The Effects of Electroflocculation Pretreatment on Fouling Mechanisms, Filtration Energy and Contaminants Removal Rates in Microfiltration

Thesis submitted for the degree of "Doctor of Philosophy"

By

Moshe Ben-Sasson

Submitted to the Senate of the Hebrew University

August, 2010
This work was carried out under the supervision of

Prof. Avner Adin
Abstract

The high rate of population growth in developing countries is expected to cause a severe fresh-water shortage in the forthcoming years with potential devastating consequences. A major obstacle in the establishment of water-purification systems in such areas is the operational cost due to high operational energy demands. Also, the more energy that is consumed, the higher air pollution intensity is. Consequently, global efforts are being made to develop low-energy operation conditions for the existing water purification methods.

Microfiltration (MF) and Ultrafiltration (UF) are currently the most reliable technologies for treating colloidal contamination. The colloids group (particles in size range of 1-1000 nanometers) includes viruses, bacteria, dissolved organic matter, industry waste products, pesticides and other common water pollutants. Still, large-scale applications of MF and UF are limited as results of their main operational problem: the colloidal fouling. Colloidal fouling is the accumulation and plugging of particles on the membrane surface or inside the membrane pores which may leads to hundreds percents increase of the consumed operational energy. There are two main types of colloidal fouling: (1) Internal fouling— plugging that leads to decrease of the membrane permeability, (2) External fouling— additional hydraulic resistance resulted from colloids accumulation on the membrane surface which leads to the creation of an additional layer ("cake").

The severe energy losses resulted by the colloidal fouling led to wide efforts that were put in order to investigate and to find methods that will reduce the fouling effects. This work investigate electroflocculation (EF) pretreatment as fouling mitigation method for MF.

Electroflocculation (EF) presents an alternative method to conventional (chemical) flocculation with several advantages: easy operation, lower quantities of produced sludge, avoidance of chemical use and, most importantly, no anions, such as chloride or sulfate need to be added to the water. Unlike conventional flocculation in which the coagulants are added to the water as salts, in the EF process, the coagulants (iron or aluminum) are added to the water by dissolving the anode in an electrochemical cell.

While the effects of conventional coagulation as fouling mitigation method were discussed in the literature and still there is a lack of knowledge, only few works were
dedicated to investigate the potential of EF as fouling mitigation method. Therefore, the understanding of the potential efficiency of the hybrid process (MF+EF) was missing. Only one article was found in the literature regarding the hybrid process of aluminum based EF and MF. It showed possible significant fouling reduction in crossflow MF, still the operational conditions for achieving this result were not discussed. Also there was not found any information regarding the effects of aluminum based EF on dead-end MF mode. Regarding iron based EF, both in crossflow and dead-end operation modes, former researchers claimed for only marginal or negligible effects on MF performances.

In addition, most of the former works involved fouling mitigation methods based their conclusions on flux comparison methods. Applying mitigation fouling methods such as EF may be costly in terms of both money and energy. It is therefore important to understand not only if a fouling-mitigation method can improve membrane filter performance (e.g. increase the flux), but also how much energy is actually saved and what the optimum operational conditions are as well. Still the current author did not find in the literature any method for filtration energy calculations and comparisons.

Consequently, the goal of this research was to study the effects of EF pretreatment on dead-end MF, by answering the following research questions: (a) How much filtration energy can be saved by the addition of EF pretreatment? (b) How are the internal and external fouling mechanisms in MF affected by EF pretreatment? (c) What is the desired flocculation mechanism—sweep coagulation or particle destabilization—in the hybrid (EF + MF) process? (d) What are the optimal operating conditions in terms of pH and electric current intensity values? (e) What are the effects of EF pretreatment on colloidal removal abilities?

In order to answer the first energetic question a new method of energy calculations was proposed to comprehend and realize the effect of EF pretreatment on energy minimization in MF. This method also enables optimized the system's operational conditions.

Three experimental sets were planed in order to achieve the research goals and to answer the above research questions.

1. First set - Silica colloids synthetic suspensions (pH 6-8) were pretreated by aluminum and iron based EF at various operation times (0 to 4 min, constant electric current of 0.4 A) followed by different slow mixing times (0 to 30 min) and MF without any sedimentation step. The purpose of this set was to investigate the effect of EF on each type of fouling mechanism (internal and
external) and to explore the dependency of the hybrid process (EF+MF) performances on the pH and the dissolved coagulant dose.

2. Second set – three types of effluents (pH 7.5) were pretreated by different operation times of iron based EF (0 to 4 min, constant electric current of 0.4 A) followed by MF or UF. This set was designed to observe the EF pretreatment effects on "real solution" which contains organic matter. In addition, the EF effects on MF and UF were compared.

3. Third set – synthetic solutions of dissolved organic matter (pH 6-8) were pretreatment by different operation times of iron and aluminum based EF (0 to 12 min, constant electric current of 0.3 A) followed by MF. This set was designed to study the effects of EF on MF contaminates removal rates.

The results showed dramatic improvement in MF performances and significant fouling mitigation by EF pretreatment in all the three types of experimental sets both by iron and aluminum, based EF. Fouling mitigation by EF was found to be dependence on fouling intensity, dominant fouling mechanism, suspension pH and EF operation time. The pictures from the scanning electron micrographs showed a thick cake that formed on the membrane surface as result of iron/aluminum based EF pretreatment. This indicate over-saturation conditions which point at the important role played in fouling mitigation by sweep-coagulation mechanism. Two new mechanisms were offered for explaining the observed fouling reduction and improvement in filtration performance: (a) the coagulant deposits form a cake on the membrane-surface which prevent the small particles from penetrating and clogging the pores of the membrane, (b) the composition of the formed cake changes as results of coagulants deposits formation during the EF treatment, this leads to building of a cake with higher porosity which decreases the hydraulic resistance for flow.

The minimum solubility of aluminum found at pH 6-6.5 led to observed lower residual aluminum in the permeate and it was needed lower EF operation time to get improvement in filtration performance, as compared to higher pH values. Also the highest energy savings were found in these pH values. Therefore the best recommended operational pH values for aluminum based EF are 6-6.5.

Regarding iron based EF, the improvement in MF performance was almost the same in all the examined pH values (pH 6-8). pH values below 7 were problematic because the permeate turned yellow as a result of significant residual iron. The
appearance of residual iron was explained by the dependency on pH of Fe$^{2+}$ oxidation to Fe$^{3+}$ reaction rates. Therefore the best recommended operational pH values for iron based EF is above 7.

The new methods for filtration energy appraisal was implemented in the first experimental set and it indicated about 90% of potential filtration energy saving at the optimum conditions of operation. Significant energy savings were observed even without the slow mixing step due to the local flocculation conditions near the membrane surface. Additional energy savings were obtained due to the significantly higher initial flux recovery rates (>90%) imposed by treating the suspension with EF. This indicates an additional benefits of the EF application: (a) lower energy and water consumptions in the cleaning procedure (b) longer operational life of the membrane, (c) reduction of the biological fouling on the membrane-surface which otherwise may leads to membrane exchanging.

In addition, unlike the information found in the literature, the results showed in the second experimental set that iron based EF can be very efficient even when the solution contain organic matter. It was also observed that the EF treatment is much more efficient and had stronger positive effect in MF as compared to UF.

The third set results revealed significant higher removal rates due to EF treatment of dissolved organic matter, both when the anode was made of iron or aluminum. The contaminants removal ability in the hybrid process (EF+MF) were most of the times superior than UF.

In summarizing all the above, MF has larger pore sizes than UF and, therefore, requires less energy consumption when compared to UF. On the other hand, the contaminant-removal abilities of MF are inferior. Therefore, the ideal membrane filtration process should have energy consumption as with MF without fouling effects and with contaminant removal abilities as UF. Following the results of the three experimental set, it can be state that the hybrid process (MF+EF) is approaching the ideal colloidal removal treatment due to its low energy consumption as MF with minimal fouling and also approved contaminants removal rate might be superior than UF.

This conclusion hints on the high potential of the hybrid process (EF+MF) as attractive method for effluent-polishing (tertiary treatment), especially in light of the operational problems found in the effluent-polishing methods commonly used today.
# Table of contents

## 1. Introduction

1.1 Background for the research ......................................................... pg. 1

1.2 Scientific background

1.2.1 Types of fouling ................................................................. pg. 2

1.2.2 Important parameters in membrane filtration ........................ pg. 4

1.2.3 The filter medium ............................................................... pg. 11

1.2.4 Observed phenomenon during membrane filtration .......... pg. 17

1.2.5 Colloidal fouling models ...................................................... pg. 20

1.2.6 Chemical coagulation ........................................................... pg. 33

1.2.7 Chemical coagulation pretreatment to membrane filtration .... pg. 35

1.2.8 Electroflocculation ............................................................... pg. 38

1.2.9 Electroflocculation pretreatment to membrane filtration ...... pg. 43

1.3 Literature review summary ........................................................ pg. 45

1.4 The research objectives ............................................................. pg. 48

1.5 The research hypothesis ............................................................. pg. 49

## 2. Methodology

2.1 Material ...................................................................................... pg. 50

2.2 Methods ..................................................................................... pg. 51

## 3. Results

3.1 First experimental set: filtration of colloidal silica ......................... pg. 54

3.1.1 Aluminum based EF experiments ........................................... pg. 55

3.1.2 Iron based EF experiments .................................................... pg. 62

3.2 Second experimental set: EF+MF for effluents polishing ............... pg. 69

3.3 Third experimental set: EF effects on DOM removal ..................... pg. 76

## 4. Discussion & Conclusions

4.1 Discussion - first experimental set ............................................. pg. 80

4.1.1 The desired flocculation mechanism .................................... pg. 80

4.1.2 EF effects on fouling mechanisms ....................................... pg. 80

4.1.3 Optimal EF operation time ................................................ pg. 81
4.1.4 Optimal pH value for operation........................................pg. 82
4.1.5 EF effect on cleaning abilities........................................pg. 84
4.1.6 The Importance of slow mixing stage.........................pg. 85
4.2 Discussion - second experimental set ..............................pg. 85
4.3 Discussion - Third experimental set...............................pg. 87
4.4 Conclusions.................................................................pg. 88

5. References........................................................................pg. 90

6. Appendixes

Appendix 1: Development of Kuberkar and Davis generalized model.................pg. 118
Appendix 2: Computer program, stage 1 of the filtration energy appraisal method....pg. 120
Appendix 3: Computer program, stage 2 of the filtration energy appraisal method....pg. 126
Appendix 4: Model reconstructions and raw filtration curves of the EF untreated
  Solutions.................................................................pg. 129
Appendix 5: Energetic calculations of the hybrid process EF+MF.................pg. 135
**PUBLICATIONS**

