

**NANOPARTICLE SEPARATION IN CROSS-FLOW FILTRATION
BY INTRODUCTION OF ELECTROPHORESIS**

by

Yachen Zhang

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Applied Sciences in Civil Engineering

Summer 2014

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ACKNOWLEDGMENTS

I am deeply thankful to my advisor, Dr. C.P. Huang for his solicitude and guide in my graduate study. Dr. Huang not only provided me with very interesting research topics, but also taught me how to be a good researcher. With the instructions of Dr. Huang, I discovered the charm of aquatic chemistry step by step and, learned the duty as being a scientific researcher. I appreciate to Dr. Choi for working together with me as one group. I thank all the members in aquatic chemistry lab, Soo hoon Choi, Kevin Wang, Jenn Fang Su, Xuesong Liu, Lu Shi Yun-Lei Hao, Tommy Chen and Rovshan Mahmudov for always giving me good advice in my research and their friendship. I also owe my sincere appreciation to Michael Davidson, for his time and great technical support. Without his support, I cannot finish my experiments so smoothly. Specifically, I am grateful to my parents as well as all my family members for their support and love during these years I have been abroad. Last but not least, I specially thank to my friends Eric Jin, Serena Fang and Constance Cheng. Without the love from you guys, I can never finish this research and the thesis. You are always my best friends.

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ABSTRACT

Membrane fouling is a long-existed problem in filtration industries. Techniques to prevent membrane fouling and improve filter performance in cross-flow filtration have been studied since early twentieth century. The research of cross-flow filtration is a milestone in filtration technique development. By applying a flow parallel to the filter medium, deposited particles on the filter can be effectively washed away. However, when particle sizes become small, like nano-sized particles, it will become much more difficult for the shear flow to remove the depositions away. Filter cakes are formed due to concentration polarization. The superimposition of an external electrical field inside the cross-flow filtration system has been proved to be able to greatly enhance the flux and particle removal efficiency. Cross-flow electro filtration (CFEF) is a hybrid separation process combining both the features of conventional cross-flow filtration and electrophoretic separation apparatus. The technique of CFEF has been applied for separation of nano-sized particles from liquids due to its high selectivity and independence of special membranes although fouling will still occur on the membrane, depending on the conditions applied in different experiments.

The major goal of this research is to minimize membrane fouling and maximize nanoparticle removal efficiency. A prototype cross-flow electro filtration module has been designed and constructed for the experiment. The CFEF module is consisted of a peristaltic pump, an external tube, a tubular shaped metal net and a concentric rod as electrodes, a circular membrane placed between the two electrodes, and a D.C. power supply connected to the electrodes. Charged particles can be

separated depending on their size distribution and surface charge density. Three kinds of particles with different pH_{zpc} and mean sizes: SiO_2 , TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ are used for this study. The influences of clogging on membrane can be ignored during each experimental running. Results demonstrate that the CFEF system can separate nanoparticles effectively. Particle removal efficiency is highly related to the electric field strength, filtration flow rate and pH of the feed solution.

A mathematical model is also developed to quantify the effects of parameters including particle sizes, solution pH, filtration flow rate and electric field strength on membrane performance. The influences of Coulomb forces among particles are also evaluated in this research, which is proved to be an essential factor affecting the removal rate and has not been considered by previous researchers. The model results suit well with experimental data, which proves that the mathematical model is highly reliable. Further, based on the results of model and experiments, it is possible to separate mixture of nanoparticle solution using the CFEF module by adjusting the pH and applied electric field strength.

Chapter 1

INTRODUCTION

1.1 Aim and Scope of the Research

Liquids and solids separation plays an important role in modern industry. It has been widely used in many fields. For example, drinking water treatment, pharmacy, food industry, coloring pigment industry, mineral processing industry, biotechnology, synthetic fertilizer, water pollution control, etc. (Weber and Stahl 2002; Domany et al. 2002).

Mechanical separation processes are mainly based on filtration and sedimentation. As one of the most widely accepted methods of separating solids from liquids, the technique of filtration has been used for many years. However, one of the most serious problems in the application of filtration is the flux decline caused by concentration polarization and membrane fouling. Specifically, due to the accumulation of colloidal or the proteinaceous solutes on the surface of a membrane, highly resistant filter cakes are formed (Iritani et al. 1991; Iritani et al. 2000). Such flux decline will then result in a series of problems, for example, an increase of the frequency of replacing the membranes and energy requirements. All these problems will make processes of filtration become uneconomic. In order to make sure the filtration processes used in industrial production to be energy-saving and economic, high flux rate should be maintained; on the other hand, polarization and fouling should be prevented. A variety of techniques have been introduced to reduce the cake formation, including cross-flow filtration, dynamic filtration, upward filtration and

inclined filtration (Murase et al. 1989; Iritani et al. 1991; Iritani et al. 2000). Among all these filtration techniques, cross-flow filtration is a process that can minimize the accumulation of particles included in solutes.

Cross-flow filtration is a procedure during which the solute deposition can be washed away due to the flow parallel to the filter, at the same time, the formation of cake layers will also be hindered. Compared with dead-end flow filtration, cross-flow filtration can get a quasi-stationary filtrate flow for a longer time (Altmann and Ripperger 1997). Cross-flow filtration is comprehensively used in many medical and chemical applications like nanoparticle separation and protein purification. Parameters including the cross-flow rate, transmembrane pressure, filter resistance, characteristics of suspended particles like their size distribution, agglomeration and deposition behavior will all influence the effects of cross-flow filtration (Altmann and Ripperger 1997). However, since there always existed limitations, it is hard to get sufficiently high cross-flow velocities; the interactions between particles in the solutions and membrane are also inevitable. Thus, concentration polarization and cake formation can still occur (Wakeman and Tarleton 1991; Altmann and Ripperger 1997). Some further techniques such as backwashing, pulsed cross-flows, flow reversal are developed for cross-flow filtration. People also use abrasives and filter aids during the processes of cross-flow filtration. All these efforts are applied for reducing the fouling, while at the same time, these techniques may make the lifetime of membrane become shorter and the filtration cycle complicated (Wakeman and Tarleton 1991). Such side effects are not expected in industrial production.

The final goal of separation is to maximize the particle removal efficiency and minimize fouling and injury on the membrane. One idea is to employ a

supernumerary force field, for example, an acoustic or electric field, within the filter. Researches have proved that the application of additional fields will greatly enhance permeate flux and as a result, improve the efficiency of conventional membrane filtration. When the particles in solute are very small, like nanoparticles, the charge of a single particle will be intensively related to the surface charge density of particle since its ratio of surface area to volume is very big. Under such circumstance, the superimposed electric fields are more selective compared with the sonic fields (Lo et al. 1983). Therefore, industries like water purification and food dispersion that need to separate very small particles from the main phase prefer to add external electric field in their filtration system. The cross-flow membrane filtration which is enhanced by a direct current electric field is called cross-flow electro filtration (CFEF). It is a separation process combined by both cross-flow filtration and electrophoresis. This technique has been studied since the 1970s (Henry et al. 1977). Since then, the technique of electrophoresis has been used in filtration industry for reducing fouling on the membrane. In CFEF, the accumulation of particles is controlled by the electrophoretic forces between the electrodes. When the charged particles are with proper polarity, with the increase of electro field strength, the electrophoretic forces increase, the charged particles will have a stronger trend to travel in a direction away from the filter and as a result, fouling on the membrane will be reduced effectively.

Filtration of nano-sized particles is a task widely existed in modern industry including oil and petroleum chemistry, food industries, pharmaceuticals and so on. Nanofiltration is a relatively new technique for nanoparticles removal. The development of nanofiltration is very fast in recent years. However, some significant disadvantages of this technique always remain. The membrane pressure needed for

nanofiltration is very high, which results in not only cost but also safety problems. Another disadvantage for nanofiltration is the membrane maintenance. Repairs and replacement of nanofiltration membranes are extremely complicated and expensive.

In cross-flow electro filtration, the core factor influencing the particle removal and flux enhancement is the particle charge. The CFEF method can suit the work of removing nanoparticles well because the particle charge is mainly related to the pH and ionic strength of the solution. Compared with plain cross-flow filtration, the membrane works more like a barrier instead of a filter. This is because the main driving force that removes the colloids away is electrophoretic force, not the pressure difference. Therefore, CFEF system can be used to separate nanoparticles without the application of nanofiltration membranes. Usually the CFEF system is built with an electric field being applied across the microfiltration or ultrafiltration membrane (Henry et al. 1977; Yukawa et al. 1983; Bros and Kroner 1990; Lentsch et al. 1993; Robinson et al. 1993; Wakeman and Sabri 1995). These membranes can be flat sheet, tubular, and spirally wound modules. Previous studies by Wakeman and Tarleton showed that CFEF system with tubular geometry uses the electrical power most effectively (Wakeman and Tarleton 1987). Studies by Bowen show that titanium coated with a thin layer of platinum is one of the best materials for anode (Bowen 1993). There are also numerous researches about removal of nanoparticles using cross-flow electro filtration. Verdegan tried to separate fine particles with diameters less than 10 μ m from nonpolar liquids using cross-flow electro filtration process. He found that CFEF has higher removal efficiency of all particle sizes, longer life, and fewer electricity requirements compared with conventional cross-flow filtration (Verdegan 1986). Lo studied the separation of aluminum oxide colloids from

nonaqueous solution with cross-flow electro filtration. According to this research, parameters including feed rate, driving pressure, electrical field strength and deposition rate on electrodes were analyzed (Lo et al. 1983). Majmudar and Manohar separated titanium dioxide from aqueous solution by electrophoretic filtration. The authors applied different voltages and flow rates in the experiments and the optimal conditions came out as 15V and 200mL/h (Majmudar and Manohar 1994). However, studies showing a complete model describing the relationship between removal efficiency and other parameters, including feed rate, filtration flow rate, applied voltage, solution pH and properties of particles. Moreover, very few articles considered the Coulomb forces interacting on each other. When the charge of a single particle reaches a level, Coulomb force on the particle will influence its movement. This effect should not be ignored.

In order to quantify the relationship between removal efficiency of nanoparticles with parameters affecting removal, this article will focus on discovering a mathematical model describing this relationship. A cross-flow electro filtration module will be used to separate nanoparticles from DI water. A comparison between experimental data and modeling results will be made. Based on these results, a method to maximize the removal efficiency as well as to minimize fouling on the membrane will be determined.

1.2 Developing of Cross-Flow Electro-Filtration Processes

1.2.1 Concentration-Polarization and Cake Formation

The separation of solute and solvent occurs at the membrane surface. During the processes, solvent goes through the membrane while solutes are retained

and accumulated, causing an increase of solute concentration at the upstream of membrane. This is the effect of concentration-polarization. Such phenomenon has been long recognized by the field of electrochemistry. It was not until the middle of 20th century had the chemists and chemical engineers paid attention on this effect.

Based on Fick's law of diffusion, a trend of solute to diffuse back into the bulk solution will take place when concentration at the membrane surface becomes higher. Assume solvent and solute are with similar densities, the diffusion coefficient is constant and the concentration slopes parallel to the membrane surface can be neglected compared to the concentration slopes vertical to the membrane surface. The following equation which describes the mass balance on the membrane surface at steady state will be obtained (Bowen and Jenner 1995):

$$J = \frac{D}{\delta} \ln \left(\frac{c_m - c_p}{c_b - c_p} \right) \quad (1.1)$$

In Eq. (1.1), J stands for the flux; D is known as the diffusion coefficient of the solute; δ stands for thickness of the boundary layer; c_p is solute concentrations in the feed flow and permeate flow; c_m and c_b are the concentrations of solute at boundary conditions: c_m is the concentration of solute on the filter, and c_b is the concentration of solute of the upstream solute.

To some extent, concentration polarization and cake formation are combined with the mechanism of pore blocking of the membrane during filtration. Studies have been made about the transition between concentration-polarization and cake formation. By the beginning of a filtration process, the transmembrane pressure increases rapidly from a low level. Once the flux exceeds a boundary level, the rate of boundary layer re-establishment and filter cake removal slows down. This boundary level of flux is called critical flux (J_{crit}). When the flux is below J_{crit} , the

transmembrane pressure difference ΔP keeps stable when increasing or decreasing the flux. Little hysteresis of flux-pressure profiles for microfiltration or ultrafiltration was shown under the operations below J_{crit} . On the contrary, when the flux is above J_{crit} , a period of instability of ΔP can be observed when changing the flux, an obvious hysteresis of flux-pressure profiles also take place (Chen et al. 1997). Such phenomenon points out the formation of a stubborn layer with very slow redispersion by the time interactions between particles are overcome.

Lu and Huang studied about mechanism of cake formation by applying the conception of the critical friction angle of particles. When a force balance is reached on the particle, a critical friction angle can be got. Based on the size of friction angle, the position of particle deposition on the cake surface can be determined (Lu and Huang 1993). According to the research, the authors operated several conditions which are known to influence cake formation and filtration rate attenuation during filtration processes, including filtration rate, cake surface porosity, fluid velocity at the cake surface and mass of instantaneous cake formation. The calculated distribution of hydraulic pressure, porosity, specific filtration resistance of a filter cake coincided very well with the experimental data.

Due to the phenomenon of concentration polarization and compact cake formation, the effectiveness and efficiency of membrane filtration are greatly reduced. Several more techniques have been developed to prevent polarization and fouling. Cross-flow filtration is a standard operation in many technical applications. It can greatly reduce the formation of layer and keep it at a low level.

1.2.2 Cross-Flow Filtration

Back to 1907, Bechhold did an experiment about filtration of colloids and fine particles (Altmann and Ripperger 1997). In this experiment, he found that the filtrate volume can be increased by applying a flow parallel to the filter medium before it is blocked by a compact cake formation. Bechhold created the shear flow across the filter medium by using a stirred filtration cell (Bechhold 1907). Today, more than 100 years have passed since Bechhold first time applied the shear flow to optimize the filtration, and this technique has been well developed as the cross-flow filtration, the basic idea is still by applying a flow which is parallel to the membrane to reduce the cake layer formation and keep it at a low level, thereby getting an accurate and stable filtrate flow.

Previous studies have concluded that cross-flow filtration is affected by quite a number of parameters: cross-flow velocity, membrane resistance, cake layer resistance, transmembrane pressure, particle form and size distribution, surface effects and agglomeration behavior of the suspended particles (Altmann and Ripperger 1997; Youravong et al. 2002). Because of the complicated relationships among all these parameters, although a lot of researches about mechanisms of cross-flow filtration have been done, there's still not a widely accepted model describing the mechanism of cross-flow filtration.

One of the investigations studying about mechanism of cross-flow filtration of suspensions with fine particles is a research done by Altmann and Ripperger. In this study, they focus on the forces caused by hydrodynamic and adhesive effects acting on a single particle. Namely, the forces are drag force of the filtrate flow, drag force of the cross-flow and lift force (Altmann and Ripperger 1997). According to their study, the balance between the drag force of filtrate flow and lift

force will determine the particle transportation to the layer. If the drag force of filtrate flow is higher than the lift force, the particle will be deposited. Both forces will increase based on the parameter of particle size. In contrast, the drag force increases faster than the lift force with the same increasing rate of particle size. As a result, small particles tend to be more likely to attach on the layer to increase the layer resistance, which in turn makes the permeate flux lower. Further, in their experiments, they observed that the formation of layer is continuous, while the removal of layer only occurs with large agglomerations or large layer fragment being removed. It can be concluded that the adhesion forces and friction forces play a dominating role compared to hydrodynamic forces for a single particle. Particle deposition on the layer is irreversible most of the time, only large particles, layer fragment and agglomerations can be removed. With higher transmembrane pressure, the increase of the filtrate flow is hardly observable, while a linear increasing relationship between the layer height and the transmembrane pressure can be observed, while with lower pressure, the filtration rate decreases linearly with the transmembrane pressure, the layer height does not show obvious changes. These phenomena indicate that only at lower membrane pressure, the filtrate flow will increase with the increase of membrane pressure, layer structure and resistance will not be influenced by the decreasing membrane pressure.

Wakeman and Tarleton did a research focusing on the fouling propensity of fine particles with process parameters being changed systematically. In this study, not only the influences of particle size, transmembrane pressure, cross-flow velocity are discussed, the authors also studied how suspension properties including pH and concentrations would affect fouling. Cross-flow velocity is a tricky part in the

processes of cross-flow filtration because by increasing cross-flow velocity, the filtrate flux can be either increased or decreased. In fact, such phenomenon is not uncommon in industry. Adequate cross-flow velocities are applied to induce high shear strength across the filter surface. Industries once usually used a cross-flow velocity of 3m/s. However, such a velocity often failed to increase the filtration rates. Today, cross-flow velocity has been increased to as high as 4 to 7m/s (Wakeman and Tarleton 1987). But in many instances, the high shear rates generated by these high velocities still cannot keep the filter surface from being fouled and can even lead to a decrease of filtration rates. Such phenomenon coincides with the results of experiments done by Wakeman. According to his study, the influences of cross-flow velocities on filtration rates are almost all due to the size and size distribution of particles in suspensions. There exists a size distribution below which the cross-flow velocity will hardly have any effects on the trend of decrease of filtration rates. This size distribution is defined as the “critical size”. The finer particles are, the sooner an equilibrium flux will be reached at lower cross-flow velocity. Further, by increasing the velocity, an obvious decline of filtration flux was observed. This can be explained as under such condition, the shear strength generated by the cross-flow velocity is not enough to overcome the forces that cause the fine particles to accumulate and form cakes at the filter surface. The ratio of membrane pore size to particle size is also considered. With membrane pore size smaller than the average particle size, the equilibrium flux or the rate of processes to equilibrium will almost not change with the change of membrane pore size; while with membrane pore size larger than particle size, the equilibrium flux reduces as the membrane pore size increase and so does the rate of processes (Wakeman and Tarleton, 1991). Characteristics of the suspension itself will also influence the

filtration flux. The charging properties of particles are highly related to the surrounding fluid environment. By changing the pH of suspension, the zeta potential of fine particles will be changed. Such effects will be discussed more specifically in the latter part about electrophoresis.

Particle size is an essential parameter in the performance of cross-flow filtration. Besides the two studies mentioned above, many researches have come up with the result that the flow resistance increases as the particle size decreases, which makes the processes of filtration time-consuming and inefficiency (Lo et al. 1983; Chen et al. 1997; Weber and Stahl 2002). Because the main removing force in cross-flow filtration is the shear strength produced by the parallel flow and the cross-flow velocity, the shear strength can seldom overcome the permeation drag forces on particles when the particle sizes are very small. This makes cross-flow velocity insignificant in the filtration processes. Some industries add processes like backwashing, back-pulsing or flow reversal in filtration processes, or apply usage of abrasive and filter aids. These techniques either make the filter operating cycle more complex, or reduce lifetime of membranes, neither of which is desired (Wakeman and Tarleton 1991).

Various techniques were developed to reduce the fouling on membrane. It has been well known that electrochemical effects can play an essential role in the prevention of fouling in cross-flow membrane filtration (Bowen 1993; Elzo et al. 1998; Huisman et al. 1998), namely, it is the technique of cross-flow electro filtration. It was Bier who first developed a filtration technique which utilizes an electrical field to dewater colloidal suspensions (Bier 1959). In cross-flow electro filtration, the imposed electrical forces can prevent the colloids from accumulation. By increasing the electric

field strength, the electrophoretic velocity to the particles in a vertical way away from the membrane surface will be increased. The characteristics of particles still play important roles in the cross-flow electro filtration, especially the particle size distribution and the surface charge density. Compared with conventional cross-flow filtration, cross-flow electro filtration is especially applicable for nano-sized particles removal.

1.2.3 Cross-Flow Electro Filtration

Electrochemical technique has been proved to be used in a variety of fields for membrane filtration. Including preventing membranes from getting fouled; assisting in cleaning fouled membrane; or aiding in selective separation of different species of particles based on their size and surface characteristics (Henry et al. 1977; Huotari et al. 1999; Webster et al. 2000; Zhang et al. 2000). Electric fields have been utilized in both dead-end flow and cross-flow filtration.

To minimize the accumulation of particles at the filter surface, the cross-flow electro filtration process is employed. The process is combined with two particle transportation mechanisms: cross-flow filtration and electro filtration (Henry et al. 1977; Radovich and Chao 1982; Yukawa et al. 1983; Radovich et al. 1985; Rios et al. 1988; Bowen and Sabuni 1992; Bowen 1993; Lentsch et al. 1993; Bowen and Ahmad 1997). The factors that influence conventional cross-flow filtration will also influence the performance of cross-flow electro filtration. However, since the superimposed electric field can cause electrical effects, these effects can make the factors like cross-flow velocity affect the filtration in a different way compared to normal cross-flow filtration. There are mainly three factors influencing particle transportation to the filter medium: bulk flow, fluid shear and electrophoretic migration. Due to the factor of

bulk flow, with the liquid phase going across and going through the filter medium, a particle will also be transported in the same direction. This will cause an accumulation of particles and decay the filtration rate-time in conventional cross-flow filtration at constant driving force. Thanks to the fluid shear, the particles can be transported either toward or away from the filter medium. Besides, since most of the particles in the electrolyte solutions are charged, an electrical field with proper polarity can drive the charged particles migrate away from the filter medium. Being different from normal dead-end flow filtration, cross-flow electro filtration process can be operated when the system is working at steady states and thus with no decay of filtration time-rate decay. Since all the three factors (bulk flow, fluid shear and electrophoretic migration) will contribute to the migration rates of particles, a balance between the migration rates of particles towards the filter medium in terms of bulk flow and away from the filter medium in terms of both fluid shear and electrophoretic migration will be reached at steady state. So it can be concluded that in cross-flow electro filtration, a higher the filtration rate can be obtained than by conventional cross-flow filtration or electro filtration alone (Henry et al. 1977).

The two most essential electro kinetic effects are electrophoresis and electro-osmosis. More specifically, for a given electric field, by influencing the trajectories of colloids and charged particles, deposition is prevented from the membrane, this phenomenon is called electrophoresis. For some instances, if the membrane is charged and has charged pore walls, counter-ions will be excessive within the pore. These counter-ions will drag the water and move in the electrical field (Huisman 1998), such water flux caused by the drag force is called the electro-osmotic flow. These mechanisms provide the power of not only improving the filtration rates

but also operating steady states for filtration of solutes with fine particles. It should be mentioned that there exist other electrical effects in the cross-flow electro filtration system, for instance, electrochemical reactions, chemical reactions, adsorption and phase formation, at the electrodes and filter medium (Jagannadh and Muralidhara 1996). But these effects don't have great effects on the results of membrane filtration.

The extent of increasing the removal efficiency and filtration flow rate in cross-flow electro filtration is highly related to the particle size distribution and their surface charge density. The surface charge density depends on the zeta potential of particles. It is the potential at the surface of the shear between the charged particle surface and the electrolyte solution determines the electrokinetic behaviours (Shaw 1991). Zeta potential is significantly related to the pH and ionic strength of electrolyte solution (Bros and Kroner 1990). Based on the zeta potential of a single particle in a solution with pH and ionic strength known, one can calculate the surface potential of the particle and thus know about the surface charge density. This makes cross-flow electro filtration especially suited for treating nano-sized particles because their zeta potential and surface charge density are highly related to the pH and ionic strength of electrolyte solution. Consider the zeta potential of different kinds of particles, particles in aqueous media are more often negatively charged than positively charged because of their negative zeta potential in a liquid. This is mainly because that anions are usually less hydrated than cations. Thereby, cations tend to be more likely to dwell in the bulk aqueous medium; while the more polarizing anions have a greater tendency to be absorbed (Shaw 1991). However, not all particles are negatively charged, for example, titanium dioxide and aluminum oxide, are positively charged at low pH due to their high pH_{zpc} (Wakeman and Sabri 1995; Tarleton 1988). Even though air

bubbles suspended in water have negative electrophoretic mobilities. This is because their adsorption of negative ions. Further, organic particles like proteins and microbial cells also have zeta potential and are usually negatively charged at high pH. But for microbial cells, their exhibitions of zeta potential are highly different regarding on their type of organism and growing conditions (Bros and Kroner 1990).

Based on the principles of cross-flow electro filtration, the technique of CFEF has been widely applied in many fields. Flux enhancement is one of these applications. It is obtained mainly due to electrophoresis. Since the formation of cakes on the filter medium can be prevented, the flux will thus be enhanced when the particles are charged with proper polarity and the applied field strength is above the critical strength (Radovich et al. 1985; Rios et al. 1988; Bowen 1993). The critical electric field strength is defined as the applied electric field strength at which the net particle migration velocity towards the membrane is zero. Not only electrophoresis, electro-osmosis can also influence the flux with an electric field applied across the membrane and proper zeta potential of the membrane (Radovich and Chao 1982; Radovich et al. 1985; Bowen 1993). Electro-osmosis can enhance the flux when the applied flux in electro filtration is below the critical pressure. The critical pressure is the pressure below which the limiting flux is obtained. Many researches have reported that parameters having an effect on the flux in cross-flow electro filtration include the electric field strength, the employed pressure and the zeta potentials of particles and filter medium.

Improving the membrane selectivity is another application by superimposing the external electric field. Similar as the enhancement of flux, when the applied field strength is higher than the critical field strength value, the charged

particles will be kept in electro filtration system and migrate away from the membrane with no effects of the membrane pore size (Akay and Wakeman 1997). Thereby, with proper applied electric field strength, particles can be kept selectively and as a result, the selectivity of membrane will be improved. Some researcher held the opinion that since the charged particle size is usually bigger than the membrane pore size and thus the employment of electric field does not affect particle retention essentially even though the permeate flux is greatly enhanced. While there are still other researchers observing membrane selectivity in their reports. For example, Yukawa et al. studied the electro filtration of gelatin with a concentration of 10g/L using polysulfone membrane. The applied membrane pressure is only 2 bar and the flow rate is low. At first, the retention slightly increased with the increase of electric field strength. When reaching or exceeding the critical electric field, the retention becomes constant (Yukawa et al. 1983). Lentsch et al. focused on the separation of bovine serum albumin from polyethylene glycol using electrical ultrafiltration. Normal ultrafiltration can hardly separate these two substances. One of the reasons is that the two substances are of almost the same size. However, the zeta potential of bovine serum albumin is highly related to pH while polyethylene glycol is not. The authors settled their experiments at the pH of 6.8. Under this condition, bovine serum albumin is rejected by the membrane while polyethylene glycol is attracted and migrated towards the membrane. The retention rate of bovine serum albumin is maintained high. The selectivity of membrane is significantly improved (Lentsch et al. 1993).

There is also an application of pulsed electric field for cross-flow electro filtration. As a matter of fact, continuous employment of electrical field requires the electrical field strength as high as 10kWh/m^3 and thereby, a great electrical power

supply is consumed (Bowen et al. 1989). In order to lower the power consumption, some studies focus on applying a pulsed electric field to restrict the electrical field strength needed for electro filtration processes. For example, Bowen et al. designed a system using membrane as one electrode with application of a pulsed electric field to clean the membrane without interrupting the separation process. They used the same values of current densities as those being used in commercial electro dialysis plants. The electric field strength of their pulsed electric field they applied in their experiments is in the range of 0.036-6.9kWh/m³, which is much lower than the minimum needed 10kWh/m³ in normal cross-flow electro filtration with constant electric field (Bowen et al. 1989).

In summary, compared with conventional cross-flow filtration, cross-flow electro filtration has the following advantages. First of all, an increased filtration rate can be obtained compared with sole cross-flow filtration or electro filtration; secondly, the filtration system can be operated at steady state without interruption of the separation process; thirdly, with the application of electric field in cross-flow filtration system, an enhancement of filtration flux and membrane selectivity can be achieved; further more, with the application of electrical fields, particles can be filtrated without utilizing the filter aid, this status can not only extend the lifetime of membrane but also avoid contamination might be caused due to the filter aids.

1.3 Model Development of Cross-Flow Electro Filtration

1.3.1 The Influence of Filter Geometry

The performance of cross-flow electro filtration can be improved by many approaches. For example, boundary layer control, membrane shape and material

modification, and also optimizing characteristics and parameters of the superimposed electrical fields, cross-flow velocity, pH of aqueous suspensions, and all the other parameters that can affect the performance of conventional cross-flow velocity. In this section, each of these approaches will be discussed specifically.

In a cross-flow electro filtration system, the electric field is always applied across the microfiltration or ultrafiltration membranes (Henry et al. 1977; Yukawa et al. 1983; Bros and Kroner 1990; Lentsch et al. 1993; Robinson et al. 1993; Wakeman and Sabri 1995). These membranes are usually in flat sheet, spirally wounds or tubular modules. A study by Wakeman and Tarleton focuses on the trajectory of particles through cross-flow microfiltration units referring to profiles of fluid velocity and electric field strength. They compared the performances of plate, tubular and multitube filters. Based on the results of their study, the tubular geometry uses the electrical power most effectively when being utilized as an aid to prevent membrane fouling. They compared the capture positions of particles entering a separator 0.05mm from the septum surface. The effects of both electrode and channel geometry were evaluated. According to the authors' theory, the greater the distance a particle remains in the suspensions, the better the system works. From the table it can be seen a single particle in tubular geometry with porous inner wall remains in suspensions the greatest distance. Besides the filter geometry, it can also be seen that with the increase of electric field strength, a significant increase of the distance a particle remains in suspensions also occurs. Such increase is much greater than the difference between different geometries under the same electric field strength (Wakeman and Tarleton 1987). This demonstrates that electric field strength plays a more essential role in preventing membrane fouling.

1.3.2 Electric Field Strength

Electric field strength is a prime parameter in cross-flow electro filtration process design and modeling. The electric field strength in a flat sheet membrane system is calculated as:

$$E = \frac{\varphi}{L} \quad (1.2)$$

In the above equation, E is the symbol for electric field strength; φ stands for the electrical potential and L is the distance between two electrodes.

Since tubular membrane system often has a better performance in fouling prevention, it is of great interest to achieve the equation expressing electric field strength. While in a tubular system, Eq. (1.2) needs to be modified. The electric field strength between two concentric cylinders is conveyed as (Wakeman and Tarleton 1987):

$$E = \frac{\varphi_o - \varphi_i}{r \cdot \ln(r_o/r_i)} \quad (1.3)$$

In Eq. (1.3), φ_o and φ_i stand for electric potential at the outer and inner electrode, respectively; r is the radial coordinate; r_o is radius of outer electrode and r_i is radius of inner electrode. Besides, this equation is built among the assumptions that the region of electric field under investigation is far away from any electrode edge without edge effects, and that the suspension is fully diluted to be a pure fluid without distortion of fluid motion.

Some authors have different idea about the calculation of electric field strength. They disagree with the methods of calculating electric field strength using the applied voltage because the voltage drop at the electrode-interfaces is not known. They came up with a method based on Ohm's law (Bowen and Sabuni 1992; Bowen and Ahmad 1997):

$$E = \frac{I}{\lambda_0} \quad (1.4)$$

In Eq. (1.4), I is known as the explicit value of current and λ_0 is the conductivity of the bulk solution.

The theory of critical electric field strength has been raised up by several authors in their researches. It is defined as the electrical field strength at which the total particle migration velocity towards the filter medium is zero and the flux is independent of the cross-flow velocity. The critical electrical field strength is obtained as:

$$E_c = \frac{J}{u_p} \quad (1.5)$$

1.3.3 Filtration Fluxes in Electro-Flitration

In the equation calculating E_c , J is the solvent flux under a given membrane pressure and u_p is the electrophoretic mobility of the particles. While J and u_p can be expressed as the following equations (Shaw 1991):

$$u_p = \frac{v_p}{E} = \frac{\varepsilon \xi}{\eta} \quad (1.6)$$

$$J = \frac{\Delta P}{\eta R_T} \quad (1.7)$$

In the expressions of Eq. (1.6) and Eq. (1.7), v_p is the velocity of a single particle or colloid; ε is known as the permittivity of electrolytes; ξ is the zeta potential of particles; η stands for the viscosity of electrolyte; ΔP is the transmembrane pressure applied in the filtration; R_T is the total resistance which is the combination of film resistance, cake resistance and membrane resistance. The studies by Henry et al. gave an expression of R_T , which is written as (Henry et al. 1977):

$$R_T = R_f \Delta P + R_M + R_C \quad (1.8)$$

$$R_f = \frac{1}{k \cdot \ln(C_s/C_b) + u_E E} \quad (1.9)$$

$$R_M = \frac{R_{0M}}{1 + K_M E R_{0M} / \Delta P} \quad (1.10)$$

$$R_C = \frac{R_{0C}}{1 + K_C E R_{0C} / \Delta P} \quad (1.11)$$

In Eq. (1.8), R_f , R_M , R_C are film resistance, membrane resistance and cake resistance, respectively. It should be mentioned that the factor R_f is multiplied by the transmembrane pressure ΔP because the flux should be independent of the transmembrane pressure in the case of film or concentration polarization control. Eq. (1.9), (1.10) and (1.11) are the expressions of film resistance, membrane resistance and cake resistance, respectively. In Eq. (1.9), C_b is the concentration of colloids or particles in the bulk fluid; C_s is the concentration of colloids or particles at the surface of filter medium or filter cake; k is the mass transfer coefficient, u_E is the electrophoretic mobility. In Eq. (1.10), R_{0M} is the membrane resistance when the electric field strength is equal to zero; K_M electroosmotic coefficient in the membrane. In Eq. (1.11), R_{0C} is the filter cake resistance at zero electric field strength; K_C is the electroosmotic coefficient in the filter cake. Thus, by combining Eq. (1.7), (1.8), (1.9), (1.10), (1.11) together, the model for flux will be (Henry et al. 1977; Radovich and Chao 1982; Bowen and Sabuni 1992):

$$J = \frac{\Delta P}{\eta \left[\frac{\Delta P}{k \cdot \ln(C_s/C_b) + u_E E} + \frac{R_{0M}}{1 + K_M E R_{0M} / \Delta P} + \frac{R_{0C}}{1 + K_C E R_{0C} / \Delta P} \right]} \quad (1.12)$$

It should be mentioned that the term R_{0C} is not a constant. It is a function of the thickness of filter cakes which is affected by the electric field strength. When

the electric field strength is increased, an expansion of the cakes will occur and the resistance of cakes will thus decrease. When the electric field strength is higher than the critical electrical field strength, the cake resistance can be ignored. Thereby, the expression of flux will be obtained as (Fane 1994):

$$J = \frac{\Delta P}{\eta \left[\frac{\Delta P}{k \cdot \ln(C_s/C_b) + u_E E} + \frac{R_{0M}}{1 + K_M E R_{0M} / \Delta P} \right]} \quad (1.13)$$

Bowen et al. discovered another model describing the total resistance of the cross-flow electro filtration system which is very similar to Eq. (1.8). However, some researchers disagree with the models by Henry or Bower for their unsatisfactory performance in quantitativity. These authors commence the model development of electro filtration flux from the steady-state. At steady-state, a mass balance equation for the dispersed particles in the concentration polarization layer can be expressed as (Yukawa et al. 1983; Radovich et al. 1985; Rios et al. 1988):

$$J C_p = (J C + D) \frac{dC}{dx} - v_p (C - C_p) \quad (1.14)$$

In the above mass balance equation, C_p is the concentration of particles in the permeate flow; C is the concentration of particles in the solution in the concentration polarization layer; D is the diffusion coefficient of particles; x stands for the distance from the membrane; v_p is known as the electrophoretic velocity of the dispersed particles. At boundary conditions, by integrating Eq. (1.14), the filtration flux then becomes:

$$J = K \cdot \ln \frac{C_g - C_p}{C_b - C_p} + u_p E \quad (1.15)$$

$$K = D / \delta_c \quad (1.16)$$

Eq. (1.15) and Eq. (1.16) show the filtration flux under boundary conditions. C_g is the particle concentration in the surface deposit; C_b is the bulk concentration of the dispersed particles; K is the particle mass transfer coefficient and δ_c is the concentration polarization layer thickness. The boundary conditions $C = C_g$ at $x = \delta_g$, $C = C_b$ at $x = \delta_c + \delta_g$. δ_g is the thickness of the cake layer. The filtration flux model of Eq. (1.15) indicates that the limiting flux enhancement owing to electric field is only dependent on the applied electric field strength and the electrophoretic mobility of the particles in suspensions.

1.4 Research Objectives

The major goal of this research is to study the parameters affecting nanoparticle separation from liquid phase by the application of cross-flow electro filtration. By optimize the experimental conditions, the best filter behavior will be performed as the minimum fouling on membrane and maximum nanoparticle removal efficiency. Specifically, the research objectives include the following:

1. Design and construct a cross-flow electro filtration module for experimental use. All parts of the system are obtained from the aquatic chemistry lab in University of Delaware. The CFEF system will overcome all the problems interrelated to conventional dead-end flow or cross-flow filtration system;
2. Study the main factors affecting the results of cross-flow electro filtration by separating nanoparticles experimentally. The effects of factors including applied electric field strength, filtration flow rate and solution pH will be focused on and assessed. SiO₂ (Aerosil 200, Evonic Degussa Cooperation Company), will be used as model nanoparticles.

3. Develop a mathematical model describing the fate and transportation of charged nanoparticles in cross-flow electro filtration system. The influences of all parameters tested in experiments will be quantified by the model. The model will be validated by matching the experimental results.

1.5 Notations

C_b	concentration of colloids or particles in the bulk fluid, g/L
C_g	concentration of particles in the surface deposit, g/L
C_p	concentration of particles in the permeate flow, g/L
C_s	concentration of colloids or particles at the surface of membrane or filter cake, g/L
D	diffusion coefficient of the particles, m^2/s
E	electric field strength, V/m
E_c	critical electric field strength, V/m
I	current density, A/m^2
J	filtration flux, m/s
k	mass transfer coefficient, m/s
K	mass transfer coefficient of particles in the concentration polarization layer, m/s
K_C	electroosmotic coefficient in the filter cake, m/s
K_M	electroosmotic coefficient in the membrane, m/s
L	distance between electrodes, m
ΔP	applied transmembrane pressure, Pa
r	radial coordinate, m
r_i	radius of inner electrode, m
r_o	radius of outer electrode, m

R_C	cake resistance, m^{-1}
R_f	filter resistance, m^{-1}
R_M	membrane resistance, m^{-1}
R_T	total resistance in electro filtration system, m^{-1}
R_{0C}	cake resistance when electrical field strength is zero, m^{-1}
R_{0M}	membrane resistance when electrical field strength is zero, m^{-1}
u_E	electrophoretic mobility, $(m/s)/(V/m)$
u_p	electrophoretic mobility of particle, $(m/s)/(V/m)$
v_p	electrophoretic velocity of particle, m/s
x	distance from the membrane, m
δ_c	thickness of concentration polarization layer, m
δ_g	thickness of cake layer, m
ϵ	permittivity of electrolytes, $C^2/J \cdot m$
ζ	zeta potential, V
η	liquid viscosity, $g/m \cdot s$
φ	electrical potential, V
φ_i	electrical potential at inner electrode, V
φ_o	electrical potential at outer electrode, V
λ_0	conductivity of the bulk solution, $A/V \cdot m$

Chapter 2

EXPERIMENTAL PROCESSES OF SEPARATING NANO-SIZED PARTICLES BY CROSS-FLOW ELECTRO FILTRATION

2.1 Abstract

The aim of this research is to separate the nano-sized from suspensions and study how parameters including electric field strength, particle surface characteristics, cross-flow velocity, etc. influence the removal efficiency and membrane fouling control. In this chapter, the experimental processes of separation are introduced. A prototype cross-flow electro filtration (CFEF) module is designed and constructed for the experiments. Nano-sized SiO_2 is used as model nanoparticles in the experiments. Further optimizations upon the parameters are done to increase the particle removal efficiency as well as minimize membrane fouling. Based on the experimental results, it is concluded that by increasing the electric field strength or decreasing the filtration flow velocity or doing both will increase the particle removal efficiency. Since the particle surface characteristics are strongly related to pH of the solutions, a curve expressing the relationship between the removal efficiency and pH of solution with constant electric field strength and filtration flow velocity is also obtained. The removal efficiency of nano-sized particles can be effectively increased by optimizing the cross-flow electro filtration system.

2.2 Introduction

The demands of separating nano-sized particles from liquid or from other kinds of colloidal suspensions are increasing. Because of the small sizes of nanoparticles, conventional filtration techniques including dead-end flow filtration and cross-flow filtration are difficult to meet the goal. For a dead-end flow filtration, both the liquid phase and the particles pass through the filter medium in the same direction. As a result, the filtration flux declines significantly due to the fast formed fouling on the membrane. Such phenomenon also indicates the limitations of dead-end flow filtration (Iritani et al. 2000). For cross-flow filtration, the flow is parallel to the filter medium. With the shear strength generated by the parallel flow, the formed cakes on the membrane can be removed effectively (Henry et al. 1977). The filtration flux is therefore maintained. However, when the particle sizes become sufficiently small, for example, nanoparticles, the shear strength generated by the parallel flow can hardly contribute to membrane fouling control. This makes the effectiveness of cross-flow filtration plummeted. Not only these traditional techniques, there are also some new techniques especially for nanoparticle removal. Nano-filtration is a newly developed technique for removing nanoparticles. However, considering the principles of nano-filtration, a very high transmembrane pressure (usually 100 psi) must be applied in order to separate nanoparticles from the liquid phase. This determines that the equipment and membranes for this technique are special made and of high cost. On the other hand, although the removal efficiency of nanoparticles is increased by the application of nano-filtration, the potential problem of membrane fouling still takes place. The cost of fouling control in nano-filtration is even higher.

One thing noticed by researchers is that particle size distribution is not the only particle characteristic can be used for particle separation. The surface

electrochemical properties of particles also need consideration. By applying an external electrical field, the particles can get charged and be collected on an electrode with opposite polarity. This method will not only increase the particle removal efficiency but also minimize fouling on the membrane (Henry et al. 1977; Yukawa et al. 1983; Verdegan 1986; Wakeman and Tarleton 1987).

Manegold was the first to study the hybrid separation process combining the features of both conventional pressure filtration and electrophoretic separation (Manegold 1937). Bier tried to dewater colloidal suspensions using a membrane technique with the application of electrical field (Bier 1959). Giddings developed a process which is named as field flow fractionation is quite similar to today's cross-flow electro filtration. The main differences between these two techniques include that in the cross-flow electro filtration, not only the electric field strength of the superimposed electrical field is used, but also there exists a fluid bulk flow going towards the membrane; Besides, the cross-flow electro filtration system does not need back wash or periodic elution when filtrating colloidal suspensions. While in Gidding's principles, his goal is to fractionate either the dissolved solutes or the suspended particles. Moulik (1976) tried to remove colloidal particles like algal cells and bentonite by applying an electrostatic field in micro-filters. The removal efficiency was proved to be very good in the experiment.

Cooper et al. modified the models of batch filtration. In their models, the effect of particle mobility in the slurry adjacent to the membrane and a revise of electro-osmosis in both the filter cakes and the membranes are included (Cooper et al. 1965). However, the influences of shear tangential to the membrane as well as the concentration polarization concepts are not considered in their models. It was Henry in

the year of 1977 coming up with a prime analysis of the cross-flow electro filtration. In the research of Henry, the three factors including bulk flow, fluid shear tangential and electrophoretic migration that can affect particle transportation toward or through the filter medium are studied. A mathematical model for the cross-flow electro filtration was developed which considers how electrophoretic mobility of particles in the suspensions affect the film resistance, membrane resistance and cake resistance (Henry et al. 1977). By the employment of this model, the performance of a separation process can be interpreted

In the experimental setup of cross-flow electro filtration, parameters including transmembrane pressure, applied voltage, filtration rate, feed concentration, pH and so on are known to have significant effects on the performance of filtration system. Lo et al. did the experiments of separating Al_2O_3 colloidal particles from non-aqueous solutions with cross-flow electro filtration processes. In this research, the effects of feed rate, driving pressure, electrostatic field strength and total solid deposition rate on the collector electrode are assessed. An extent of fouling decrease upon the filter medium is carried out (Lo et al. 1983). Majmudar and Manohar separated TiO_2 from aqueous solution utilizing electrophoretic filtration. The experiments were conducted at different applied electrical field strength and flow rates. They found the critical electric field strength at a certain flow rate that the maximum separation rate can be obtained (Majmudar and Manohar 1994). Zumbusch et al. focused on the factors related to electrostatic field. The study not only included electric field strength, but also frequency and conductivity. Their results indicate that with low frequency, high conductivity at limiting electrolytic currents and high electrostatic field strength the best performance of electro-filtration will be obtained

(Zumbusch et al. 1998). Sung et al. built a cross-flow filtration module with low operation pressure and a large pore-size membrane. This system showed good performance in nano-sized particle removal with the assistance of electrical field (Sung et al. 2007). Du et al. intensified cross-flow electro filtration with a novel electrode configuration. In this research, DEP was first time introduced to suppress fouling in filtration. Results showed that the membrane working life and permeate flux were great increased (Du. et al. 2013).

In this research, a cross-flow electro filtration module is designed and constructed. By the application of this module, the separation of nano-sized particles from liquid samples will be practiced and analyzed. The following objectives will be aimed: Maximize the removal efficiency and minimize fouling on the membrane by experiments; Developing a mathematical model describing the relationship between the filtration removal efficiency and parameters influencing the performance of electric field and membrane, testing the model using experimental data; Based on the theories from the developed model, separating different kinds of mixed nanoparticles from water samples.

2.3 Experimental Design and Results

2.3.1 CFEF Module Design and Setup

The following figures shown are a photo of the equipment used in the research and a schematic figure describing the total arrangement of the CFEF module. The main parts of the apparatus include a feeding tank, a peristaltic pump, a D.C. power supply, a pH controller, several flow meters and a cross-flow electro filtration unit.

The CFEF unit consists of an external tube, a reel-type metal net and a concentric rod as electrodes, a tubular membrane is inserted between cathode and anode. The inner diameter of the external tube is 8.8 cm, the distance from the center of tube to the edge of the metal net electrode is 3.35 cm, the inner diameter of the tubular membrane is 1.55 cm, the radius of the concentric rod electrode is 0.5 cm. The length of the module is 22.5 cm. Cathode and anode are connected to a D.C. power supply (Model: E861, Consort, Belgium) with a highest output voltage of 600 volts. This power supply is used to provide a stable electric field across the electrofiltration system. In order to prevent membrane fouling by the generation of gas and air bubbles by electrolysis or heat generation, the current and power are limited at their maximum value, 1000 mA and 300 W, respectively. Further, the metal net electrode is placed outside the membrane with a distance of 3 mm from the membrane outer surface so that the gas bubbles will be washed away by the cross flow stream.

An electrical resistance box is connected with the system. The main applications of this thing are to control the electrical current and alternate polarity of the electrodes more conveniently. If the colloidal particles being separated are charged positively, then the collector electrode should be a cathode; if the particles are charged negatively, the collector electrode should be an anode. The filter used in this experiment is FXUSC rev. 2 (General Electric Company) which are purchased in Home Depot. The pore size of this membrane is between $xx\mu\text{m}$ to $xx\mu\text{m}$. Since the pore size of the membrane is much larger than the particle size, such membrane is just applied as a barrier. The cross-flow electro filtration module used in this research is a tangential flow filtration system made by Millipore and the model is ProFlux M12. A pressure sensor is installed so that the inlet and outlet pressures can be read.

The following figures are sketch of the arrangement and photograph of the CFEF Module, respectively:

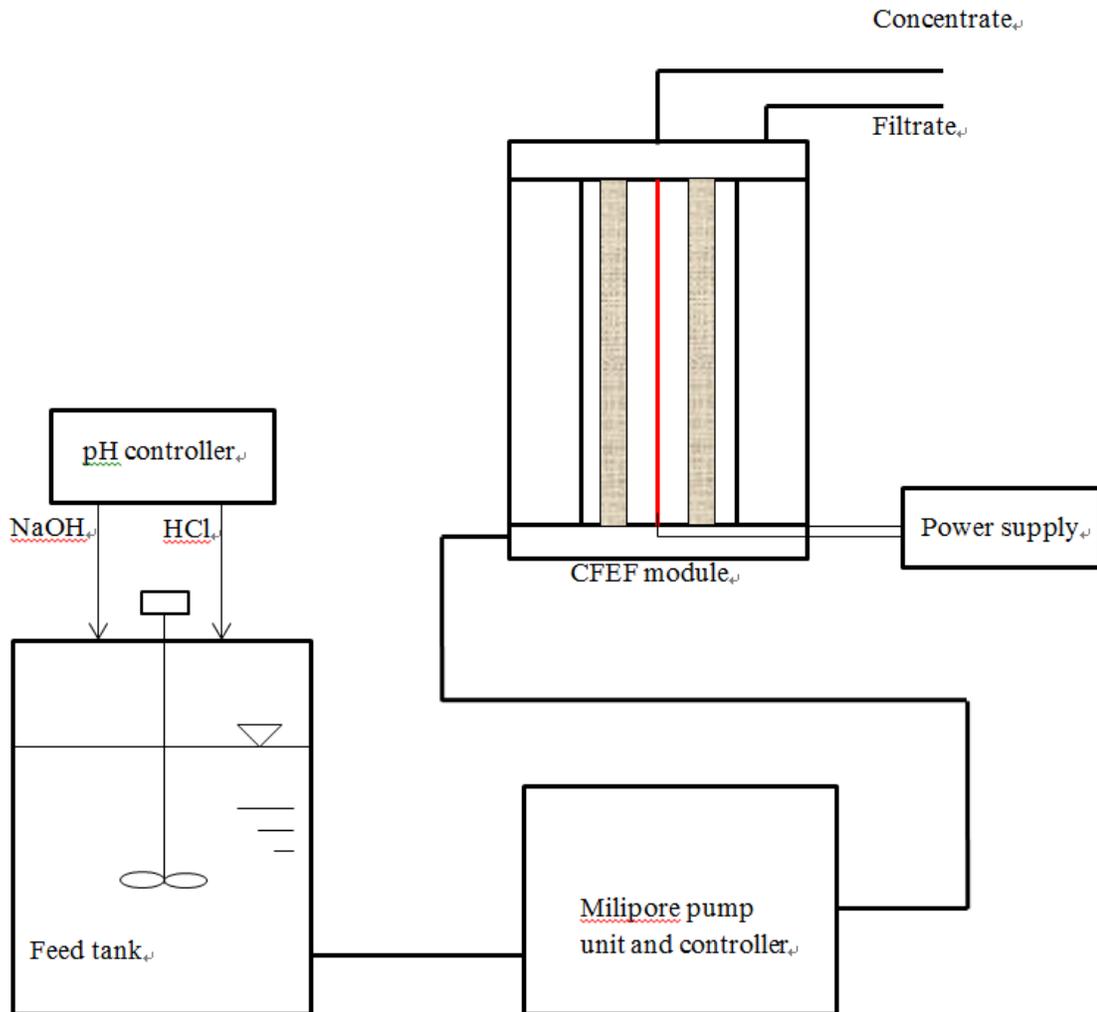


Figure 2.1 Sketch of the arrangement of CFEF Module



Figure 2.2 Photograph of the whole arrangement of the CFEF Module

2.3.2 Materials and Chemical Analysis

SiO₂ is used as the model nanoparticle in this experiment. The SiO₂ particles are aerosil 200 which are purchased from Evonic Degussa Coporation Company (NJ, USA).

The colloidal particles are suspended in electrolyte. The electrolyte are sodium chloride (NaCl) solution with an ionic strength of 10⁻² mol/L based on distilled and deionized water. The pH value is adjusted by HCl and NaOH to a desired value.

In order to get the removal efficiency, the following equation can be used:

$$\eta = \left(\frac{C_0 - C_t}{C_0} \right) \times 100\% \quad (2.1)$$

In Eq. (2.1), η is the removal efficiency; C_0 stands for the feed concentration at the very beginning; C_t is particle concentration in filtrate flow at a given time. It should be noted that the suspended colloidal particles will give turbidity to the water solution. The unit of turbidity is nephelometric turbidity unit (NTU). Before running the experiment, a calibration curve describing the relationship between suspension concentration and turbidity is made. Results show that concentration of SiO_2 is linearly related to their turbidity, and the linear correlation coefficient R^2 is bigger than 0.99. Thus, a linear relationship between suspension concentration and turbidity can be determined. By knowing the turbidity of a suspension, the particle concentration can be calculated then be used to get the removal efficiency η . The turbidity of suspension is measured using a turbidity meter (2100P Portable Turbidimeter, HACH, USA).

2.3.3 Experimental Operation

Before doing the experiments, some preparations are necessary. The membrane should be sunk in water for 24 hours. The colloidal nanoparticles are weighted and distilled with DI water. Then the suspension will be put onto an ultrasonic oscillator for 3 hours to make sure the particles are fully dispersed in the solutes and prevent particle agglomeration. Then the suspension will be diluted to the preferred concentration with DI water in a 100L plastic container. This container is used as the feed tank in the experiment. When running the experiment, a stirrer is applied into the colloidal solution to make sure the solution is homogeneous. The pH

controller is also connected with the feed tank, HCl and NaOH will be added into the suspension when needed.

Performances of the cross-flow electro filtration system will be tested by controlling the following parameters: applied voltage, filtrate flow rate and pH of solution. The applied voltage can be set up using the control pad on the E861 D.C. power supply before the system starts to run. The module should be reset when a different voltage is needed. In this experiment, the applied voltage is from 0 to 400V. Based on the distance between the two electrodes, one can calculate that the applied field strength ranges from 0 to 14829 V/m. Three flow meters are installed upon the system, one is used to read the total inlet feed rate, the other two are used to read the concentrate flow rate and permeate flow rate, respectively. The feed flow rate is related to the pumping speed, the concentrate and permeate flow rate can be adjusted by the pressure valve installed on the pipes. There is a control pad on the module which can be used to control the pumping speed and read the inlet pressure, outlet pressure and pressure difference. The pumping speed (S, %) of the pump is also linearly related to the feed flow rate (Q, L/min) with the equation: $Q = 0.081S - 0.215$. In this experiment, a pumping speed of 10%, an inlet pressure of 2 Psi, an outlet pressure of 1Psi and the transmembrane pressure difference (ΔP) of 1 Psi is maintained.

A group of performance tests have been done to evaluate the clogging status of the membrane during the cross-flow electro filtration processes. The test uses brand new membranes, the solution is 100 mg/L SiO₂, the pH of solution is 6.2, pumping speed is 10% and the feed rate is 0.6 L/min, initial inlet and outlet pressure are 2 and 1 Psi, respectively, the applied voltages varies from 0 to 400 voltages.

Results show that when the applied voltage is higher than 400 V, there is no difference occurred at the inlet or outlet pressure for more than 10 hours. When the applied voltage is 300 V, the transmembrane pressure maintains stable for 6 hours. After 6 hours, the transmembrane pressure will become higher and the flux is decreased. This indicates that for the first 6 hours, no clogging is observed. When the applied voltage is 100 V, the transmembrane pressure will start to increase within 3 hours. Since each experiment will be run for one and half hours, there is no need to backwash or backpulse the filter during the experiment. When each running is finished, the module will be splitted, the glass cell, electrodes and membranes will all be washed.

During the first 30 minutes of the experiment, samples from the concentrate flow and permeate flow will be collected every 5 minutes. From 30 to 90 minutes, samples will be collected every 10 minutes. When the concentration differences between a sample (concentrate flow or permeate flow) and the next samples (concentrate flow samples compared with concentrate flow samples and same for permeate flow samples) are less than 2%, a steady state is considered to be reached. The removal efficiency at the steady state is recognized as the final removal efficiency of the experiment. During each test, the pH and temperature of the feed solutions are kept constant and the temperature is around 20 °C.

2.3.4 Results

2.3.4.1 Effect of Applied Electric Field Strength

An experiment of particle removal efficiency versus different electric field strength has been conducted. The result is shown in the following figure. The applied voltage is operated to increase from 0 to 400 V (or from 0 to 14829 V/m). It

can be seen that the charged nanoparticle removal efficiency is significantly related to the applied electric field strength. The experimental results also indicate a fact that it takes about 15 minutes for each electro filtration run to reach a near-steady state, which is 4 times of a hydraulic circulation time period. After 15 minutes, the turbidity of filtrate flow keeps stable.

To focus on the effect of applied field strength on membrane performance in CFEF, we conduct the experiment with stable filtrate flow rate, transmembrane pressure, feed turbidity and pH. The following figure is SiO₂ removal efficiency with initial concentration of 100 mg/L. The pH is 6.2, and the filtrate flow rate is 0.2 L/min. Because the p*H*_{zpc} of silica dioxide is less than 2, the SiO₂ particles are negatively charged when pH is 6.2. Thus, in order to remove the SiO₂ nanoparticles, we make the outer electrode as cathode and the inner concentric rod as anode. It can be seen that when no electric field is applied, the particle removal efficiency is almost 0. The reason that the particle removal efficiency is extremely low is mainly due to the size difference between nanoparticles and membrane pores. The membrane pore size is between 30 to 50 μm while the silica dioxide used in experiment only has a particle diameter of 12 nm. Such big size difference can cause all the particles to pass through the membrane without being removed. When the electric field is applied, the process of nanoparticle removal using this system becomes much viable compared with the condition of absence of electric field. In this study, we applied an electric voltage as low as 50 volts and the electric field strength is about 1854 V/m at the very beginning. The applied field strength was increased step by step in later parts of experiments. It can be seen from the results that the particle removal efficiency shows a very strong relationship with the applied electric field strength. The particle removal efficiency

increases obviously with the increase of applied field strength. In Figure 2.3, the particle removal efficiency is 5.2, 14.9, 24.7, 33.8, 47.1, 54.6, 64.3, 73.7 and 84.3% with the applied field strength of 0, 1854, 3707, 5561, 7414, 9268, 11122, 12975 and 14829 V/m (or 0, 50, 100, 150, 200, 250, 300, 350, 400 V as applied voltages), respectively. Such results indicate high removal efficiency at high electric field strength as expected.

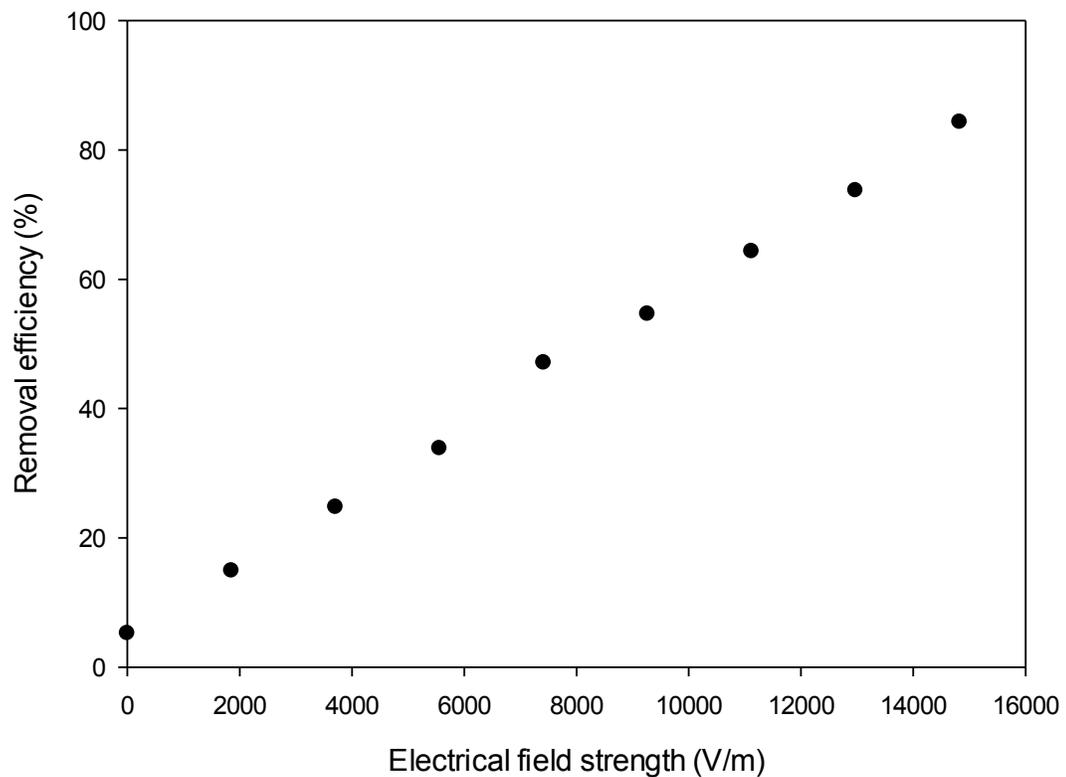


Figure 2.3 Aerosil 200 removal efficiency at different applied electric field strength. Particle concentration: 100 mg/L; pH = 6.2; Filtration flow rate: 0.2 L/min.

2.3.4.2 Effect of Filtrate Flow Rate

To study the effect of filtrate flow rate on particle removal efficiency, we conduct the experiment under the conditions of: 100 mg/L SiO₂ colloidal solution, pH = 6.2, electric field strength is 11122 V/m. The filtrate flow varies from 0.2 L/min to 0.6L/min. Results of this series of experiments are shown in the figure below. The SiO₂ nanoparticle removal efficiency is 64.3, 53.4, 42.1, 34.2, 26.1% with the filtrate flow rate of 0.2, 0.3, 0.4, 0.5, 0.6 L/min, respectively. The maximum removal efficiency was obtained when the filtrate flow rate is the lowest. It can be seen that the particle removal efficiency shows a trend of decrease with the increasing filtrate flow rate.

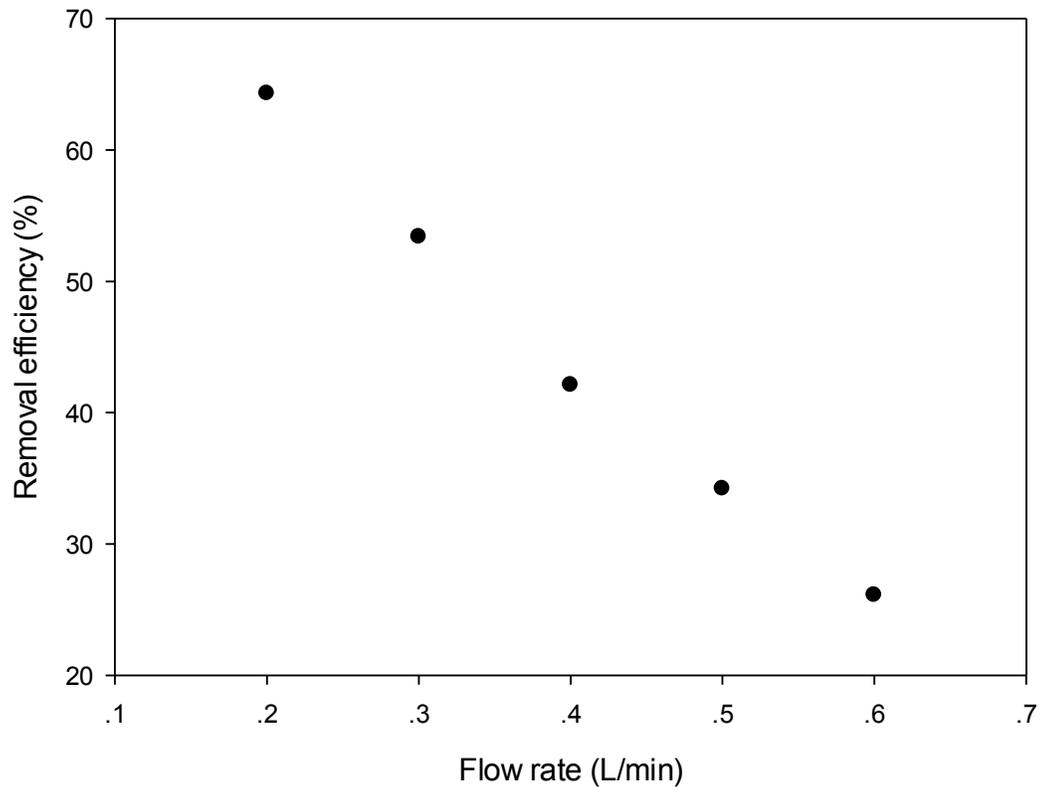


Figure 2.4 Aerosil 200 removal efficiency at various filtration flow rate. Particle concentration: 100 mg/L; pH = 6.2; Applied field strength: 11122 V/m.

2.3.4.3 Effect of pH

Since the zeta potential of colloidal nanoparticles varies at different pH, therefore, the surface charge density of a single particle is also different when pH changes. Such difference can result in membrane performance divergence at different pH level in cross-flow electro filtration. Because the pH_{zpc} of SiO_2 is less than 2, when the pH is greater than 2, the bigger the pH is different from pH_{zpc} , the greater the particle is charged. Figure 2.5 shows the particle removal efficiency versus different pH values. In this series of experiment, the feed concentration is 100 mg/L; electric field strength is 8823.5 V/m; the filtrate flow rate is 0.2 L/min. pH ranges from 3.5 to 8.4. The SiO_2 nanoparticle removal efficiency is 26.6, 33.7, 41.1, 64.3, 72.3 and 82.0% with the pH of 3.5, 4.3, 5.1, 6.2, 7.1 and 8.4, respectively. It can be seen that when the pH reaches 8.4, the removal efficiency is as high as 85%, indicating the significance of pH in electro filtration.

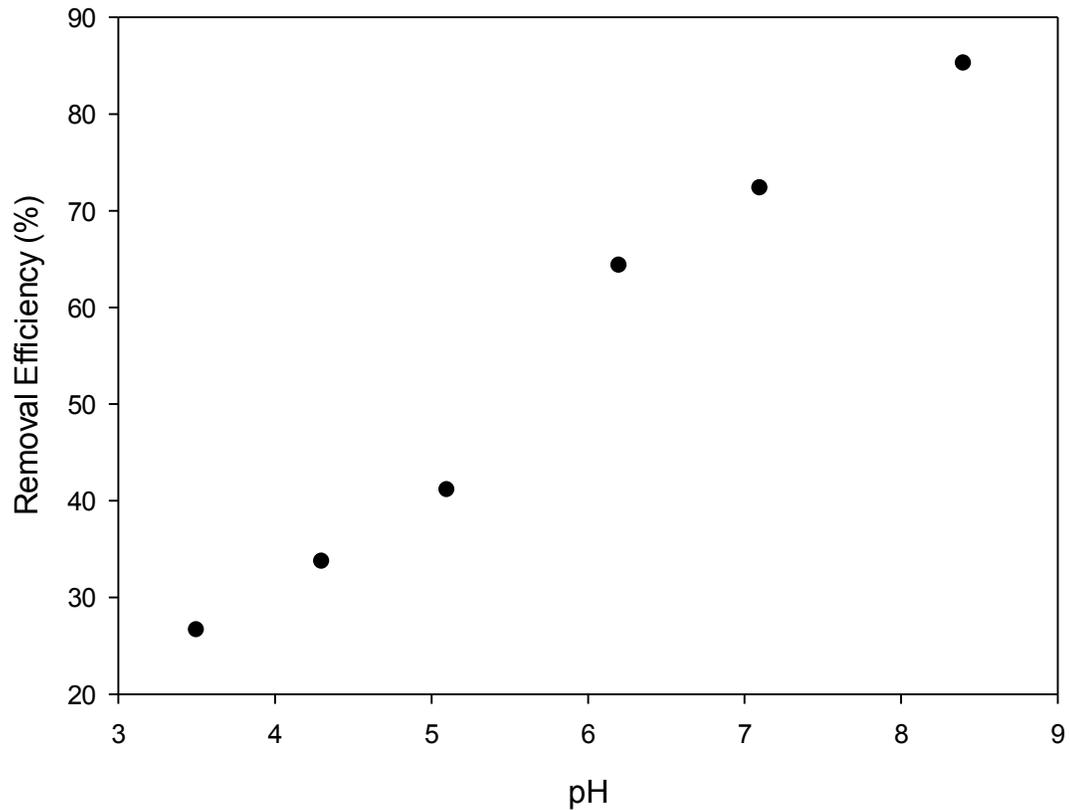


Figure 2.5 Aerosil 200 removal efficiency at different pH values. Particle concentration: 100 mg/L; Filtration flow rate: 0.2 L/min; Applied field strength: 11122 V/m.

2.4 Summary

In this section, we design and build a cross-flow electro filtration module for nanoparticle removal. Results have proved that the CFEF system works effectively. No serious clogging problem occurred, especially at higher applied electric field strength. However, when the electric field strength is low, clogging may still take place after 2 hours run. The transmembrane pressure also stayed the same when no

clogging occurs. Since each experimental run usually takes only one and half hours, so there is no need to backwash in the processes.

Parameters influencing the nanoparticle removal efficiency are studied. In the experiments, SiO₂ (aerosil 200) was utilized as model particles. The solid concentration remains 100 mg/L for both particles. The pumping speed remains 10%, which makes the feed flow rate 0.6 L/min; the inlet and outlet pressure are 1 and 2 psi, respectively and the pressure difference is 1 psi; the applied electric field strength varies from 0 to 14829 V/m; filtrate flow rate is controlled from 0.2 L/min to 0.6 L/min; the pH is adjusted from 3 to 9 by HCl and NaOH. Results indicate that the system will reach a near-steady state at around 15 minutes, which is 4 times of a hydraulic circulation time period.

Results indicate that all the three parameters studied above have great effects on the removal efficiency of particles. In the study about applied field strength, the filtrate flow rate was maintained as 0.2 L/min, pH was 6.2. An experiment without external electrical field was operated at the beginning and results showed that the removal efficiency was extremely low due to the big size difference between membrane pores and nanoparticles. The applied field strength was then raised up step by step from 1854 V/m to 14829 V/m. As expected, the particle removal efficiency increases fast with the increase of the applied field strength. When the applied electric field strength reaches 14829 V/m, the removal efficiency reaches more than 80%. In the study of filtrate flow rate, the applied field strength stayed as 11122 V/m, pH was 6.2. Results indicate that with the decrease of filtrate flow rate, the particle removal efficiency will increase. The effect of pH was also studied. The influence of pH lies upon the influences of particle surface charge density and zeta potential. When the pH

is increased to 8.6, the experimental removal efficiency of SiO_2 is as high as 90%, which proves that pH plays an essential role in cross-flow electro filtration.

In the next chapter, we will focus on quantifying the effects of the parameters studied above and develop a mathematical model to describe the transportation of a nanoparticle in the cross-flow electro filtration system.

Chapter 3

THEORETICAL ANALYSIS OF NANOPARTICLE TRANSPORTATION IN CROSS-FLOW ELECTRO FILTRATION

3.1 Abstract

Many authors have modified conventional cross-flow filtration mathematical models to obtain theories for electro filtration. Model development for describing charged particle transportation in cross-flow electro filtration is still quite rare. In this chapter, a mathematical model predicting particle transportation in CFEF unit is developed. Effects of parameters including particle size, surface charge density, flow rate, solution pH and applied electric field strength on membrane performance are evaluated. Besides, compared with previous studies, the effect of Coulomb forces between a single particle and all the other particles is also discussed. Results demonstrate that the effect of Coulomb forces influence the model behavior a lot and it cannot be ignored. Predicting curves of the membrane performance are generated based on the mathematical model. These curves match well with the experimental results shown in Chapter 2. The experimental operation can be optimized to maximize the nanoparticle removal efficiency and minimize the membrane fouling based on the model. Further, it is possible to separate mixed nanoparticle solution according to the model and previous experimental results by adjusting the pH and applied electric field strength.

3.2 Introduction

Cross-flow filtration overcomes many disadvantages of dead-end flow filtration, such as short membrane life time, low removal efficiency and high decrease rate of flux. However, the main limitation of conventional cross-flow filtration is the particle size. When dealing with nano-sized particles, a heavy solid deposition of particles is achieved on the membrane which is hard to be removed by cross-flow. The application of external force field, like an electric field to obtain the cross-flow electro filtration system is an effective method for nanoparticle separation.

In the CFEF unit, a capture zone is defined. It contains the collector electrode and the concentrate flow area. When proper parameters are applied, the charged particles will be removed away from the membrane surface and collected in the capture zone. The electrophoretic separation is only related to the total charge of every single particle, which is determined by their surface charge density in the solution and particle size and has nothing to do with their materials. Theoretically, if the electric field strength is high enough and the particles are charged sufficiently, all the particles will be caught completely in the capture zone without transporting towards the membrane. As a result, the membrane will not get fouled at all.

Previous researchers have developed a variety of mathematical models about the cross-flow filtration. Some authors modified these models for electro filtration. These electro filtration models are mostly extension of cross-flow filtration film theory and resistance prediction (Henry et al. 1977; Radovich et al. 1985; Rios et al. 1988; Bowen 1993). Kim and Zydney analyzed the effects of electrostatic, hydrodynamic and Brownian forces on particle trajectories and sieving in normal flow filtration and cross-flow filtration. Their models emphasized the motion state of a single particle in filtration system. But the study was only limited in normal filtration

and conventional cross-flow filtration (Kim and Zydney 2003; Kim and Zydney 2006). Study focusing on transportation of a single charged particle in cross-flow electro filtration system is very rare. One comprehensive model describing the model behavior in cross-flow electro filtration is the mathematical model by Yao Tung Lin. In his study, a sensitivity analysis has been employed to assess the influences of several parameters, like particle size distribution, surface charge and applied electric field strength on model performance (Yao-Tung et al. 2007). However, there are still some imperfect handling and wrong assumptions in his research. His theory needs further consummation.

In this chapter, a mathematical model describing the filter performance based on the fate of a single charged particle in the cross-flow electro filtration system will be developed. Experimental results will be applied to fit the model to test its reasonability.

3.3 Model Development

In order to develop a mathematical model evaluating the removal efficiency of nanoparticles in the CFEF system, the following assumptions are made (Lo et al. 1983; Yao-Tung et al. 2007):

1. Steady state operation;
2. The electrical force is the main driving force on the nanoparticles;
3. The physical and transportation properties are constant;
4. Flow in the CFEF system is considered as laminar flow due to the Reynolds numbers are low;
5. The nanoparticle is considered as being removed when its final position is within the capture zone.

Figure 3.1 is the motion state of a single particle in the CFEF system. The particle is assumed to be negatively charged and the inner electrode and outer electrode are assumed to be anode and cathode, respectively. On the r-axis, the motion of particle can be divided into two velocities: the filtration flow velocity v_f and the velocity generated by electrostatic force, which is marked as v_e . While on the x-axis, the only speed influencing the motion of particle is the velocity of inlet flow, marked as v_x . r_0 is the distance from the anode to the cathode; r_i is the radius from the central electrode to the inner side of the cylindrical filter. The capture zone is defined as the space within r_i .

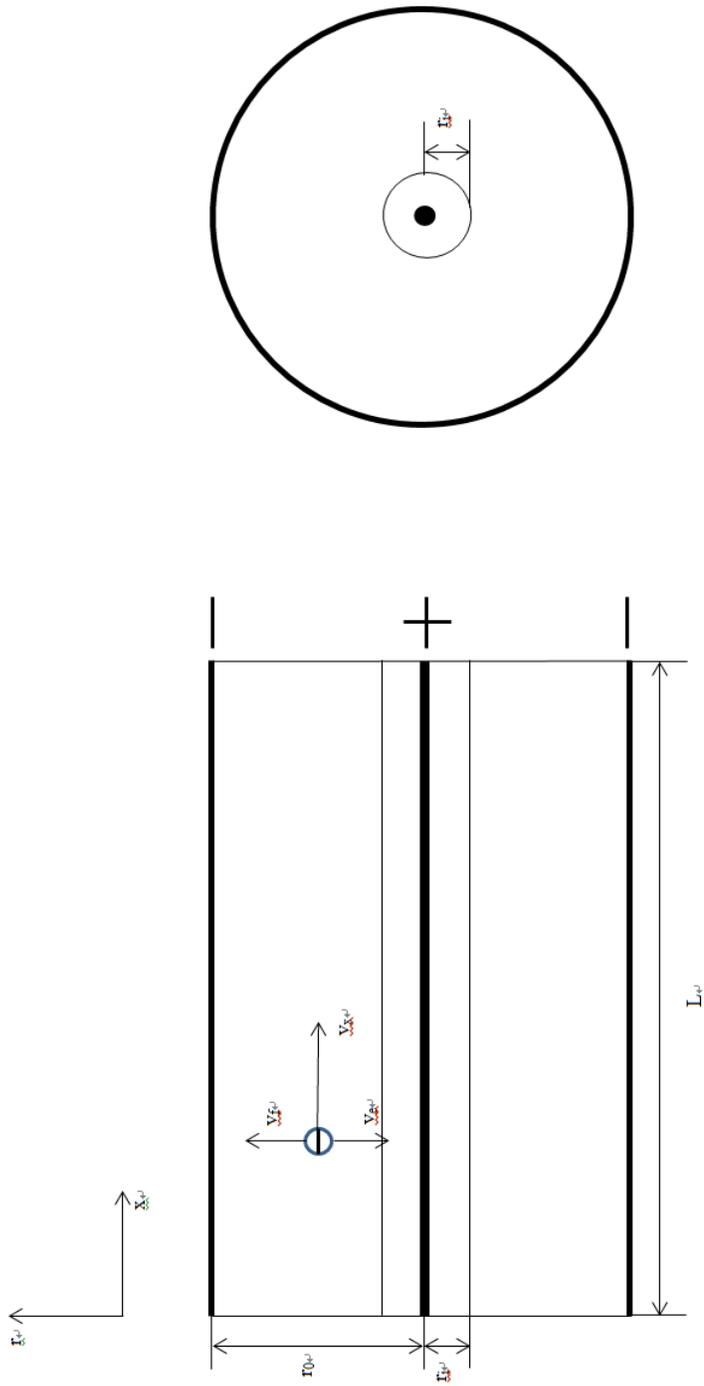


Figure 3.1 Sketch of the collection section of the CFEF Module

To discuss the motion state of a single charged particle in the CFEF system, we will first define the vector of particle velocity relative to the fixed coordinate as \mathbf{v}_p . The trajectory of a single particle is evaluated based on Newton's law. The particles are assumed to be spherical. The value of \mathbf{v}_p and equation of motion can be written as following:

$$v_p = v_e + v_f \quad (3.1)$$

$$m_0 \cdot \frac{dv_p}{dt} = \mathbf{F}_E + \mathbf{F}_D \quad (3.2)$$

\mathbf{F}_E and \mathbf{F}_D are electrostatic force and drag force on the particle, respectively. To make the model easy to calculate, we only consider the horizontal and vertical directions (r-axis and x-axis in the above figure). While \mathbf{F}_E is influenced by two electric fields: the applied external field (E_0) and the field generated by the charged particles themselves ($E_{q(r)}$), which are of opposite directions. Mark the charge of a single charged particle as q_p , so on the vertical direction, the value of \mathbf{F}_E can be written as:

$$F_E = q_p(E_{q(r)} - E_0) \quad (3.3)$$

The drag force \mathbf{F}_D is proportional to the particle velocity relative to the flow; the direction of \mathbf{F}_D is opposite to that of the \mathbf{v}_p . So the value of \mathbf{F}_D can be expressed as:

$$F_D = -3\pi\mu d_p(v_p - v_f) \quad (3.4)$$

In Eq. (3.4), μ is the viscosity of solution; d_p is the diameter of a nanoparticle; v_f is the filtration velocity. By combining the above equations, a numerical integration of Newton's equation of motion will be obtained as:

$$m_0 \cdot \frac{dv_p}{dt} = 3\pi\mu d_p(v_f - v_p) + q_p(E_0 - E_{q(r)}) \quad (3.5)$$

In order to analyze the electric field within the CFEF system, Gauss's law should be applied:

$$\oint E dA = \frac{q}{\epsilon_0 \epsilon_r} \quad (3.6)$$

While in Eq. (3.6), q is the total charge within the surface A , ϵ_0 is permittivity constant and ϵ_r is dielectric constant of the medium. In the region between radius r and $r+dr$ of the CFEF system, based on Gauss's law, one has:

$$E_{q(r+dr)}A(r + dr) - E_{q(r)}A(r) = \frac{q_r \cdot A dr}{\epsilon_0 \epsilon_r} \quad (3.7)$$

$$E_{q(r+dr)} \cdot [2\pi(r + dr)L] - E_{q(r)} \cdot 2\pi r L = \frac{q_r \cdot 2\pi r L \cdot dr}{\epsilon_0 \epsilon_r} \quad (3.8)$$

Eq. (3.8) is an expression of Gauss's law in the CFEF system. $A(r)$ is the surface area at r position; q_r is the charge density within r . Expand $E_{q(r+dr)}$ in Taylor's series:

$$E_{q(r+dr)} = E_{q(r)} + \frac{E'_{q(r)}}{1!} dr + \frac{E''_{q(r)}}{2!} (dr)^2 + \dots$$

$$E_{q(r+dr)} - E_{q(r)} = \frac{E'_{q(r)}}{1!} dr + \frac{E''_{q(r)}}{2!} (dr)^2 + \dots \quad (3.9)$$

Neglect high order terms in Eq. (3.9), the following equation will be obtained:

$$E_{q(r+dr)} - E_{q(r)} = \frac{dE_{q(r)}}{dr} \cdot dr \quad (3.10)$$

Back to Eq. (3.8), this equation can be rearranged as:

$$E_{q(r+dr)} \cdot dr + [E_{q(r+dr)} - E_{q(r)}] \cdot r = \frac{q_r \cdot r dr}{\epsilon_0 \epsilon_r} \quad (3.11)$$

Insert Eq. (3.10) into Eq. (3.11), the following expression will be obtained:

$$(E_{q(r)} + dE_{q(r)}) \cdot dr + dE_{q(r)} \cdot r = \frac{q_r \cdot r dr}{\epsilon_0 \epsilon_r} \quad (3.12)$$

Ignore high order terms and rewrite Eq. (3.12), the equation will become:

$$E_{q(r)} + \frac{dE_{q(r)}}{dr} \cdot r = \frac{q_r \cdot r}{\varepsilon_0 \varepsilon_r} \quad (3.13)$$

Eq. (3.13) is a differential equation about $E_{q(r)}$. $E_{q(r)}$ can be solved as:

$$E_{q(r)} = \frac{C_1}{r} + \frac{q_r r}{2\varepsilon_0 \varepsilon_r} \quad (3.14)$$

Use the boundary condition at $r=r_i$. r_i is the radius of the capture zone, within which all the charged nanoparticles will be removed. q_{ri} can be calculated based on the total charge within r_i . The result will be:

$$E_{q(r_i)} = \frac{C_1}{r_i} + \frac{q_r r_i}{2\varepsilon_0 \varepsilon_r} \quad (3.15)$$

$$E_{q(r_0)} = \frac{q_T \cdot \eta}{\varepsilon_0 \varepsilon_r \cdot (2\pi r_i L + 2\pi r_i^2)} \quad (3.16)$$

In Eq. (3.15) and (3.16), q_T is the total charge of all the particles in the module; L is the length of the module, respectively. q_T and q_r can be written as the following equations:

$$q_T = \frac{q_p \cdot C \cdot \pi R^2 L}{m_0}$$

$$q_r = \frac{q_T \eta}{\pi r_i^2 L}$$

While C stands for the concentration of particle influencing the movement of single charged particle in the solution. With the expression of q_T and q_r , combine Eq. (3.15) and (3.16), C_1 can be solved as:

$$C_1 = -\frac{q_T \eta r_i}{2\varepsilon_0 \varepsilon_r \pi L (L + r_i)}$$

So the result of $E_{q(r)}$ as a function of r will become:

$$E_{q(r)} = \frac{q_T \eta r}{2\varepsilon_0 \varepsilon_r \pi r_i^2 L} - \frac{q_T \eta r_i}{2\varepsilon_0 \varepsilon_r \pi L (L + r_i) r} \quad (3.17)$$

Back to Eq. (3.5), consider the particle will go through the module with the flow, which indicates that the particle velocity on the x-axis will only be influenced by the flow rate of the system. Any position on x-axis can be expressed as a function of time. While the particle velocity v_p of a single particle is related to its position on the x-axis. So v_p can be written as a function of time, defined as $f(t)$. Eq. (3.5) then becomes:

$$m_0 \cdot \frac{df(t)}{dt} = -3\pi\mu d_p [f(t) - v_f] + q_p \left(\frac{q_T \eta r}{2\varepsilon_0 \varepsilon_r \pi r_i^2 L} - \frac{q_T \eta r_i}{2\varepsilon_0 \varepsilon_r \pi L(L+r_i)r} - E_0 \right) \quad (3.18)$$

Rewrite Eq. (3.18), it will become:

$$\frac{df(t)}{dt} + \frac{3\pi\mu d_p f(t)}{m_0} = \frac{3\pi\mu d_p v_f}{m_0} + \frac{q_p}{m_0} \left(\frac{q_T \eta r}{2\varepsilon_0 \varepsilon_r \pi r_i^2 L} - \frac{q_T \eta r_i}{2\varepsilon_0 \varepsilon_r \pi L(L+r_i)r} - E_0 \right) \quad (3.19)$$

Eq. (3.19) is a differential equation about $f(t)$. $f(t)$ can be solved as:

$$f(t) = C_2 \cdot e^{-\int \frac{3\pi\mu d_p dt}{m_0}} + e^{-\int \frac{3\pi\mu d_p dt}{m_0}} \cdot \int \left[\frac{3\pi\mu d_p v_f}{m_0} + \frac{q_p}{m_0} \left(\frac{q_T \eta r}{2\varepsilon_0 \varepsilon_r \pi r_i^2 L} - \frac{q_T \eta r_i}{2\varepsilon_0 \varepsilon_r \pi L(L+r_i)r} - E_0 \right) \right] \cdot e^{\int \frac{3\pi\mu d_p dt}{m_0}} dt \quad (3.20)$$

Rearrange Eq. (3.20), the expression of $f(t)$ will become:

$$f(t) = C_2 \cdot e^{-\frac{3\pi\mu d_p t}{m_0}} + \frac{q_p}{3\pi\mu d_p} \left(\frac{q_T \eta r}{2\varepsilon_0 \varepsilon_r \pi r_i^2 L} - \frac{q_T \eta r_i}{2\varepsilon_0 \varepsilon_r \pi L(L+r_i)r} - E_0 \right) + v_f \quad (3.21)$$

In Eq. (3.21), C_2 is a constant. To determine C_2 , the boundary condition at $t=0$ should be applied. It should be mentioned that for a single particle, its particle velocity v_p is determined by two other velocities: the electrophoretic velocity v_e and filtration flow velocity v_f . The relationships are:

$$v_p = v_e + v_f \quad (3.22)$$

$$v_e = \frac{2\varepsilon_0 \varepsilon_r \zeta E}{3\mu} \quad (3.23)$$

$$\mathbf{v}_f = \frac{Q_f}{A_f} \quad (3.24)$$

In Eq. (3.23) E stands for the total electric field strength; Eq. (3.23) is the theory from Hückel, E. (1924) (Hückel 1924); Q_f is filtration flow rate and A_f is filtration area. When t is equal to zero, the particle enters into the cross-flow electro filtration system, we have:

$$f(0) = \frac{2\varepsilon_0\varepsilon_r\zeta}{3\mu} \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) + \frac{Q_f}{2\pi r_i L} \quad (3.25)$$

$$f(0) = C_2 + \frac{q_p}{3\pi\mu d_p} \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) \quad (3.26)$$

Combine Eq. (3.25) and (3.26), C_2 can be solved as:

$$C_2 = \left(\frac{2\varepsilon_0\varepsilon_r\zeta}{3\mu} - \frac{q_p}{3\pi\mu d_p} \right) \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) + \frac{Q_f}{2\pi r_i L} \quad (3.27)$$

Insert the result of C_2 into Eq. (3.20), the function of particle velocity $f(t)$ can be written as:

$$f(t) = \left[\left(\frac{2\varepsilon_0\varepsilon_r\zeta}{3\mu} - \frac{q_p}{3\pi\mu d_p} \right) \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) + \frac{Q_f}{2\pi r_i L} \right] e^{-\frac{3\pi\mu d_p t}{m_0}} + \frac{q_p}{3\pi\mu d_p} \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) + \frac{Q_f}{2\pi r_i L} \quad (3.28)$$

Next, we will focus on the displacement of a single particle on r-axis during the period it transports in the CFEF module. The total travel time can be calculated as:

$$t_t = \frac{L}{Q_t/A_c} \quad (3.29)$$

In Eq. (3.29), Q_t is the total inlet flow rate from the feed tank; A_c is the cross-sectional area. So the displacement of a single particle will be:

$$s = \int_0^{t_t} f(r, t) dt$$

$$s = -\frac{m_0}{3\pi\mu d_p t} \left[\left(\frac{2\varepsilon_0\varepsilon_r\zeta}{3\mu} - \frac{q_p}{3\pi\mu d_p} \right) \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) + \frac{Q_f}{2\pi r_i L} \right] e^{-\frac{3\pi\mu d_p t}{m_0}} \Big|_0^{t_t} + \frac{q_p t}{3\pi\mu d_p} \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) \Big|_0^{t_t} + \frac{Q_f t}{2\pi r_i L} \Big|_0^{t_t} \quad (3.30)$$

$$s = -\frac{m_0}{3\pi\mu d_p t} \left[\left(\frac{2\varepsilon_0\varepsilon_r\zeta}{3\mu} - \frac{q_p}{3\pi\mu d_p} \right) \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) + \frac{Q_f}{2\pi r_i L} \right] \left(e^{-\frac{3\pi\mu d_p t_t}{m_0}} - 1 \right) + \frac{q_p t_t}{3\pi\mu d_p} \left(\frac{q_T\eta r}{2\varepsilon_0\varepsilon_r\pi r_i^2 L} - \frac{q_T\eta r_i}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r} - E_0 \right) + \frac{Q_f t_t}{2\pi r_i L} \quad (3.31)$$

Eq. (3.31) is the expression of displacement. Since the capture zone is the area within the radius of r_i . If the final position of the particle is within the radius of r_i , the particle will be considered as being removed. The final position can be calculated as the sum of the starting position and displacement of a single particle. Mark the starting position at which the single particle will be exactly removed as r_c . We assume that the particles are evenly distributed when entering the CFEF module. For r_c , there should be:

$$r_i = r_c + s \quad (3.32)$$

$$\eta = \frac{r_c^2}{r_i^2} \quad (3.33)$$

To make the equations easy to write, we define:

$$a_1 = \frac{q_p t_t}{3\pi\mu d_p}$$

$$a_2 = \frac{m_0}{3\pi\mu d_p}$$

$$a_3 = e^{-\frac{3\pi\mu d_p t_t}{m_0}} - 1$$

$$a_4 = \frac{2\varepsilon_0\varepsilon_r\zeta}{3\mu} - \frac{q_p}{3\pi\mu d_p}$$

$$a_5 = \frac{Q_f}{2\pi r_i L}$$

$$a_6 = \frac{q\tau}{2\varepsilon_0\varepsilon_r\pi r_i^4 L}$$

$$a_7 = \frac{q\tau}{2\varepsilon_0\varepsilon_r\pi L(L+r_i)r_i}$$

$$a_8 = \frac{Q_f t_t}{2\pi r_i L}$$

Combine Eq. (3.31), (3.32) and (3.33) together, r_c can be expressed as:

$$(a_1 - a_2 a_3 a_4) a_6 r_c^3 + (1 + a_2 a_3 a_4 a_7 - a_1 a_7) r_c + (a_2 a_3 a_4 E_0 - a_1 E_0 - a_2 a_3 a_5 - r_i + a_8) = 0 \quad (3.34)$$

Eq. (3.34) is a cubic equation of r_c . Based on the theory of Fan Shengjin (Shengjin 1989), we define:

$$a = (a_1 - a_2 a_3 a_4) a_6$$

$$b = 0$$

$$c = 1 + a_2 a_3 a_4 a_7 - a_1 a_7$$

$$d = a_2 a_3 a_4 E_0 - a_1 E_0 - a_2 a_3 a_5 - r_i + a_8$$

$$A = b^2 - 4ac$$

$$B = bc - 9ad$$

$$C = c^2 - bd$$

If $B^2 - 4AC > 0$, r_c will be solved as:

$$r_c = \frac{-b - (\sqrt[3]{Y_1} + \sqrt[3]{Y_2})}{3a}$$

$$Y_{1,2} = Ab + 3a \left(\frac{-B \pm \sqrt{B^2 - 4AC}}{2} \right)$$

So the removal efficiency η will be:

$$\eta = \frac{\left(\sqrt[3]{3a \left(\frac{-B + \sqrt{B^2 - 4AC}}{2} \right)} + \sqrt[3]{3a \left(\frac{-B - \sqrt{B^2 - 4AC}}{2} \right)} \right)^2}{9a^2 r_i^2}$$

If $B^2 - 4AC < 0$, r_c will be solved as:

$$r_c = \frac{-b + \sqrt{A} \left(\cos \frac{\theta}{3} + \sqrt{3} \sin \frac{\theta}{3} \right)}{3a}$$

$$\theta = \arccos \frac{2Ab - 3aB}{2 \sqrt[3]{A}}$$

The removal efficiency η will thus become:

$$\eta = \frac{A \left(\cos \frac{\theta}{3} + \sqrt{3} \sin \frac{\theta}{3} \right)^2}{9a^2 r_i^2}$$

3.4 Model Validation

The technique of cross-flow electro filtration has been applied by many researchers to separate colloidal solids from liquid phases. In this article, experimental data from this experiment and previous researches will be applied to validate the mathematical model (Lo et al. 1983; Majmudar and Manohar 1994; Yao-Tung et al. 2007). These experiments were run with varying conditions: applied electrical field strength; pH value and filtration flow rate.

Figure 3.2 is the predicted and experimental results of the effects of electrical field strength on particle removal efficiency. γ -Al₂O₃, SiO₂ (aerosil 200) and SiO₂ (snowtex 20L) were used as model colloids. Results indicate that the particle

removal efficiency increases with the increase of the electrical field strength as expected. When no electrical field was applied, the particle removal efficiency was near 0. Fig. 2(a) was the result of γ -Al₂O₃ removal. The removal efficiency from the experiments were 3.5, 23, 46, 60, 68, 72, 80% with the electrical field strength of 0, 1933, 3866, 5760, 7733, 9666, 11599 V/m, respectively. Fig. 2(b) was the result of SiO₂ (aerosil 200) removal. The experimental results were 5.2, 14.9, 24.7, 33.8, 47.1, 54.6, 64.3, 73.7, 84.3% with the electrical field strength of 0, 1854, 3707, 5561, 7414, 9268, 11122, 12975, 14829 V/m, respectively. Fig. 2(c) was the result of SiO₂ (snowtex 20L) removal. The experimental results were 3, 31, 60, 70, 93, 97% when the electrical field strength were 0, 3866, 7733, 11599, 15466, 19332 V/m. The shape of the predicted curve is a linear one, which is the same as the result from Lo. (1983). It can be seen that the curve fits well with the experimental result.

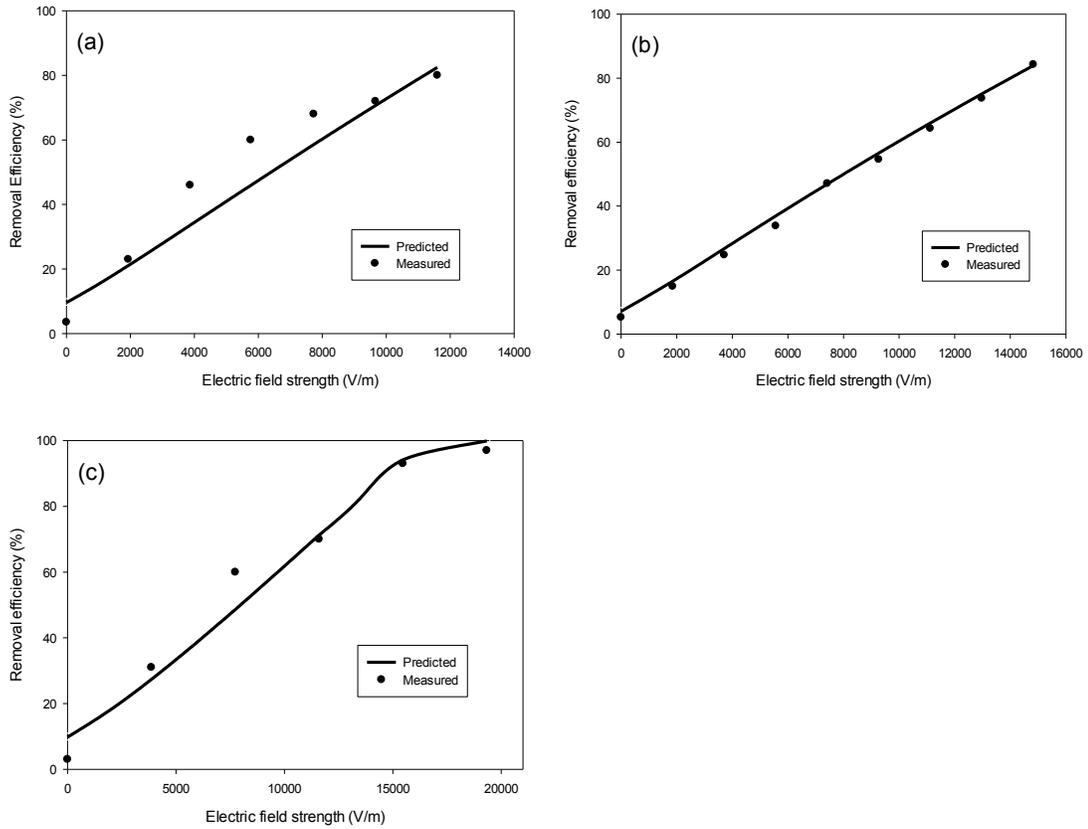


Figure 3.2 Relationship between electric field strength and removal efficiency of γ -Al₂O₃, aerosil 200 and Snowtex 20L. Experimental conditions for (a): 100 mg/L γ -Al₂O₃, pH = 5.6, filtration flow rate 0.3 L/min; (b): 100 mg/L SiO₂ (aerosil 200), pH = 6.2, filtration flow rate 0.2 L/min; (c): 242 mg/L SiO₂ (snowtex 20L), pH = 5, filtration flow rate 0.3 L/min.

Figure 3.3 is the predicted and experimental results of the effects of filtration flow rate on particle removal efficiency. It can be seen that with the increase of the filtration flow rate, the particle removal efficiency performs a trend of decrease. In Fig. 3(a), the removal efficiency of γ -Al₂O₃ were 80, 64, 53, 45, 46% when the filtration flow rates were 0.3, 0.42, 0.54, 0.66, 0.78 L/min, respectively. In Fig. 3(b), the removal efficiency of SiO₂ (aerosil 200) were 64.3, 53.4, 42.1, 34.2, 26.1% with

the filtration flow rates as 0.2, 0.3, 0.4, 0.5, 0.6 L/min. It can be seen that with the increase of filtration flow rate, the removal efficiency decrease fast at first. With the increase of filtration flow rate, the decrease rate of the removal efficiency becomes slower. The calculation results of removal efficiency also showed the same trend. The curve went down sharply and became constant with the increase of the filtration flow rate value. It can be predicted that at a certain filtration flow rate, the removal efficiency of the particles will become constant.

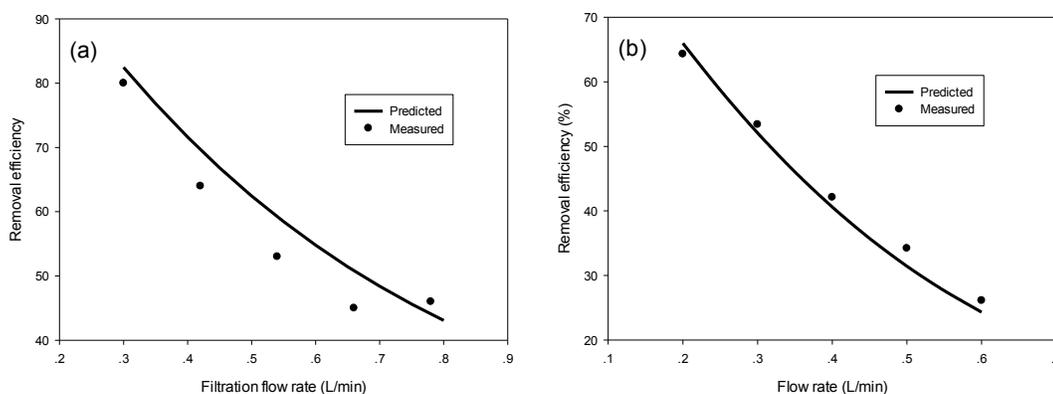


Figure 3.3 Relationship between filtration flow rate and removal efficiency of aerosil 200 and $\gamma\text{-Al}_2\text{O}_3$. Experimental conditions for (a): 100 mg/L $\gamma\text{-Al}_2\text{O}_3$, pH = 5.6, electrical field strength 11599 V/m; (b): 100mg/L SiO_2 (aerosil 200), pH=6.2, electrical field strength 11122 V/m.

Figure 3.4 is the influence of the pH value to the removal efficiency of SiO_2 (aerosil 200) nanoparticles. The removal efficiency showed a trend of increase with increase of the pH value of the feed solution. With the applied pH value of 3.5, 4.3, 5.1, 6.2, 7.1 and 8.4, the particle removal efficiencies were 26.6, 33.7, 41.1, 64.3, 72.3 and 85.2%, respectively. The pH_{zpc} of SiO_2 is smaller than 2. The larger the pH difference from pH_{zpc} is, the more charged the nanoparticles will be. In this

experiment, the applied pH values of the feed solution were kept higher than pH_{zpc} , SiO_2 nanoparticles were negatively charged. Both results from experiments and the model indicated that nanoparticles with higher charge are more easily removed at a given filtration flow rate and electrical field strength. Fig. 3.4 shows a good correspondence of the predicted results with the experiments.

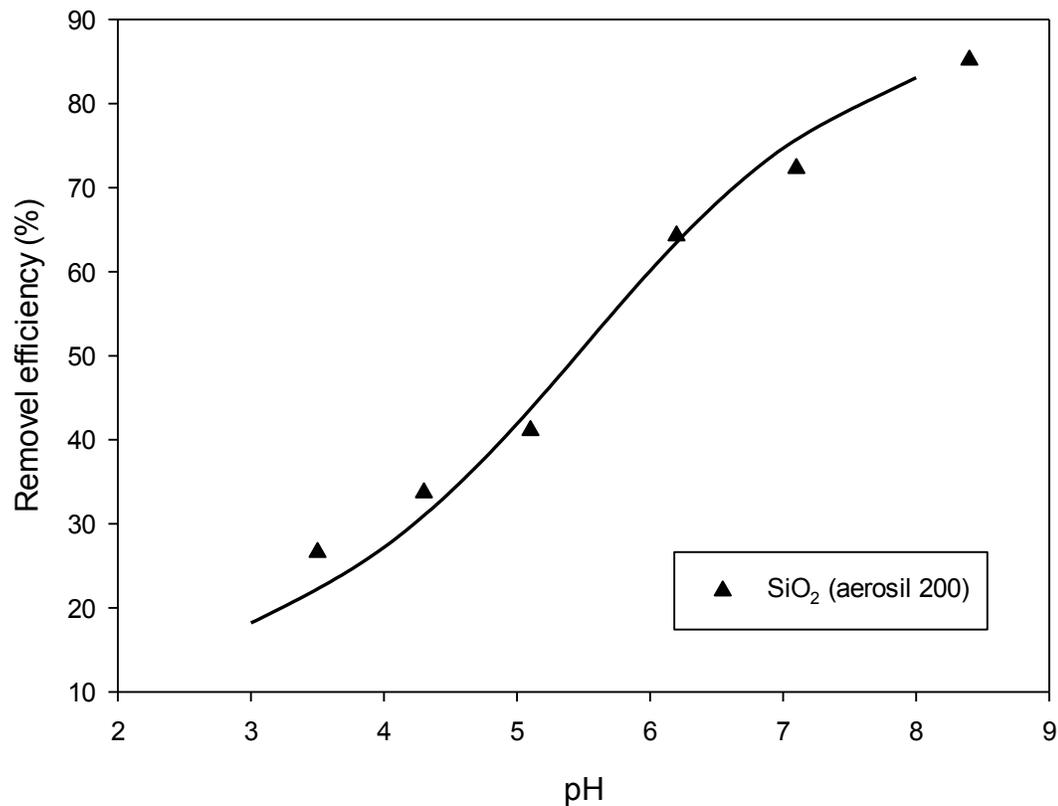


Figure 3.4 Relationship between solution and removal efficiency of aerosil 200. Experimental conditions: 100 mg/L, electrical field strength 11122 V/m, filtration flow rate 0.2 L/min.

Figure 3.5 is a series of experiments on the removal of TiO_2 nanoparticles with an electro filtration system. The influences of applied voltages and flow rates

were evaluated. According to the results of the experiments, the removal efficiencies at different applied voltages and flow rates did not vary a lot. As for the influence of field strength, the applied voltages were from 30 to 50 and the electrical field strength were calculated to be 2000, 2666.7 and 3333.3V/m, respectively. The results still showed an increase of particle removal efficiency with the increase of applied field strength. Compared with other experiments, the differences of applied field strength are not big enough. It can be predicted that with lower applied voltages, the particle removal efficiency will be lower. For the flow rate, the filtration flow rate was kept constant in this experiment. Only the feed flow rate was adjusted. The particle removal efficiency from experimental results were 90.5, 90.3 and 87.9% when the flow rates were 128, 190 and 288mL/h. Figure 3.5 shows that both the predicted results as well as the experimental results displayed that the increase of total flow rate would not influence the particle removal efficiency much. The results proved that the influence of filtration flow rate was much higher than that of the feed flow rate.

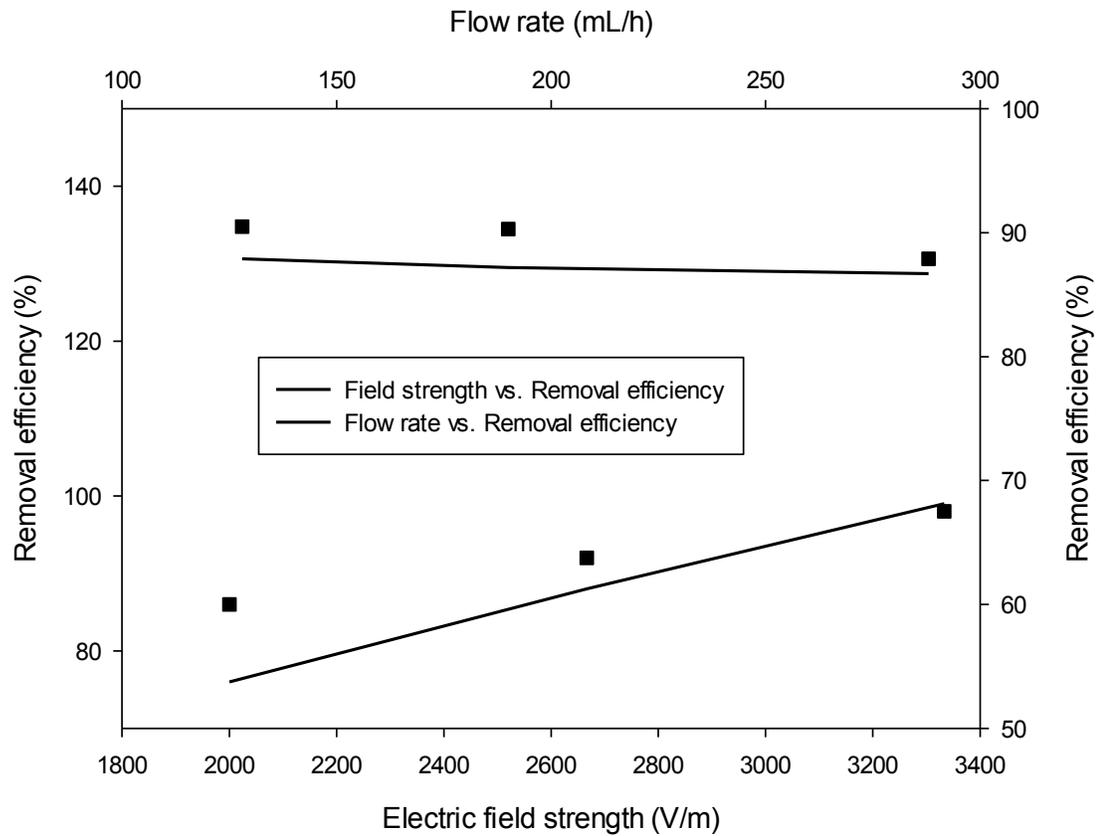


Figure 3.5 Removal of TiO_2 at different electric field strength and flow rate. Data from: Majmudar and Manohar

3.5 Notations

- A_f Cross-sectional area of the filtrate flow, m^2
- C Concentration of the feed solution, g/L
- C_1 An algebra constant for calculation
- d_p Particle diameter, m
- E Total electric field strength, V/m
- E_0 Applied electric field strength, V/m
- $E_{q(r)}$ Electric field strength generated by charged particles in a region of the whole CFEF module with a radius of r , V/m

$E'_{q(r)}$	Electric field strength with a ratio to $E_{q(r)}$, the value of ratio is equal to d_p/L , V/m
$f(t)$	The function form of particle velocity v_p , m/s
F_d	Drag force acting on a single charged particle, N
F_e	Total electrical force acting on a single charged particle, N
L	Length of the CFEF module, m
m	An algebra constant for calculation
m_0	Weight of a single nanoparticle, kg
q_p	Charges on a single particle, C
$q(r)$	Particle charge density in a region of the whole CFEF module with a radius of r , C/m ³
$q(r)_T$	Total charge of all particles in a region of the whole CFEF module with a radius of r , C
Q	Total charge all particles in the whole CFEF sytem, C
Q_f	Flow rate of the filtrate flow, m ³ /s
Q_{in}	Flow rate of the feed solution, m ³ /s
r	radius, m
r_0	Distance from the center of CFEF module to the metal net electrode, m
r_c	Critical radius, m
r_i	Distance from the center of CFEF module to the inner porous wall of membrane, m
t_l	Time for a single charged particle to migrate away from the module, s
t_r	Time for a single charged particle to migrate into the capture zone, s
v_l	Velocity of a single charged particle on l-axis, m/s

v_r	Velocity of a single charged particle on r-axis, m/s
ϵ_0	Permittivity constant, $8.85 \times 10^{-12} \text{ C}^2/\text{J}\cdot\text{m}$
ϵ_r	Dielectric constant of medium, 78.85
ζ	Zeta potential, V
η	Particle removal efficiency, %
μ	Viscosity of solution, $\text{kg}/\text{m}\cdot\text{s}$

Chapter 4

CONCLUSIONS

4.1 Research Summary

A cross-flow electro filtration (CFEF) module has been built for this research to study the main factors influencing the membrane performance in processes of cross-flow electro filtration. The research used SiO₂ nanoparticles to make the test. A D.C. power supply with maximum output voltage, current and power of 600V, 1 amp and 300W, respectively is utilized for the research. Particle concentration of colloidal solution is reflected through turbidity based on the linear relationship between solution turbidity and particle concentration.

The experimental processes are expressed in chapter 2. The effects of applied electrical field strength, filtrate flow rate and pH value of feed solution. Results indicate that the studied parameters all have great influences on the membrane performance in cross-flow electro filtration. With the increase of applied field strength, the particle removal efficiency increases obviously and the loss of particles shows a trend of decrease due to the electrophoretic effects provided by the electric field. By decreasing the filtration flow rate, particle removal efficiency increases and fouling on the membrane decreases, indicating a better performance of membrane. The effect of pH is related to the pH_{zpc} of each kind of nanoparticle. The pH_{zpc} of SiO₂ is smaller than 2. When the solution pH is equal or very close to pH_{zpc} of the nanoparticle, the removal efficiency is very low because the particle is or nearly zero charged. When the pH value is getting further from the pH_{zpc} value, the zeta potential and surface

charge density of particles increase. The particle removal efficiency gets highly improved as expected. Based on the results, the system can be optimized to maximize the nanoparticle removal efficiency and minimize the fouling on membrane.

In chapter 3, a mathematical model is developed to analyze the fate of nanoparticles in the CFEF module. Effects of parameters including applied electric field strength, filtration flow rate zeta potential and surface charge density that may influence the membrane performance are quantified and evaluated. A sensitivity analysis has been conducted to study the model behavior. A validation study is also done to compare the experimental data and model outcome under the same condition. Results indicate that the model can make an accurate prediction in the cross-flow electro filtration system.

In summary, both experimental study and model development prove that cross-flow electro filtration is effective in separating nano-sized particles from liquid phase. By optimizing the applied condition, the colloidal particle removal efficiency can be well increased and the membrane fouling can be minimized. Compared with other filtration techniques, this technique is not only effective but also economic. Cross-flow electro filtration can be further studied to eliminate the naturally occurred nanoparticles in many areas like water purification and separating different kinds of nanoparticles.

4.2 Further Study

The effectiveness and feasibility of cross-flow electro filtration for nanoparticle separation have been studied and proved in this article. Based on the principles of this study, it is possible to separate different kinds of nanoparticles from a mixture of colloidal particle solution. A study focusing on building an equipment to

separate mixing nanoparticles can be conducted in the future. Besides, before designing the future research, some improvement of the CFEF module should be operated first.

The CFEF module built for this experiment generally works well. However, it also displayed a few problems during the experiment. There are mainly three problems. The first one is that the system cannot treat solutions with high ionic strength because the current may exceeded the current limit of the D.C. power supply and the power supply will thus stop working. This problem can be solved by increasing the electrical resistance between the two electrodes. Secondly, electrochemical reactions cannot be fully prevented during the electro filtration cycle. The filtration suspension property is thus changed. Applying an ion-exchange membrane can solve this problem. Last but not least, the cleaning difficulty of the module always remains. When each filtration cycle is finished, rusty dirt appeared on the membrane.

The CFEF module can be applied to separate various particles based on their different pH_{zpc} and size distribution. Different particles are with total different charge property at the same pH value. By treating the particle mixture using cross-flow electro filtration, the size distribution of the mixed colloidal particles should be different before and after the treatment. The size distribution can be observed by utilizing a light scattering. The ideal result is that the two different particles are more than 99 percent separated. This result can be achieved by optimizing the experimental condition, mainly the pH and applied electric field strength. Further, it is possible two separate more than three kinds of nano-sized colloidal particles step by step with the application of cross-flow electro filtration.

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