF from 0.47 to 8.05%. While at lower or medium dosage, the fitting precision of VRRWS achieved by POAZF was high within the settling time of 15 min, and followed by a drastic decrease, down to 56.95% at dosage of 186 mg L^{-1} and 94.38% at dosage of 372 mg L^{-1}, respectively. So, probably it will be inferred that the fitting precision of VRRWS achieved by POAZF will be good within 5 min. Therefore, the VRRWS of POAZF within 15 min may be roughly predicted according to the polynomial fitting curves, which will be of significance for production rate and volume reduction rate of wet sludge in the actual wastewater treatment process. Of course, this deserves to be further studied in the future.

The fitting precision of VRRWS of PAZF between the experimental data and fitting data was higher than that of PAC, with the error range of PAZF from 0.15

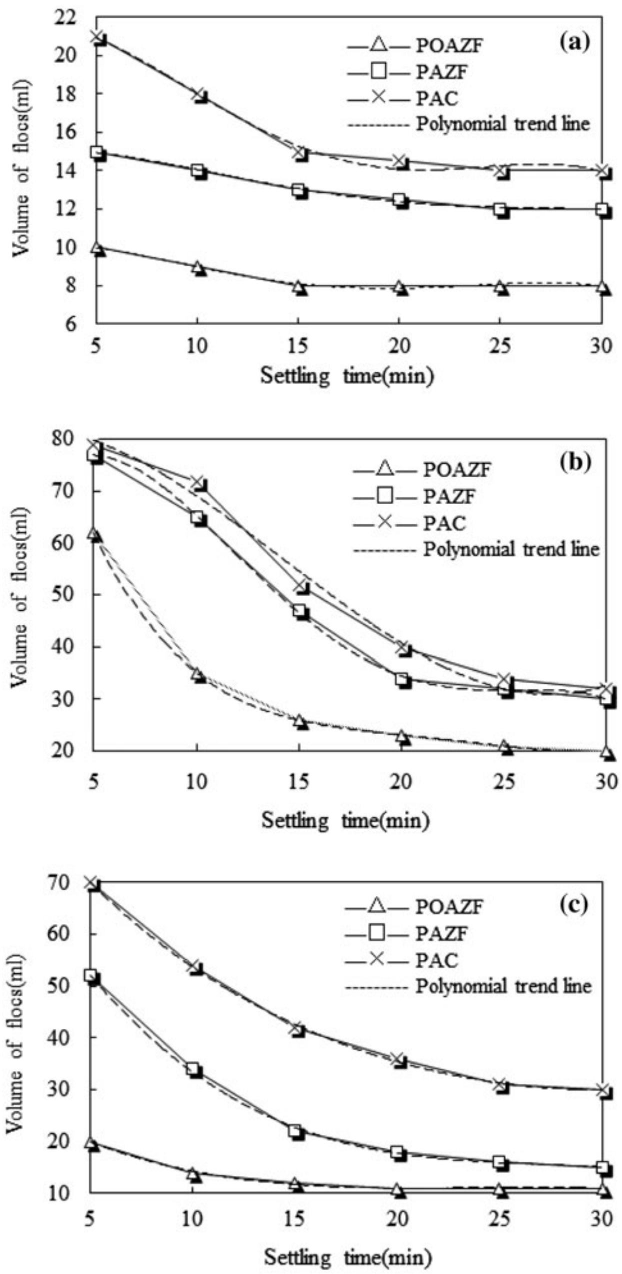

Fig. 3. Influence of set cling time from 5 to 30 min and dosage of (a) 60 mg L^{-1}, (b) 186 mg L^{-1}, and (c) 372 mg L^{-1} on settling performance of POAZF, PAZF, and PAC in treating sewage.

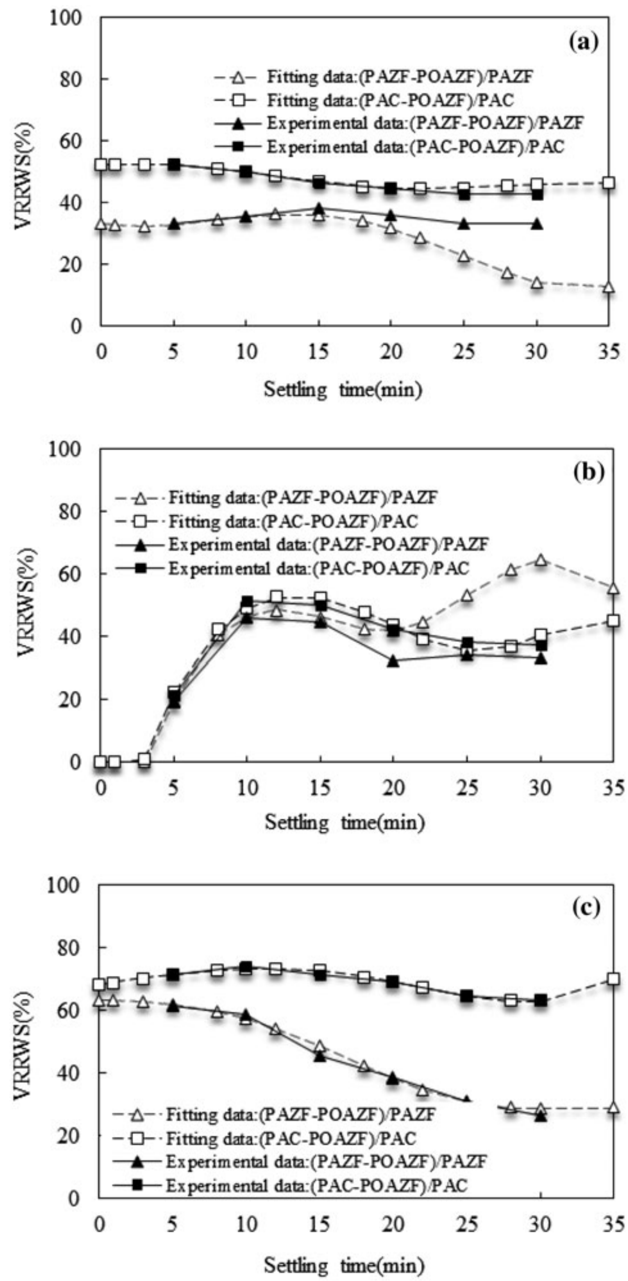

Fig. 4. Comparison of VRRWS of POAZF between experimental data and calculating data in treating sewage at different dosages of (a) 60 mg L^{-1}, (b) 186 mg L^{-1}, and (c) 372 mg L^{-1} and different settling times from 5 to 30 min (comparison with that of PAZF and PAC). VRRWS: volume reduction ratio of wet sludge.

to 7.69%, 2.9 to 8.2%, and 0 to 0.88% at dosage of 62, 186, and 372 mg L^{-1}, respectively.

3.3. Surface morphology and mass reduction of dry sludge

3.3.1. Surface morphology of dry sludge

To analyze the essential reason for which POAZF achieved certain mass reduction in dry sludge, surface morphology of dry sludge formed by POAZF was studied by FESEM at 20 K magnification times, compared to that by PAZF and PAC. Fig. 5 displays the different morphology of dry sludge formed by the three coagulants.

As seen from Fig. 5, the surface morphology of dry sludge formed by POAZF was obviously different from that by PAZF or PAC. The surface morphology of dry sludge of POAZF consisted of some sort of ball-like or coral-like loose floc structures and bulk crystal-like structures with some shallow slit or deep trench-type structures among them (Fig. 5(a)), in which crystal structures presented a kind of layered distribution and appeared to be a very compact texture. The surface morphology of the dry sludge of PAZF contained crystal structures, ball-like or coral-like loose floc structures, in which the amount of crystal structures was much less than that of POAZF and the amount of ball-like structures was much more than that of POAZF. Similarly, there are also some small slit-type structures arranged among the surface structures in PAZF (Fig. 5(b)). The surface morphology of dry sludge formed by PAC appeared to be some block, floc and soft-cloth structures, among which there are some deep trench structures distributed (Fig. 5(c)).

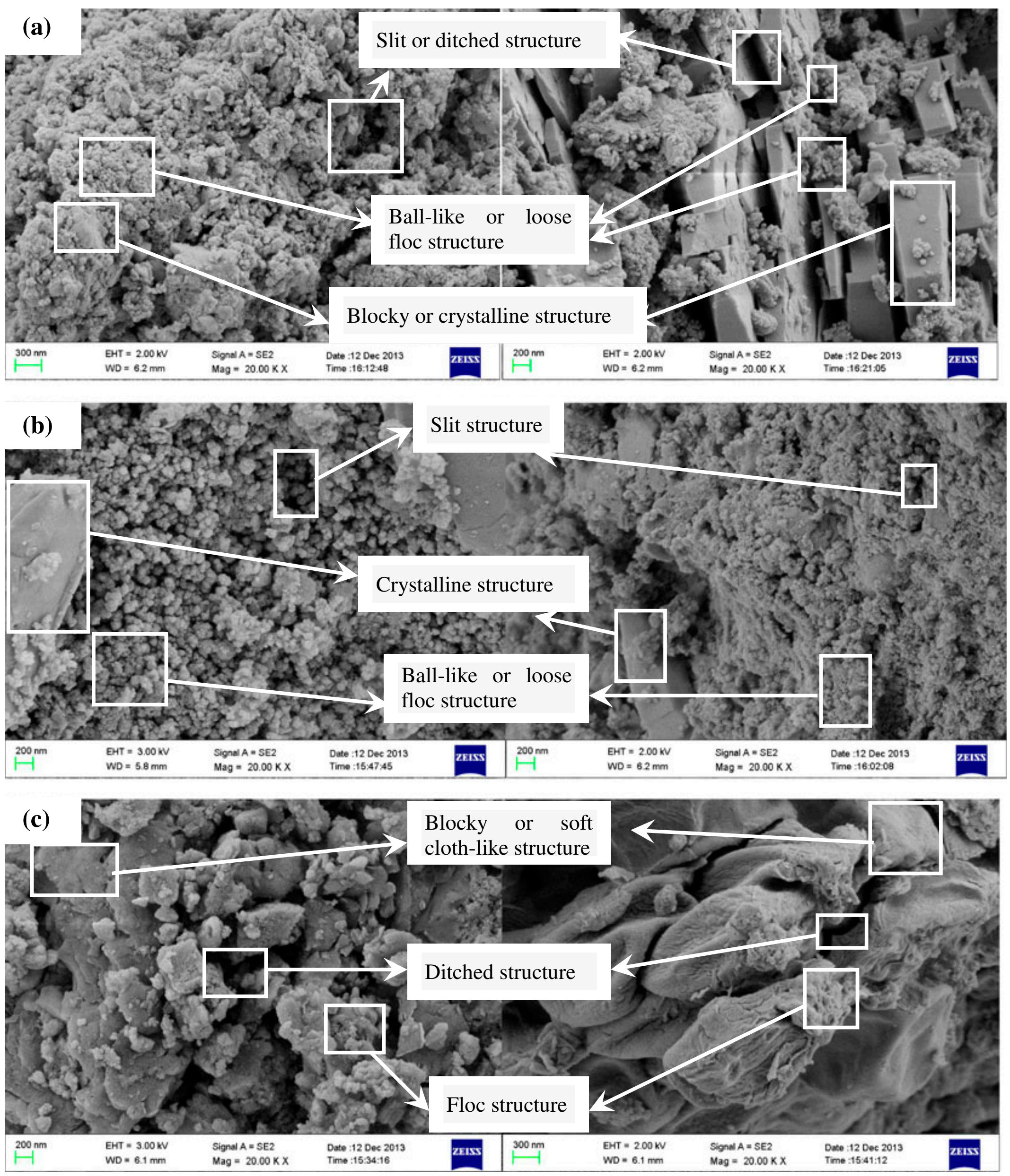

Fig. 5. Surface morphology of dry sludge formed by (a) POAZF, (b) PAZF, and (c) PAC in treating sewage (magnifies 20,000 diameters). Dosage = 186 mg L^{-1}.

For the surface morphology of dry sludge, POAZF gave two different points from that of PAZF and PAC. (1) Surface morphology of dry sludge will be closely related to some factors, such as structures, composition, and morphology of hydrolysis species of coagulant itself, apart from types and amount of impurities in water samples and so on. Therefore, according to the analysis obtained from Fig. 5, POAZF may give lots of similarities to PAZF during its hydrolysis process, in which most of hydrolysis species of POAZF may be the same as that of PAZF with different amount of each hydrolysis species, thus leading to POAZF giving similar composition of surface morphology of dry sludge to PAZF with very different amount of each type of hydrolysis species. The type and composition of hydrolysis species of POAZF and PAZF were different from those of PAC, thus leading to a different composition of their surface structures in dry sludge. Therefore, different hydrolysis species and different species composition led to different density of dry sludge formed by the three coagulants, in which the density of dry sludge of POAZF was larger than that of PAZF and the dry sludge density of POAZF or PAZF was larger than that of PAC; (2) According to the comparison between Figs. 2 and 5, it can be inferred that the connection between the flocs and between the floccules in flocs formed by POAZF and PAZF was tighter than that by PAC, and the combination of morphology of dry sludge formed by POAZF and PAZF was also relatively tighter and harder than that by PAC. Therefore, the resistant capacity of POAZF and PAZF against the disturbance or shear force during the coagulation process will be greater than that of PAC, which was consistent with the results of the previous study [39].

3.3.2. Mass reduction of dry sludge

Fig. 6 shows the relationship between mass of dry sludge formed by POAZF, PAZF, PAC and dosage within dosage range from 62 to 372 mg L^{-1}. As indicated in Fig. 6, the mass of dry sludge formed by POAZF was almost equivalent to or greater than that by PAZF and PAC at the same dosage, which may be due to the two following reasons. First, according to the removal rate of pollutants in Fig. 1, POAZF was combined with a greater amount of substance of turbidity and organic matters than the other two coagulants within the experimental dosage range after their addition into water samples. Second, according to the comparison between Figs. 2 and 5, it can be inferred that the density of flocs of POAZF was greater than that of PAZF and PAC.

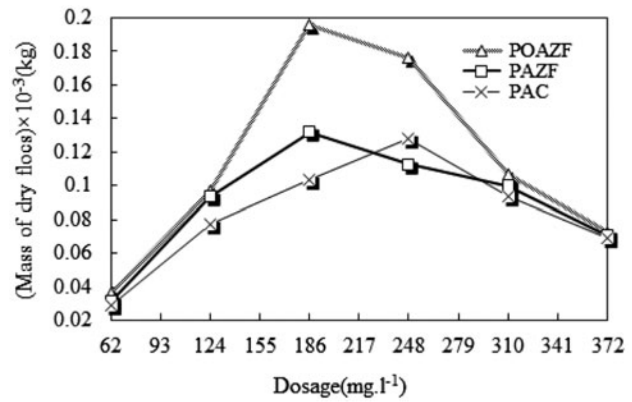

Fig. 6. Influence of dosage on mass of dry sludge formed by POAZF, PAZF, and PAC in treating sewage.

In the following sections, the dry sludge reduction of POAZF (compared with that of PAZF and PAC) will be mainly analyzed according to the comparison between Figs. 6 and 1 when achieving the same coagulation effect.

As shown in Fig. 1(a), if turbidity removal was up to 90%, the required dosage was 62, 90, and 112 mg L^{-1} for POAZF, PAZF, and PAC, corresponding to the final dry sludge mass (Fig. 6) of 0.036, 0.061, and 0.067 g, respectively.

As seen from Fig. 1(b), if the removal efficiency of COD_{Cr} was up to the maximum value of 66.5% by PAC, the required dosage was 100, 123, and 248 mg L^{-1} for POAZF, PAZF, and PAC, corresponding to the dry sludge mass (Fig. 6) of 0.072, 0.093, and 0.125 g, respectively. And then reduction percentage of dry sludge (namely, reduction rate of dry sludge (REDS)) formed by POAZF will be calculated using Eqs. (1) and (2), based on PAZF and PAC, respectively.

$$y_1 = \frac{w(\mathrm{PAZF}) - w(\mathrm{POAZF})}{w(\mathrm{PAZF})} \times 100\% \quad (1)$$

$$y_2 = \frac{w(\mathrm{PAC}) - w(\mathrm{POAZF})}{w(\mathrm{PAC})} \times 100\% \quad (2)$$

where, y_1 and y_2 represents the REDS of POAZF compared to that of PAZF and PAC, and *w*(*POAZF*), *w* (*PAZF*), and *w*(*PAC*) represents the mass of dry sludge formed by POAZF, PAZF, and PAC, respectively.

The REDS of POAZF was calculated at different removal rates of turbidity and organic matters, and then was displayed in Fig. 7. The dotted curve in Fig. 7 was not the actual trend of REDS curve, which means that only POAZF reached this high removal rate, while PAZF and PAC did not reach this removal effect; so, the REDS of POAZF at this removal rate range could not be calculated.

As seen from Figs. 1(a) and 7(a), the dry sludge mass of POAZF was smaller than that of PAZF and PAC at both dosage of 62–147 mg L^{-1} and turbidity removal of 90–95%, i.e. the REDS of POAZF was in positive value range, in which the REDS of POAZF reached 41 and 46.3% at both lower dosage (62 mg L^{-1}) and same removal rate of turbidity (90%) (Fig. 1(a)), based on PAZF and PAC, respectively. However, just like the above statement, when the dosage was from 153 to 223 mg L^{-1}, PAZF or PAC could not reach that very higher turbidity removal rate which could be achieved by POAZF; therefore, the REDS of POAZF could not be calculated over this dosage range (as a dotted line in Fig. 7). With the continuous increasing of dosage, turbidity removal declined due to the occurrence of re-stability phenomena, and the dry sludge mass of POAZF was larger than that of PAZF when reaching the same turbidity removal rate by this two coagulants; so, the REDS of POAZF was within a negative value range as displayed in Fig. 7(a). And then, with the further increasing of dosage, turbidity removal decreased again down to about 95%, while the dry sludge mass of POAZF reduced again based on PAZF and PAC.

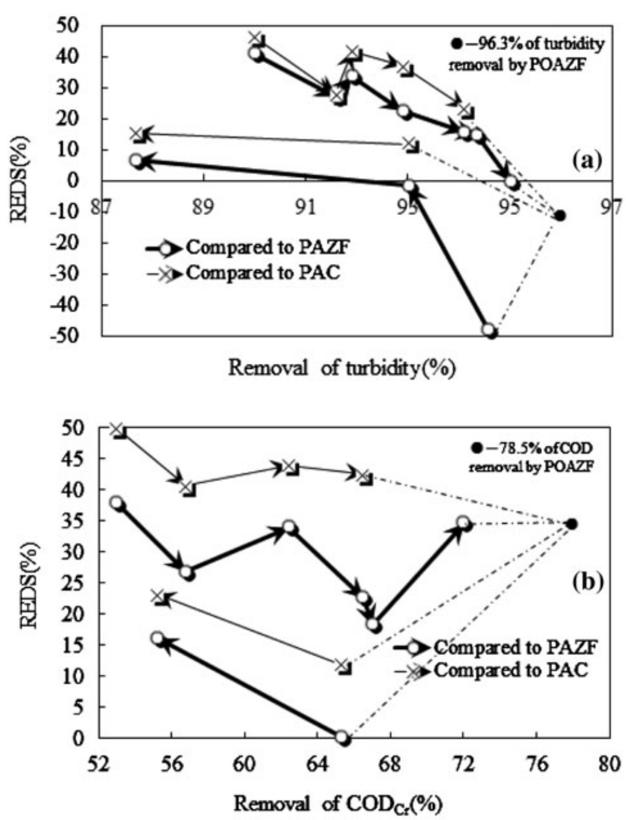

Fig. 7. Influence of removal of (a) turbidity, and (b) organic matters on REDS of POAZF in treating sewage (in contrast to PAZF and PAC). REDS: reduction rate of dry sludge.

As seen in Fig. 7(b), the dry sludge mass of POAZF was also smaller than that of PAZF and PAC according to the removal of organic matters. When the dosage was from 62 to 122 mg L^{-1} and COD_{Cr} removal was from 56.74 to 72%, the REDS of POAZF achieved 38 and 49.9% at both lower dosage of 62 mg L^{-1} (Fig. 1(b)) and same COD_{Cr} removal of 53% (Fig. 1(b)) based on PAZF and PAC. If COD_{Cr} removal by PAZF and PAC reached the maximal value of 72.8 and 66.8% at both dosage range and COD_{Cr} removal range mentioned above, the REDS of POAZF was upto 34.8 and 42.4% based on PAZF and PAC, respectively. And then the dosage was up to a range from 124 to 252 mg L^{-1}, in which the REDS of POAZF could not be calculated when COD_{Cr} removal ranged from 72.8 to 78.5%. And then re-stability phenomena occurred, COD_{Cr} removal decreased, and the REDS of POAZF increased gradually.

For actual coagulation process, reduction of dry sludge is of practical value only before re-stability phenomena occurs; for instance, the dosage range in Fig. 1 which was only from 62 to 122 mg L^{-1} has its practical significance. Therefore, in contrast to PAZF and PAC, the REDS of POAZF was from 15 to 41 and 23.2 to 46.3% over the dosage range from 62 to 122 mg L^{-1} based on turbidity removal. While based on COD_{Cr} removal, the REDS of POAZF was from 18.4 to 38 and 40.6 to 49.9% compared to PAZF and PAC, respectively. However, from the removal of turbidity and organic matters point of view, the REDS of POAZF ranged from 18.4–38% and 23.2–40.6% compared to PAZF and PAC, respectively. The important reasons that POAZF gave larger REDS were as follows. POAZF gave lower dosage than PAZF and PAC when achieving the same coagulation effect, which was particularly evident in the removal of organic matters. For instance, when COD_{Cr} removal was upto 62%, the required dosage of POAZF, PAZF, and PAC was 87, 118, and 186 mg L^{-1}, respectively. POAZF dosage was 31 and 99 mg L^{-1} less than PAZF and PAC when achieving the same COD_{Cr} removal of 62%, probably because POAZF appeared to be some distinctive structures of hydrolysis species and species composition. This can be inferred from the analysis derived from Fig. 5 that POAZF gave most of the same hydrolysis species to PAZF with different amount of each species, and gave different hydrolysis species and species composition from PAC, thus leading to the different dosage when reaching the same coagulation effect.

In addition, just as the analysis obtained from Fig. 5 shows, the dry sludge of POAZF maybe gave larger density than that of PAZF and PAC, which increased the mass of dry sludge formed by POAZF to some extent. Otherwise, POAZF probably will have greater REDS based on PAZF or PAC, which may be one of the reasons that REDS (mass reduction rate) of POAZF was lower than its VRRWS (volume reduction rate).

4. Conclusions

POAZF gave tighter connection between the flocs and between the floccules in flocs than PAZF in their strip-like structures which were different from the image of PAC flocs.

The settling performance of POAZF flocs was far superior to that of PAZF and PAC. POAZF had the VRRWS ranging from 33.3 to 38.5%, 19.5 to 46.2%, and 26.7 to 61.5% (compared to PAZF), and ranging from 42.9 to 52.4%, 21.5 to 51.4%, and 63.3 to 74.1% (compared to PAC) at dosage of 62, 186, and 372 mg L^{-1}, respectively. The settling curve of flocs of POAZF was drawn using the fitting data which were calculated from some polynomials obtained by fitting process to predict VRRWS of POAZF. The fitting precision of VRRWS of POAZF was higher at high dosage (372 mg L^{-1}), and was higher within settling time of 15 min at lower or medium dosage, in contrast to that of PAZF. The tighter connection between the flocs and between the floccules in flocs of POAZF may be the important reason that POAZF had less water content and larger density than PAZF and PAC.

The surface morphology of dry sludge formed by POAZF was different from that by PAZF and PAC: some sort of ball-like or coral-like loose floc structures and bulk crystal-like structures in POAZF, crystal-like structures, ball-like or coral-like loose floc structures in PAZF, and some block, flocs, and soft-cloth structures in PAC. The amount of each structure in PAZF was different from that in POAZF. The dry sludge of POAZF gave larger density than that of PAZF, and both of them gave larger density than PAC.

From the removal of turbidity and organic matters, the REDS of POAZF was from 18.4 to 38% and 23.2 to 40.6% compared to PAZF and PAC at dosage range from 62 to 122 mg L^{-1}, respectively. The important reason for which POAZF had larger REDS was that POAZF had lower dosage than PAZF and PAC as achieving the same coagulation performance. While the reason for which POAZF gave lower dosage was that POAZF maybe gave most of the same hydrolysis species to PAZF with different content of each species and gave varying hydrolysis species and species composition from PAC, thus influencing the dosage.

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