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Development of a new poly silicate ferric coagulant and its application to coagulation-membrane filtration hybrid system in wastewater treatment

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ABSTRACT

Coagulation is one of the effective pretreatment stages in membrane filtration of wastewaters to produce clean water. Using a suitable coagulant, one can mitigate membrane fouling. Membrane fouling is a process where particles deposit onto a membrane surface or into membrane pores in a way that degrades the membrane's performance. Research in this area is currently being focused on development of improved coagulation reagents such as poly silicate ferric (PSiFe), which has a high molecular weight and large number of positive surface charges with high efficiency at low doses. In this paper, PSiFe was prepared by following two approaches: (a) acidification of water glass solution using HCl followed by $FeCl_3$ addition (old-PSiFe); (b) acidification of water glass solution by passing it through an acidic ion exchange resin followed by fresh $FeCl_3$ addition under different Fe/Si molar ratios (new-PSiFe). These coagulants were characterised by X-ray diffraction and scanning electron microscopy. According to coagulation jar test results when Fe/Si = 1, the best performance was achieved in terms of turbidity, total organic carbon (TOC) and UV254 removals. Another aspect is the comparison of the old-PSiFe, FeCl3 and new-PSiFe which showed that in a membrane filtration system, using the new-PSiFe not only reduces the required transmembrane pressure (TMP) due to lower fouling, but also improves the TOC removal efficiency.

Keywords: Coagulation; Poly silicate ferric; Membrane fouling; Membrane filtration; Transmembrane pressure

1. Introduction

Water is not an infinite resource in many countries across the world. To have a sustainable and clean water resource, wastewater can be viewed as a resource if it is treated to remove pollutants. Some wastewater professionals are reusing treated wastewater and have found it to be a reliable alternative water source even for drinking purposes. Most of the wastewaters are usually polluted with inorganic and organic particles, as well as contaminants associated

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with these particles in dissolved forms. The removal of these pollutants is essential as their presence deteriorates water quality. If the treatment complies with applicable and appropriate rules, treated wastewater can be used for many beneficial purposes such as landscape irrigation, agricultural irrigation, aesthetic uses, groundwater recharge, industrial uses, fire protection, household uses and drinking purposes.

Coagulation is generally known as the core process in any type of water treatment; its absence would lead to unfavourable downstream process such as membrane treatment that would in turn greatly increase the operation and maintenance cost, especially in industries where massive quantities of wastewater are required for thorough treatments on a daily sustainable basis. It is applied to destabilise and then in the sedimentation of colloidal particles and dissolved contaminants in water. Traditionally iron and aluminum salts are used as coagulants, then an improved coagulant, such as poly metal salts (e.g. poly ferric or poly aluminum chloride or sulfates), is being used. As residual aluminum is believed to be harmful to human and other living organisms, iron-based coagulants have attracted more interest and attention [1,2].

Among the coagulant types, PSiFe, which is an inorganic poly metal silicate, has been shown to be a very effective coagulant due to its high charge, high molecular weight and environmental friendliness. The hydrolysis/polymerisation of Fe-polysilicate coagulants has been investigated extensively by many chemists and water treatment specialists [3–5]. There have been several studies conducted using different modifications in the preparation of inorganic poly silicate metal coagulants, such as adding new components to polymerised silicate solution [6–8]. According to the studies, adding a modifier, such as poly silicate (PSi), increases molecular size and aggregation process as well as stability and durability [9–11].

A new type of coagulation reagent known as poly inorganic flocculants (PIFs), such as poly silicate ferric (PSiFe), have higher charge and molecular weight than the previously used polyvalent metal salts, and therefore their higher coagulation ability is currently being investigated by many researchers [3,4,12]. Due to the complex nature of the silica used in the preparation of PSiFe, various preparation methods were proposed [5]. It can be noted that each preparation method may give different performances under the same name of PSiFe. New research is required for quantifying suitable silica characteristics and improving the method of preparation of PSiFe, which is to be employed as an effective coagulant [3,6]. Different methods were considered to optimise Si/Fe ratios, basicity factors, the heating temperature and the ageing time.

Most researchers followed one of the currently available procedures using an inorganic or an organic acid or a modifier such as poly ferric sulphate (PFS) or poly ferric chloride as the polymerisation agent. In many developed methods, these additions were made at very low pH (around 2) [4,6,13]. To the best knowledge of the authors, there is no evidence that researchers have precisely investigated the methodology of the polymerisation of silica with alternative acidification using acidic resin to produce improved aggregation characteristics and reach the main goal in particle sedimentation. In this study, all these factors including initial concentration of silica, acidification method, temperature and suitable time of aggregation of turbidity particles, speed and optimum pH for Fe addition have been investigated. Obviously all these factors directly or indirectly would result in having minimum consumption of the material, high charge neutralisation ability, bridging/sweeping and other necessary characteristics for the optimisation of coagulation.

Another original aspect of this research is the use of PSiFe coagulants in a hybrid system consisting of coagulation and a submerged membrane to determine the efficiency of this coagulant (PSiFe) on the performance of the membrane, such as membrane fouling. All these factors directly or indirectly would result in having minimum consumption of the materials and high charge neutralization ability, bridging of the particles and all necessary characteristics for the optimisation of coagulation. Consequently a steady, reliable and durable membrane treatment system will be developed. The outcome of this research will provide a sustainable coagulation/membrane filtration system with lower chemical consumption, lower waste and minimum operation and maintenance cost.

2. Experimental program

An array of experiments were conducted in this study. In this section, preparation details and characterisations of PSiFe are described. In addition, jar test-based coagulation experiments as well as the details of a bench-scale hybrid system of coagulation–membrane filtration are explained.

2.1. Preparation of PSiFe

In the first step, PSiFe was prepared pursuing an available procedure [6]. The procedure involves polymerisation of diluted water glass solution (6% w/w SiO_2) with hydrochloric acid followed by metal addition. The PSiFe prepared based on this procedure is called old-PSiFe in this paper. After a detailed literature survey on silica polymerisation methods, the test procedure was improved and a new PSiFe was prepared. This product is called new-PSiFe in this paper. The steps used in the preparation of the new-PSiFe are summarised as follows:

(1) Dilution of water glass solution.
(2) Heating the diluted water glass solution to 80–100℃ for 10 min to improve the aggregation ability.
(3) Passing the solution through an acidic resin to prepare poly silicate acid (PSiA) without Na^+ which otherwise causes dispersion instead of aggregation and improves the stability of the solution.
(4) Heating the PSiA to 80–100℃ for 10 min and aging for 24 hours to increase the molecular size of the polymer.
(5) Adding various amounts of $FeCl_3$ (1 M) to the specific volume of PSiA to prepare four products with different Si/Fe ratios [5,6,7,9,10,14,15].

2.2. Characterisation of PSiFe

The structure and morphology of PSiFe coagulants were determined using X-ray diffraction (XRD), and scanning election microscopy (SEM). The effectiveness of the destabilisation ability of PSiFe was investigated by measuring different factors of the in-situ flocculation product at the sedimentation stage [13]. The most important measurement of PSiFe is to determine the proportions of different polymeric species by the ferron-time spectroscopy method that has been reported previously by a number of researchers [3,13,15].

2.3. Coagulation experiments (jar test)

The coagulation experiments were carried out using a jar test apparatus with six paddles. Synthetic wastewater (SW) was prepared with specific contaminants as shown in Table 1 [16]. The jar test consisted of initial 15 min rapid mixing (90 rpm) to allow particle destabilisation followed by 15 min slow mixing for the flocculation period and the final sedimentation period, which lasted 30 min. The samples were withdrawn from 20 mm below the water surface for the analysis. The total organic compound (TOC) and turbidity factors were evaluated in the jar test.

2.4. Bench scale inline coagulation-membrane hybrid system

After determining the best Si/Fe ratio and the optimum dose of PSiFe by the jar test, a hybrid system, a combination of coagulation and membrane module (hollow fibre) was prepared. This system was used to examine the effect of coagulation with this chemical on the performance of the membrane system for durability and fouling based on a series of standard physical and chemical tests (Fig. 1). The analysis involved TOC, turbidity and durability of the critical transmembrane pressure (TMP). TMP was measured using a pressure gauge at the outlet of the membrane; TOC was measured after coagulation but before membrane filtration.

Table 1
Synthetic wastewater composition

Component name	Concentration (mg/l)
Beef extract	1.8
Peptone	2.7
Humic acid	4.2
Tannic acid	4.2
Sodium lignin sulphate	2.4
Sodium lauryl sulphate	0.94
Acacia gum powder	4.7
Arabic acid (poly sacharide)	5
$(NH4)_2SO_4$	7.1
KH_2PO_4	7
NH_4HCO_3	19.8
$MgSO_4 \cdot 3H_2O$	0.71

2.5. Analytic methods

Turbidity measurements of the suspended solids are made using a turbidity metre, HACH 2100. TOC using MultiN/C 3100 (analytik Jena).

UV254 was used to measure the dissolved organic compounds by UV light absorbance at 254 nm using Schimadzu UV-1700 Low absorbance corresponds to high removal of dissolved organic matter.

All the measurements were compared with SW using the following formula (Eq. (1)):

$$\begin{aligned}&\%\ \text{Removal of TOC, Turbidity, and UV254}\\&\quad = [(\text{Sample result} - \text{SW result})/\text{SW result}]\\&\qquad \times 100\end{aligned} \tag{1}$$

3. Results and discussion

3.1. XRD patterns of PsiFe

Data acquired from XRD tests showed that the old-PSiFe had large amounts of NaCl impurity, whereas the new-PSiFe had no NaCl crystals. The

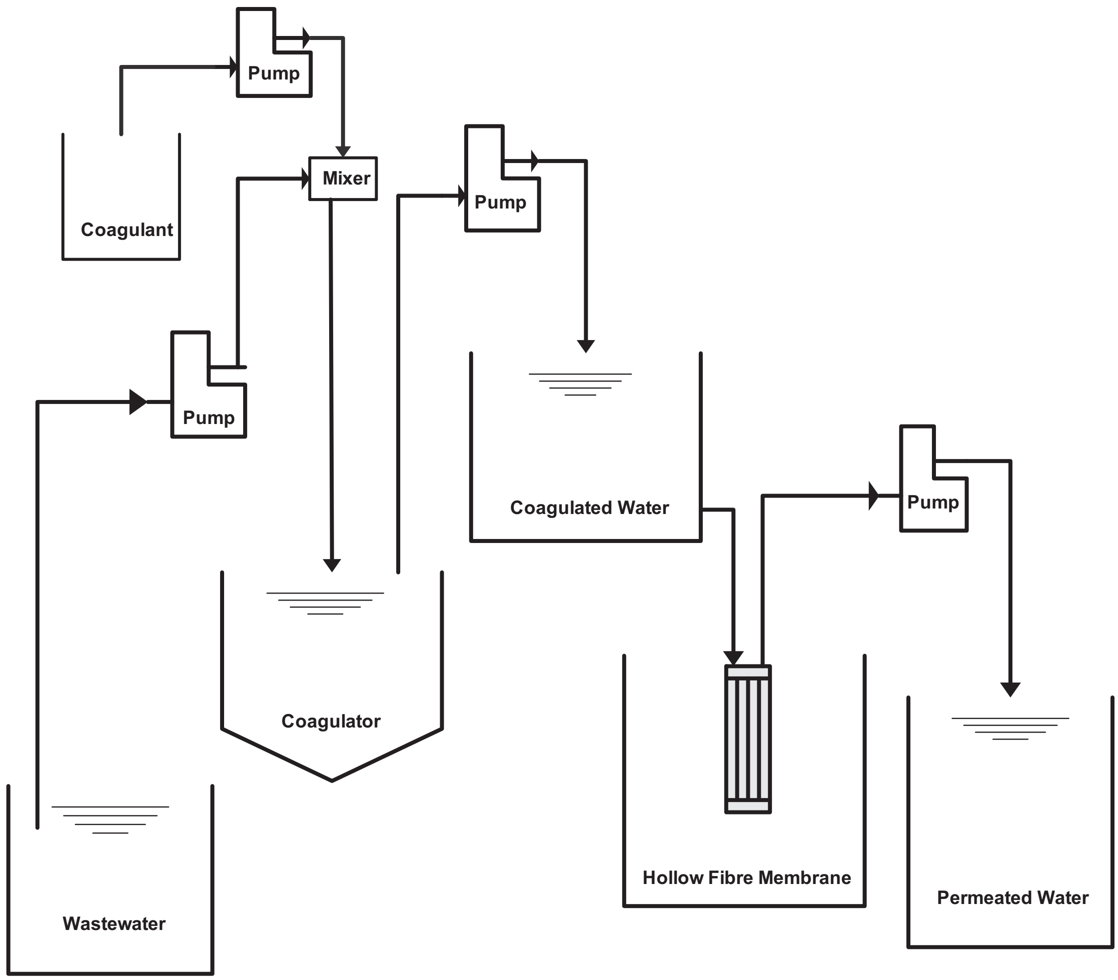

Fig. 1. Coagulation-membrane filtration hybrid system.

presence of Na^+ not only reduced the attachments of the polymer units at the aggregation stage but also produced less bridging at the final preparation stage. Furthermore, it caused salinity in the treated water. Therefore the new-PSiFe with no salt can be considered a better coagulant.

The XRD patterns show that the old-PSiFe had large amounts of NaCl crystal impurity, whereas the new-PSiFe had no visible NaCl peaks(Fig. 2). SEM peaks also show that the new PSiFe had no NaCl crystals, whereas the old-PSiFe had large amounts of NaCl (Fig. 3). Presence of NaCl causes less external bridges in the polymer that is not helpful for coagulation.

3.2. *Jar test*

After performing several jar tests, the selected results of the jar tests for the removal of TOC, turbidity at different Si/Fe ratios are summarised in Table 2 and Figs. 4 and 5. The results show that turbidity removal was the highest for Si/Fe = 1 (94%), TOC removal was the highest for Si/Fe = 0.5 (84%). The main cause of membrane fouling in the coagulation membrane filtration hybrid system is excessive turbidity. Therefore, the Si/Fe ratio which produced the greatest turbidity removal (Si/Fe = 1) was considered to be the best ratio for the new-PSiFe coagulant.

Negative numbers in turbidity mean increasing the turbidity after adding the coagulant.

3.3. *Bench-scale inline coagulation-membrane hybrid system*

Three different coagulants were tested in this experiment. $FeCl_3$, old-PSiFe, and new-PSiFe with the ratio of Si/Fe = 1 were prepared and were fed into the membrane system. In these experiments, cumulative

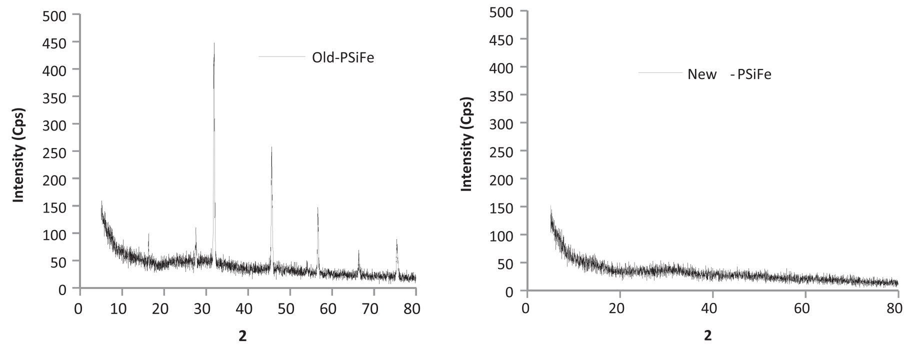

Fig. 2. XRD patterns of Old-PSiFe and New-PSiFe.

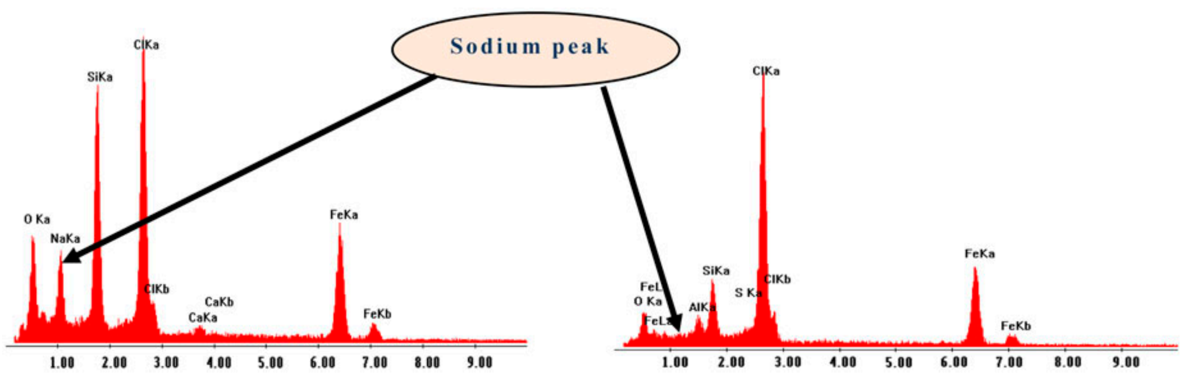

Fig. 3. SEM peaks for Old-PSiFe and New-PSiFe.

volume of permeate versus TMP (the difference between inlet and outlet pressure of the membrane) was found for different target coagulants at a dose of 17 Fe (mg /l) with a membrane flux of 20 L/m^2h (Fig. 6). Furthermore, the TOC removals were compared for the above-mentioned coagulants at two sampling points, after coagulation and after membrane filtration (Fig. 7).

Fig. 6 shows that new-PSiFe causes lower pressure drop in membrane with high cumulative volume compared to $FeCl_3$ and old-PSiFe. This means that by coagulation with new-PSiFe prior to membrane filtration, we can have more flow through membrane with lower outlet pressure.

Fig. 7 shows that the new-PSiFe provided the highest TOC removal in the coagulation stage among old-PSiFe and ferric chloride. It causes less TOC treatment load on the membrane system, which consequently causes low fouling on membrane.

Among the coagulants calculated from the same amount of ferric ion with the specific amount of wastewater in the coagulator, two samples are taken before and after the membrane filtration to compare the TOC removal of these coagulants.

4. Conclusions

The main conclusions that can be drawn from this study are:

- The results indicate that the new-PSiFe has superior coagulation efficiency than $FeCl_3$ and a PSiFe prepared based on a common existing method (old-PSiFe).
- Structure and morphology analysis of PSiFe samples carried out using XRD patterns showed that the new-PSiFe had no measurable NaCl peaks, whereas the old-PSiFe had large amounts of NaCl crystals. The results confirmed this finding. This point can be explained as Na^+ can be removed by the acid exchange resin in the preparation of the new-PSiFe.
- The new-PSiFe with Si/Fe = 1 is highly efficient in removing the TOC and turbidity. Therefore, the new-PSiFe coagulant provides a lower potential of fouling in downstream membrane filtration treatment.
- The precoagulation with the new-PSiFe has higher effect on the physico-chemical factors of membrane

Table 2
Comparison of TOC and turbidity data for different Si/Fe ratios

Fe (mg/l)	Si/Fe = 0.2 % Turbidity removal	Si/Fe = 0.2 % TOC removal	Si/Fe = 0.5 % Turbidity removal	Si/Fe = 0.5 % TOC removal	Si/Fe = 1 % Turbidity removal	Si/Fe = 1 % TOC removal	Si/Fe = 2 % Turbidity removal	Si/Fe = 2 % TOC removal
5	−32	8	16	32	21	24	−10	40
10	−32	53	38	38	45	27	33	51
15	−54	58	−12	32	51	52	24	72
20	−42	64	52	82	55	75	79	73
25	−42	70	90	84	91	67	83	79
30	46	80	−24	71	94	73	−81	56

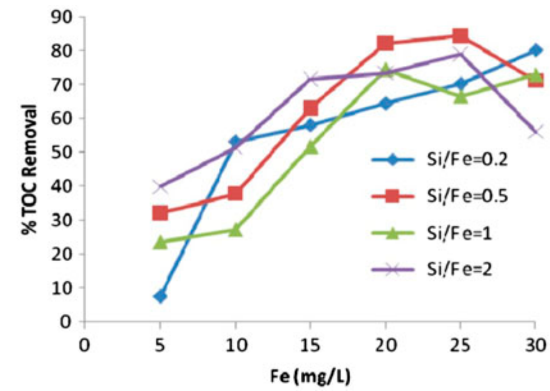

Fig. 4. Jar test TOC removal data for new-PSiFe at different Si/Fe ratios.

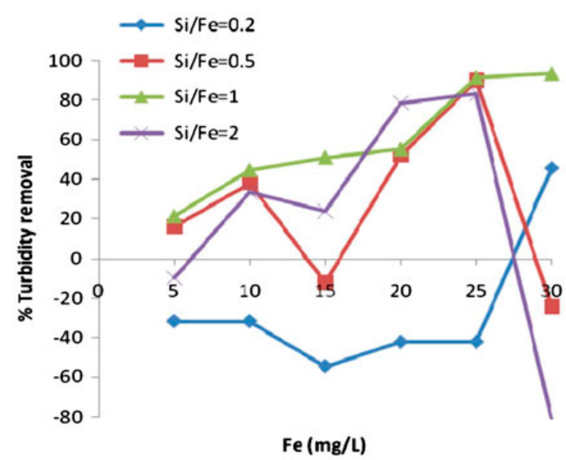

Fig. 5. Jar test Turbidity removal data for new-PSiFe at different Si/Fe ratios.

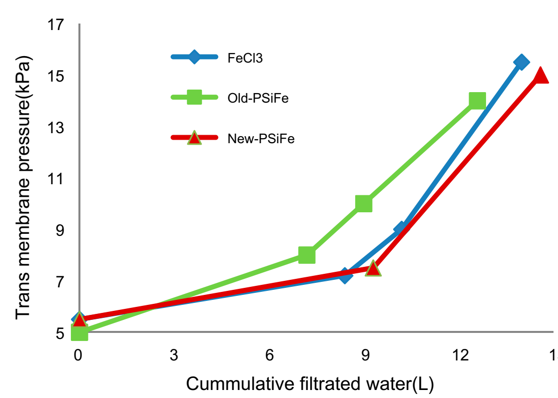

Fig. 6. TMP against cumulative membrane outlet volume of treated water for three different coagulants.

filtration such as TMP reduction and TOC removal compared to traditional coagulants ($FeCl_3$ and old-PsiFe).

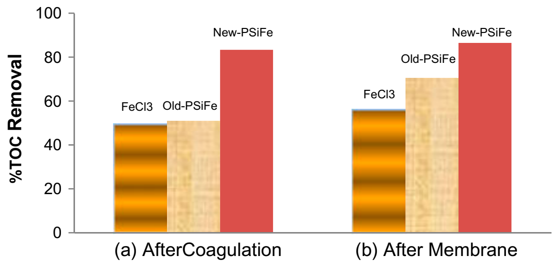

Fig. 7. TOC removal using three different coagulants (a) after coagulation but before passing through the membrane (b) after membrane filtration.

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