



**Development of a Novel Polysilicate Ferric
Coagulant and Its Application to Coagulation-
Membrane Filtration Hybrid System in
Wastewater Treatment**

by

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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ABSTRACT

Coagulation is one of the effective pretreatment stages in membrane filtration of wastewater to produce clean water. Using a suitable coagulant can mitigate membrane fouling. Membrane fouling is a process where solute or particles deposit onto a membrane surface or into membrane pores in a way that degrades the membrane performance. Research in this area is currently being focused on development of improved coagulation reagents such as polysilicate ferric (PSiFe), which has a high molecular weight and large number of positive surface charges with high efficiency at low doses. In this thesis, PSiFe has prepared based on the following approaches: (a) acidification of water glass solution using HCl followed by FeCl_3 addition and (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. 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 the turbidity, the total organic carbon (TOC) and UV_{254} removals.

In this study, a thorough experimental program has been carried out to compare the performance of three different coagulants including the existing PSiFe, FeCl_3 and the modified PSiFe. The results clearly

indicated that in a membrane filtration system using the modified PSiFe not only reduces the required transmembrane pressure (TMP) due to lower fouling, but also improves the TOC removal efficiency.

The outcome of this research provides an efficient coagulant, which can create a sustainable coagulation-membrane filtration system with a lower consumption of chemicals compared to traditional coagulants, and lower fouling that consequently leads to minimum operating and maintenance costs. The findings of this research have also revealed that the performance of the target coagulant, PSiFe- γ , is superior to conventional reagents. Hence, this coagulant and the developed procedure in this study can be used in industry to enhance the coagulation process for achieving a more effective wastewater treatment procedure.

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JOURNAL ARTICLES PUBLISHED

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Sanghyng. J., **Nateghi, F.**, Nguyen, **T.V. and** Vigneswaran, S. (2011). “Pretreatment for seawater desalination by flocculation: Performance of modified poly ferric silicate and ferric chloride as flocculants”, *Desalination*, vol. 283, pp. 106-111.

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Nateghi, F., Loganathan, P., Khabbaz, H., Nguyen, T.V., Vigneswaran, S. (2011). “Development of iron based coagulants and their applications to coagulation-membrane hybrid system in wastewater treatment”. In *Proceedings of the 7th International Chemical Engineering Congress & Exhibition (ICHEC 2011)*, Kish Island, Iran.

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LIST OF ABBREVIATIONS

ATR-FTIR: Attenuated total reflection–Fourier transforms infrared spectroscopy

COD: Chemical oxygen demand

DI: De-ionized

DO: Dissolved oxygen

DOC: Dissolved organic carbon

DON: Dissolved organic nitrogen

EDX : Energy dispersive spectroscopy

HA: Humic acids

HOC: Hydrophobic organic carbon

HPC: Heterotrophic plate count

HPI (HF): Hydrophilic

HPO (HB): Hydrophobic

HRT: Hydraulic retention time

HS: Humic substances

MBR: Membrane bio-reactor

MF: Microfiltration

NF Nanofiltration

MQ: Mili-Q water

MW: Molecular weight

NOM: Natural organic matter

NPD: Normalized pressure drop

OM: Organic matter

PolyDADMAC: Polydiallyldimethylammonium chloride

PSA: Polysilicate acid

PSiFe: Polysilicate ferric

SS: Suspended solids

SUVA: Specific ultraviolet absorbance

SWW: Synthetic wastewater

TMP: Trans-membrane pressure

TOC: Total organic carbon

TSS: Total suspended solids

UF: Ultrafiltration

UF-MFI: Ultrafiltration-modified fouling index

UV: Ultraviolet

UV₂₅₄: Ultra violet at 254 nanometer absorption

XRD: X-ray diffraction

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