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A combined process of short-time coagulation+sedimentation+filtration behavior and mechanism of poly-Si-Fe (PSF) coagulant

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ABSTRACT

Poly-Si-Fe (PSF) was used as the main coagulant, compared with polyferric aluminum (PFA). Actual images of the flocs formed in short-time coagulation+sedimentation (StCS) were probed with ordinary camera in treating a synthetic humic acid (HA) water by jar test, compared with that in conventional coagulation+sedimentation (CCS), and suitable export height of water sample (EHWS) below the surface of supernatant after StCS was determined. The behavior of StCS+filtration (StCSF) and pollution situation of filter materials were investigated with an assembled facility including a six-unit multiple stirrer and a self-made filter device, and ordinary camera and scanning electron microscope (SEM), respectively, compared with that of CCS+filtration (CCSF). The results showed the flocs size of PSF in StCS were basically the same or similar to that in CCS, and both precipitated quickly and were obviously larger than that of PFA. The suitable EHWS was 10–11 cm. The filtration rate and flux of both PSF and PFA in StCSF were lower than that in CCSF. For PSF, the turbidity and organic matters removal in StCSF were almost the same as that in CCSF, meeting the quality requirements of drinking water; the pollution of the filter materials in StCSF was almost similar to that in CCSF, in which the flocs basically covered the top and near top filter materials, reducing the difficulty of backwashing and facilitating the flux recovery. For PFA, much smaller flocs flowed out of the filter materials along with water flow, resulting in serious decreasing of water qualities. The superior behavior of PSF in StCSF was determined by its hydrolysis product distribution, microscopic characteristics and oxidative behavior, and PSF StCSF can be applied in many situations where PFA could not be used.

Keywords: Short time; PSF coagulant; Combined process; Coagulation+sedimentation+filtration; Behavior; Mechanism

1. Introduction

Coagulation+sedimentation+filtration is an important three-units combined process commonly used in drinking water treatment or advanced treatment of wastewater [1,2], in which the previous unit has a profound impact on the behavior and cost of the subsequent processes. There are many factors impacting the behavior of the three units, mainly including coagulants and hydraulic conditions [2,3], such as coagulation time, mixing speed, precipitation time, filtration time and speed, thickness of filter materials, other related factors, etc. The literatures [4–11] reported some general empirical value ranges of representative parameters (such as coagulation time and sedimentation time) in CCS: conventional coagulation time of generally from 11 to 33 min, and sedimentation time of generally from 10 to 60 min (60 min is often needed for most flocs to settle completely). In CCSF, some relative factors, such as coagulation time, precipitation

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time, filtration time, etc., are required to reach certain values due to treating requirements, thus leading to a large volume of facilities in the three units. Therefore, it is necessary to study a combined process having the characteristics of tight connection and small floor space, especially for China which has a large population and less land area. In recent years, some researchers at home and abroad have successively carried out some studies on high-efficient water treatment technologies based on coagulation and sedimentation in the field of water treatment and applied them in actual processes [12–15]. For instance, Lv et al. [12] reported a magnetic seeding coagulation+flocculation process by adding the composite poly-aluminium chloride/magnetic particles first followed by polyacrylamide: turbidity, UV_{254} and total phosphorus were removed up to 96.7%, 80.8% and 95.7% in 5 min under applied magnetic field. In addition, there are some typical coagulation+sedimentation processes having characteristics of high efficiency, high sedimentation speed and occupying small floor space, such as Densadeg technology of Deliman Company in France [13,14] and Turbo-LME high-speed sedimentation tank of Passawang-Lorgues Company in Germany [15]. The above efficient technologies were studied only from treating processes or reactors. However, the research on StCS and further optimizing the subsequent filtration based on high-efficient advantages of coagulants has rarely been reported.

The StCSF can not only decrease the floor space occupied by water treating facilities but also improve the flexibility and applicability of the facilities. In addition, StCSF also facilitates the development of integrated equipment, mobile facilities or modular water treatment facilities in a limited space with less land area [16–21]. Especially for some special places, it is difficult for traditional water treatment facilities constructed with civil structures to be applied [18], such as disaster areas, expressway service areas, etc. In these places, water supply is complex, thus resulting in poor applicability of traditional water treating facilities. In addition, there were many problems in traditional water treating facilities used in rural areas in China, such as complex structures, lack of operation and maintenance personnel, and less centralized water supply system, etc. Integrated or mobile or modular water treating facilities [19–22] are characterized by having advantages of short construction period, high flexibility, high degree of automation and high degree of integration, especially of suitability for these special places or scattered rural areas [23,24]. For some wastewater treatment in industries or residential areas, water reuse or other occasions, land area or space was often limited, therefore, high efficiency of short-time and less land area are necessary for water treating facilities or processes, moreover, the application of integrated or mobile or modular water treatment facilities also has strong applicability and flexibility for these places. Therefore, it is of great significance to probe StCSF process based on high-efficient coagulants and to further optimizing filtration. But until now, this aspect has rarely been reported.

PSF, as one of efficient coagulants composed of Fe and Si, has been studied since the late 20th century in Japan [25]. PSF has almost been studied in China simultaneously with Poly-aluminum silicate, and some valuable results have been obtained [4,26–28]. PSF gave the advantages of large fractal dimension in flocs, high sedimentation speed, non-toxicity, and greater removal of organic matters. However, PSF has not been able to be applied extensively in the field of water and wastewater treatment in China due to various reasons.

In this work, PSF prepared [4] was used as the main coagulant in treating a synthetic HA water sample, compared with PFA. The behavior of StCSF, and pollution situation of the filter materials were probed with Jar test, and Ordinary camera and SEM, compared with that of CCSF. The behavior mechanism of PSF in StCSF was also analyzed. This work is expected to provide a theoretical basis for efficient application and process optimization of integrated or mobile or modular water treating facilities having small space occupation, and for accelerant improvement of safe drinking water supply in rural areas, and also provide effective process parameters for large-scale application of such type of coagulants.

2. Materials and methods

2.1. StCSF test

2.1.1. Tested water

The tested water was a synthetic water made from both humic acid (HA, analytical grade, China) stock solution and Kaolin (analytical grade, China) stock solution. HA stock solution was made as follows: 1 g HA and 0.4 g NaOH were dissolved in 100 mL double-deionized water under stirring 30 min to obtain a mixed solution. And then the mixed solution was added to 1 L double-deionized water to obtain the HA stock solution with concentration 1.0 g L^{-1}, which was stored below 4°C before using. Kaolin stock solution was made as follows: 5 g Kaolin were dissolved in 1 L double-deionized water under stirring 30 min, followed by 30 min settlement, and then the supernatant was taken out as the Kaolin stock solution. Some HA stock solution and Kaolin stock solution were added to double-deionized water to obtain the tested water with the following qualities: turbidity = 28.5–39.8 NTU, color = 0.296–0.395 A, UV_{254} = 0.253–0.663 cm^{-1}, COD_{Mn} = 8.85–10.5 mg L^{-1}, pH = 7.99–8.93, temperature = 17.2°C–29.2°C.

2.1.2. Experimental process and facilities

The combined process of StCSF was applied in this work, in which an assembled facility composed of a six-unit multiple stirrer (ZR4-6 flocculator, Zhongrun, China) and a self-made filter device was used, as seen in Fig. 1.

The coagulation−sedimentation test was performed on the six-unit multiple stirrer system. PSF and PFA (liquid, w(Al + Fe) = 10.26%, Zibo Lujing, China) were selected as coagulants, and the dosage was selected as the preferred dosage of 6 mg L^{-1} (PSF as Fe, and PFA as Al) according to the previous experiment results. (1) The coagulation procedure of StCS based on the previous experiment results was as follows: coagulant was added to the tested water (1 L), and rapid mixing was performed at 200 r min^{-1} for 1 min. The slow mixing stage of 4 min at 40 r min^{-1} was conducted to build up microflocs to large and dense flocs. A sedimentation stage of 3 min was followed. And then the supernatant was withdrawn from a certain position (EHWS) below the surface, as the influent of the filter device in StCSF. (2) The procedure of CCS was almost the same to (1), only the flocculation time and sedimentation time were 10 and 10 min, respectively, and then the supernatant from the EHWS was used as the influent of the filter device in CCSF.

The filtration test was conducted on the self-made filter device including influent tank, motor + mixer, peristaltic pump (BT100, Baoding, China), filter column (diameter = 3 cm, height = 150 cm) with an overflow hole at 3 cm from the top, Rotameter (LZB, Changzhou, China), Valves, Effluent tank, etc. Quartz sand with a particle size from 0.5 to 1.0 mm was selected as the filter materials. The initial filtration rate was set to be 7 m h^{-1}, the thickness of the filter layer was 70 cm, and pebbles were selected as the support layer for the filter materials with a thickness of 10–20 cm.

The valve was first opened to the maximum flow, thus leading to the deionized water passing through the filter materials at full speed for 30 min, in order to remove the bubbles among the filter materials. Then, the supernatant above EHWS after coagulation+sedimentation (in Section 2.1.2) was carefully (to avoid breaking the flocs) introduced into the influent tank, followed by a slow stirring to avoid settling of flocs. Last, the water sample was introduced into the filter column by a peristaltic pump.

2.2. Behavior of StCS

2.2.1. Actual images of flocs

The actual images of the flocs formed by PSF and PFA after both StCS and CCS in Section 2.1.2 were studied with EOS M100 camera (Canon, Japan), respectively. The supernatant after precipitation was carefully and slowly poured out in order not to disturb the flocs, and then the flocs at the bottom of the test Jars were vertically photographed to compare the differences of the floc images between StCS and CCS of PSF and PFA.

2.2.2. Determination of EHWS after StCS and analysis of effluent water qualities

2.2.2.1. Determination of EHWS

The procedure of coagulation+sedimentation was as follows: PSF and PFA with dosage of 6 mg L^{-1} were added to the tested water (1 L), and rapid mixing was performed at 200 rpm for 1 min; the slow mixing time of 4 min for StCS and 10 min for CCS at 40 rpm was conducted, respectively, and followed by a sedimentation stage of 1–13 min. And the supernatant was then withdrawn from the positions of 4, 7 and 10 cm below the surface for the analysis of turbidity and color, respectively, to determine the suitable EHWS.

2.2.2.2. Effluent qualities from StCS

The water sample derived from above EHWS was used as the influent to the filter device in StCSF. The influent qualities were analyzed as follows: turbidity, color and COD_{Mn} were measured with 2100AN turbidity meter (HACH, USA) and $KMnO_4$ method, respectively. Some supernatant was first filtered through 0.45 μm filters (Shanghai, China) and then was measured by 752S UV spectrophotometer (China). All tests were performed in three runs. The results represented the averages of the test.

2.3. Behavior of StCSF and pollution of filter materials

2.3.1. Behavior of StCSF

Filtration rate and flux, turbidity, color, UV_{254} and COD_{Mn} of the effluent from StCSF were analyzed every 1 h: filtration rate was measured with LZB Rotameter, and flux was calculated according to Eq. (1). Filtration time was approximately determined according to filtration rate (reduced to 2 m h^{-1}) or COD_{Mn} (reduced to 3 mg L^{-1}) or residual turbidity (reduced to 1 NTU).

$$W = V \times \pi R^2 \tag{1}$$

where w: flux, mL min^{-1}; v: filtration rate, m h^{-1}; π: 3.14; R: radius of filter column, m.

2.3.2. Pollution of filter materials

The actual images and surface morphology of the filter materials after filtration for 18 h in both StCSF and CCSF in Section 2.1.2 were studied to observe the material pollution situation.

Actual images. 1 cm thickness of filter materials of at 0, 5, 35 and 70 cm from the top were taken out, sealed with plastic film, and frozen in a refrigerator at –18°C for 6 h, and then followed by 24 h freezing again at –70°C in SCIENTZ-10N freeze dryer (Ningbo, China). Last, the filter materials dried were photographed with EOS M100 Canon camera (Japan, Canon) to observe the pollution difference of filter materials at different filter layers between StCSF and CCSF.

Surface morphology. 1 cm thickness of filter materials of at 0 and 35 cm from the top were taken out, and was frozen with the same method to Section 2.3.2, and then were observed by EVO/LS15 SEM (ZEISS, German) at 2,000 times magnification under accelerating voltage of 10 kV.

3. Results and discussion

3.1. Behavior of StCS

3.1.1. Actual images of flocs

The actual images of the flocs formed by PSF and PAF in both StCS and CCS are shown in Fig. 2. PSF flocs (Fig. 2a1) formed in StCS showed to be a sort of branch-like or net-like images having larger volume, and almost gave the same size and structure to that formed in CCS (Fig. 2a2), thus suggesting that PSF produced larger size flocs which had greater precipitation speed in a short time and gave better removal of pollutants, which is one of the main reasons for which PSF had excellent coagulation behavior in StCS (as seen in Table 1). The size of the flocs formed by PSF in both StCS (Fig. 2a1) and CCS (Fig. 2a2) was obviously larger than that by PFA (Figs. 2b1 and b2), which is closely related to the essential characteristics of PSF (size characteristics) [4]: PSF gave a larger size, further forming larger flocs, which made it have better bridging ability. In addition, the flocs

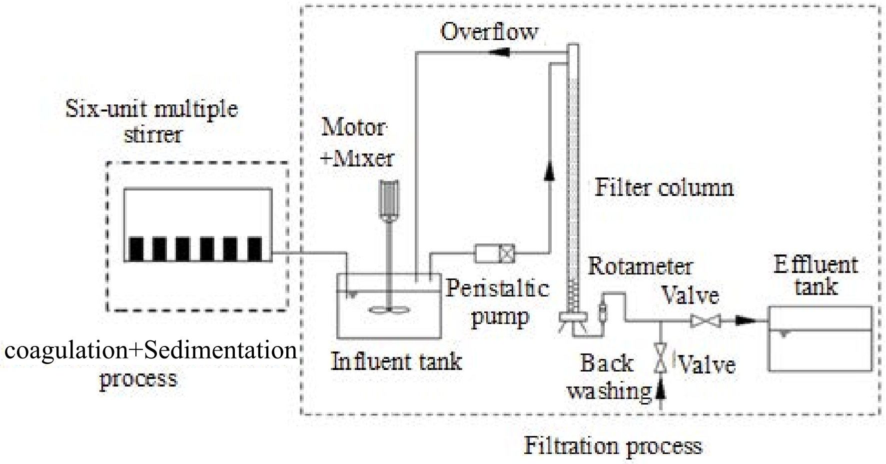

Fig. 1. Schematic diagram of experimental facility of "StCSF".

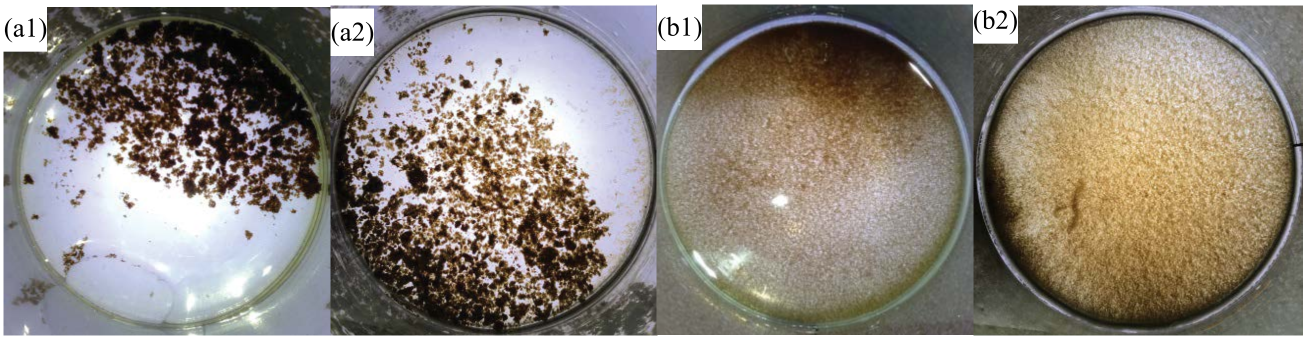

Fig. 2. Actual images of flocs formed by (a) PSF and (b) PFA in both StCS and CCS. (a1) PSF StCS, (a2) PSF CCS, (b1) PFA StCS, (b2) PFA CCS. StCS: short-time coagulation+sedimentation; CCS: conventional coagulation+sedimentation.

Table 1
Qualities of influent (coming from both "StCS" and "CCS") to filter device

Coagulants		Turbidity (NTU)	Color (A)	UV_{254} (cm^{-1})	COD_{Mn} (mg L^{-1})	pH	Temperature (°C)
PSF	"StCSF"	3.69	0.068	0.061	3.06	8.76	17.3
	"CCSF"	2.78	0.08	0055	3.06	8.76	17.3
PFA	"StCSF"	11.8	0.16	0.126	3.67	8.65	20.5
	"CCSF"	4.78	0.12	0.134	3.3	8.6	21

formed by PFA in StCS (Fig. 2b1) was also smaller than that in CCS (Fig. 2b2), therefore, it took a long period of time for PFA flocs to precipitate in StCS (Fig. 2b1), which makes it difficult for PFA to meet the requirements of water qualities in StCS.

3.1.2. Determination of EHWS and qualities of influent to filter device

Fig. 3 shows the impact of both sedimentation time and EHWS on turbidity removal by PSF and PFA in StCS (slow mixing time = 4 min) and CCS (slow mixing time = 10 min), respectively.

As seen in Fig. 3, the EHWS almost gave no impact on turbidity removal by PSF in both StCS and CCS (Fig. 3a), especially when precipitation time was less than 3 min, turbidity removal by PSF at EHWS of 4, 7, and 10 cm in both StCS and CCS almost tended to be a constant, because PSF could form larger size flocs in a short time, thus leading to rapid precipitation to the bottom of the test jars (Fig. 2a1). While the EHWS and sedimentation time had great influence on turbidity removal by PFA (Fig. 3b): reaching the maximum and the minimum turbidity removal at 4 and 10 cm, respectively, and then basically tending to be stable at sedimentation time greater than 5 min. This indicated that the flocs formed by PFA were small, so turbidity removal by PFA was closely related to the EHWS. So, 10–11 cm was selected as the suitable EHWS according to the following reasons: residual turbidity was one of the main parameters

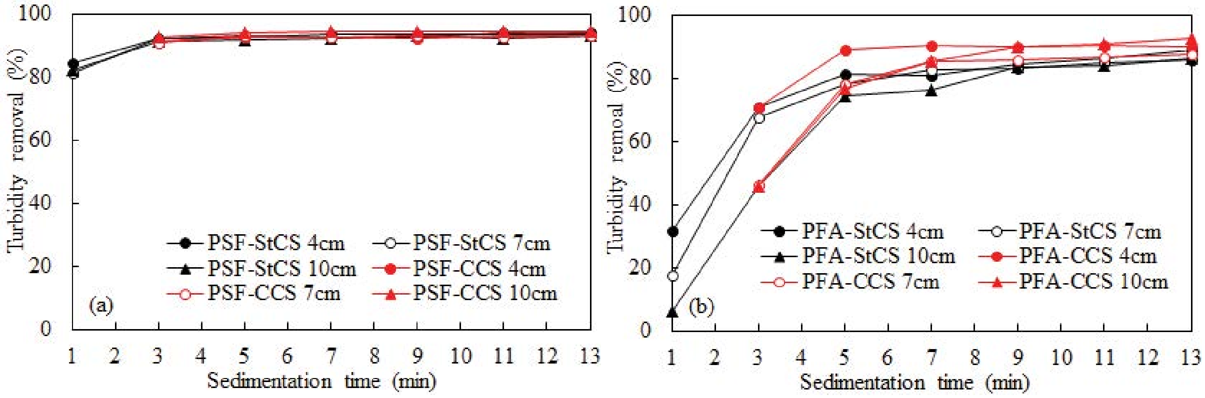

Fig. 3. Influence of EHWS and precipitation time on turbidity removal by (a) PSF and (b) PFA in StCS and CCS. Dosage = 6 mg L^{-1}; EHWS: export height of water sample after StCS. StCS: short-time coagulation+sedimentation (slow mixing time = 4 min); CCS: conventional coagulation+sedimentation (slow mixing time = 10 min).

in coagulation+sedimentation process, PSF was the main coagulant used in this work, and as more water samples as possible needed to be taken out from both StCS and CCS processes. When the EHWS was 10 cm, PSF gave higher 45.7% turbidity removal than PFA in StCS at precipitation time of 3 min, thus resulting in worse qualities of the influent to the filter device of PFA in StCSF.

The qualities of the influent to the filter device are summarized in Table 1, which also was the comparison of pollutants removal between PSF and PFA in StCS and CCS, respectively, and also referred to the starting point of the filtration test (that is, the value at 0 h). As seen in Table 1, for the water samples from EHWS, PSF basically gave the similar behavior in both StCS and CCS; while the removal of the parameters by PFA in StCS was lower than that in CCS apart from UV$_{254}$. Moreover, the behavior of PFA in CCS was lower than that of PSF in CCS, therefore, the coagulation behavior of PFA in StCS was far lower than that of PSF in StCS, thus leading to much better of the water qualities by PSF entering the filtration unit than that by PFA.

3.2. Behavior of StCSF and pollution of filter materials

3.2.1. Behavior of StCSF

Fig. 4 shows the comparison of behavior of StCSF and CCSF between PSF and PFA with the increasing of filtration time, in which the behavior referred to the cumulative results of coagulation+sedimentation and filtration.

The values at 0 h in Fig. 4 refers to the residual values of the parameters (such as turbidity, color, etc.) or removal rate of the parameters after coagulation+sedimentation, which are also the initial values entering the filtration unit, in which the initial filtration rate and flux of PSF and PFA were all 7 m^3 h^{-1} and 82 mL min^{-1}, respectively (Fig. 4a), and the other parameters are shown in Table 1. As also seen in Fig. 4, the duration of the filtration time for PSF in CCSF was 27 h according to the test requirements (in Section 2.3.1), which was the longest in this work, compared with 18 h or so in the other processes.

As shown in Fig. 4a, with the increasing filtration time, the filtration rate and flux of PSF and PFA in StCSF were smaller than that in CCSF, indicating that the pollution situation in the former may be more serious than that in the latter. For CCSF, the filtration rate and flux of PSF was similar to that of PFA in the first 7 h of filtration, but gradually lower than that of PFA after 7 h. The reasons were as follows. First, the residual flocs of PSF after coagulation–sedimentation was less (Table 1) than that of PFA, so there were less flocs of PSF entering in the filtration unit (Table 1), but the size of the residual flocs may be larger (Fig. 2a), so the probability of clogging the gaps among the filter materials was slightly larger than that of PFA, resulting in more flux reduction in PSF. Second, the size of the flocs formed by PFA during coagulation+sedimentation was smaller (Fig. 2b) than that by PSF. Moreover, as described in the previous studies [29]: we almost cannot see the value of PFA's K_A (flocculation coefficient) for flocs whose size is smaller than 2 mm, because K_A of PFA is so very small (K_A of PFA is equivalent to 0.00057 × 10^3) that it almost does not present in Fig. 9 (Comparison of aKA and bKB between PSF and PFA in treating surface water) (in [29]) at this size range. However, K_A of PSF is equivalent to 0.4 × 10^3 as shown in Fig. 9 [29]. Therefore, K_A of PSF is larger four magnitudes or so than that of PFA when flocs's size is smaller than 2 mm, so, it is reasonable to infer that the residual flocs of PFA after coagulation+sedimentation were also smaller than that of PSF. Therefore, the smaller residual flocs of PFA could flow out of the filter materials through the filter gaps, which could be seen from Fig. 4b: the turbidity of PSF effluent out of CCSF was basically less than 0.4 NTU during the entire filtration time, but, the residual turbidity of PFA before 7 h was lower than 0.3 NTU, followed by a quick increasing (up to more than 0.6 NTU after 7 h), indicating that much more PFA flocs flew out of the filter layer, so, PFA gave lower probability of clogging the gaps among the filter materials than PSF, leading to a slightly greater flux and filtration rate than that of PSF.

But for StCSF, the filtration rate and flux of PSF were similar to that of PFA (Fig. 4a). For PFA, much more smaller flocs flowed out of the filter materials through the filter gaps in StCSF, moreover, the residual flocs of PSF after StCS was much less than that of PFA, so the gaps among the filter materials of PSF after intercepting flocs was similar to that of PFA, thus leading to a similar or slightly larger

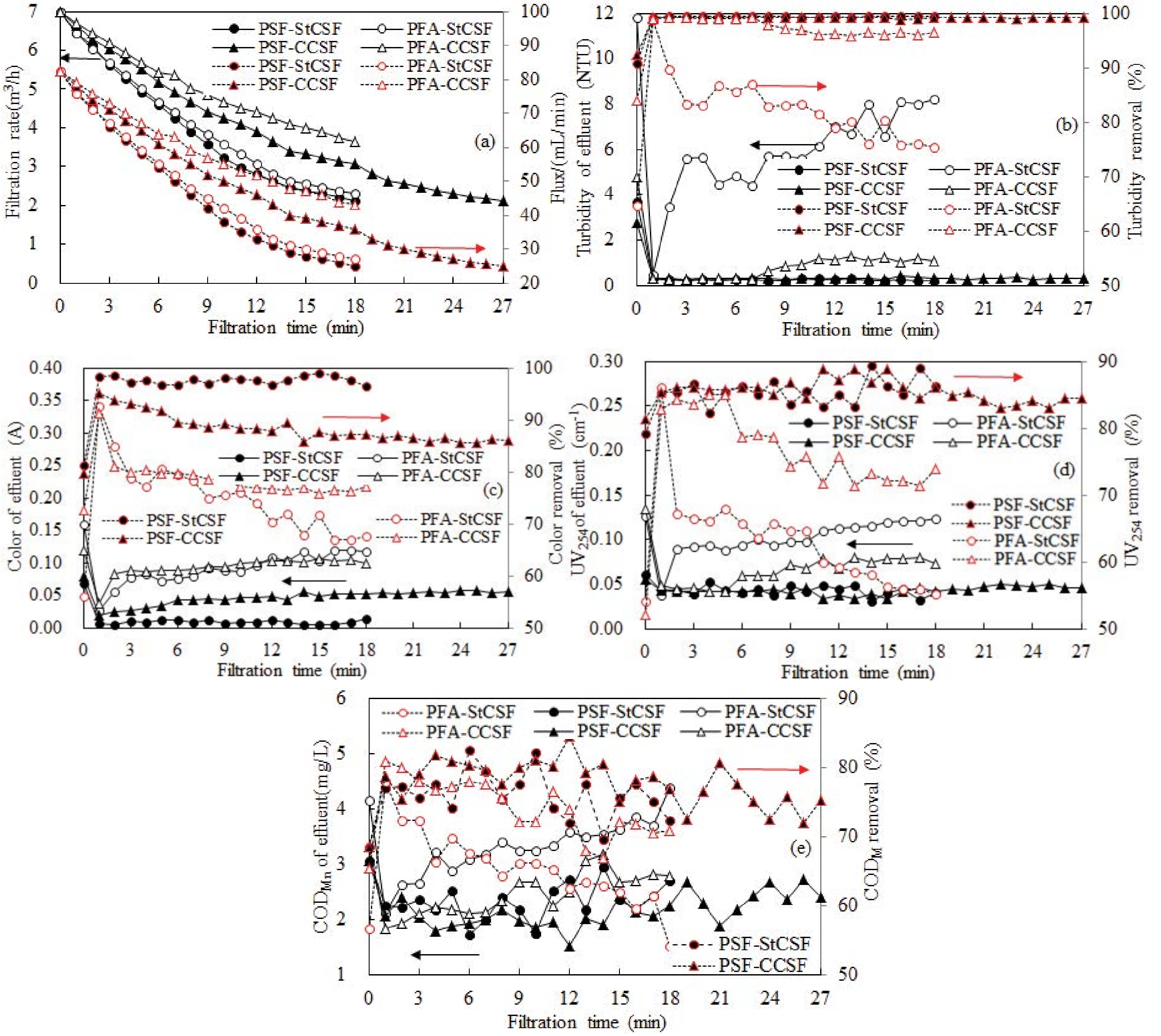

Fig. 4. Comparison of behavior of PSF and PFA between StCSF and CCSF. Dosage = 6 mg L^{-1}. StCSF: short-time coagulation+ sedimentation+filtration; CCSF: conventional coagulation+sedimentation+filtration.

flux of PFA to or than that of PSF, however, the turbidity removal of PFA was far lower more than that of PSF after StCSF (Fig. 4b). As for why the filtration rate and flux of PSF during StCSF was smaller than that during CCSF, the explanation will be done at the end of this section due to the similar size of the flocs in Fig. 2 and similar filter material pollution in the subsequent detection in Figs. 5 and 6 for PSF in both StCSF and CCSF.

As shown in Fig. 4b, PSF gave similar turbidity removal (almost more than 99%) in both StCSF and CCSF within experimental filtration time (CCSF of 27 h and StCSF of 18 h): residual turbidity of both was all less than 0.5 NTU. While turbidity removal by PFA in CCSF was obviously larger than that in StCSF: turbidity removal was more than 94% and residual turbidity was less than 2 NTU in the former, but turbidity removal decreased to lower than 89.7% and 75.4% and residual turbidity increased to 3.44 and 8.2 NTU at filtration time of 2 and 18 h in the latter, respectively. Therefore, although the flux of PSF was although similar to that of PFA in StCSF, turbidity removal by PSF was much better than that by PFA. PSF met the quality requirements of drinking water during the entire filtration time, while PFA did not meet the standard after filtering 2 h.

As seen in Fig. 4c, PSF gave better color removal in StCSF than that in CCSF: color removal in StCSF after filtrating 18 h was higher (10.4%) than that in CCSF after filtrating 27 h. The decolorization advantage of PSF in StCSF overcomes its own weakness of less color removal in CCSF due to the color of PSF itself in most water treatment. PFA gave lower color removal in CCSF than that in StCSF. This

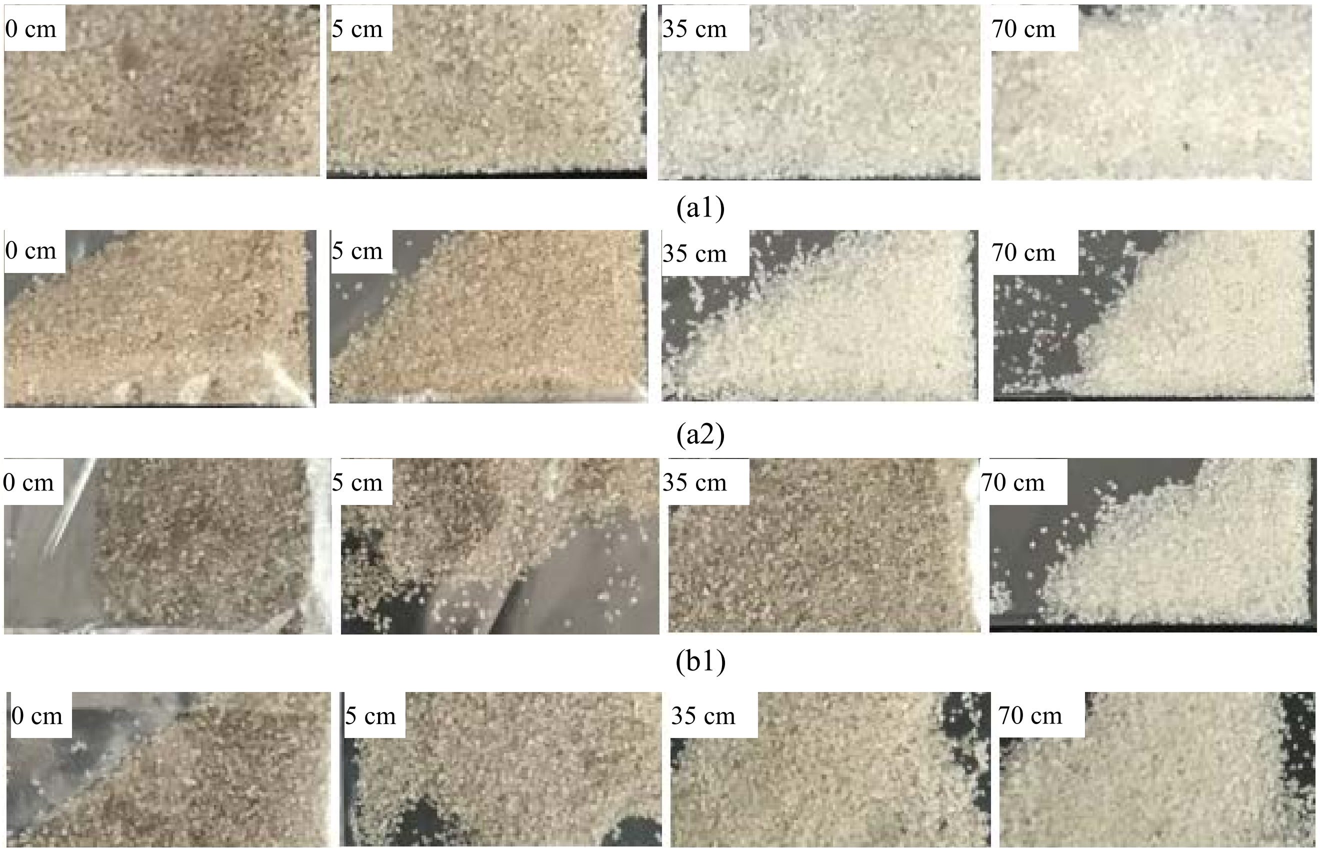

Fig. 5. Comparison of pollution of filter materials at different filter layers between (a) PSF and (b) PFA in both StCSF and CCSF. (a1) PSF StCSF, (a2) PSF CCSF, (b1) PFA StCSF, (b2) PFA CCSF. StCSF: short-time coagulation+sedimentation+filtration; CCSF: conventional coagulation+sedimentation+filtration.

indicated that PSF in StCSF gave greater color removal, but PFA in CCSF was conductive to color removal. In addition, PSF gave higher color removal in both StCSF and CCSF than PFA: PSF posed higher 28.8% color removal than PFA at 18 h in StCSF, and higher 12.1% at 27 h in StCSF than PFA at 18 h in CCSF.

Figs. 4d and e show that PSF gave similar removal of UV_{254} and COD_{Mn} in both StCSF and CCSF with the increasing of filtration time: UV_{254} removal was more than 83% and COD_{Mn} removal ranged between 72% and 82%. PSF gave far greater removal of UV_{254} and COD_{Mn} than PFA, especially for StCSF, PSF had larger advantages in removing organic matters, because UV_{254} and COD_{Mn} removal by PFA in CCSF was better than that in StCSF, and UV_{254} and COD_{Mn} removal by PSF was better than that by PFA in CCSF. As also seen in Figs. 4d and e that PSF almost gave relatively stable removal of UV_{254} and COD_{Mn} in both StCSF and CCSF with the increasing of filtration time: UV_{254} and COD_{Mn} removal in CCSF ranged from 85.4% and 78.7% at 1 h to 84.4% and 75.3% at 27 h, respectively. While UV_{254} and COD_{Mn} removal by PFA decreased from 82.8% and 80.8% at 1 h to 73.9% and 70.8% at 18 h in CCSF, respectively, and decreased from 86.2% and 78% at 1 h to 55.3% and 54.1% at 18 h in StCSF, respectively. Therefore, removal of organic matters by PSF was little influenced by process conditions, but PFA was greatly influenced and gave larger decrease in removing organic matters in StCSF. PSF has an excellent removal of organic matters because PSF is an oxidative coagulant by having a synergistic effect of oxidization and coagulation properties in removing organic matters [4,30,31]. This further proved that PSF in StCSF gave advantages not only in removing turbidity and color but also in eliminating organic matters or dissolved organic matters.

The filtration rate and flux of PSF during StCSF was smaller than that during CCSF (Fig. 4a), some explanation was as follows. (1) The turbidity of the influent entering into the filter unit in both CCSF and StCSF was 2.78 and 3.69 NTU, respectively. With the increasing filtration time, the residual turbidity of PSF in StCSF was basically slightly lower than that in CCSF, decreasing to 0.214 NTU for the former at 18 h and to 0.307 NTU for the latter at 27 h, respectively, and the average during the entire filtration period was 0.238 and 0.295 NTU, respectively. (2) The COD_{Mn} of the influent entering into the filter unit in both CCSF and StCSF was the same (Table 1) with 3.06 mg L^{-1}. With the increasing filtration time, the residual COD_{Mn} for both flocculated between 1.5 and 3 mg L^{-1}. But, the average CODMn of the entire filtration period was 2.142 and 2.309 mg L^{-1} in CCSF and StCSF, respectively. Therefore, the filtration period for PSF in StCSF and CCSF was determined as 18 and 27 h, respectively, according to residual turbidity and COD_{Mn} which all meet the measurement indicators in Section 2.3.1,

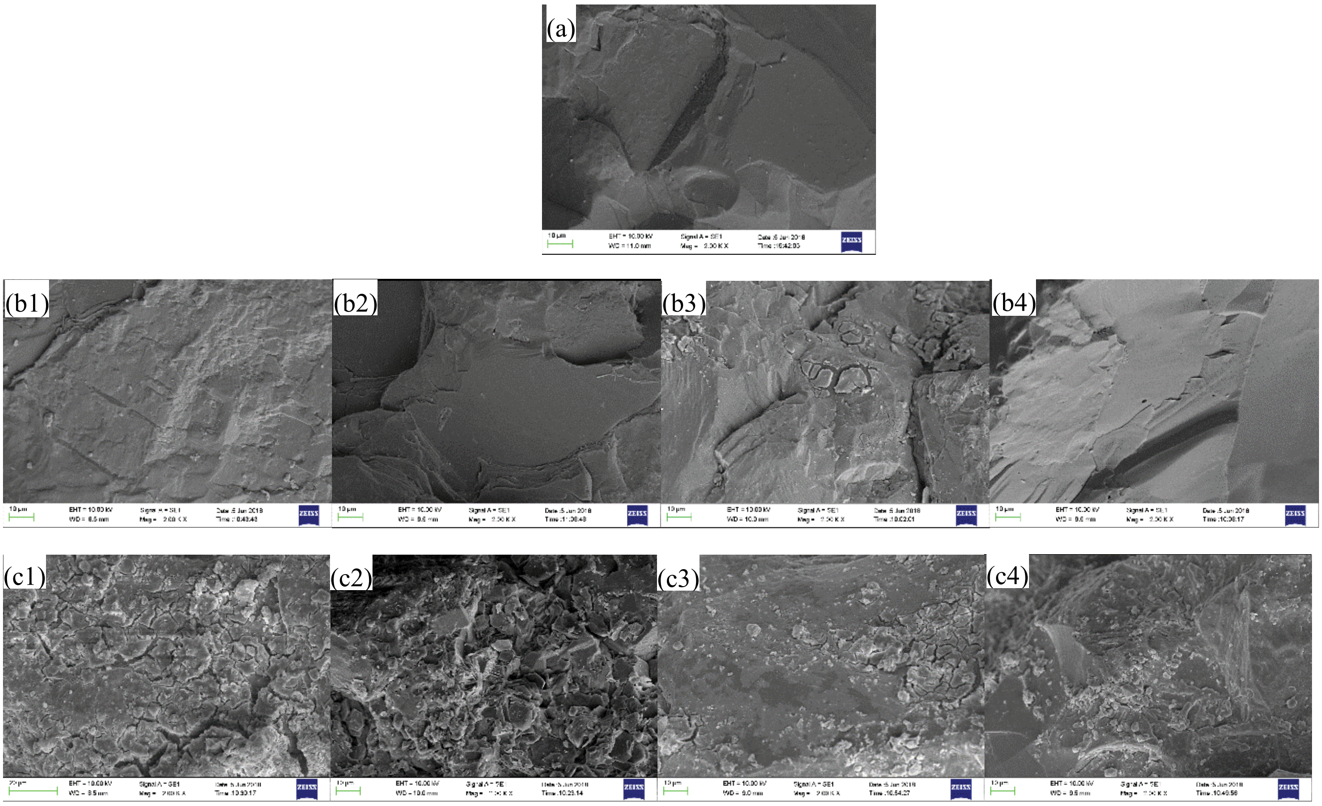

Fig. 6. Comparison of surface morphology of filter materials at different depths among (a) fresh filter materials, (b) PSF and (c) PFA in both StCSF and CCSF under magnification of 2,000 times. (b1) PSF StCSF at 0 cm, (b2) PSF StCSF at 35 cm, (b3) PSF CCSF at 0 cm, (b4) PSF CCSF at 35 cm, (c1) PFA StCSF at 0 cm, (c2) PFA StCSF at 35 cm, (c3) PFA CCSF at 0 cm, (c4) PFA CCSF at 35 cm. StCSF: short-time coagulation+sedimentation+filtration; CCSF: conventional coagulation+sedimentation+filtration.

which maybe different from actual operation, but it has guiding significance in this work or for the future work.

3.2.2. Surface morphology of filter materials

Fig. 5 shows the pollution level of the filter materials at different layers of PSF between StCSF and CCSF, compared with that of PFA. Fig. 6 shows the surface morphology of the filter materials in different layers of PSF in both StCSF and CCSF, in comparison with that of PFA.

As seen in Fig. 5, for both PSF and PFA, the top filter materials (0 cm) was polluted seriously, and pollution degree was all gradually lightened with deepening of filter layers downward. The pollution situation of each layer of PSF was lower than that of PFA, indicating that the amount of PSF flocs entering the filter device was less, consistent with the results in Table 1 and Fig. 5a. The pollution situation of the filter materials at deeper layers of PSF (Figs. 5a1 and a2) was obviously lighter than that of PFA (Figs. 5b1 and b2), such as 35 cm, because the size of PFA flocs was obviously smaller than that of PSF, thus resulting in more gaps or channels among the filter materials covered by PFA flocs, as a result, the other flocs were likely to flow out of the filter materials through the filter gaps. For PSF, the pollution situation at all depths of the materials in StCSF was similar to that in CCSF (Fig. 5a), moreover, the materials at 35 and 70 cm were only slightly polluted, because the size of PSF flocs in StCSF was almost the same to that in CCSF according to the real images in Fig. 2a, thus leading to a similar pollution in the two processes of PSF. As also seen in Fig. 5a, there were less flocs of PSF flowing out of the filter layers, thus leading to far less pollution of the deeper filter materials. While as seen in Fig. 5b, the filter materials at 35 cm of PFA in StCSF (Fig. 5b1) was seriously polluted than that in CCSF (Fig. 5b2), because the size of PFA flocs in StCSF was obviously smaller than that in CCSF according to the real images in Fig. 2b, so, the filter materials of PFA at deeper parts were likely to be contaminated by the smaller PFA flocs in StCSF, moreover, much more PFA flocs flowed out of the filter materials through the filter gaps, resulting in worse water qualities of the effluent, which was consistent with the results in Fig. 3 and Table 1.

As seen in Fig. 6a, the surface morphology of the fresh filter materials appeared to be a sort of rock characteristics by having relatively smooth surface structure.

The filter materials of PSF at 0 cm in both StCSF (Fig. 6b1) and CCSF (Fig. 6b2) (top layers) were clearly covered by less flocs having relatively larger size, thus resulting in smaller gaps or channels among the materials and more reduction of flux. The surface morphology of the filter materials at 35 cm of PSF in both StCSF (Fig. 6b2) and CCSF (Fig. 6b4) were similar to that of the fresh filter materials, indicating that there was less flocs covering the surface of the filter materials of PSF at slightly deeper filter layers for both StCSF and CCSF, which was almost consistent with the actual images having slight pollution at deeper layers in Figs. 5a1 and a2.

As seen in Fig. 6c, the surface of the filter materials was almost covered by PFA flocs in both StCSF and CCSF: the flocs size in StCSF (Figs. 6c1 and c2) was obviously smaller than that in CCSF (Figs. 6c3 and c4), resulting in much more gaps or channels among the filter materials in StCSF than that in CCSF. In addition, apart from the top filter materials (Figs. 6c1 and c3), the deeper filter materials (Figs. 6c2 and c4) were also covered by a large amount of flocs, in which the flocs in StCSF (Figs. 6c1 and c2) gave smaller size, larger amount and more gaps than that in CCSF (Figs. 6c3 and c4), further suggesting that probably there were more gaps among the filter materials in StCSF than that in CCSF. The covering situation of the filter materials in the deeper part of PFA in both StCSF and CCSF further indicated that there may be much more flocs flowed out of the filter layers through the gaps among the materials, resulting in worse water qualities of the effluent, which was also consistent with the results in Table 1 and Figs. 4 and 5.

The comparison of the pollution situation between PSF and PFA in CCSF or StCSF further suggested that most of the residual PSF flocs after CCS was basically intercepted and adhered by the top and near top filter materials, which will reduce the difficulty of filter layers's backwashing, in which the flux would be easily recovered as long as the top and near top filter materials was cleared. Compared with PSF, the filter materials of PFA was more difficult to be cleared by backwashing due to the following reasons: (1) the surface of PFA filter materials was covered by much more smaller flocs which maybe was adhered to the materials firmly, and (2) the filter materials at different depths were almost attached or adhered by much flocs.

3.3. Performance mechanism and feasibility analysis of PSF in StCSF

According to the literature [4,30–32], the reasons for which PSF had superior behavior in StCSF were mainly analyzed according to the hydrolysis products distribution, microscopic characteristics and oxidation performance. First, the analysis was for StCS process. As reported in the study by Fu and Yu [32], PSF is a high polymer copolymerized by polysilicic acid (PS) and Fe. Various hydrolysis products (Fe^{3+}, $Fe(OH)_2^+$, $Fe(OH)^{2+}$, $Fe(OH)_4^-$ and $Fe_2(OH)_2^{4+}$) were formed at lower pH side or at higher pH side. When the pH of water was larger than 5 and lower than 9 (the pH of the tested water in this work was lower than 9), the main hydrolysis products contained $Fe(OH)^{2+}$ and Fe^{3+} having positive charges, and poly-nucleus hydrolysis products of solid hydroxide of $Fe(OH)_3$, in which $Fe(OH)_3$ (its total amount was lower than 50%) represented the total amount of all other Fe^{3+} products combined with Si firmly, some poly-nucleus hydrolysis products of Fe and other hydrolysis solid sediment, apart from various hydrolysis products of Fe^{3+} (such as Fe^{3+}, $Fe\ (OH)_2^+$, $Fe(OH)^{2+}$, $Fe(OH)_4^-$, $Fe_2(OH)_2^{4+}$, etc.); moreover, $Fe(OH)_3$ carried some positive charges. So, $Fe(OH)_3$ gave ability of both bridging and charge-neutralization/destabilization simultaneously for impurities negatively charged due to its electrical attraction, species and size characteristics. In addition, as also stated in the study by Fu and Yu [32], three hydrolysis products of Fe namely, $Fe(OH)_3$, $Fe(OH)^{2+}$ and Fe^{3+} coexisted stably in water samples at $5 < pH < 9$, in which $Fe(OH)^{2+}$ and Fe^{3+} posed relative lower molecular weight and high positive charges, so, PSF gave a combination of enhanced charge-neutralization/destabilization and bridging due to double action of $Fe(OH)_3$ and the coexistence of three products of Fe ($Fe(OH)_3$, $Fe(OH)^{2+}$ and Fe^{3+}) described above. Also, the species of PSF was characterized by having multi-branched structure with larger size, wider molecular weight and bigger fractal dimension [4], so PSF gave greater larger surface area and higher surface energy, having stronger binding ability with impurities. While PFA was a conglomerate of some sphere or stick-like shape with almost the same size and lower fractal dimension than PSF [4], giving less adsorption sites connected to the impurities [4,32,33], hence PFA had no enough bridging ability, resulting in smaller size of flocs (Fig. 2). In addition, from the viewpoint of coagulation dynamics, the effective hydrolysis products formed by PSF after adding water samples were very stable, so, the time was sufficient for the products to transfer to the surface of impurities, and exerted destabilization with positive charges of average of 1.75 mV [4] on impurities negatively charged and the larger products complexed with Si played bridging function. Therefore, the combination of electric neutralization/destabilization and bridging also could be fully exerted by PSF in StCSF.

Second, the analysis was for StCSF. As shown in Table 1, the qualities of the influent of PSF entering the filter unit was much better than that of PFA, and PSF flocs formed in StCSF was obviously larger and precipitated more easily than PFA flocs, thus resulting in a large amount of smaller flocs of PFA flowing out of the filter unit through the gaps among the materials, so further resulting in a cumulatively higher turbidity removal of PSF in StCSF than that of PFA (Fig. 4).

As also reported in the literature [4,30,31], the oxidation ability of PSF (the redox potential [RP] of PSF and PFA was 750 and 450 mV, respectively [4]) was an important reason for which PSF had excellent removal of organic matters. While for dissolved organic matter (DOM) [4,30], real water samples in fact contained both colloid impurities carrying large amount of organic matters and DOMs dispersed in solution, apart from containing colloid or particulate-like organic matters. The migrating speed of the hydrolysis products of coagulants onto the surface of colloid impurities mainly depended on the rapid mixing time during the coagulation process. This rapid mixing time for inorganic coagulants was often selected as 60–90 s [4], so destabilization of impurities almost occurred within 60 s. In fact, only 0.01–1 s was needed for destabilization of impurities [31] if the hydrolysis products of coagulant once were adsorbed onto the surface of impurities. HA was almost oxidized within 120 s by PSF [4], and a continuous oxidization of PSF on DOMs dispersed in solution (uncombined with coagulant or colloid impurities) occurred, which improved the continuous adsorption of HA on the flocs formed. This may be one of the important reasons for which PSF gave superior UV_{254} removal during StCS (Fig. 4d). After StCS, PSF still gave oxidizing function in StCSF due to PSF's continuous oxidization ability. Combined with the adsorption of filter materials, the oxidizing ability of PSF was the most important reason for which PSF had greater organic matters removal (especially DOMs) than PFA in StCSF.

According to the pollutants removal in Figs. 4b–e and flux changes in Fig. 4a, and the analysis of performance mechanism above mentioned, after StCSF by PSF, the residual values of turbidity, color and organic matters in the effluent almost met the quality requirements of drinking water. In addition, some flocs of PSF had been basically intercepted by the top filter materials according to Figs. 5 and 6, thus reducing the difficulty in backwashing, so the flux was easy to be recovered as long as the top filter materials was once cleared. While PFA could not meet the quality requirements of drinking water in terms of turbidity and organic matters after StCSF, so, as a widely used inorganic coagulant in China's market, PFA will not be applied in StCSF. In summary, the StCSF by PSF is feasible and can be applied in many sites where PFA cannot be used. The StCSF has a far-reaching application significance in special occasions (such as disaster areas, high-speed service areas, etc.), modular or mobile water treatment plants.

4. Conclusions

The suitable EHWS after StCS was 10–11 cm below the surface of the supernatant in the test jars. For the effluent obtained from this height, the behavior of PSF in StCS was basically similar to that in CCS, while the behavior of StCS by PFA was much worse than that by PSF.

The filtration rate and flux of both PSF and PFA in StCSF were lower than that of CCSF. For PSF, the removal of turbidity, COD_{Mn} or UV_{254} in StCSF were almost the same as that in CCSF: during the filtration time (StCSF of 27 h and CCSF of 18 h), the residual turbidity was lower than 0.5 NTU and the turbidity removal was all more than 99%, always meeting the quality requirements of drinking water; the UV_{254} removal reached more than 82% and COD_{Mn} basically fluctuated between 72% and 82%. But the color removal of PSF in StCSF was better than that in CCSF, overcoming its weakness in removing less color due to the color of PSF itself. While for PFA, the residual turbidity in StCSF reached 3.44 NTU after 2 h of filtration, followed by a gradual increase, and then up to 8.2 NTU at 18 h; the removal of UV_{254} and COD_{Mn} decreased from 86.2% after 2 h to 55.3% after 18 h, and from 78% after 2 h to 54.1% after 18 h, respectively.

The pollution of filter materials in StCSF by PSF at different depths of the filter materials was similar to that in CCSF, in which the pollution of the filter materials of PSF in the deeper part was obviously lighter than that of PFA. The flocs of PSF were basically intercepted by the top and near top filter materials, reducing the difficulty of backwashing, further facilitating the recovery of flux. While For PFA, there were much smaller flocs flowing out of the filter layers, resulting in poor water qualities of the effluent.

The excellent behavior of PSF in StCSF was determined by its hydrolysis product distribution, microscopic characteristics and oxidation ability. After PSF StCSF, the residual values of turbidity, color and organic matter in the effluent were able to meet the quality requirements of drinking water; moreover, PSF in StCSF gave the characteristics of easy backwashing and easy recovery of flux. So, the StCSF by PSF is feasible and can be applied in many sites where PFA could not be used.

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