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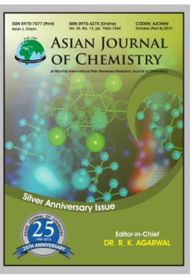

Properties and Coagulation Behaviour of Polyferric Silicate Sulphate by Different Preparation

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Polyferric silicate sulphate (PFSS) can be used in wastewater treatment as modified inorganic polymeric coagulant. Polyferric silicate sulphate is prepared through following steps: (1) alkalization of the mixture consisting of ferric sulphate and polysilicate (PFSSa) and (2) oxidation of the mixture consisting of ferrous sulphate and polysilicate (PFSSo). The typical properties (*e.g.*, pH, ζ-potential and morphology) of PFSSa and PFSSo were characterized. The coagulation performances of the two PFSS samples were studied by using synthetic wastewater and paper wastewater. PFSSa exhibits excellent coagulation performance in comparison with PFSSo and polymeric ferric sulphate for turbidity removal. PFSSo have better ratio COD removal than PFSSa for paper wastewater treatment. It is evident that methods of production play a significant role in the structure and property of polyferric silicate sulphate coagulants.

Key Words: Coagulant, Alkalization, Oxidation, Polyferric silicate sulphate, Wastewater treatment.

INTRODUCTION

Various kinds of coagulants are used in the coagulation process, which is one of the most important processes of wastewater treatment for the destabilization of colloidal suspensions and for the removal of suspended solids and natural organic matter (NOM)[1]. Coagulants mainly consist of organic and inorganic compounds. As an inorganic coagulant, iron salt coagulants are extensively used in wastewater treatment. Because of its superior ratio of efficiency-cost, polymeric ferric sulphate (PFS) is becoming the main coagulant used in wastewater treatment. Nevertheless PFS is difficult to preserve and prone to produce iron hydroxide sedimentation. Thus, many modified PFS was studied on labs[2,3].

Polyferric silicate sulphate (PFSS) as a novel coagulant was found in the 2000's[4-6]. There are two PFSS preparation methods, *i.e.*, (1) alkalization of the mixture of ferric sulphate and polysilicate, producing alkaline polyferric silicate sulphate(PFSSa) and (2) oxidation of the mixture of ferrous sulphate and polysilicate, producing oxidative polyferric silicate sulphate (PFSSo). Few research papers considered the preparation and properties of polyferric silicate sulphate. In particular, the comparison of the preparation methods and the properties of produced coagulants has not been discussed[7].

In this paper, the two synthesis methods (alkalization and oxidation) of polyferric silicate sulphate were investigated. The major properties of PFSSa and PFSSo obtained, such as pH, ζ-potential and morphology were characterized. And their coagulation behaviours were assessed by using synthetic wastewater and paper wastewater.

EXPERIMENTAL

All used reagents were analytically pure chemicals. Deionized water with conductivity lower than 0.5 μS/cm was used to prepare all the solutions.

Preparation of PFSSa: Polysilicate solution (PS) with a SiO_2 concentration of 10 % (w/w) was prepared as follows sodium silicate solution was introduced slowly to sulphuric acid (1:4) under magnetic stirring conditions at room temperature. Then sodium hydroxide solution (10 %) was used to control pH at 3.0 and the polysilicate solution was aged at 45 ºC. Then, ferric sulphate solution was added to the polysilicate solution and mixed rapidly at 60 ºC to give the Si/Fe ratio 1:1. Subsequently, sodium hydroxide solution (25 %) was added as alkali. The B (B = OH/Fe) molar ratios were decided by the volume of alkali. The PFSSa samples were taken out after aging for 2 h.

Preparation of PFSSo: Ferrous sulphate solution was added to the polysilicate solution as mentioned above and mixed rapidly at 20 ºC to give the Si/Fe ratio 1:1 and B = 0. Then, hydrogen peroxide (25 %) was added as the oxidant. PFSSo samples were prepared after aging for 3 h.

Detection method: Liquid PFSSa and PFSSo with Si/Fe ratio 1:1 were dried at 55 °C in an oven for more than 24 h and were ground using a laboratory mortar and pestle for the analysis of characterization.

The pH and zeta (ζ) potential were measured by using PHS-3C (Weiye Instrument Co., LTD. China) and DelsaNano S (Beckman Coulter INC. USA).

The surface morphology of two PFSS powder samples was examined by SEM microphotographs, using a KYKY 1008B (KYKY Technology Development LTD. China) scanning microscope under accelerating voltage of 15 kV.

Samples of PFSS powder were characterized by X-ray diffraction (XRD) for the determination of crystalline phases using a D/max/2400 X-lay diffractomater (Rigaku Industrial Corporation. Japan) with CuK radiation in the range of 5-65° 2θ at a scan rate of 1°/min.

One milligram of PFSS powder was mixed with 250 mg KBr and respective discs were analyzed with Nicolet380 FT-IR Spectrum Meter (Thermo Fisher Scientific Inc. USA) under the conditions of, He-Ne laser light source, 2 cm^{-1} resolution and 60 times of scan range of 4000-400 cm^{-1}.

The degree of silicon polymerization (Si) was determined by timed complexation spectrophotometry with molybdate as a colour reagent. The measurements were performed on WFZ UV-2000 UV-VIS spectrometer (Unico Instrument Co., Ltd. China) at 410 nm. The different species of silicon can be classified into three categories, respectively, Sia (silicates), Sib (oligomers) and Sic (polymers)[8-14].

Jar test for coagulation performance: The synthetic wastewater was made from the surface water with clay added (300 mg/L) with 100NTU and pH = 7.8. Turbidity was determined by WGZ-200 turbid meter (Shanke Instrument Co., China).

Coagulation experiments were conducted in 500 mL beakers using a jar test apparatus MY 3000-6A flocculator (Qianjiang Meiyu Co., China) with a variable speed six-paddle gang stirrer with flat paddle impellers. The experimental conditions were that the initial vigorous stirring time was set to 45 s at the paddle speed 200 rpm to allow coagulant uniform distribution, then the flocculation period (set to 10 min and with paddle speed at 30 rpm) and the final sedimentation period, which settled for 10 min. The supernatant samples after settling were withdrawn from a position of 2 cm below the surface of the tested water samples.

RESULTS AND DISCUSSION

Analysis of morphology: As shown in Fig. 1(b), the surface morphology of PFSSa sample (Fe/Si = 1) consists of the plane of the bulge,which is different from that of PFS [Fig. 1(a)], with a curl chain-net structure. On the other hand, the PFSSo sample prepared with Fe/Si ratio = 1 [Fig. 1(c)] consists of fold surface. Thus the microstructures of PFSSo, PFSSa and PFS are completely different each other.

XRD analysis: Fig. 2 illustrates the XRD spectra of solid PFSSa, PFSSo and PFS samples. There are no single, sharp, intense and well recognizable peaks but only broad, low-intense and not clearly recognizable peaks. It is evidenced that the PFSSo and PFSSa samples are amorphous with rather obscure traces of crystallinity. The same trend has also been observed by Moussas. Compared to the XRD spectra with PFS, the PFSSo and PFSSa samples have a broad intense shoulder at around 8° 2θ. A study of the peaks reveals that a new compound has been formed (at 29° and31° 2θ), containing both silicon and silica, while the rest of the peaks can be attributed to silicon oxide, sodium sulphate and iron species[7]. Thus, the addition of polysilicate within the ferric solution leads to the formation at some extent of the bonds Fe-O-Si and significantly alters the PFS rather than a simple mixture of the raw materials.

FTIR spectra of PFSS and PFS: As shown in Fig. 3, the spectra at 3500-3190 cm^{-1} can be assigned to the stretching vibration of dissociative -OH and -OH attached to Fe and Si[15]. The spectra at 1640-1634 cm^{-1} can be assigned to the bending vibration of water absorbed, complexed and crystallized in coagulant[16]. Significant variations between PFSS and PFS were observed in the bond at 1380-950 cm^{-1}. There have a series of peaks. In particular, the peak at 1225 cm^{-1} (for PFS, B = 0.1) corresponds to the stretching vibration of -OH attached to Fe[17]. The bond around 979 cm^{-1} (for PFSSa, Fe/Si = 1.0, B = 0) and at 984 cm^{-1} (for PFSSo, Fe/Si = 1.0, B = 0) are associated with a Si-O-Fe bond. The peak at 1043 cm^{-1} (for PFSSa, Fe/Si = 1.0, B = 0 and PFSSo, Fe/Si = 1.0, B = 0) is related to asymmetric Si-O-Si stretching vibrations and the peak at around 530 cm^{-1} correspond to the stretching vibrations of Fe-O and Si-O bond[9,18].

For comparing PFSSa (Fe/Si = 1.0, B = 0) sample with PFSSo (Fe/Si = 1.0, B = 0) and PFS (B = 0.1), it was more than evident that the spectrum of PFSSo was similar to that of

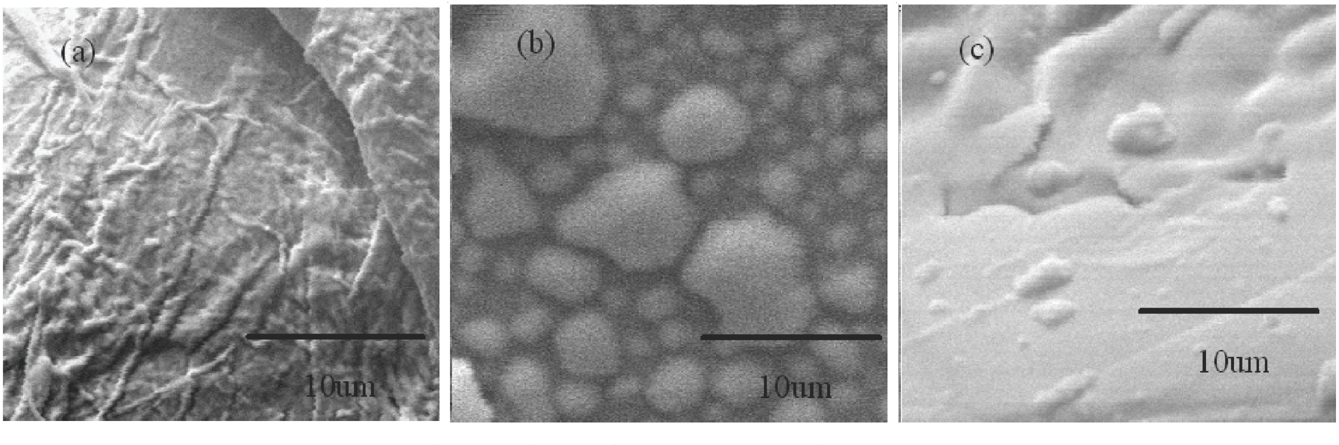
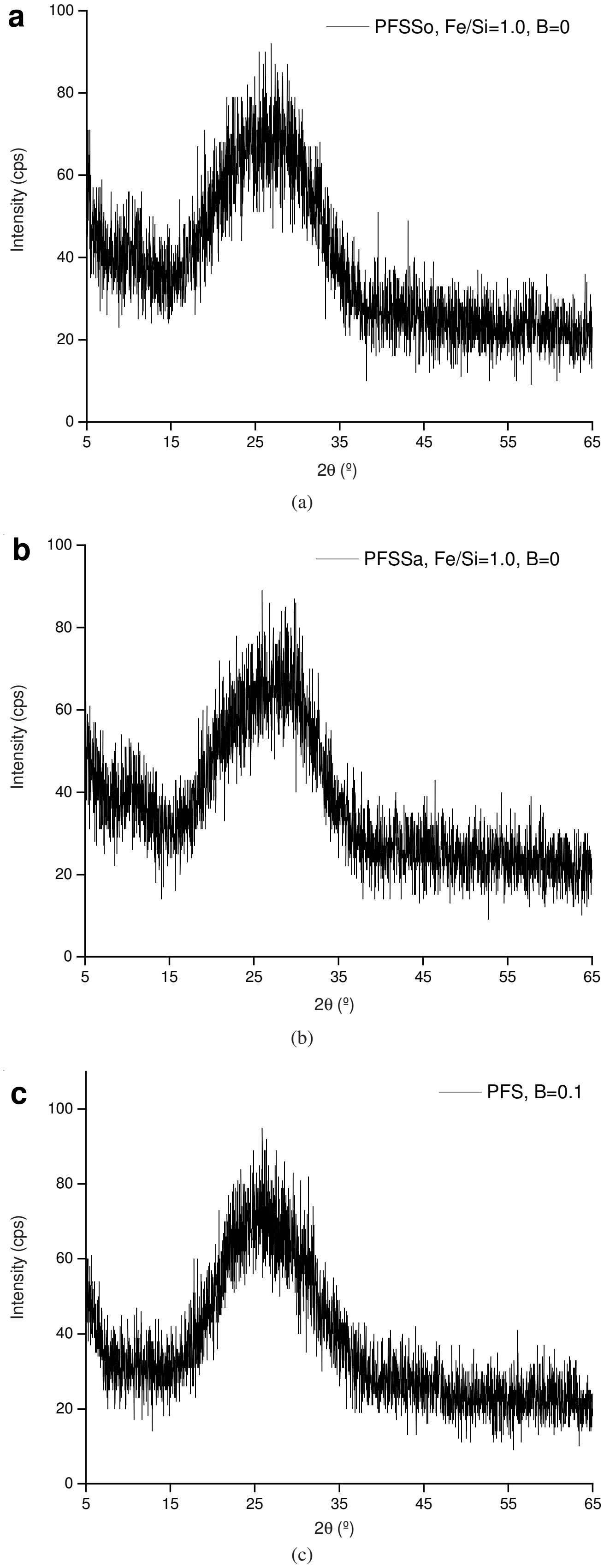


Fig. 1. SEM images of PFS (a), PFSSa (b) and PFSSo (c)



(a)

(b)

(c)

Fig. 2. X-Ray diffractomater scan of PFSSo (a), PFSSa (b) and PFS (c)

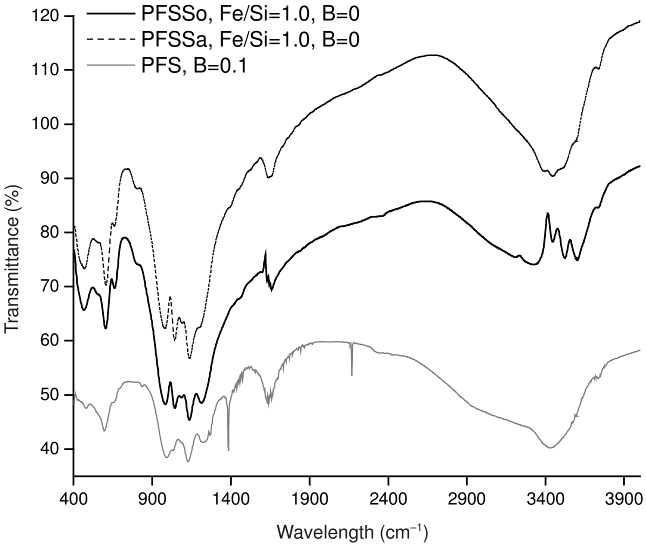


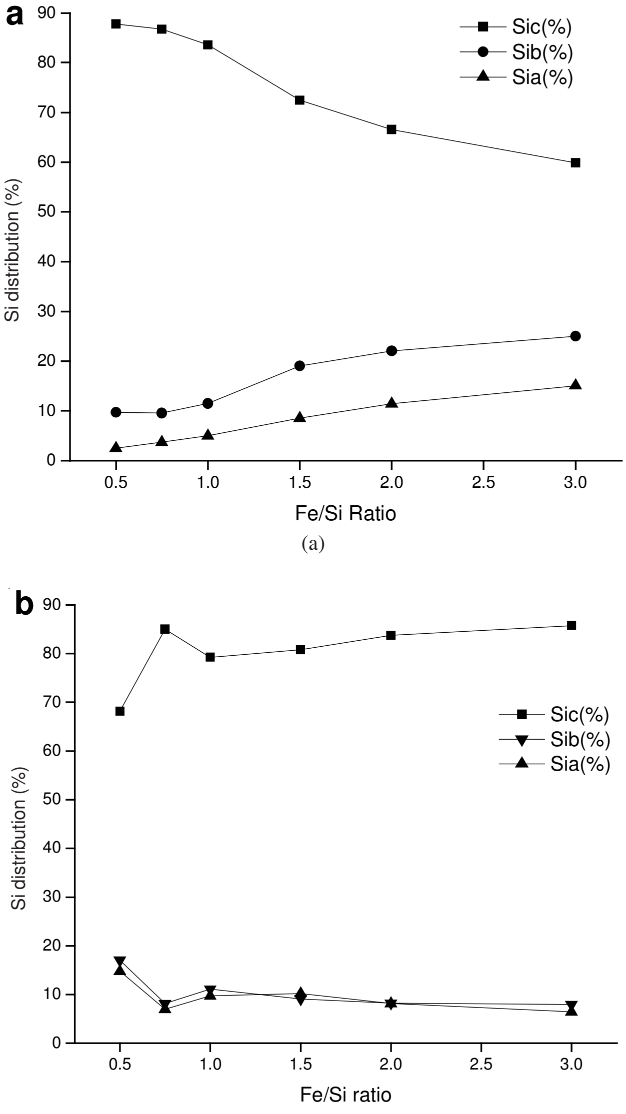
Fig. 3. FTIR spectra of PFSS (Fe/Si = 1.0, B = 0) and PFS (B = 0.1)

PFSSa, whereas distinct from PFS. In the case of the PFSSo and PFSSa, the peaks corresponding to Si-O-Si, Si-O-Fe, Si-OH and Si-O vibration were observable, indicating when the silicate was added, the Fe-O-Fe bond is replaced by Si-O-Si and transformed to a Si-O-Fe bond. Furthermore, the peaks of Si-OH and Fe-OH were stronger and more at PFSSo than at PFSSa. It could be explained that when the oxidant was added into mixing solution of silicate and ferrous sulphate for PFSSo, Si-OH bond in polysilicate was not destroyed and Fe-OH bond product at PFSSo. However, at PFSSa with sodium hydroxide adding, pH value increasing, parts of Si-OH bond in polysilicate was destroyed and Fe, Si and -OH synthesis uniformed Si-OH and Fe-OH solution. Overall, the finding of FTIR analysis supports the statement that new chemical species consisting of iron and silica were formed, which was in total agreement with the conclusion withdrawn from XRD analysis.

Speciation of silicon polymerization: The speciation of all samples was conducted after aging. The results obtained from the application of molybdic acid method are presented graphically in Fig. 4. Before any sort of conclusion made by the application of this method, it is very important to investigate whether the ferric will react on molybdic acid and have any effect on the assay method. Therefore, polyferric sulphate samples at different concentrations were added into the molybdic acid reagent and the absorbance of each sample were recorded at 410 nm. The results showed that ferric did not affect the absorbance of molybdic method.

As shown in Fig. 4(a), the amount of the silicates (Sia) and oligomers (Sib) increased with the increase of Fe/Si values for PFSSa. At the same time, the amount of polymers (Sic) decreased rapidly[7,19], although it is lower than that reported by Wang for a polyferric silicate chloride coagulant. In comparison with the results obtained for PFSS product, the same trend of species distribution is observed by Wang[8] and Zouboulis[20].

However, it can be noticed that the different trend was shown for PFSSo coagulants in Fig. 4(b). By increasing of Fe/Si values the amount of silicates and oligomers decrease. Amount of polymers increase at the same time. Overall, the species distribution of silica in PFSSo changes more smoothly than PFSSa. Furthermore, the data showed that the degree of silicon polymerization for PFSSa coagulants have been more



(a)

(b)

Fig. 4. Distribution of Si species of PFSSa (a) and PFSSo (b)

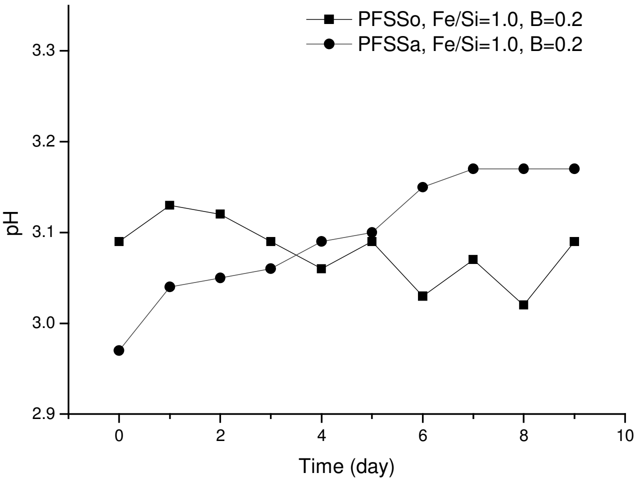


Fig. 5. pH evolution of PFSSa (Fe/Si = 1.0, B = 0.2) and PFSSo (Fe/Si = 1.0, B = 0.2)

greatly affected by Fe/Si ratio than PFSSo, which can be attributed to the different preparation method. It is suggested that mixing polysilicate with ferrous sulphate and then the addition of oxidation (hydrogen peroxide) do not affect polymerization of silicate at PFSSo; this is due to silicate ion is stable and can not be oxidized by oxidation. On the other hand, in the case of PFSSa the sodium hydroxide for alkalinization ferric sulphate change pH value of polysilicate solution, thus polymerization of polysilicate is changed[20]. Finally, The result that methods of production play a significant role in the structure of PFSS coagulants was obtained.

pH evolution and effect of Fe/Si ratio on ζ-potential value: Fig. 5 showed the pH evolution of PFSSo (Fe/Si = 1.0, B = 0.2) and PFSSa (Fe/Si = 1.0, B = 0.2). It can be noticed that for initial (one day) the preparation of the samples, the pH value increase. Lange and Spencer[21] suggested, this is due to silicon polymerization still in progress. It leads to pH increasing that the progress of silicon polymerization release -OH. As PFSSo, ferrous sulphate mixed with polysilicate and then oxidant was added in. Ferrous ion co-polymerizing with polysilicate was oxidized. Ferrous-silicate polymeric was destroyed and ferric-silicate polymeric was composed. The procedure of oxidation affected composition of ferric-silicate copolymer. Quantity of -OH reduced and pH was released. On the other hand, pH value of PFSSa samples increases continuously. It was due to ferric-silicate polymeric was composed and polysilicate released -OH generally. This trend is explained by Tang and Werner[22] that the hydrolysis and polymerization procedure continues in progress.

Fig. 6 demonstrated the effects of pH on the ζ-potential values. It can be revealed that ζ-potential decreased with pH increasing. The ζ-potential decreased steeply at pH values (5, 7 and 8) for PFSSa, PFSSo and PFS, respectively. Addition of polysilicate decrease ζ-potential of samples and compromises the charge neutralization ability of the prepared samples because charge neutralization occurs when polysilicate species of opposite charge were combined with hydrolyzed ferric sulphate.

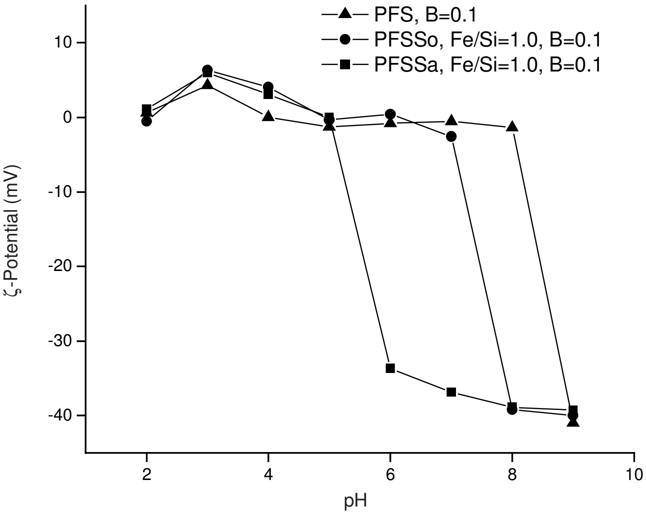


Fig. 6. Effect of pH on ζ-potential values

Evaluation of coagulation efficiency: Fig. 7 displayed the comparison of coagulation efficiency between PFSSo, PFSSa and PFS. Optimal dose was 5 mg/L (as Fe) for PFSSo, PFSSa and PFS and turbidity removal was 96.9, 93.2 and 87 %, respectively. Clearly, turbidity removal performances of PFSSo

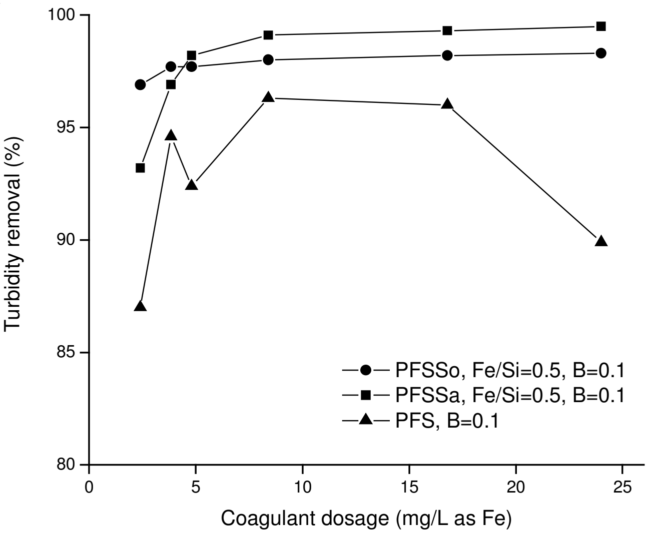


Fig. 7. Comparison of coagulation efficiency between PFSSo, PFSSa and PFS

and PFSSa samples were better than that of PFS. PFSSa had the best capacity in turbidity removal, which could be attributed to the higher degree of its polymerization as assay by pH evolution.

Fig. 8 displays the COD removals of PFSS and PFS for paper wastewater (COD = 438 mg/L). The COD removal of PFSSo and PFSSa were obviously higher than PFS. PFSSo showed excellent COD removal efficiency and stability of COD removal. Thus, PFSSo was most appropriate for COD removal for paper wastewater treatment.

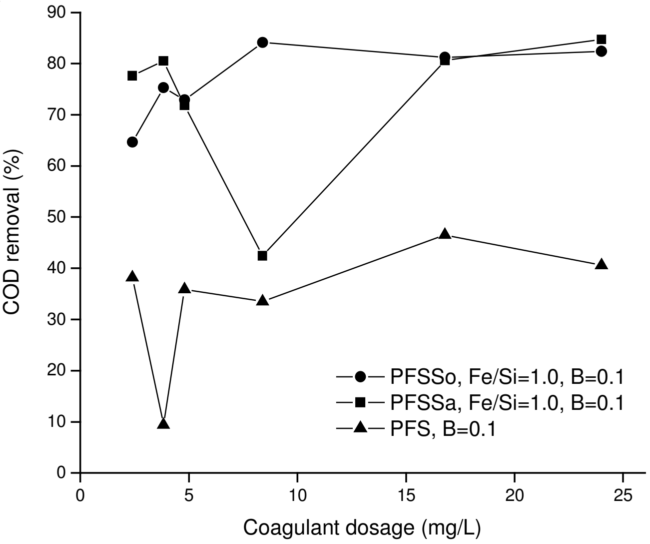


Fig. 8. Treatment of paper wastewater with PFSSo, PFSSa and PFS

Conclusion

The modified inorganic polymeric coagulants PFSS were prepared by two different methods, *i.e.*, (1) alkalization of the mixture of ferric sulphate and polysilicate, producing PFSSa and (2) oxidation of the mixture of ferrous sulphate and polysilicate, producing PFSSo. Compared with PFSSo, the PFSSa coagulants display a better coagulation performance for turbidity removal. The speciation by the molybdic acid assay showed that in the case of PFSSa the co-polymerization of iron and polysilicate resulted in the formation of larger polymeric species than PFSSo did. But, PFSSo has stable removal of COD for paper wastewater. Overall, PFSSa and PFSSo are new modified inorganic polymeric coagulants in comparison with PFS coagulant. PFSSa and PFSSo have different structural features and exhibit different coagulation performance.

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