

Coagulation Chemistry of Ceramic Membranes

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Abstract

This paper focuses on electro-coagulation coupled with ceramic membrane filtration, which can have significant environmental and financial benefits. Water Corporation has tested ceramic membranes but found that both for drinking water and wastewater applications the membrane would foul uncontrollably if a coagulant was not used. This was a disadvantage, as polymeric membranes operated without coagulants. Water Corporation's interest in ceramic membranes is due to their longer lifespan, being able to withstand harsher cleaning chemicals and delivering a higher flux which results in a lower surface footprint. This paper proposes pre-treatment electro-coagulation, to enable ceramic membranes. Electro-coagulation works by having a cathode and a sacrificial anode connected to an electrical supply that will produce metal ions, causing flocculation and mitigating membrane fouling. Advantages of electro-coagulation include the production of less sludge, minimal impact on the pH, and ease of transport and storage. The key outcome is operating effectively with an aluminium anode with an optimal set-up of 1.7A, 200 L/m²h filtrate flux, 550 L/m²h backwash flux, 30 s backwash time, 30 min filtration cycles, and aeration on backwashes. Aluminium was found to perform significantly better in a continuous flow setting than iron.

1. Introduction

Water Corporation has recently undertaken pilot trials using ceramic membrane filtration for water and wastewater alongside pre-treatment processes of coagulation and ozone. This has shown promising results, with the membrane being able to operate at high flux rates. The flux is denoted as L/m²hr (LMH), and a higher flux is desirable as it can decrease the amount of area needed for filtering a certain volume. However, for a wastewater recycling application, this has been deemed insufficient incentive to switch over to ceramic membranes, as the process uses coagulant to decrease irreversible fouling, which is an expensive product at a large scale. Irreversible fouling is a foulant that can only be removed by chemical cleaning, and reversible fouling is removed by pushing the filtrate in the opposite direction, called a physical backwash. Water Corporation is looking for alternatives that may decrease and potentially eliminate the usage of chemical coagulants as a whole. Investigating the use of ceramic membranes is of interest due to their long lifespan (>20 years), and ability to withstand harsher cleaning chemicals and deliver higher fluxes, which results in a smaller plant footprint. One of the possible alternatives is the use of electro-coagulation (EC). This is in line with the Water Corporation's goal of being environmentally sustainable as climate changes.

1.1 Electro-coagulation

EC works by having a cathode and a sacrificial anode, made from materials such as aluminium or iron, connected to an electrical supply that will produce sufficient amounts of metal ions that can coagulate organic matter. Coagulation is the process of introducing a positively charged species to attract negative particles such as organic matter to form larger flocs. These larger flocs mitigate membrane fouling by being less likely to go deep into the membrane's pores. The greater the current, the more metal ion is produced, as shown by equation 1, increasing flocculation (Bhadana et al., 2022).

$$m = \frac{M * I * t}{z * F} \quad \text{Eq. 1}$$

Where the mass of metal generated is m in grams and I is the current. The M is the molecular weight of the atom, t is the time, z is the number of electrons transferred per metal ion and F is Faraday's constant, 96,486 C/mol. The different metal ions behave uniquely for the various water conditions but a general trend is that iron produces smaller, "fluffier" flocs that are more difficult to settle (Song et al., 2015). EC has several advantages, one being that it produces less sludge, a by-product of the coagulation process, compared to using inorganic chemical coagulants (Al-Hanif & Bagastyo, 2021). Having less sludge produced will mean that there will be less material that needs to be disposed of, which gives EC a potentially lower operating cost. Secondly, electro-flotation can occur, where the hydrogen bubbles from the cathode adsorb with the flocs and float to the surface. Another advantage is that EC has minimal effect on pH while inorganic chemical coagulants, such as Aluminium sulphate or Ferric sulphate, cause pH to decrease (Bhadana et al., 2022; Song et al., 2015). Decreasing pH requires supplemental lime, such as soda ash or caustic soda, to be added to maintain an acceptable pH level. Keeping the pH near 7 eliminates the need for pH adjustment using lime, which will decrease the chemical supply costs. The third major benefit is the fact that EC will have less liquid chemical demand as the coagulant agent is now being produced on-site (Al-Hanif & Bagastyo, 2021). This will save significant costs of transportation, storage and management of large amounts of chemicals and is also a greener approach as it reduces potentially hazardous or toxic chemicals (Bhadana et al., 2022).

1.2 Project Objective

The purpose of this research is to investigate alternative operation methods for ceramic membranes that can minimise or eliminate the usage of coagulants.

An operation method identified as promising and worth further investigation is using EC to decrease reliance on chemical coagulants. When the correct voltage is supplied the anode will produce metal ions to promote flocculation. EC will be tested using a ceramic flat sheet membrane, a structure of ceramic membrane never previously tested by Water Corporation, and measuring the transmembrane pressure (TMP) to indicate the rate of fouling.

2. Process

The effect of EC on ceramic membrane performance has been investigated using the experimental rig depicted in Figure 1. The rig uses a laboratory scale submerged flat sheet ceramic membrane module. Data was recorded and manipulated using MS Excel.

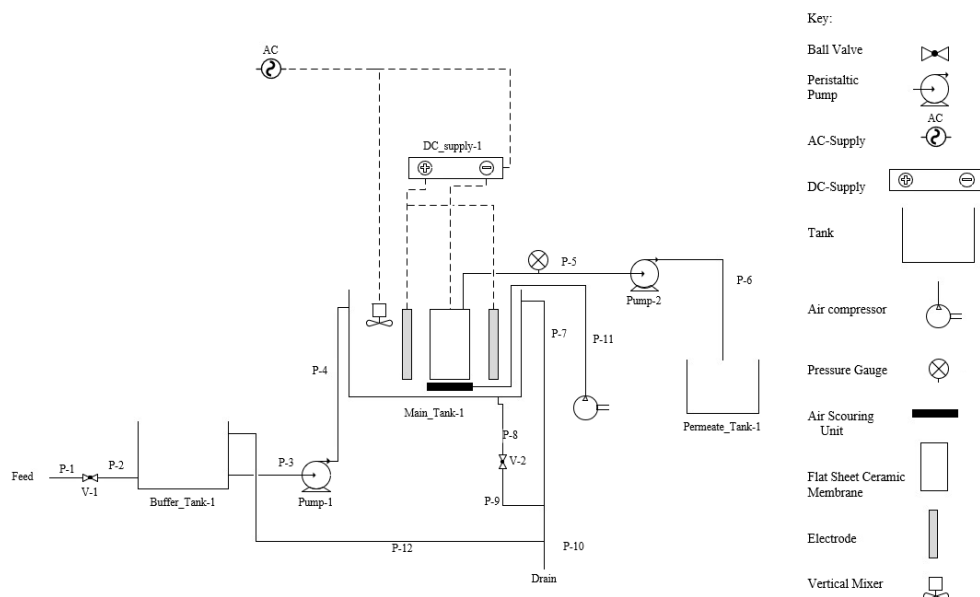


Figure 1 P&ID of the experimental setup. P-7 is the overflow pipe that allows for a constant water level to be achieved for the main tank. P-12 is also another overflow pipe for the buffer tank.

Reclaimed effluent from the Water Corporation's Subiaco wastewater treatment plant is used to test the antifouling potential of EC. The experiment comprises running the ceramic membrane at different operating conditions which include various filtrate flux, backwash flux, filtration time, backwash times, DC-supply currents and EC rest times. The EC rest time is the length of time the EC is turned on before the filter pump is turned on. The buffer tank was critical as the reclaimed effluent flow rate would change throughout the day and the inlet flow rate would greatly change the effectiveness of the EC. The setup is used to simulate a continuous wastewater pre-treatment process in a potential water recycling plant.

2.1 Restoration Procedure

A rigorous membrane cleaning method is required between each trial. There are three main types of cleaning; Cap cleaning, Chemical enhanced backwash (CEB) and Cleaning in place (CIP). The most common cleaning (recommended by the manufacturer) was the Cap cleaning. This involved spraying the membrane surface with 6% NaOCl (for organic fouling) or 6% HCl (for inorganic fouling), leaving it for 2 min, then rinsing with tap water. Cap cleaning removes most of the irreversible foulant shallow in the pores, and usually gets the membrane to 90-95% of the original value. The next most commonly used cleaning was CIP, which involved soaking the membrane in a 1000 parts per million NaOCl or 2 pH HCl solution overnight. This cleaning was used when the membrane was fouled significantly and Cap cleaning couldn't restore it. CEB was used rarely but involves backwashing with the solution with the same concentration as the CIP. The membrane was considered restored when it was at least 90% of its original TMP, as outlined by the manufacturer.

3. Results and Discussion

Both aluminium and iron were tested as the material for the sacrificial anode. The operating conditions for each experiment are shown in the graph. The normalised TMP is a ratio of the initial TMP and the current TMP and all of the data is triplicated.

2.1 Aluminium anode optimisation

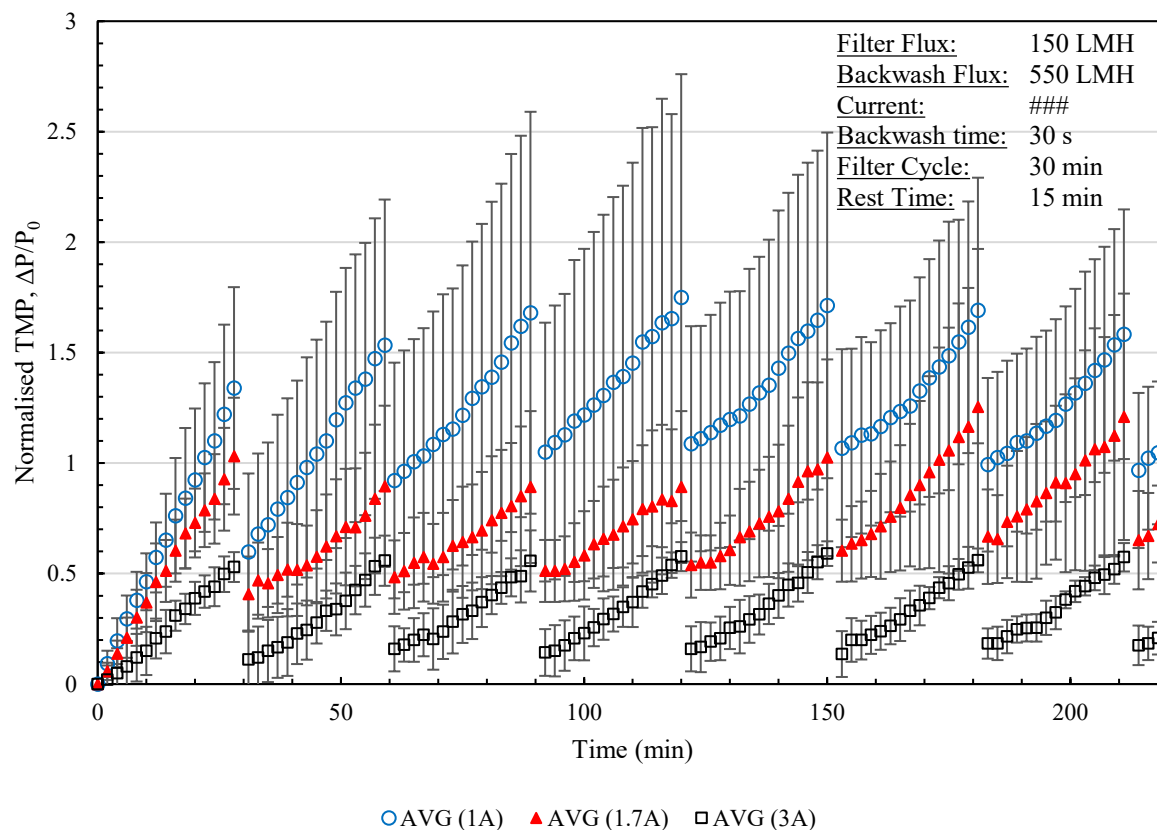


Figure 2 Normalised TMP versus time at 150 L/m²hr (LMH) with the aluminium anode at varying currents.

The current is linked to the number of metal ions generated, and thus it is expected that varying the current will affect the amount of fouling occurring. In Figure 2 this trend is observed by the normalized TMP not increasing as much when a higher current is used. The 3A graph is almost able to recover fully after each cycle while at 1A there is more irreversible fouling occurring after each cycle. The greater recovery is further emphasised at 220 minutes, the 3A is roughly 5 standard deviations (σ) below the 1.7A and 11 σ below the 1A graph.

The first cycle contributes the most difference in gradient between the 3 currents. The 1A data increases dramatically for this cycle which is a large factor in not able to effectively recover in the following backwashes, since it is already significantly irreversibly fouled. Looking at the 1.7A data, the gradient is almost identical to the 3A data after 30 min and the 1A data has a similar gradient to the 3A data at around 120 min. This suggests that the lower current needs to have a longer period to generate enough metal ions so there are more and larger flocs that will prevent irreversible fouling. By optimising the length of the rest period the system may be reliably operated at a lower current, but further investigation is required. A lower current is preferred as this results in lower power consumption, resulting in lower operating costs. Taking into account operating costs, performance and advice from the manufacturers of the membrane, a longer trial involving a higher LMH and current of 1.7A was performed with a longer rest period, explored in the next experiment.

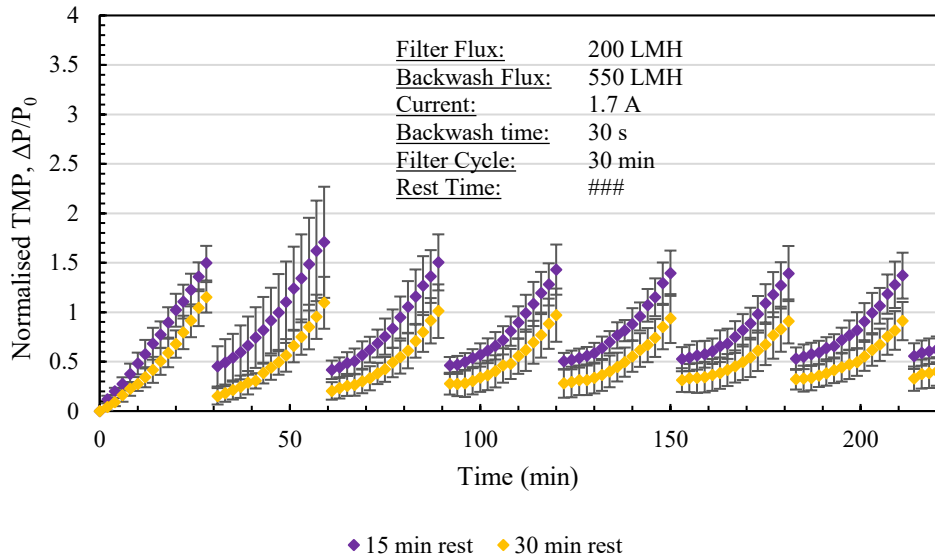


Figure 3 Normalised TMP versus time at 15 min and 30 min rest periods.

From Figure 3, it can be observed that the 30 min rest period performs better than the 15 min rest period. Firstly, the longer rest period at the start allows for a higher concentration of metal ions in the solution. The higher concentration leads to greater flocculation, causing less irreversible fouling and was observed clearly with the larger amount of electro-flotation occurring. At 30 min, the 30 min rest data can recover almost to its original value after the physical backwash, while the 15 min rest data is approximately two times higher than the 30 min rest data. Secondly, a greater amount of electro-flotation occurring before the filter results in fewer foulants being present in the solution as it floats on the surface. The decreased amount of foulants in the solution results in the TMP increasing more slowly as there's less probability for the pore to be blocked. This effect can be observed in the first cycle of Figure 3, where the gradient for the 30 min rest data is smaller than the 15 min rest data. The 30 min rest setup appeared capable of achieving stable performance over 8hr, only reaching a max TMP of 175, which is only half of the manufacturer’s maximum in a 6hr period.

2.1 Comparing the iron anode and aluminium anode

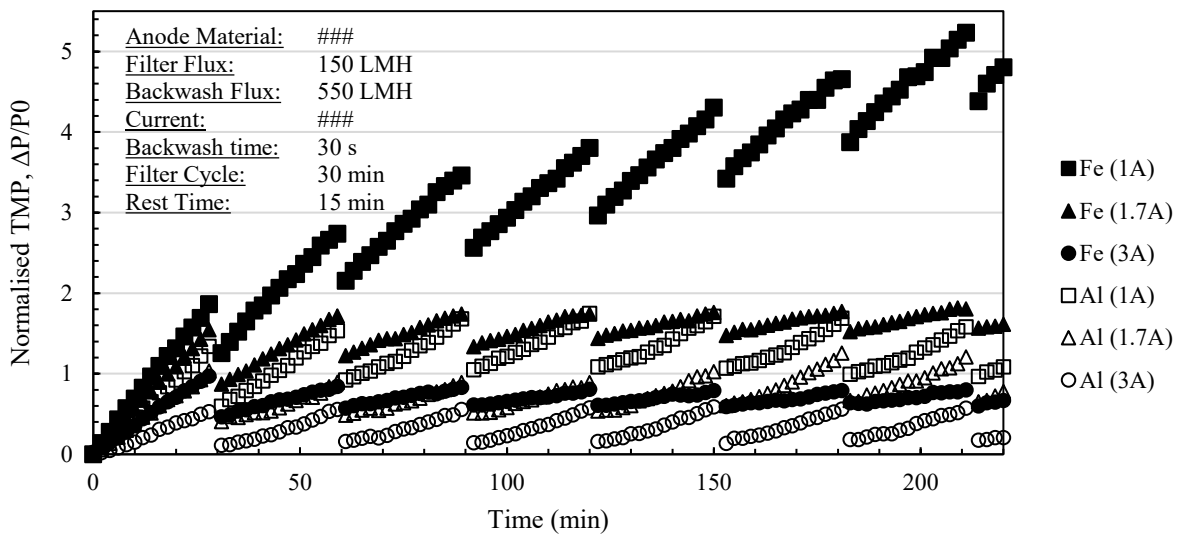


Figure 4 Normalised TMP versus time comparing the iron and aluminium anode.

From Figure 4, aluminium performs better than iron at all currents. Aluminium can maintain a fairly constant recovery even at 1A, while iron cannot at 1A and the 3A data from the iron almost performs identically to the aluminium 1.7A. There are several reasons why we observe the trend of aluminium performing better than iron. Firstly, is that aluminium metal ions can produce larger flocs compared to iron metal ions, which produce “fluffier”, more difficult-to-settle, flocs, at similar metal ion concentrations. The smaller particle size of the floc leads to more irreversible fouling as it gets lodged deeper into the pores, making it difficult to remove.

Another difference is the effect of passivation on the dissolution rate of the sacrificial anode. Leaving the iron anode in the air overnight resulted in substantial rust on the surface, decreasing the release of metal ions into the solution (Lakshmanan, Clifford, & Samanta, 2009). Aluminium did not encounter this issue as the data was still repeatable over multiple weeks of usage with no cleaning of the anode surface. It was observed that the iron anode caused metal ions to leak into the filtrate while the aluminium did not encounter this issue. Under the same operating conditions, with no cleaning between runs, aluminium performed better.

4. Conclusions and Future Work

This paper presents a viable and alternative method of operating the flat sheet ceramic membrane with the use of EC. Both aluminium and iron anodes were investigated, and it was found that for a continuous process, the aluminium performed better and more reliably. The optimum operating condition identified for aluminium was at 1.7A, 200 LMH filtrate flux, 550 LMH backwash flux, 30 s backwash time, 30 min filtration cycles and aeration on backwashes.

Future work could involve testing both anode materials in a batch process setup, further testing the effects of aeration on the iron anode to reduce iron leakage into the filtrate, and possible operation with different feed water such as seawater for pretreatment to a desalination plant.

5. Acknowledgements

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6. References

- Al-Hanif, E. T., & Bagastyo, A. Y. (2021). Electrocoagulation for drinking water treatment: a review. *IOP conference series. Earth and environmental science*, 623(1), 12016. doi:10.1088/1755-1315/623/1/012016
- Bhadana, B., Ebrahimi, M., Gernaey Krist, V., Gholami Shirkoohi, M., Karimi Estahbanati, M. R., Khosravanipour, M. A., . . . Kumar, L. R. (2022). *Electro-Coagulation and Electro-Oxidation in Water and Wastewater Treatment* (1st ed. ed.): American Society of Civil Engineers.
- Lakshmanan, D., Clifford, D. A., & Samanta, G. (2009). Ferrous and Ferric Ion Generation During Iron Electrocoagulation. *Environmental Science & Technology*, 43(10), 3853-3859. doi:10.1021/es8036669
- Song, Y., Dong, B., Gao, N., & Deng, Y. (2015). Comparative Evaluation of Aluminum Sulfate and Ferric Sulfate-Induced Coagulations as Pretreatment of Microfiltration for Treatment of Surface Water. *Int J Environ Res Public Health*, 12(6), 6700-6709. doi:10.3390/ijerph120606700