Removal of Heavy Metal Ions from Aqueous Solution by Alkaline Filtration

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Thesis submitted to the University of Ottawa

in partial Fulfillment of the requirements for the

Master of Applied Science in Chemical Engineering

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Abstract

An innovative approach for the removal of heavy metal ions such as Pb^{2+} and Cd^{2+} from aqueous solution was evaluated. It was established that alkaline filtration, which is in essence the combination of alkaline precipitation and membrane filtration, could drastically increase both the efficiency and completeness of Pb^{2+} or Cd^{2+} ions removal, producing water whose metal concentration satisfying drinking water standard from a simulation wastewater containing 5 ppm or more Pb^{2+} or Cd^{2+} ions. Filtration with three different membranes, including microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) membranes, were studied at three different pH levels, i.e., 7.0, 8.5, and 10, in terms of metal ion rejection, flux, and permeate pH and at varied dissolved inorganic carbon (DIC) concentration. Increasing the pH of the feed in the tested range would lead to the decrease of metal ion concentration in permeate while flux was in general unaffected. When the feed pH was 10, the Pb^{2+} concentration in permeate was below 10 ppb regardless of the DIC concentration and membrane for filtration. The effects of DIC concentration were significant but complex. It was found that MF, UF, NF could all effectively reject Pb^{2+} ions at pH 8.5 and pH 10 although only NF was charged. A hypothesis was proposed to explain the mechanism of alkaline filtration based on experimental data.

Key Words: membrane filtration, alkaline precipitation, lead, cadmium

Résumé

Une nouvelle méthode d 'élimination des ions métalliques lourds tels que Pb^{2+} et Cd^{2+} dans l' eau a été évaluée. Confirmé que le filtrage alcalin, essentiellement lié à la précipitation alcaline et au filtrage de membrane, il permet d'augmenter profondémment l' efficacité et l 'intégrité de Pb^{2+} ou Cd^{2+} de déplacement des ions en produisant de l 'eau à partir d' eaux usées contenant 5 ppm ou plus Pb^{2+} ou Cd^{2+} ions présentant des concentrations métalliques satisfaisant aux normes d 'eau potable. Filtration avec trois membranes différentes, inclure microfiltration (MF), ultrafiltration (UF), et nanofiltration (NF) membranes, étudié les variations des valeurs de PH, i.e., 7.0, 8.5, et 10, et selons la rejection des ions métalliques, le flux et la perméabilité de pH, et différente concentrations de carbone inorganique dissous (DIC). Une augmentation du pH du liquide d'alimentation dans l'essai entraîne une réduction de la concentration d' ions métalliques dans le liquide perméable, le flux n'est généralement pas affecté. Lorsque le pH d'admission est de 10, la concentration Pb^{2+} dans le liquide perméable est inférieure à 10 ppb, quelle que soit la concentration de DIC et l'épaisseur de membrane filtrant. Les effets de DIC concentration sont remarquables mais complexes. Les résultats montrent que le MF, UF et NF, peuvent tous refuser efficacement le Pb^{2+} Ions dans les conditions pH 8.5 et pH 10, mais ne chargent que le NF. Sur la base des données expérimentales, des hypothèses concernant le mécanisme

de filtration alcaline ont été avancées.

Mots clés: filtration sur membrane, précipitation alcaline, plomb, cadmium

Acknowledgement

I would like to express my heartfelt and sincere appreciation to my supervisor and co-supervisor, Dr. Christopher Lan and Dr. Takeshi Matsuura, for their support, patient guidance and background knowledge. Special thanks to Dr. Dipak Rana for his patient guidance and help.

My gratitude also goes to all staff in the Department of Chemical and Biological Engineering, Faculty of Engineering, University of Ottawa, especially Sylvie Saindon, Francine Pétrin and Franco Ziroldo for their valuable help in administrative and technical affair.

I specially acknowledge the Centre for Catalysis Research and Innovation in our university through Dr. Yun Liu for her support and help with TEM and SEM analysis.

Special graduate to all members of microalga group and our membrane group especially Dr. Johnson E. Efome, Zhelun Li, Rufan Zhou and Zeqing Bao for their inspiring and helping in my project.

Finally, I am grateful to my beloved parents, grandfather and girlfriend for their love, guidance, unconditional support and encouragement in my life.

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Nomenclature

A_{sample}	Area of membrane sample for porosity test (cm^{-2})
A	Effective area of membrane (m^2)
C_b	Solute concentration in feed ($g \cdot L^{-1}$)
C_f	Lead concentration in feed (ppm)
C_{p-3}	Lead concentration in permeate filtrated by 3 μm filter paper (ppm)
C_p	Solute concentration in permeate ($g \cdot L^{-1}$)
C_{p-10}	Lead concentration in permeate filtrated by 10 μm filter paper (ppm)
DIC	Dissolve inorganic carbon
J	Flux of membrane ($m^3 \cdot m^{-2} \cdot s^{-1}$)
k_{a1}	Acid dissociation constant of H_2CO_3 (M)
k_{a2}	Acid dissociation constant of HCO_3^- (M)
k_{sp,H_2O}	Solubility product constant of H_2O ($mol^{-2} \cdot L^{-2}$)
$k_{sp,Pb(OH)_2}$	Solubility product constant of $Pb(OH)_2$ ($mol^{-3} \cdot L^{-3}$)
$k_{sp,PbCO_3}$	Solubility product constant of $PbCO_3$ ($mol^{-3} \cdot L^{-3}$)
l	Thickness of the dry membrane sample (cm)
$m_{>10\mu m}$	The amount of lead in the particles whose diameter more than 10 μm (g)
m_{feed}	The amount of lead in the feed solution (g)
$m_{permeate-10}$	The amount of lead in permeate filtrated by 10 μm filter paper (g)
m_{total}	The total amount of lead in solution (equal to the amount of lead in feed solution, g)

ΔP	Transmembrane pressure difference (Pa)
R	Rejection of membrane
$r_{<3\mu m}$	Proportion of particles whose diameter are less than 3 μm
$r_{>10\mu m}$	Proportion of particles whose diameter are more than 3 μm
$r_{3\sim10\mu m}$	Proportion of particles whose diameter are between 3 and 10 μm
t	Filtration time (h)
V_f	Volume of feed (ml)
V_{p-10}	Volume of permeate filtrated by 10 μm filter paper (ml)
w	Weight of permeate collected (g)
w_d	Weight of membrane sample after drying in porosity test (g)
w_w	Weight of wet (wetting by n-butanol) membrane sample (g)
μ	Viscosity of the permeate (mostly water, Pa·s)
ε	Porosity of membrane
ρ	Density of permeate ($kg \cdot m^{-3}$)
$\rho_{butanol}$	Density of n-butanol ($g \cdot cm^{-3}$)

Chapter 1. Introduction

In the 20th century, the world's population increased by nearly 6 folds[1] and freshwater consumption increased by about 7 times[2]. Most significantly, the industrial water usage increased by 19 folds[2] during the same period. Consequently, the per capita fresh water resource at the end of the 20th century was only 1/6 of that at the beginning of the century. It is predicted that about 60% of world population will be affected by water shortage By 2025[3,4].

Heavy metals such as lead and cadmium pose a hazard to the natural environment, ecosystems and human health due to their toxicities, making them a source of concern for food safety and ecological safety. The effective treatment of excessive heavy metals in water is thus an important environmental issue[5–8].

Owing to many advantages such as normal temperature operation, no phase change, small equipment volume, high cost-efficiency, high energy efficiency, and environmentally friendliness, membrane separation technology is used in water treatment such as seawater desalination, drinking water purification, industrial wastewater and domestic sewage treatment and reuse. The membrane technology is also widely used in separation, purification and concentration in the chemical, pharmaceutical, food and other industries[9,10].

Among membrane separation processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), the pore sizes of MF and UF membranes are too large to remove heavy metal ions from aquatic system, while RO membrane has pore sizes small enough to remove metal ions. The separation efficiency of the RO membrane is high, and the impurity removal range is wide. However, the pressure required for the RO membrane is high, leading to relatively high energy consumption and complicated pre-treatment requirement and frequent membrane regeneration. The pore sizes of the NF membrane are between UF and RO membranes and their carry surface charges, which makes them suitable for the partial separation of mono- and divalent ions[11–15].

Chemical precipitation is widely used in industrial wastewater treatment. It is a relatively mature and low-cost method for removing heavy metal ions. However, for some heavy metal ions, the use of less toxic agents to precipitate heavy metal ions produces fine particles that are hard to settle. Most of the chemical agents with better sedimentation effect have certain toxicity, and improper treatment will cause secondary environmental pollution[16–19].

The objective of this work is to investigate the hybrid precipitation-membrane separation process for the removal of heavy metal ions such as lead and cadmium.

In this thesis, the source and the hazard of the heavy metal contamination are first reviewed, and the methods to remove heavy metal contamination are discussed. Then, results of studies on the removal of heavy metal ions (lead and cadmium) by alkaline filtration are systematically discussed.

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Chapter 2. Literature Review

2.1. Introduction

Heavy metals in the context of environment and health mainly refer to mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As) and other bio toxic elements. They also include copper (Cu), zinc (Zn), cobalt (Co), and nickel (Ni)[1,2]. Heavy metals exist in a variety of physical and chemical forms in environments such as water, soil, and atmosphere, and migrate and accumulate in the environment. Anthropogenic pollution sources of heavy metals are mainly mining, metal smelting, metal processing and chemical production wastewater, pesticide and fertilizer, and domestic garbage[1,3,4]. The bioaccumulation of excessive heavy metals in the food chain poses a hazard to the natural environment, ecosystems and human health, and is related to food safety, biosafety and ecological safety. The effective treatment of excessive heavy metals in water is the key to reducing the heavy metal content of other animals and plants in the biological chain. Therefore, heavy metal pollution treatment has gradually become a serious issue. People have adopted various methods to treat heavy metal wastewater and pollution[1,5,6].

This article reviews the sources of heavy metals and the hazards to people and ecosystems. It describes several water treatment methods for removing heavy metals,

such as precipitation, coagulation and flocculation, ion exchange, adsorption, electrochemical treatment, flotation and membrane separation. The classification, mechanism, materials and processes of membrane separation technology are briefly described.

2.2. Heavy metal contamination

Accompanying the remarkable industrial achievements during the last century, some toxic chemicals are inevitably used in the industrial process and discharged into the environment. Heavy metals are one of these harmful chemicals. As the awareness of environment protection grows, governments of the developed countries began to control the emission of waste liquid and solid containing heavy metals. However, the heavy metals pollution still threatens the health of human and the ecology system in the developed and developing countries and regions.

2.2.1. Common Heavy Metal Contaminants

Heavy metals are commonly defined as the metallic elements whose density is more than 5 g/mL[1]. The most common heavy metals that are harmful are mercury, lead, cadmium, chromium, aluminium and arsenic (arsenic is a metalloid, but it is usually classified as heavy metal considering its chemical properties.)[1,7].

Lead is extensively used in metallurgy, electroplating, mining, batteries, paints and

cosmetics. The sources of lead contaminants are widely distributed. In the past, the use of lead contained gasoline was the main source of lead exposure. While lead containing gasoline has been phased out in high-income countries (HIC), the lead accumulated in soil and surface water due to the past usage of it still has a negative influence on the environment. Particularly, such a negative influence is much more pronounced in the low- and middle-income countries (LMIC) since the usage of lead contained gasoline[8,9] was forbidden much later in those countries. As well, the incineration and land filling of municipal solid waste (MSW) is a serious source of lead pollution in LMIC, since the lead containing wastes such as electronic components, circuit boards and batteries are not collected due to poor MSW classification management[10]. The incineration of MSW with lead will disperse lead into atmosphere as microparticles. Then, those microparticles will precipitate and accumulate in the soil and surface water. In the mining industry, lead smelting and electroplating are the important sources of lead exposure in LMIC. The usage of lead-induced paint is also the source of lead exposure in both LMIC and HIC. In the past, the lead-induced paint had been widely used in building construction until its use for home painting was banned. For example, the Australian government started to ban the sale of lead-induced paint as early as 1922, and restriction was strengthened nationwide in 1970s. However, the lead-induced paint still remains in old homes. The lead containing materials used in drinking water pipelines and pipefittings are the important sources of lead exposure both in LMIC and

in HIC. The lead in the pipelines can diffuse into drink water and chlorine, used for the disinfection of drinking water in China, facilitates the lead diffusion [11–13].

Cadmium is widely used in metallurgy, electroplating, batteries, and mining and chemical industry. There are many sources of cadmium as contaminants. The exploitation of nonferrous metal mines, especially the lead-zinc ore, causes the contamination by cadmium. The dust containing cadmium disperses into atmosphere by wind from spoil-heap material and extracted ores. When cadmium-containing dust is blown by air, cadmium accumulates in the soil and surface water near the nonferrous metal mines. The thermal smelting and electrolytic extraction of nonferrous metal (including the ores and cadmium containing recycled metal scraps such as iron scrap, lead scrap and copper scrap) are also the significant sources of cadmium contaminants. Those processes can discharge a large quantity of cadmium-rich dust into the atmosphere. The wastewater with low cadmium concentration is released from thermal smelting plants and often discharged into environment without any treatment. The emissions from electroplating plants are also the main sources of cadmium pollution. The improper disposal of cadmium-containing products, such as stabilizers, pigments, alloys and nickel-cadmium battery, are other important sources of cadmium contaminants. These cadmium containing municipal wastes usually are landfilled or incinerated. Some research also showed that the combustion of coal releases a lot of

cadmium particles. Some phosphate fertilizers which are produced from rock phosphate as the raw material can be adsorbed by crops and accumulated in soil and aquatic system[4,14].

Mercury is widely used in instrument manufacturing, salt electrolysis, precious metals refining, fluorescent lamp manufacturing, dental amalgam and cosmetics. In the developed countries or regions, such as U.S. or the European Union, coal-fire power plants are the largest sources of the mercury contaminants. In U.S. 44.0% of mercury contaminants were contributed by electricity generation by coal in 2014. The coal-fire power plant, ferrous metal industry, municipal waste disposal are the main sources of mercury pollution in U.S. In the European Union, the main sources of mercury are coal combustion, landfilling of municipal waste, wastes from chlor-alkali industry and waste from incinerator slag. In developing countries and some Asian countries, the combustion of coal is still the largest source of mercury contamination. The other main sources in those countries and areas are zinc extraction, ferrous metal extraction, medical waste incinerators, industrial waste incinerators, municipal waste landfilling or incinerators, chlor-alkali and electroplating industry. Due to the insolubility in water and high volatility of mercury, the mercury in the mercury containing waste spreads over a large area. The usage of mercuric fungicides in paint and mercury containing battery have been phased out in most areas. However, their usage in the past

accumulated a lot of mercury in the soil and aquatic system[15–17].

Chromium is extensively used in leather tanning, electroplating and ceramic industry. It is also used as catalysts and industrial pigments. Chromium is the essential micronutrient element for the metabolism of humans and animals. The low concentration of chromium is nontoxic, but at high concentration the divalent chromium ions will transform to hexavalent ions which are toxic for both organisms and microorganisms. The main sources of hexavalent chromium are chrome electroplating, evaporation cooling towers, chromite chemical manufacturing and chromite mining and refining[18–20].

Arsenics are widely used in mining, metallurgy, transistor manufacturing and pharmaceutical industries. The main sources of arsenic contaminants are mine tailing, mine effluents, base-metal refinery or metallurgical facilities, coal processing or combustion, the usage of arsenical pesticides and the usage of arsenical wood preservatives. Most of arsenic discharges (over 90%) are from coal combustion and metallurgical facilities. In the last century, the usage of arsenic product increased rapidly, especially as arsenical pesticides and arsenical wood preservatives. Although the arsenical pesticides and wood preservatives have been banned, the arsenic accumulated in the soil is still being released into aquatic system and adsorbed by microorganisms and plants, which human can take in through the food chain[3,21–23].

2.2.2. Threats of Heavy Metals to the Ecosystem, Animals and Humans

Most of heavy metals are harmful to the ecosystem and organisms including humans. Some heavy metal ions can cross the cell membrane and react with proteins, enzymes, and DNA molecules. This destroys the structure of biological macromolecules, causing them to lose their function and biological activity. It also causes DNA mutations to induce cancer. Long time intake or exposure to low concentration of heavy metals causes cancer and acute heavy metal poisoning. Exposure to high concentration of heavy metals even causes death[5]. In the natural environment, unlike organic contaminants, heavy metal contaminants are not biodegradable. They tend to accumulate in living organisms, will be enriched through the food chain, and eventually be taken in by humans through the food they consume.

Long-term low concentration lead exposure gives rise to nervous system damage, memory deterioration, consciousness reducing and kidney damage. Recent researches also showed that the intelligence of children who are exposed to low lead concentration for a long time will be lowered. High-level lead exposure can damage the proximal renal tubule, which can cause kidney disease[24].

Intake of cadmium can be life threatening, sometimes it will cause acute pulmonary damage and death. Cadmium exposure can induce kidney damage. Some researches

showed that cadmium caused irreversible tubular dysfunction of kidney, which makes the kidney lose the ability to reject small molecular weight proteins in the blood[14,25]. Long-term cadmium exposure also increases the risk of skeletal damage and cardiovascular disease[14,26].

The long-term mercury exposure can cause reversible chronic poisoning and kidney damage. A high dietary intake of mercury can increase the incidence of coronary heart disease. Metallic mercury also is an allergen, which may give rise to contact eczema[27]. The inorganic mercury can be converted to organic mercury in organisms or microorganisms. The organic mercury such as methyl mercury is highly toxic to animals and humans. It was shown that the exposure to methyl mercury can cause acute nervous system damage. High dose exposure even causes death[28].

Since trivalent chromium does not easily permeate through or is absorbed by cell membranes, its toxicity is small. Hexavalent chromium can easily cross the cell membrane and is a strong oxidant and therefore highly toxic[29]. Hexavalent chromium can be absorbed by the digestive system and lung and even by skin[30]. The hexavalent chromium exposure or intake causes kidney damage, male reproductive system damage, ulcers in the digestive system, anemia and cancer[5].

The arsenic is acutely toxic. The arsenic can cause disturbance or damage of the central

nervous system, digestive system and cardiovascular system, and eventually causes death. The long-term arsenic exposure increases the risk of skin cancer, bladder cancer, lung cancer and kidney cancer[31].

2.2.3. Standards for Lead, Cadmium and Other Important Heavy Metal Contaminants

Table 2-1 shows the drinking water standards and guidelines of common heavy metals in U.S. and Canada, and those recommended by the World Heath Organization (WHO).

Table 2-1 Drinking water standards and guidelines of U.S. Canada and WHO

Chemicals		U.S.[32]		Canada[33]	WHO[34]
		MCL (ppm)	MCLG (ppm)	MAC (ppm)	ppm
As	Arsenic	0.01	Zero	0.01	0.01
Cd	Cadmium	0.005	0.005	0.005	0.003
Cr	Chromium	0.1	0.1	0.05	0.05
Pb	Lead	0.015	Zero	0.01	0.01
Hg	Mercury	0.002	0.002	0.001	0.006

MCL: Maximum Contaminant Level

MCLG: Maximum Contaminant Level Goal

MAC: Maximum Acceptable Concentration

2.3. Conventional Heavy Metal Removal Technology

The methods to remove heavy metals include precipitation, coagulation and flocculation, adsorption, ion exchange, electrochemical treatment, flotation and membrane filtration.

2.3.1. Coagulation and Flocculation

Coagulation and flocculation are widely used in the purification of drinking water and sewage treatment. Coagulation is a process in which coagulants neutralize the repulsive force between colloids or particles in the solution to destabilize the colloids. The widely used coagulants are solid aluminum sulfate, liquid aluminum sulfate, alum, poly-aluminum chloride, ferric chloride and ferrous sulfate. Although the coagulants are workable for suspended particles and hydrophobic colloids, it is difficult to remove heavy metal ions by regular coagulants. Thus, some researchers used polyethyleneimine grafted with the sodium xanthogenate group as a coagulant. This coagulant, as an amphoteric polyelectrolyte, can reduce heavy metal ions concentration while coagulating negatively charged colloids[35].

Flocculation is the process in which the flocculants adsorb flocs or particles, forming a bridge to bind the flocs or particles into big clumps or agglomerates that can be removed by filtration. Usually the suspended particles in the solution have the same surface charges that prevent the particles from agglomerating due to the repulsive force. The repulsive force is determined by the thickness of electric double layer and strength of the surface charge. During flocculation, the flocculants are adsorbed on the particles, which can neutralize the surface charge and reduce the thickness of electric double layer to facilitate agglomeration. Thus, the ionic radius, ionic strength and ion valence of the

flocculants will affect the flocculation. Normally, the flocculants of high ion valence is more effective. The flocculation rate of fine particles (particle diameter is smaller than 0.1 μm) are dominated by diffusion speed or Brownian motion. This flocculation process lasts for a short time. Larger particles, affected by solution flow, constantly agglomerate and break up until equilibrium is reached. The common flocculants can be classified into three categories; i.e. iron flocculants such as ferric sulfate, polyferric chloride (PFC), and polymeric ferric sulfate (PFS); aluminum flocculants such as aluminum sulfate, polyaluminum chloride (PAC), polyaluminum sulfate (PAS) and organic polymer flocculants such as polyacrylamide (PAM). Similar to coagulants, the regular flocculants can not remove heavy metals from wastewater. Some researches have shown that a new kind of flocculants, mercaptoacetyl chitosan made from the reaction of chitosan with mercaptoacetic acid, could not only reduce the turbidity, but also remove the heavy metal ions from wastewater[36].

Generally, coagulation and flocculation can not remove heavy metal ions completely from wastewater. These processes need to be combined with other heavy metal removal methods to treat wastewater.

2.3.2. Adsorption

2.3.2.1. Activated Carbon

The activated carbon has strong adsorption ability of heavy metals due to its high specific surface area, and large mesopore and micropore volume. It was shown that additives such as tannic acid, alginate, surfactants or magnesium[37,38] had significant influence on the heavy metal adsorption of activated carbon. Furthermore, activated carbon is relatively expensive.

2.3.2.2. Carbon Nanotubes

Carbon nanotubes (CNTs) are promising adsorbents for heavy metal removal. Many researches proved that CNTs have a high potential in the removal of heavy metals such as lead, chromium and cadmium[39,40]. The CNTs adsorb metal ions mainly by chemical interaction, electrostatic attraction and sorption. Depending on the molecular structure, CNTs can be classified into two types, multi-wall CNTs and single-wall CNTs. Although the metal ion adsorption capacity of CNTs is relatively small, the adsorption capacity of CNTs is significantly improved by the treatment with oxidants such as $KMnO_4$, NaClO or HNO_3 solution[41].

2.3.2.3. Zeolites

Natural zeolites are abundant and low cost materials and are widely applied in

adsorption, building industry, soil remediation, agriculture, catalysis and energy[42]. Natural zeolites are crystalline hydrated aluminosilicate minerals with microporous structure. The micropores of natural zeolites are occupied by alkaline, alkaline earth cations and water and have high ability for molecular sieves and cation exchange. Thus, natural zeoites are good adsorbents in separation and purification industries. The adsorption ability of natural zeolites depends on their cation exchange capacity, which are affected by several factors, including ion size and shape, ionic charge, concentration of the external electrolyte solution, framework structure and charge density of the anionic framework[42].

In recent year, the modified forms of natural zeolites are widely investigated, showing that they also have good performance in anions and organics removal from the water system. The common modification processes are acid-base treatment and surfactant modification[43].

In acid-base treatment, the impurities that block the pores of the natural zeolite can be removed, and the cations are replaced by hydrogen ions gradually. Finally, the dealumination takes place. Usually, the acid treatment will decrease the cation-exchange capacity due to dealumination and improve capacity to adsorb non-polar molecules from water system. Cheng etc. investigated the performance of natural zeolites, stilbite, in China. They found that after treating in hot HCl solution, the stilbite

exhibits thermal stability up to 1000°C and has high ion exchange capacity of Ag ions[44].

Due to negative charge on the framework, the natural zeolites usually have low affinity for anions. Thus, they have low ability for adsorption of organics in water. Organic surfactants are the chemicals widely used in surfactant modification of natural zeolites[45].

2.3.2.4. Biosorption

Using biomaterials as adsorbents to adsorb heavy metals is relatively new technique and has a promising prospect. The biosorption is efficient and has a good performance in treating low heavy metal containing wastewater. The biosorbents are inexpensive and have abundant sources such as microbial biomass, alga biomass and non-living biomass.

Microbial biomass includes fungi, yeasts, and bacteria. They are easy to multiplicate and grow, resulting in high biomass yield[46]. The alga biomass has been widely researched, due to its low cost, easy availability and high heavy metal adsorption capacity. It was shown that the alga biomass has a good removal effect for heavy metals. For example, *caulerpa lentillifera*, dried marine green macroalga, can effectively remove cupper, cadmium and lead ions from aquatic system[47], *Caulerpa lentillifera*, a green alga, can adsorb dilute chromium ion from wastewater[48]. The non-living biomass is easy to obtain at low cost. The non-living biomass such as coffee husks, eggshell, potato peel and sawdust have also been investigated by many researchers[49–52].

Although the biosorbents are very efficient and inexpensive, they are still under investigation in the laboratory and not applied in the industry.

2.3.3. Ion Exchange

The ion exchange process removes heavy metal ions from wastewater uses cation exchange resins by exchanging their cations such as sodium ions with heavy metal cations in the wastewater. Ion exchangers include natural and synthetic resins. The latter is more widely used in water treatment. Recently materials such as naturally occurring silicate minerals and natural zeolites have been widely researched, because they have good cation exchange capacities, and are abundantly available and inexpensive. Carboxylic acid groups (-COOH) and the sulfonic acid groups ($-SO_3H$) are the common functional groups for ion exchange. The acid groups can supply hydrogen ion in exchange of the metal cation in the water while it flows through the ion exchange column. Thus, temperature, wastewater flowrate, flow phase pH and initial metal concentration have significant influences on the removal of heavy metal by the ion exchange process[53,54].

2.3.4. Electrochemical Treatment

During the electrochemical process, heavy metal ions in wastewater are reduced and precipitated on to the cathode surface. The electrochemical treatment has the

advantages of no need to add any oxidants, flocculants and other chemicals; no or little secondary pollution generation; easy and small-size operation. However, electrochemical treatment also has the shortages such as relatively large capital investment, intensive electricity consumption, and formation of oxygen and hydrogen as byproducts, which is flammable and explosive gas. The commonly used electrochemical methods include electrodeposition, electro-flotation and electro-coagulation.

During the electrodeposition processing, the heavy metal ions in wastewater are reduced to metal elements at cathodes. The electrodeposition is effective in treating wastewater containing complexing agents[55].

During the electroflotation processing, oxygen and hydrogen gas are generated from water electrolysis and form tiny bubbles. These bubbles can float the micro particles out of the water. Electroflotation is widely used in heavy metal removal of industries wastewater[56].

The electrode of electrocoagulation normally is iron electrode or aluminum electrode. During electrocoagulation processing, the ion or aluminum electrode will be electrolyzed to ferric ions (Fe^{3+}), ferrous ions (Fe^{2+}) or aluminum ions (Al^{3+}). Then those ions are hydrolyzed to form ferric hydroxide ($Fe(OH)_3$), ferrous hydroxide

($Fe(OH)_2$) or aluminum hydroxide ($Al(OH)_3$). As coagulants, and those hydroxides can coagulate and precipitate the heavy metals in the wastewater. The electrolysis occurs at the anode. With the generation of metal ions (Fe^{3+}, Fe^{2+} or Al^{3+}) at the anode, the hydrogen gas is released from the cathode that also can float the flocculated particles out of the water[57].

2.3.5. Flotation

Flotation is now widely used in wastewater treatment. The first application of flotation is in mineral processing. The flotation uses the different physical and chemical properties of the substance surface to separate particles. The main flotation methods are precipitation flotation, ion flotation and dissolved air flotation. The dissolved air flotation attaches tiny air bubbles to suspended particles dispersed in water to form agglomerates with a density less than that of water. Due to the low density, these agglomerates accumulate on the surface of the liquid. These agglomerates are finally removed mechanically[58]. The precipitation flotation removes heavy metal ions by precipitating heavy metals and then removing those precipitates by attachment to air bubbles[59]. The ion flotation makes the heavy metal ions in the wastewater hydrophobic by surfactant, and then separates these hydrophobic substances by bubbles[60].

2.3.6. Membrane Separation

Membrane separation processes are efficient, energy saving, simple, and easy to control. It is widely used in food, medicine, biology, environmental protection, chemical metallurgy, energy and other fields. Separation membranes can be classified according to their pore size: microfiltration membrane (MF), ultrafiltration membrane (UF), nanofiltration membrane (NF), reverse osmosis membrane (RO), membrane distillation etc. Usually, the microfiltration and ultrafiltration membranes can effectively remove the heavy metal containing particles in water. On the other hand, heavy metal ions in water system can be removed by reverse osmosis and membrane distillation.

2.3.6.1. Performance of Membranes

The performance of membrane is usually judged by its flux and rejection. Flux is the rate of liquid permeation through a membrane at a certain pressure and temperature, which is the volume of liquid collected as the permeate per unit membrane area per unit time. Flux can be calculated by equation (2-1).

$$J = \frac{V}{A \cdot t} \qquad (2\text{-}1)$$

Where J is flux ($L \cdot m^{-2} \cdot h^{-1}$), V is the volume of permeate phase (L), A is the effective area of membrane (m^2) and t is the filtration time (h).

Rejection is the ratio of the difference between the concentration of a specific substance in the feed and its concentration in the permeate to the concentration in the feed. Rejection reflects the ability of the membrane to cut off a certain substance. Rejection can be calculated by the following equation.

$$R = 1 - \frac{c_p}{c_b} \tag{2-2}$$

Where R is the rejection, c_p is the solute concentration in permeate, c_b is the solute concentration in feed.

2.3.6.2. Microfiltration Membrane and Ultrafiltration Membrane

Both microfiltration (MF) and Ultrafiltration (UF) belong to the pressure driven membrane separation process. MF membrane usually is used to separate the particles whose diameter is bigger than 0.1 μm. UF membrane usually is used to separate the particles whose diameter is between 1 nm and 20 nm. The flux of microfiltration is much higher than traditional filtration since the MF membrane has lower thickness and higher porosity. Compared to ultrafiltration (UF) membrane, MF membrane has lager pore size, therefore the resistance of MF membrane is lower than UF membrane. Because of this reason, the operating pressure of MF membrane is much lower than that of UF membrane and the flux of MF membrane is much higher. Compared to the MF membrane, the UF membrane can more effectively remove smaller substances such as

colloids, proteins, viruses and organic macromolecules. Nowadays, the MF membranes and UF membranes are extensively used in sewage treatment, air sterilization and biological products purification.

Since the separation mechanism of the MF and UF membrane is the molecular sieve principle, the size of the pore size plays a significant role in microfiltration. The mechanisms of particle removed by MF and UF membrane include straining by membrane pore, adsorption, cake filtration, entrapment by membrane pore and electrostatic interaction[61–67].

1. Straining by membrane pore

Straining by membrane pore is the main mechanism of MF and UF membrane to reject the particles. At the surface of the membrane, the pore of MF and UF membrane prevents the particles larger than the pore size from crossing the membrane. The solvent and the particles smaller than the pore size can cross the membrane. This process is also known as sieving mechanism.

2. Adsorption

MF and UF membrane can adsorb portion of particles and solutes on the membrane surface or inside the membrane pore. This adsorption can be either chemical adsorption or physical adsorption. By the adsorption mechanism, membrane can remove the

particles smaller than the pore size.

3. Cake filtration

As filtration proceeds, the particles rejected by membrane can form a dense layer on the surface of membrane. Since cake (also known as fouling layer) has smaller pore size than the membrane, even the particles smaller than the membrane pore size can be rejected during filtration.

4. Entrapment by membrane pore

Entrapment occurs inside the membrane pore. Since the pores of membrane have tortuous channels, the particle can be entrapped by these tortuous paths after passing the surface. It was found that, comparing the membrane with straighter pores, the membranes with highly tortuous pores could effectively reject the particles that were much smaller than membrane pore size.

5. Electrostatic interaction

Some MF and UF membranes have charges on the surface, which causes electrostatic interaction between membrane surface and charged particles. Because of this phenomenon, the membrane with charged surface can reject the charged particles much smaller than the pore size of membrane. The behavior between the membrane surface with charge and the charged particles can be described by the Donnan effect.

2.3.6.3. Materials and Fabrication

The MF and UF membranes are mostly prepared from the following six polymers, cellulose, polyolefin, polysulfone, polyamide, polyester and inorganic material[68–70].

1. Cellulose and cellulose derivatives material

Cellulose is the main component of plant cell wall and the most abundant natural polymeric material. It is hydrophilic and not soluble in water or common organic solvents. The membrane made of cellulose has relatively high flux, but is easy to be corroded by microorganism and oxidized. Cellulose membrane becomes denser, while being used and the flux decreases as a result. Better materials for membrane can be obtained by modifying the chemical structure of cellulose. The most common cellulose derivatives used for membrane are cellulose acetate (CA), cellulose triacetate (CTA), cellulose acetate propionate (CAP) and regenerated cellulose (RCE), (CN).

Nitrocellulose is the product of the esterification of cellulose by nitric acid. There is a strong adsorptive interaction between nitrocellulose and nucleic acids or proteins. However, nitrocellulose is easy to burn. Nitrocellulose membrane is widely used in western blot analysis.

Cellulose acetate can be obtained by partially esterifying the hydroxyl groups of cellulose with acetic acid. The properties of cellulose acetate depend on the level of

esterification. Cellulose acetate is widely used for MF and UF membrane, since it is cheap, easy to produce and friendly to environment. The cellulose acetate membrane is hydrophilic and the flux is high. However, cellulose acetate is easily corroded by microorganisms and poor in heat and oxidation resistance. Cellulose acetate membranes are often used for separating plasma or serum proteins, as well as the purifying of enzymes and drugs.

Regenerated cellulose is made by dissolving natural cellulose into a solvent and then precipitating cellulose. The membrane made of regenerated cellulose has high heat resistance, good anti-fouling ability and is easy to clean. However, the regenerated cellulose membrane is easily corroded by microorganisms, has poor resistance against acid or alkaline and the flux is relatively low. The regenerated cellulose membrane can be used for industrial wastewater pre-treatment[71,72].

2. Polyolefin material

Polyolefin is a polymer of olefins, including polyethylene, polypropylene, etc. Polyolefin has the advantages of chemical resistance, low cost, high mechanical strength, low relative density. Polyolefin based separation membranes are widely used in water treatment, gas separation and biopharmaceutical concentration. However, they are poor in hydrophilicity and poor in fouling resistance, and therefore it is usually required to be modified. The common methods to modify the polyolefin membranes

are surface grafting, plasma treatment, surface ozone treatment and supercritical carbon dioxide treatment[73].

3. Polysulfone material

Polysulfone is a polymer which contains sulfone and aromatic group in the main chain. Because the sulfur atom in polysulfone is in the highest oxidation state, polysulfone membrane has high oxidation resistance and good heat and mechanical properties. Commonly used polysulfones for fabricating MF and UF membranes are polysulfone (PSE), polyethersulfone (PES), sulfonated polysulfone (SPSF) and polysulfone amide (PSA). PES membrane is widely used for steam sterilization due to its good heat resistance. PES membrane can be operated continuously at 140^{o}C.

4. Polyamide material

Commonly used polyamide for fabricating MF or UF membranes is polyarylamide (PA). PA separation membranes have good thermal stability, chemical resistance and mechanical stability, but are easily damaged by free chlorine and have poor fouling resistance.

5. Polyester material

By containing ester functional groups in the main molecular chain, polyester has high mechanical strength and has good heat and chemical solvent resistance. Polyester is

usually used for fabricating nuclear track-etched membranes. The common polyesters used for fabricating MF and UF membrane are polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and polycarbonate (PC). PET is usually used as a support layer for the membrane, since it is hydrophobic and poor solubility makes PET not usable for the fabrication of membrane by the phase inversion method. PBT is not widely used in membrane fabrication due to its high cost.

6. Inorganic material

The inorganic materials for the synthesis of separation membranes include ceramics, zeolite, glass, metals and metal oxides. The inorganic separation membrane has good thermal stability, chemical resistance, antimicrobial and mechanical properties. Thus, inorganic membranes are widely used in the system at high temperature, high pressure, and containing strong acid or alkaline[74].

2.3.6.4. Nanofiltration Membrane

Nanofiltration (NF) has a pore size between that of ultrafiltration (UF) and reverse osmosis (RO). The typical pore diameter of NF membranes is usually about 1 nm. The NF membranes usually can effectively remove divalent and high ionic ions, organic molecules with a molecular weight greater than 200 $g \cdot mol^{-1}$. Most of monovalent inorganic salt can permeate through NF membrane. Thus the NF membranes are widely used in food industry, medicine and biochemistry etc. The select layer of NF

membranes usually is composed of polyelectrolyte. Thus, NF membranes have charged surface layer. NF membranes can reject uncharged substances by steric interaction and reject charged substances by steric interaction and electrostatic interaction[75–78].

2.3.6.5. Reverse Osmosis Membrane

Reverse osmosis (RO) uses pressure to overcome the osmotic pressthe ure caused by concentration gradient of the solution, driving the solvent to permeate from the high concentration side to the low concentration side. Compared to the traditional separation technology such as evaporation and freeze drying, RO has the following advantages: 1. High separation efficiency, 2. Can remove a variety of impurities, 3. Low energy consumption, aince no phase change occurs during processing and no heating is required.

There are many model explanations for the mechanism of the RO separation process, including solution-diffusion model, preferential sorption-capillary flow model and irreversible thermodynamic approach[65,79].

In solution-diffusion model, the solvent and solute in the high pressure side solution are first dissolved in the membrane and then permeate through the membrane by molecular diffusion under the action of the chemical potential difference. The diffusion of solvents and solutes in the membrane obeys Fick's law. This model considers that both solvents

and solutes may be soluble in the membrane surface, so the permeability of the material depends not only on the diffusion coefficient, but also on its solubility of solute in the membrane. The diffusion coefficient of solute is much smaller than the diffusion coefficient of water molecules, so the amount of water molecules passing through the membrane is greater than the amount of solute that passes through the membrane[65,66].

In preferential sorption-capillary flow model, the RO membranes are hydrophilic. The solute is repelled at the surface of the membrane. Water molecules are preferentially adsorbed to the surface of the membrane and form a pure water thin film on the surface of membrane. Driven by pressure, water molecules in this film pass through the RO membrane through capillary pores. The thickness of the pure water film is usually 1 to 2 water molecules, which is 0.5 to 1 nm. The maximum flux rate is obtained when the effective diameter of the capillary pores on the surface of the membrane is twice the thickness of pure water film. When the capillary pore diameter is bigger than this diameter, the solute will leak from the center of the capillary[80,81].

2.3.7. Chemical Precipitation

Due to its efficiency, low cost and simple operation, chemical precipitation is widely used in industrial wastewater treatment. During chemical precipitation, the chemical additive reacts with heavy metal ions in wastewater to form insoluble particles or precipitates[82]. These precipitates or particles can be separated by filtration,

sedimentation or flocculation.

2.3.7.1. Hydroxide (Alkaline) Precipitation

Hydroxide precipitation is the most widely used precipitation process in industrial wastewater treatment. The hydroxide precipitation process is relatively cheap and easy to operate by adjusting the pH value. The optimal pH for hydroxide precipitation usually is between 8 to 11[83]. The addition of coagulants such as polymers, alum and iron salts can obviously increase the efficiency of precipitation and removal of heavy metal ions in wastewater. The coagulants can reduce the solubility of heavy metal ions in water[84]. Although the hydroxide precipitation is widely used in wastewater treatment, it still has some disadvantages. First, the hydroxide precipitation can not remove heavy metals when the complexing agents in wastewater inhibit the formation of metal hydroxide. Second, the hydroxide precipitation generates lots of sludge containing high proportion of water, which is hard to dispose of. Third, when there are multiple metal ions in wastewater, the pH that can precipitate one metal ion can dissolve some other metal hydroxide sediments, since some metal hydroxides are amphoteric[85].

2.3.7.2. Sulfide Precipitation

Comparing to the metal hydroxides, the metal sulfides have much lower solubility in water and are not amphoteric. The sulfide precipitation can be operated in a wide range

of pH. The sludge generated from sulfide precipitation also contains lower proportion of water, which means that it is easy to dewater. The combination of sulfide precipitation and sulfate-reducing bacteria (SRB) has been investigated by some researchers. SRB can transform sulfates to hydrogen sulfides under anaerobic conditions. The hydrogen sulfide reacts with heavy metal ions and generate insoluble metal sulfide sediment[86]. Although sulfide precipitation is very efficient, it still has disadvantages. First, during the sulfide precipitation, toxic hydrogen sulfide gas (H_2S) is formed easily. Second, the sulfide precipitation has a tendency to form colloidal precipitates, which are hard to separate from water.

2.3.7.3. Chelating Precipitation

Chelating precipitation is a relatively new technique for heavy metal removal from industrial wastewater. There are still a lot of works needed to be done to find a chelating precipitation agent with many binding sites for chelating and more environment friendly[87].

2.3.8. Chemical Precipitation Combined with Other Methods

Adding other heavy metal removal methods as the supplement of chemical precipitation can make up the limitations of chemical precipitation. Combination of chemical precipitation with nanofiltration; electro-Fenton process and ion exchange process have

been investigated by many researchers. It was shown that the combined processes can effectively decrease the heavy metal concentration in wastewater to meet recycling conditions and emission standards[88].

2.3.9. Chemical Precipitation Combined with Membrane Filtration

The research about combining chemical precipitation and membrane filtration are less. Gonzalez-Munoz et al. reported remove heavy metal ions by combining sulfide precipitation and nanofiltration. The result indicates that the combination of sulfide precipitation and nanofiltration can successful reduce the metal concentration and yielded permeate capable to directly reused in factory[89].

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Chapter 3. Alkaline and Carbonate Filtration for Lead Removal

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Abstract

In this study, the removal of Pb^{2+} ions by alkaline filtration, which is in essence the combination of alkaline precipitation and membrane filtration, was investigated. Three different membranes, i.e., microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) membranes, and three different alkalis, i.e., sodium hydroxide, sodium carbonate, and equimolar sodium carbonate and sodium bicarbonate mixture, were tested for this purpose at three different pH levels, i.e., pH 7, pH 8.5, and pH 10. The performance of alkaline filtration was evaluated by measuring the flux, the lead concentration in the permeate and the permeate pH. The morphology of particles in feed under different conditions was characterized by transmission electron microscopy (TEM) and particle size distribution estimated by fractionation with membranes of different pore sizes. It was established that under the optimal conditions, i.e., Na_2CO_3, pH 8.5-10, and UF membrane, the permeate lead level could be brought to below the drinking water standard, i.e., 10 ppb, when the feed contained 5 ppm Pb^{2+}. A hypothesis was proposed based on experimental evidences to explain the mechanism of alkaline filtration.

Key Words: membrane filtration, alkaline precipitation, lead, heavy metal removal

3.1. Introduction

There are 1.4 billion cubic kilometers water on planet earth. However, only 2.5% of it is freshwater. Furthermore, due to current technology limitations and distribution of freshwater, only less than 1% of the fresh water is readily available for the humanity and ecosystem. As a result, according to a survey of World Health Organization (WHO), the life of about 40% of people is affected by water shortage[1–3]. Even the limited water resource is now facing severe and fast increasing pressure of contaminations including heavy metal pollution.

Heavy metal contamination usually comes from industrial activities such as mining, smelting, combustion of coal and pipelines for water transportation. For instance, a public health crisis due to lead contamination of drinking water erupted in the City of Flint, Michigan, in 2014, when the municipality changed its water source from Lake Huron to the Flint River[4]. Flint River water had high chloride, high chloride-to-sulfate mass ratio, and no corrosion inhibitor, triggering a perfect storm of lead leaching into drinking water. Other major pathways for heavy metals to pollute water system include industrial wastewaters pathway and the air pathway, that is, heavy metals enter atmosphere through industrial exhaust emissions and then precipitate with rain or

natural settlement into soil or water systems[5].

Unlike organic matters, heavy metals are not biodegradable. They will circulate in ecosystem for a long time and be enriched by organisms moving up the food chain, which is a process called bioaccumulation. Consequently, these heavy metals may ultimately be picked up by human through food supply and be absorbed at a level much higher than they exist in contaminated water bodies [6–8]. Heavy metals can interfere the functionality or destroy the structure of proteins in organisms by complexing and cause a variety of acute or chronic diseases[9]. For examples, lead can destroy the nervous system and the immune system and cadmium can destroy liver and kidney[10–13].

Conventional technologies for heavy metal ions removal include coagulation and flocculation, adsorption, ion exchange, electrochemical treatment, flotation, membrane filtration, and chemical precipitation [14–17]. Coagulation and flocculation are widely used in water treatment, due to their low cost. However, coagulants and flocculants such as aluminum sulfate, alum, poly-aluminum chloride, ferric chloride and ferrous sulfate cannot remove heavy metal completely[18,19]. Most regular adsorbents, such as activated carbon[20] and zeolites, are expensive for treatment of large volumes of contaminated waters[21,22]. Bioadsorbents are relatively inexpensive but they are of low efficiency in wastewater treatment[20,23,24]. Common ion exchange resins have low capacity for exchanging heavy metal ions and need frequent regeneration, which ensues high

operation cost[21,25]. Electrochemical treatment can remove heavy metal ions efficiently, but it consumes plenty of electricity and might produce toxic and flammable gases during the operation[19,26,27].

As for membrane separation processes, conventional microfiltration (MF) and ultrafiltration (UF) membranes cannot remove heavy metal ions since they do not have surface charge and their pore sizes are too large for that purpose. Nanofiltration (NF) membranes have surface charges and much smaller pores but their pore sizes are still much larger than the size of hydrated heavy metal ions and can only partially reject them [28,29]. Reverse osmosis (RO) membranes can be used for heavy metal removal, but the flux of RO membranes is low and the required operating pressures are high, leading to high operating cost and energy consumption[30].

Chemical precipitation includes hydroxide precipitation (i.e., alkaline precipitation), carbonate precipitation[31], sulfide precipitation and chelating precipitation[14,18]. It can efficiently remove heavy metal ions at high concentration, but its effect is limited when metal concentration is low. Furthermore, chemical precipitation tends to form fine particles, which are slow to settle down by gravity or expensive to remove by centrifugation.

In this research, the combination of alkaline/carbonate precipitation and membrane

filtration was investigated. For convenience, we treat Na_2CO_3 and $NaHCO_3$, which are the agents used in carbonate precipitation, as two types of alkalis and name the process alkaline filtration. In particular, the removal of lead ions was studied at three different pH, i.e., 7, 8.5 and 10, using three different commercial membranes, i.e., MV020 (MF), UH050 (UF) and NF270 (NF), and three different alkalis, i.e., NaOH, Na_2CO_3 and the equimolar mixture of Na_2CO_3 and $NaHCO_3$, to adjust the feed pH and dissolved inorganic carbon (DIC) concentration. It is demonstrated that by combining with alkaline precipitation, both MF, UF and NF membrane could effectively remove lead ions and not surprisingly, MF offered the highest fluxes.

3.2. Materials and Methods

3.2.1. Material

Three commercial membranes, MV020 (MF membrane), UH050 (UF membrane) and NF270 (NF membrane) purchased from Sterlitech Corporation (WA, USA) were used in this work. N-butanol was purchased from Fisher Scientific (Fair Lawn, NJ). 3.0 μm filter paper (mixed cellulose esters (MCE) membrane) and 10 μm filter paper (Polytetrafluoroethylene (PTFE) membrane) were purchased from MF-Millipore (Etobicoke, Canada).

3.2.2. Preparation of Feed Solution

Lead (II) nitrate with the purity of 99% (ACS) was purchased from Strem Chemical Inc. (MA, USA). Nitric acid with purity of 68%-70% ACS, sodium hydroxide with purity of 98.9% ACS and sodium bicarbonate with purity of 99% FCC were purchased from Fisher Scientific (Fair Lawn, NJ). Sodium carbonate with purity of 99.5% ACS was obtained from Sigma Aldrich Inc. (St. Louis, MO). N-butanol was purchased from Fisher Scientific (Fair Lawn, NJ).

Stock lead nitrate solution of 100,000 ppm Pb^{2+} was prepared and diluted to 5 ppm by using deionized water of 17 MΩ·cm^{-1} resistivity before removal rests. The pH of solution was further adjusted to 7, 8.5 and 10 by adding a certain amount of one of the three alkaline solutions, i.e., 0.5 M NaOH, 0.5 M Na_2CO_3, or the mixture of equal volumes of 0.5 M Na_2CO_3 and 0.5 M $NaHCO_3$.

3.2.3. Solubility of Lead Ions in Feed

Alkaline precipitation could be described by the following equation:

$$Pb^{2+} + 2 \cdot OH^- \xleftrightarrow{k_{sp,Pb(OH)_2}} Pb(OH)_2 \quad (3\text{-}1)$$

$$k_{sp,Pb(OH)_2} = [Pb^{2+}] \cdot [OH^-]^2 \quad (3\text{-}2)$$

Therefore, the lead concentration at a given pH at 25°C can be calculated by the following equations,

$$[Pb^{2+}] = \frac{k_{sp,Pb(OH)_2}}{[OH^-]^2} \quad (3\text{-}3)$$

Where $[OH^-]$ and $[Pb^{2+}]$ are the concentration of OH^- and Pb^{2+} ions, respectively. $[OH^-]$ can be calculated by ionization balance of water.

$$H^+ + OH^- \overset{k_{sp,H_2O}}{\longleftrightarrow} H_2O \quad (3\text{-}4)$$

$$k_{sp,H_2O} = [H^+] \cdot [OH^-] = 10^{-pH} \cdot [OH^-] \quad (3\text{-}5)$$

$$[OH^-] = \frac{k_{sp,H_2O}}{[H^+]} = \frac{k_{sp,H_2O}}{10^{-pH}} = 10^{pH} \cdot k_{sp,H_2O} \quad (3\text{-}6)$$

Where k_{sp,H_2O} is solubility product constant of water, which is 1.01×10^{-14} $mol^{-2}\cdot L^{-2}$ at 25°C[32]. Combine Equations (3-3) and (3-6), $[Pb^{2+}]$ can be calculated by following equation (the unit of $[Pb^{2+}]$ is M).

$$[Pb^{2+}] = \frac{k_{sp,Pb(OH)_2}}{[OH^-]^2} = \frac{k_{sp,Pb(OH)_2}}{\left(10^{pH}\cdot k_{sp,H_2O}\right)^2} \quad (3\text{-}7)$$

Solubility of $PbCO_3$ is described by the following equilibrium. Where $k_{sp,PbCO_3}$ is solubility product constant (K_{sp}) of $PbCO_3$ which is 7.4×10^{-14} $mol^{-2}\cdot L^{-2}$ at 25°C[33].

$$Pb^{2+} + CO_3^{2-} \overset{k_{sp,PbCO_3}}{\longleftrightarrow} PbCO_3 \quad (3\text{-}8)$$

$$k_{sp,PbCO_3} = [Pb^{2+}] \cdot [CO_3^{2-}] \quad (3\text{-}9)$$

There are three DIC species, i.e., dissolved CO_2 (dCO_2), which is equivalent to H_2CO_3, bicarbonate HCO_3^-, and carbonate CO_3^{2+}. Among these DIC species, the following dissociation equilibriums are maintained[34].

$$H_2CO_3 \overset{k_{a1}}{\leftrightarrow} H^+ + HCO_3^- \quad (3\text{-}10)$$

$$H^+ + HCO_3^- \overset{k_{a2}}{\leftrightarrow} 2 \cdot H^+ + CO_3^{2-} \quad (3\text{-}11)$$

From the equilibrium (3-10) and (3-11), the following equations can be deduced.

$$k_{a1} = \frac{[H^+]\cdot[HCO_3^-]}{[H_2CO_3]} \quad (3\text{-}12)$$

$$k_{a2} = \frac{[H^+]^2\cdot[CO_3^{2-}]}{[H^+]\cdot[HCO_3^-]} = \frac{[H^+]\cdot[CO_3^{2-}]}{[HCO_3^-]} \quad (3\text{-}13)$$

Where k_{a1} and k_{a2} are the acid dissociation constant of H_2CO_3 (4.3×10^{-7} mol L^{-1}) and HCO_3^- (4.8×10^{-11} mol L^{-1}), respectively[33]. [The total [DIC] is given by the following equation:

$$[DIC] = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (3\text{-}14)$$

$$1 = \frac{[H_2CO_3]}{[DIC]} + \frac{[HCO_3^-]}{[DIC]} + \frac{[CO_3^{2-}]}{[DIC]} \quad (3\text{-}15)$$

Combine Equations (3-12), (3-13) and (3-14)[34], and use pH instead of $[H^+]$,

$$[H_2CO_3] = \frac{[DIC]}{1+\frac{k_{a1}}{[10^{-pH}]}+\frac{k_{a1}\cdot k_{a2}}{[10^{-pH}]^2}} \quad (3\text{-}16)$$

$$[HCO_3^-] = \frac{[DIC]}{1+\frac{[10^{-pH}]}{k_{a1}}+\frac{k_{a2}}{[10^{-pH}]}} \quad (3\text{-}17)$$

$$[CO_3^{2-}] = \frac{[DIC]}{1+\frac{[10^{-pH}]}{k_{a2}}+\frac{[10^{-pH}]^2}{k_{a1}\cdot k_{a2}}} \quad (3\text{-}18)$$

When precipitation occurs [DIC] is no longer the initial DIC, which is called $[DIC]_{start}$, since CO_3^{2-} co-precipitates with lead and [DIC] decreases. [DIC] after the lead ion precipitation, which is called $[DIC]_{final}$ is therefore smaller than $[DIC]_{start}$. Considering

that the decrease of the molar concentration of CO_3^{2-} by precipitation is equal to the decrease of the molar concentration of Pb^{2+} according to equation (3-8), $[DIC]_{final}$ becomes:

$$[DIC]_{final} = [DIC]_{start} - [Pb^{2+}]_{precipitate} \quad (3\text{-}19)$$

$$[DIC]_{final} = [DIC]_{start} - \left([Pb^{2+}]_{start} - [Pb^{2+}]_{final}\right) \quad (3\text{-}20)$$

Where $[Pb^{2+}]_{precipitate}$, $[Pb^{2+}]_{start}$ and $[Pb^{2+}]_{final}$, respectively, denote the decrease of Pb^{2+} concentration due to precipitation, initial Pb^{2+} concentration in the feed, and finial Pb^{2+} concentration in the feed.

It should be noted that, in the case of the addition of Na_2CO_3 or the equimolar mixture of Na_2CO_3 and $NaHCO_3$, two solutions of $[Pb^{2+}]$ were obtained either via Equation (3-7) or via Equations (3-9), (3-18) and (3-20). The smaller value of the two was adopted as the predicted dissolved lead concentration.

Equations (3-21) and (3-22) show the relationship between partial pressure of carbon dioxide in the atmosphere and dissolved CO_2 (H_2CO_3).

$$P_{CO_2} = K_{CO_2} \cdot [H_2CO_3] = K_{CO_2} \cdot \left[CO_{2(aq)}\right] \quad (3\text{-}21)$$

$$P_{CO_2} = P_{atm} \cdot [CO_2]_{\%} \quad (3\text{-}22)$$

Where K_{CO_2} is the Henry's constant of CO_2 (29.41 L·atm·mol^{-1} at 25°C[33]), P_{CO_2} indicates partial pressure of CO_2 (atm), P_{atm} is the atmosphere pressure which is 1

atm and $[CO_2]_{\%}$ is the fraction of CO_2 in atmosphere. Combine the equation (3-16), (3-21) and (3-22) the [DIC] can be calculated at certain atmosphere pressure, CO_2 content in air and pH of solution. The CO_2 content in room usually between 0.05% and 0.07% at 25°C.

3.2.4. Alkaline Filtration

Alkaline filtration experiments were carried out with a static filtration cell illustrated in Figure 3-1, where V_1, V_2, V_3, G_1, G_2 and G_3 are valves and pressure gauges for controlling pressure of the feed chamber. A membrane with an effective area of 0.0013 m^2 is mounted at the bottom of the filtration cell on a filter paper placed at the surface of a sintered metal plate. Above the membrane there is a feed chamber with a capacity of 325 mL equipped with a magnetic stirrer. Pressure is applied to the feed chamber from a nitrogen cylinder via a pressure regulator. An operating pressure of 43.5 psig was applied when the membranes were NF270 (NF membrane) or UH050 (UF membrane), while 15 psig was applied for MV020 (MF membrane). The permeate weight is automatically recorded by computer every ten seconds in this filtration system.

The membrane was washed by deionized water before being mounted to the filtration cell. After assembling the filtration system, 300 mL of feed solution was loaded into the feed chamber. Then, the pressure was adjusted to the predetermined value and the magnetic stirrer was turned on. Upon starting filtration, the initial 10 g of permeate was

collected and discarded. Then, 10 g of permeate was collected and its lead ion concentration was measured by Flame Atomic Absorption Spectrometer (FAAS, Thermo Fisher Scientific) after adding 0.2 mL of nitric acid (68%-70%) to dissolve the lead containing particles and stabilize lead ions in permeate. Furthermore, 3 g of permeate was collected to measure pH by a pH meter (Fisher Scientific).

After collecting the above samples, the permeate was collected into a vessel placed on a balance and the permeate weight was recorded automatically by a computer every 10 s until the amount of the collected permeate became 100 g. Then, the used membrane was removed from the filtration cell, rinsed with deionized water and its surface was cleaned with a rubber scarper. The membrane was rinsed again with deionized water, before being stored in deionized water.

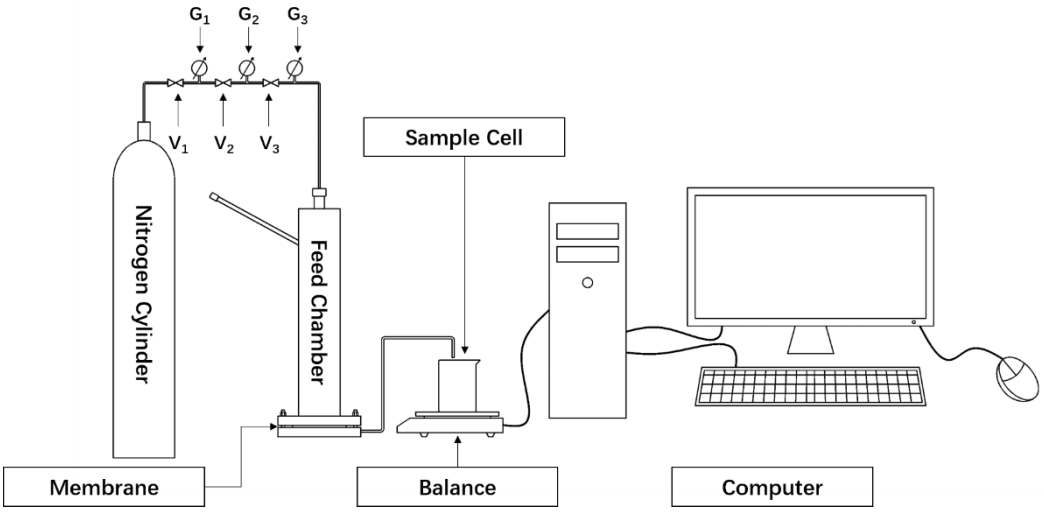

Figure 3-1 Setup for filtration

The average flux of the membranes can be calculated by following equation[35].

$$J = \frac{w}{\rho t A} \quad (3\text{-}23)$$

Where J is the flux ($m^3 \cdot h^{-1} \cdot m^{-2}$) of the membrane, w is the weight (kg) of permeate collected during filtration time t (h), ρ is the permeate density (kg m^{-3}) and A is the effective area (m^2) of membrane, which was 0.0013 m^2.

3.2.5. Fouling Estimation

To estimate the membrane fouling in association with the alkaline filtration at pH 8.5 with Na_2CO_3 for pH adjustment, pure water permeation experiments were carried out with fresh membrane coupons; then, the same membrane was used in alkaline filtration of 5 ppm Pb^{2+} lead nitrate solution at pH 8.5 with Na_2CO_3 for pH adjustment; and finally the membrane was removed from the filtration cell, rinsed with deionized water, surface-cleaned using a rubber scraper, and rinsed again with deionized water before being subjected to a second pure water permeation test.

3.2.6. Alkaline Precipitation

Alkaline precipitation was simulated by centrifuging feed solution adjusted to pre-determined pH values using a selected 0.5 M alkaline solution. Centrifugation was carried out within 30 min of pH adjustment and 50 mL of feed solution was centrifuged for 45 min at 6000 rpm (×3420 g). Then, 10 mL of the supernatant was collected and 0.1 mL nitric acid (68%-70%) was added to stabilize the lead ions before the sample

was subjected to the flame ionization analysis.

3.2.7. Particle Fractionation with Membranes of Different Pore Sizes

The size distribution of precipitating particles in the feed solution was estimated by fractionation using two membranes with pore diameters of 10 and 3 μm, respectively. Alkaline solution (either Na_2CO_3 or NaOH) was added to 200 mL of the feed solution to adjust pH to a desired value, followed by suction filtration with 10 μm membrane. Then, 200 μL of 70% HNO_3 was added to 10 mL of the filtrate sample, followed by the lead concentration measurement by AAS. The proportion of particles whose diameters are 10 μm or larger is calculated by the following equation.

$$r_{>10\mu m} = \frac{m_{>10\mu m}}{m_{total}} = \frac{m_{total} - m_{permeate-10}}{m_{total}} = 1 - \frac{m_{permeate-10}}{m_{total}} \quad (3\text{-}24)$$

Where $r_{>10\mu m}$ is the proportion of the particles whose diameters are bigger than 10 μm, $m_{>10\mu m}$ is the amount of lead in the particles whose diameters are bigger than 10 μm, m_{total} is the total amount of lead in the solution (= the amount of lead in feed solution) and the $m_{permeate\text{-}10}$ is the amount of lead in the filtrate. The amount of lead in the feed and filtrate is calculated by,

$$m_{total} = m_{feed} = C_f \cdot V_f \quad (3\text{-}25)$$

$$m_{permeate-10} = C_{p-10} \cdot V_{p-10} \quad (3\text{-}26)$$

Where m_{feed},, C_f and V_f are the amount of lead, lead concentration (ppm) and volume,

respectively, of the feed solution and $C_{p\text{-}10}$ and $V_{p\text{-}10}$ are lead concentration (ppm) and volume, respectively, of the filtrate. Since $V_{p\text{-}10} \approx V_f$,

$$r_{>10\mu m} = 1 - \frac{m_{permeate-10}}{m_{total}} \tag{3-27}$$

$$r_{>10\mu m} = 1 - \frac{C_{p-10} \cdot V_{p-10}}{C_f \cdot V_f} \approx 1 - \frac{C_{p-10} \cdot V_f}{C_f \cdot V_f} = 1 - \frac{C_{p-10}}{C_f} \tag{3-28}$$

Similarly, the proportion of particles whose diameters are 3 μm or larger, $r_{>3\mu m}$, and the proportion of particles whose diameters are less than 3 μm, $r_{>3\mu m}$, can be calculated, respectively, by

$$r_{>3\mu m} = 1 - \frac{C_{p-3}}{C_f} \tag{3-29}$$

$$r_{<3\mu m} = 1 - \left(1 - \frac{C_{p-3}}{C_f}\right) = \frac{C_{p-3}}{C_f} \tag{3-30}$$

Where $C_{p\text{-}3}$ is the lead concentration in the filtrate of 3 μm filter membrane. Since the Pb^{2+} is present in the feed solution, $r_{>3\mu m}$ includes not only the particles whose diameter is less than 3 μm but also unprecipitated Pb^{2+}, which is ignorable when pH is 8.5 or higher.

Then, the proportion of the lead particles whose diameters are between 3 and 10 μm, $r_{3\sim10\mu m}$ is,

$$r_{3\sim10\mu m} = 1 - \left(r_{>10\mu m} + r_{<3\mu m}\right) \tag{3-31}$$

$$r_{3\sim10\mu m} = 1 - \left(1 - \frac{C_{p-10}}{C_f} + \frac{C_{p-3}}{C_f}\right) = \frac{C_{p-10}}{C_f} - \frac{C_{p-3}}{C_f} \tag{3-32}$$

3.2.8. Zeta-Potential

The zeta-potential of the lead containing particles was measured by Zetasizer Nano Z (Malvern Panalytical, Worcestershire, UK). The feed samples whose pH was adjusted 7, 8.5 and 10 by adding Na_2CO_3 or NaOH solution were subjected to Zeta potential measurement.

3.2.9. TEM

For the feed lead nitrate solution whose pH was adjusted to 8.5 by adding Na_2CO_3 solution, the morphology of particles in feed was investigated by transmission electron microscopy (TEM) (JEM-2100F FETEM, JEOL, Japan).

3.2.10. Membrane Characterization

The porosity of the membrane was measured by the wet dry method[35]. Briefly, the support layer of MF, UF and NF membranes were peeled off from the top layer carefully using a plastic tweezer, when applicable. The membrane (or the top layer of the membrane) was cut into three 1×1 cm square samples and the thickness of each sample was measured by a Vernier caliper. Then, the sample was immersed in n-butanol for 24 h, ensuring that n-butanol completely wetted the membrane pores. N-butanol on the surface of the membrane sample was wiped by a rubber scraper, followed by weighing of the wet membrane sample. After drying the membrane sample in an oven for 24 h at

50°C to completely evaporate the n-butanol, the dry sample was weighed. The overall porosity of membranes can be calculated by following equation[35].

$$\varepsilon = \frac{w_w - w_d}{A_{sample} \cdot l \cdot \rho_{butanol}} \quad (3\text{-}33)$$

Where ε is the overall porosity, w_w is the weight (g) of the wet membrane sample, w_d is the weight (g) of the membrane sample after drying, A_{sample} is the area of the membrane sample (cm^2), l is the thickness (cm) of the dry membrane sample and $\rho_{butanol}$ is the density ($g \cdot cm^{-3}$) of n-butanol. Three samples were used for the measurement and the average value was reported.

Water contact angle of the membranes was measured by the sessile method using the VCA Optima Surface Analysis System (AST Product, Inc. Billerica, MA, US) at 20°C. 2 μL deionized water droplet was placed on the surface of the dry membrane to measure the contact angle. The measurement was made at 5 random spots of the membrane surface and the average value was reported.

The membrane surface was investigated by scanning electron microscopy (SEM) (JSM-7500F FESEM, JEOL, Japan). The accelerating voltage was 2 kV and the working distance was 10 mm.

3.3. Results and Discussion

3.3.1. Alkaline Precipitation of Pb^{2+} by NaOH and Na_2CO_3

Alkaline filtration is in essence the combination of alkaline precipitation and membrane filtration. It is therefore of interest to exam lead removal by alkaline precipitation as the baseline. Table 3-1 summarize the [Pb^{2+}] in supernatant under different alkaline precipitation conditions. The calculated values were determined using equations presented in Section 2.3 while the experimental values were obtained by determining the [Pb^{2+}] in the supernatant of centrifuging feed solution two hours after adjusting its pH to a pre-set value, i.e., 7, 8.5 or 10, using one of the three alkalis. Two hours was pre-determined to be sufficient for the feed solution to reach equilibrium. It should be noted that the [Pb^{2+}] of NaOH precipitation was calculated using Equations (3-7) with the assumption of no existence of DIC in the solution and that of Na_2CO_3 precipitation (low DIC) and mixed alkaline (i.e., equimolar $NaHCO_3$ and Na_2CO_3) precipitation were calculated using obtained by Equations (3-9), (3-17) and (3-18) because the solubility of $PbCO_3$ is much lower than that of $Pb(OH)_2$ or $Pb(HCO_3)_2$ under the same conditions. All three anions, i.e., OH^-, HCO_3^-, andCO_3^{2-} , were available in alkaline precipitation where DIC was involved. The [HCO_3^-] and [CO_3^{2-}] under different conditions are also listed in Table 3-1 for reference.

As can been seen from Table 3-1, the calculated supernatant [Pb^{2+}] (i.e., the saturation [Pb^{2+}]) decreased exponentially with pH no matter what alkali was used. However, the experimental supernatant [Pb^{2+}] were largely unchanged except for experimental errors while compared for the same alkali at different solution pH. Furthermore, the experimental supernatant [Pb^{2+}] were similar to each other when DIC was involved, i.e., in both the low DIC and high DIC precipitation, which was much lower than that of NaOH, i.e., non-DIC, precipitation. These result indicate that the experimental supernatant [Pb^{2+}] was controlled not by the solubility of lead salts but by the completeness of centrifugation, which relied heavily on particle size and morphology. In other words, a significant portion of the fine $PbCO_3$ or $Pb(OH)_2$ particles formed under these conditions could not be removed by centrifugation under the specified conditions. It is worth noting that the supernatant lead concentration were 18-170 times of the drinking water standard of Canada, which is 10 ppb[36].

Table 3-1 Effect of pH and alkali on permeate lead concentration by experiment (n=3) and calculation

pH			7	8.5	10
Lead concentration (ppm)	NaOH	Calculated	29570.4	29.57	2.96×10^{-2}
		Experimental	1.45±0.0050	1.21±0.0008	1.70±0.0021
	Na_2CO_3	Calculated	1.011	2.25×10^{-2}	1.82×10^{-4}
		Experimental	0.18±0.0001	0.39±0.0053	0.36±0.0059
	Mix solution	Calculated	0.651	1.04×10^{-2}	9.95×10^{-5}
		Experimental	0.37±0.0020	0.50±0.0127	0.36±0.0001
DIC Concentration (M)	Na_2CO_3	HCO_3^-	3.17×10^{-5}	4.5×10^{-5}	1.76×10^{-4}
		CO_3^{2-}	1.52×10^{-8}	6.81×10^{-7}	8.44×10^{-5}
	Mix solution	HCO_3^-	4.92×10^{-5}	9.71×10^{-5}	3.22×10^{-4}
		CO_3^{2-}	2.35×10^{-8}	1.47×10^{-6}	1.54×10^{-4}

3.3.2. Properties of Membranes

Table 3-2 lists the properties of the three membranes used in this study, including the porosity and contact angel, which were measured in this study, and other properties that were specified by manufacturers. The porosity was 43.0%, 69.6% and 70.0% and the contact angle 40.6°±3.57°, 70.91°±4.66° and 16.84°±0.97°, for MF, UF, and NF membranes, respectively. The NF membrane was made of hydrophilic polymer polyamide (PA) and was of the lowest contact angle among the three, i.e., 16.84°±0.97°. MF and UF were both made of hydrophobic polymers, i.e., polyvinylidenefluoride (PVDF) and polyethersulfone (PESH), respectively. As a result, their contact angles were much higher than the NF, i.e., 40.6°±3.57° and 70.91°±4.66° for the MF and UF membrane, respectively. These contact angles are nonetheless both smaller than 90°, probably due to the existence of pores and surface roughness of the membranes.

Figure 3-2 shows the SEM images of unused MF, UF and NF membranes at magnifications of ×5000 and ×50000. The MF membrane has a large number of pores at surface, while pores were not observed for UF and NF membranes even at ×50000 magnification. The surface of UF membranes are relatively smooth and that of the NF membranes are rough with many circular up-lifts.

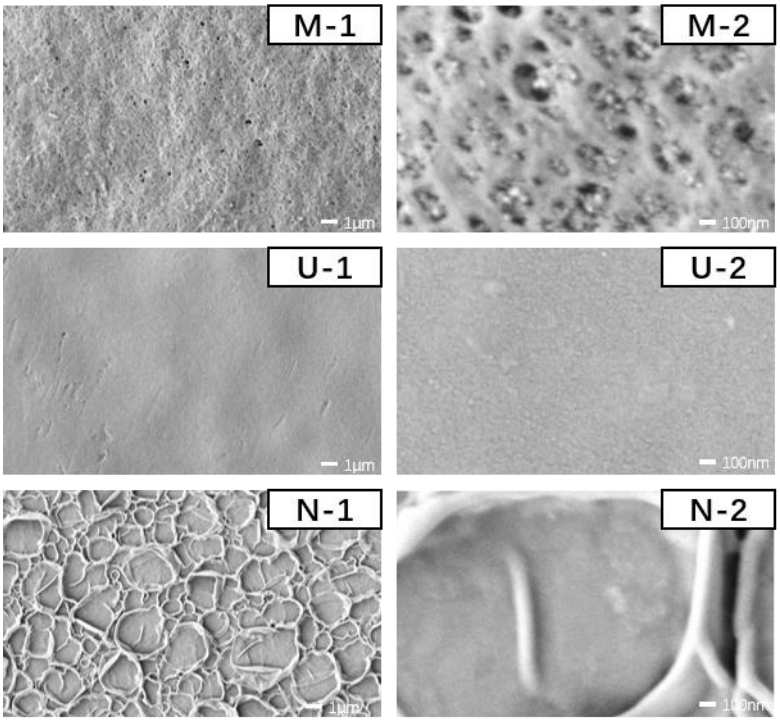

Figure 3-2 SEM images at different magnifications for membranes before filtration. M, U and N represent MF, UF and NF membranes

Table 3-2 Properties of membrane coups

Membrane	MF	UF	NF
Manufacturer	Microdyn Nadir	Microdyn Nadir	Dow Filmtec
Product Series	MV020	UH050	NF270
Material*	PVDF	PESH	PA
Operating pH at 25°C	2-11	0-14	2-11
Pore size/MWCO*	0.2 μm	50,000 Da	200-400 Da
Porosity (%)**	43.0	69.6	70.0
Contact Angle**	40.6°±3.57°	70.91°±4.66°	16.84°±0.97°

* Abbreviations: PVDF, poly vinylidenefluoride; PESH, polyethersulfone of high molecular weight; PA, polyamide; MWCO, cutoff molecular weight.

** Membrane properties measured experimentally in this study; others were provided by manufacturers

3.3.3. Flux of Alkaline Filtration

Table 3-3 summarizes the permeate flux and [Pb^{2+}] of alkaline filtration under different

conditions. The fluxes were several times higher with MF than with UF, which were magnitudes higher than with NF, when other conditions were the same. This is quite natural due to the vastly different pore sizes of these three membrane as shown in Table 3-2. On the other hand, the effects of pH and alkali on permeate flux were mixed without clear trends. One rather unusual observation is that the permeate fluxes of alkaline filtration with MF and NF decreased dramatically when feed pH increased from 8.5 to 10 with NaOH, while the flux changes in association with the same pH change were much less with NF or with alkalis rather than NaOH.

Table 3-3 Effect of pH and alkali on the permeate flux ($kg \cdot h^{-1} \cdot m^{-2}$) and [$Pb^{2+}$] in permeate (ppb) of alkaline filtration with MF, UF, and NF membranes when [Pb^{2+}] in feed was 5000 ppb (n=3)

		pH 7		pH 8.5		pH 10	
		[Pb^{2+}]	Flux	[Pb^{2+}]	Flux	[Pb^{2+}]	Flux
MF	Non-DIC	1926.4±420.3	6480±55	439.1±284.7	7242±45	**ND***	440±51
	Low-DIC	319.5±57	8418±46	38.4±19.9	4348±46	44.0±14.4	4630±13
	High-DIC	382.4±33.2	9748±21	134.3±32.8	6471±35	56.5±23.9	7791±22
UF	Non-DIC	1955.2±533.3	899±17	386.2±192.8	1350±12	**3.2±5.5**	171±25
	Low-DIC	246.5±13.5	1310±11	6.4±9.3	1071±15	28.4±4.6	1172±11
	High-DIC	299.7±14.0	1117±6	130.5±25.1	878±13	28.3±32.5	864±17
NF	Non-DIC	2267.2±262.6	30.57±3.2	746.7±194.8	46.76±5.5	**ND**	35.66±4.5
	Low-DIC	412.0±52.2	38.89±3.7	11.4±14.9	45.19±4.1	8.3±5.5	33.24±1.2
	High-DIC	334.2±23.4	26.10±3.6	270.4±93.7	27.92±2.0	10.6±18.4	20.67±1.7

* ND - not detectable

As also summarized in Table 3-3, different membranes did not show significant influence on Pb^{2+} rejection when other conditions were the same. Whereas increasing pH from 7.0 to 8.5 and then to 10.0 was always associated with increase of lead rejection, i.e., decrease of [Pb^{2+}] in permeate. On the other hand, the effects of different

types of alkalis were mixed, depending on the pH of feed solution. From the lead rejection perspective, the lead concentration in permeate was lower than the drinking water standard of Canada, i.e., 10 ppb, in MF/UF/NF filtration with NaOH (i.e., non-DIC) at pH10, and NF filtration with Na_2CO_3 at pH10. Another two conditions, i.e., UF filtration with Na_2CO_3 at pH8.5 and NF filtration with Na_2CO_3 at ph10 may also produce permeate with lead concentration lower than 10 ppb but the variation of results are too large for reliable water treatment.

3.3.4. Permeate pH

Figure 3-3 shows the permeate pH at different conditions of alkaline filtration. The dotted columns are the initial pH of feed solutions and the Feed* columns depict the pH of feed solutions 2 hours after the initial pH measurement, which is called equilibrium feed pH in this study. Under all conditions, the equilibrium feed pH was significantly lower than the initial feed pH. On the other hand, the equilibrium did not show significant difference from the permeate pH no matter what membrane was used for filtration. These results are reasonable because none of MF, UF nor NF could reject HO^- or H^+. Whereas formation of precipitating $Pb(OH)_2$ or $PbCO_3$ would cause pH decrease by either removing OH^- or releasing H^+ via the following reactions:

$$Pb^{2+} + 2 \cdot OH^- \rightarrow Pb(OH)_2 \quad (3\text{-}34)$$

$$Pb^{2+} + HCO_3^- \rightarrow PbCO_3 + H^+ \quad (3\text{-}35)$$

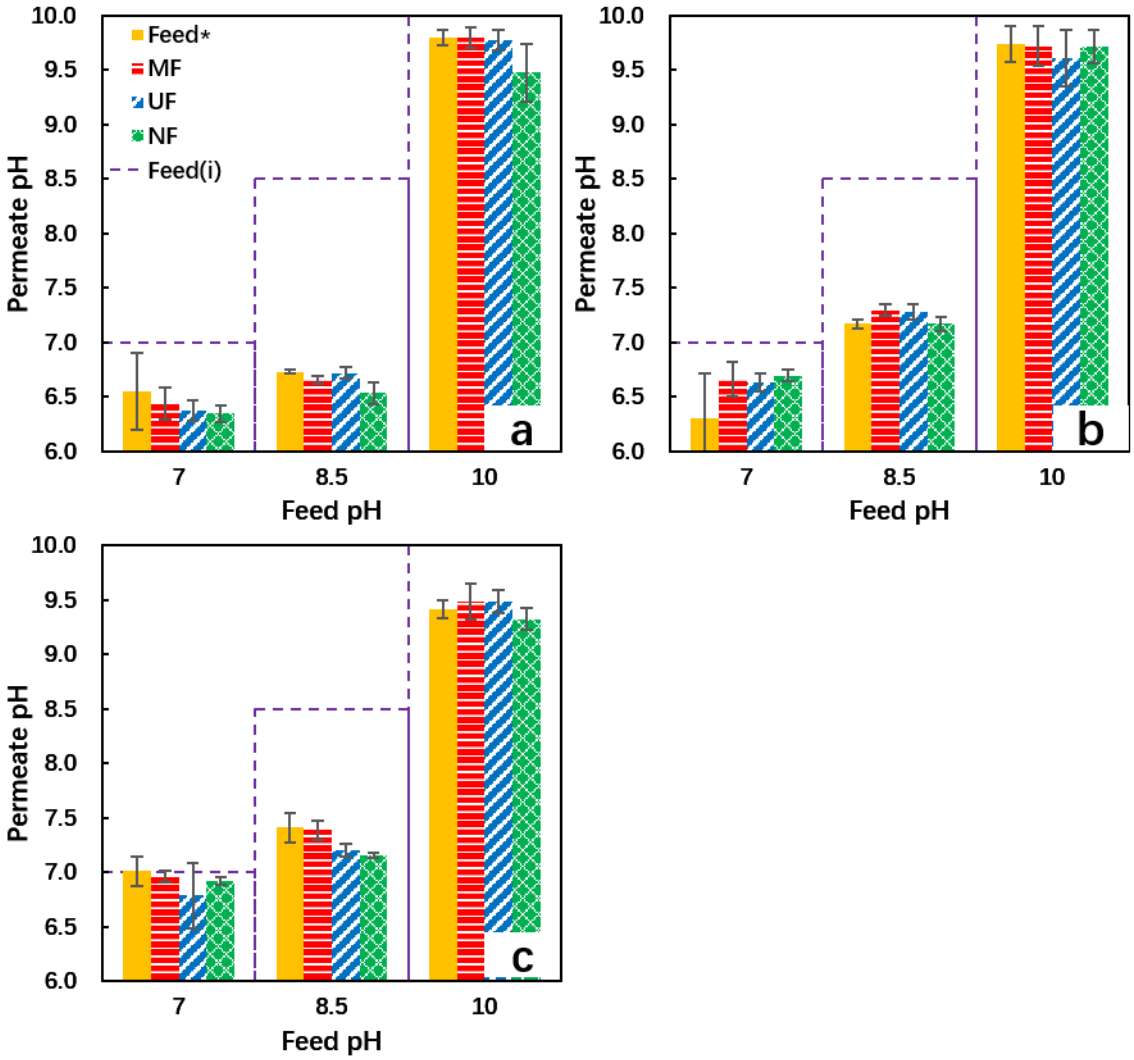

Figure 3-3 Permeate pH at different initial feed pH values when alkaline filtration was carried out with MF, UF, or NF with: (a), 0.5 M NaOH (i.e., Non-DIC); (b), 0.5 M Na_2CO_3 (i.e., Low-DIC); and (c), mixture of 0.25 M Na_2CO_3 and 0.25 M $NaHCO_3$ (i.e., High-DIC). Feed(i) is the initial pH of feed right after alkali addition and Feed* is the pH of feed after stabilization by standing still for 2 hours or longer.

It is obvious that the pH decreases at initial pH 8.5 was the largest no matter what kind of alkali was used for pH adjustment. This observation could be explained as follows.

At pH 7, the saturation concentration of Pb^{2+} ions was all much higher than 5 ppm no matter what of the three alkalis was used for pH adjustment. Consequently, only a very

small amount of precipitation could be formed because of local high NaOH or Na_2CO_3 concentration in the pH adjusting process when alkali solution was added drop by drop. Therefore, very little precipitation would be formed and hence the small decrease of pH.

On the other hand, at pH 10, $[OH^-]$ was 1×10^{-4} M, which was 6.64 times of the Pb^{2+} concentration in feed, i.e., 5 ppm (or 1.506×10^{-5} M). As a result, the impact of OH^- consumption or H^+ release in association with the formation of $Pb(OH)_2$ or $PbCO_3$ was limited.

When the initial feed pH was 8.5, the $[OH^-]$ was 3.16×10^{-6} M, which was only 21% of the initial Pb^{2+} concentration. Therefore, the formation of $Pb(OH)_2$ precipitation had a significant impact on solution $[OH^-]$ and hence the large pH decrease. In fact, these results indicate that the OH^- existed in the feed solution with an initial pH of 8.5 was not sufficient to completely remove 5 ppm Pb^{2+}. This could partially explain the high Pb^{2+} concentration in permeate when NaOH was used to adjust initial feed pH to 8.5, in comparison to that when Na_2CO_3 was used to adjust feed to the same pH (Table 3-3) The latter did reply on formation of $Pb(OH)_2$ for lead removal.

3.3.5. Fractionation of Particles in Feed by Membranes of Different Pore Sizes

Table 3-4 shows the percentage of lead removal by alkaline filtration using MF membranes of pore sizes of 10 and 3 μm sequentially at different pH levels using NaOH or Na_2CO_3 for pH adjustment. Feed solution was first filtrated through the 10 μm membrane and then the permeate was filtered through the 3 μm membrane. Since the primary lead rejection mechanism of alkaline filtration is the size rejection of $Pb(OH)_2$ or $PbCO_3$ particles by membrane, these data could also be interpreted as a rough estimation of the size distribution of particles under different conditions. This approach was used to estimate the particle size distribution because the amount of particles formed with 5 ppm was too small for measurement using conventional approaches.

As shown in Table 3-4, both pH and alkali had significant influence on particle size distribution and therefore lead removal. When Na_2CO_3 was the alkali for pH adjustment, more than 97% lead removal could be achieved by the 3 μm membrane at all three pH levels. On the other hand, when NaOH was the alkali, the 3 μm membrane could remove 90.18% of lead at pH 10 but only about 49.25 and 56.50% at pH 7 and pH 8.5, respectively. These results suggest that NaOH as alkali led to formation $Pb(OH)_2$ that were finer than the $PbCO_3$ particles formed when Na_2CO_3 was the alkali. These results are in accordance to the alkaline precipitation results (Table 3-1), which registered

much higher supernatant lead concentration when NaOH was used for pH adjustment than when Na_2CO_3 or equimolar mixture of Na_2CO_3 and $NaHCO_3$ was used for pH adjustment.

Table 3-4 Particle size distribution of feed

pH		7	8.5	10
Na_2CO_3	10 μm	49.69%	25.04%	7.48%
	3 μm-10 μm	47.44%	72.38%	91.45%
	<3 μm & ions	2.87%	2.58%	1.07%
NaOH	10 μm	25.33%	29.40%	46.84%
	3 μm-10 μm	23.93%	27.10%	43.34%
	<3 μm & ions	50.75%	43.50%	9.82%

3.3.6. Zeta Potential

As shown in Figure 3-4, the zeta potentials of particles in feed solutions were zero at pH 7 but negative at pH 8.5 and pH 10 with either NaOH or Na_2CO_3 as the alkali. However, the negative zeta potential of particles at the same basic pH, i.e., 8.5 or 10, in the feed solution containing Na_2CO_3 were magnitudes higher than that in the feed solution when NaOH was the alkali. When NaOH was the alkali, the average Zeta potential was 0 mV at feed pH 7, -0.46 mV at 8.5 and -9.65 mV at pH 10. When Na_2CO_3 was the alkali, on the other hand, the average Zeta potential was -0.1, -32 and -62.8 mV at pH 7, 8.5 and 10, respectively. The larger negative Zeta potential for Na_2CO_3 is likely due to the higher negative valence of CO_3^{2-}, which is a bivalent anion, whereas OH^- is a monovalent anion. The CO_3^{2-} groups at the $PbCO_3$ particle surfaces would therefore

have larger negativity than the OH^- groups at the $Pb(OH)_2$ particle surfaces. The fact that larger portion of $PbCO_3$ particles were large particles in comparison to that of $Pb(OH)_2$ particles (Table 3-4) may also contributed to the different zeta potential as observed.

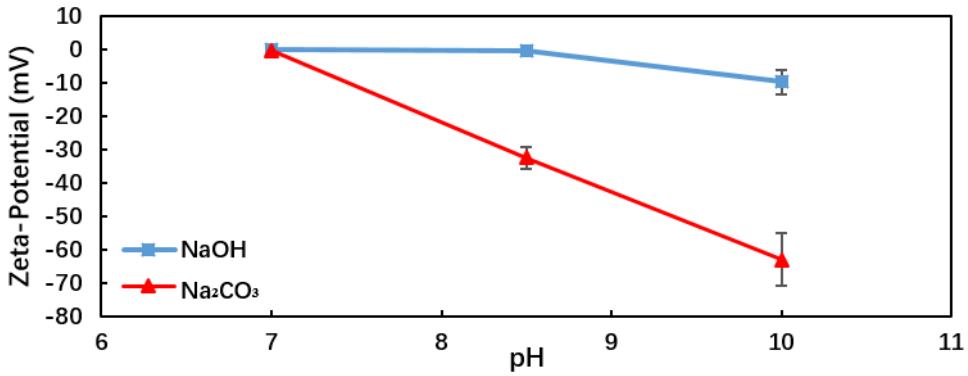

Figure 3-4 Zeta potential of particles in the feed solution

3.3.7. Particle Morphology

Figure 3-5 shows the morphology of $Pb(OH)_2$ particles (i.e., the particles with NaOH as the alkali) and $PbCO_3$ particles (i.e., particles obtained using Na_2CO_3 as the alkali) in feed solution at initial pH 8.5. The TEM image shows that by adjusting feed solution pH to 8.5 using 0.5 M Na_2CO_3, the formed $PbCO_3$ particles were thin snowflake-like particles. The particles were so thin that the darkening of the shadow could be observed at the overlap of two particles. These particles may form an agglomerate layer with small pores on the surface of the membrane, which would be able to reject fine particles. This might have facilitated the adsorption of free Pb^{2+} cations in solution on to the

partially negatively charged particle surfaces. Fine particles whose diameter was smaller than 30 nm could also be observed in feed solution.

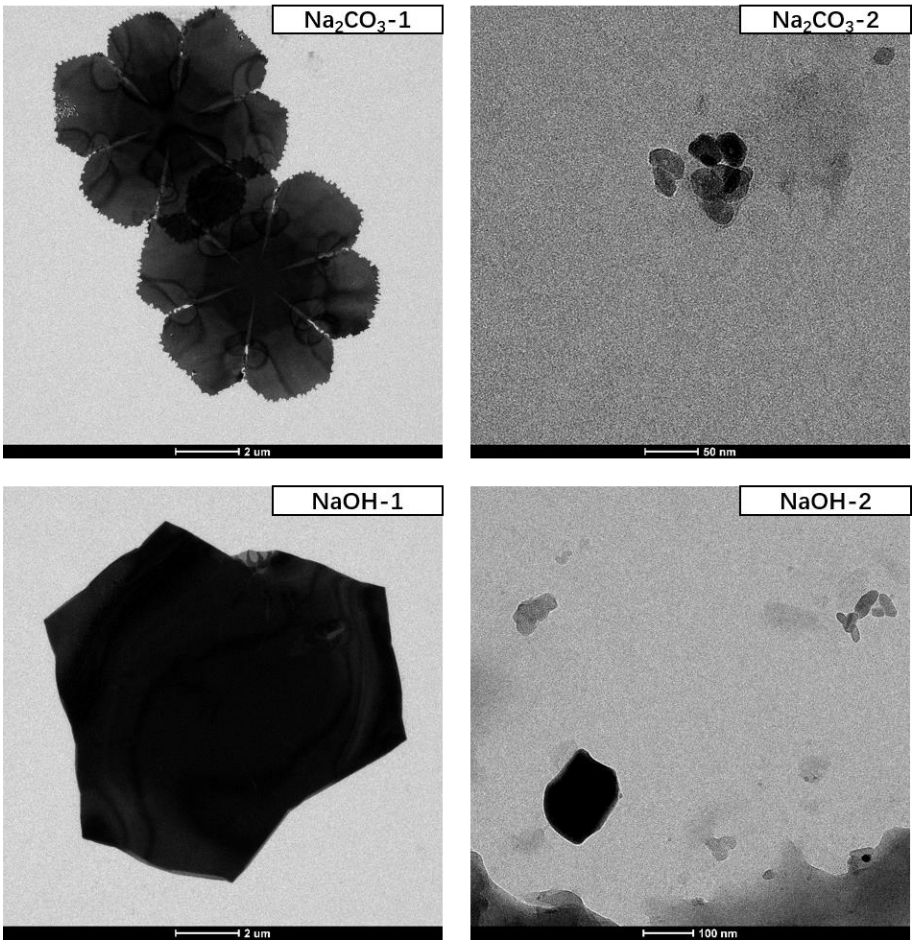

Figure 3-5 TEM image of lead particles in feed at different magnifications adjusting pH to 8.5 by adding sodium hydroxide or sodium carbonate

When NaOH was the alkali for pH adjustment, the $Pb(OH)_2$ precipitation tend to form denser particles. Fine particles whose diameter smaller than 20 nm were also observed in the feed solution.

3.3.8. Fouling of Different Membranes

Figure 3-6 shows the relationship of permeate weight and time in alkaline filtration at pH 10 using NaOH or Na_2CO_3 as the alkali for pH adjustment and MF membrane (a) or UF membrane (b) for filtration. It is clear that the permeate flux as indicated by the slope of the NaOH curve were much larger than that of the Na_2CO_3 with either MF or UF membrane, indicating that NaOH alkaline filtration had a much larger flux than Na_2CO_3 alkaline filtration, which is consistent with the data reported in Table 3-3. In all four cases, the slopes decreased continuously in the early stage of filtration, indicating a strong fouling effect in the early stage, after which the curves became linear, indicating the formation of a stable fouling layer on membrane surface. In Na_2CO_3 filtration, the fouling stage lasted for only 20-50 seconds for the MF membrane and 200-310 seconds for the UF membrane. In NaOH filtration at pH 10, however, the fouling period was about 600 s for MF membranes and 1600 s for UF membranes. The fouling time can be regarded as the time a fouling layer was built up at the membrane surface under individual conditions.

The different fouling time of Na_2CO_3 filtration and NaOH filtration could be tentatively explained by the morphology and particle size distribution of particles in these two different scenarios. As aforementioned, more than 97% of the $PbCO_3$ particles formed in Na_2CO_3 filtration were retained by 3 μm membrane while approximately 43.50% of

$Pb(OH)_2$ particles formed in NaOH filtration could pass the same membrane. Furthermore, the flake-shaped morphology of $PbCO_3$ particles may be beneficial for fast formation of the fouling layer.

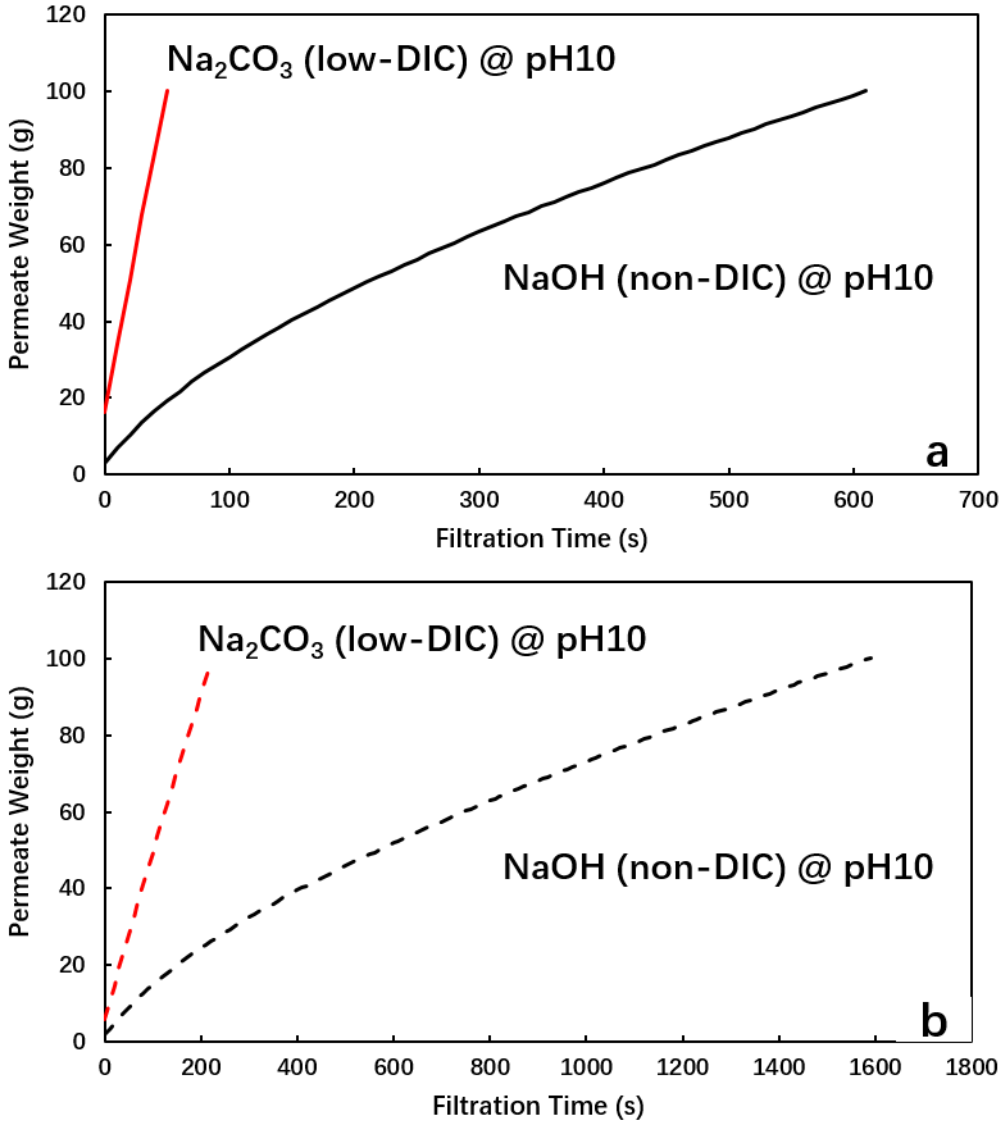

Figure 3-6 Permeate weight change with time in alkaline filtration with NaOH or Na_2CO_3 at pH 10 with MF (a) and UF membranes (b)

3.3.9. Mechanism of Lead Rejection in Alkaline Filtration

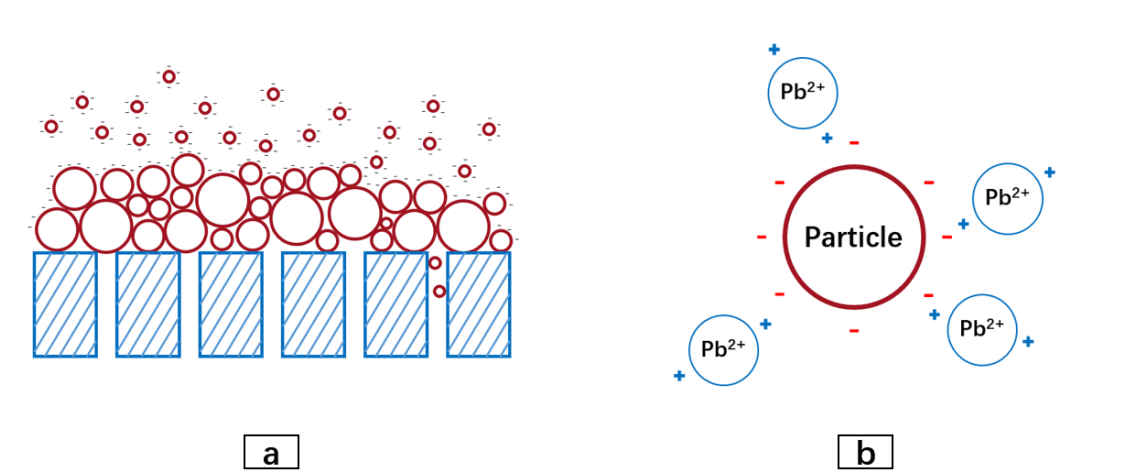

Figure 3-7 Mechanism diagram for fouling layer rejection (a) and adsorption of lead ion at the particle surface (b)

Lead ion has a radius of 1.22 A and hydrated lead ion has a radius of 2.61 A. Apparently, they cannot be retained by NF, UF or MF by size rejection. According to the experimental data described in previous sections, we propose the following mechanism to explain alkaline filtration.

First of all, fractionation results (Table 3-4) indicate that a significant portion (49.25-98.93%) of the particles in feed solution after pH adjustment could be retained by a membrane with a pore size of 3 μm. Therefore, it is logical to assume that even more particles would be retained by the MF membrane used in alkaline filtration, which had a pore size of 0.2 μm (Table 3-2), the UF membrane, or the NF membranes. In the early stage of alkaline filtration, the $PbCO_3$ particles in DIC filtration or $Pb(OH)_2$ particles in NaOH filtration would form a fouling layer (cake) on membrane surface, which is

confirmed by the results of fouling experiments.

Second, both $PbCO_3$ and $Pb(OH)_2$ particles were negatively charged, although at different extent (Figure 3-7), and the pores of the cake would be smaller than the membrane. As a result, the static electric interaction between the negatively charged layer and fine particles, in addition to the enhanced size rejection, would allow the fouling layer to reject the fine particles that were much smaller than those could be rejected by any of the three membranes.

Third, the fouling layer with a negative zeta potential would be able to adsorb positively charged Pb^{2+}. This mechanism might not be meaningful at high pH (e.g., pH 10) alkaline filtration, where the Pb^{2+} solubility was much smaller than the [Pb^{2+}] in permeate of alkaline filtration. However, it might played an important role in reducing the permeate [Pb^{2+}] to below the solubility of Pb^{2+} under certain conditions. For instance, for NaOH filtration at pH 7 (Table 3-1), the saturation [Pb^{2+}] at 25°C is 29570.4 ppm but the experimental [Pb^{2+}] was only 1.45 ppm. The partial lead rejection in alkaline filtration under such conditions might be achieved through the formation of small amount of particles due to local high alkali concentration in the mixing process and the adsorption of Pb^{2+} ions by the negatively charged particles in suspension and on membrane surface.

3.4. Conclusion

In this study, the removal of lead from aqueous system using alkaline filtration was investigated. It was demonstrated that this is an efficient technology with the potential of using conventional MF or UF membrane to remove lead ions from aqueous solutions to satisfy drinking water standard when conditions are optimized. The best conditions emerged from this study is pH 8.5 with Na_2CO_3 as the alkali for pH adjustment and UF as the membrane for filtration. The mechanism of this technology hypothetically involved the formation of negatively charged particles that were larger than the pore size of the membrane, which would prevent the passage of fine particles of the same charges by electric rejection and adsorb positively charged Pb^{2+}.

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Chapter 4. Cadmium Removal by Alkaline Filtration

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Abstract

The removal of Cd^{2+} from aqueous solution by alkaline filtration was evaluated with three different membranes, including microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) membranes at three different feed pH, i.e., 7, 8.5 and 10, and two different alkalis, i.e., sodium hydroxide and sodium carbonate. Permeate cadmium concentration, permeate pH, and permeate flux were measured to evaluate the performance of alkaline filtration. While different types of membranes seem to have similar cadmium rejection, feed pH was found to be dominating and drastic increase of cadmium rejection was observed with pH increase when other conditions were the same.

Key Words: membrane filtration, alkaline precipitation, cadmium, heavy metal removal

4.1. Introduction

Heavy metal pollution is one of the most serious water pollution problems. Heavy metals enter the water bodies through mining, metal smelting, metal processing and chemical production wastewater, fossil fuel combustion, application of pesticides and household wastes, and other natural sources such as geological erosion[1–6].They are highly toxic, cannot decomposed in the environment, can be easily bio-accumulated,

and have bio-magnification effects. They thus constitute serious threats to the health of humans and aquatic organisms[1,7–10].

Since the discovery of cadmium in the early 19th century, the production of cadmium has increased year by year. Cadmium is widely used in the electroplating industry, chemical industry, electronics industry and nuclear industry. Cadmium is a by-product of the smelting industry and is mainly used in batteries, dyes or plastic stabilizers, and is more easily adsorbed by crops than other heavy metals. A large amount of cadmium is discharged into the environment through waste gas, wastewater and waste slag, causing pollution. The main sources of pollution are lead-zinc ore, as well as non-ferrous metal smelting, electroplating and cadmium compounds as raw materials or catalysts[3,11]. When the environment is contaminated with cadmium, cadmium can be enriched in the organism, causing chronic poisoning through the food chain. After cadmium is absorbed by the body, it forms cadmium-sulfur protein in the body and selectively accumulates in the liver and kidney. Among them, the kidney can absorb nearly one-third of the cadmium in the body, which is the target organ of cadmium poisoning. As cadmium damages the renal tubules, the patient develops diabetes, proteinuria and amino aciduria. It is particularly detrimental to bone metabolism, causing a series of symptoms such as osteoporosis, atrophy and deformation. Various methods have been developed to treat and repair heavy metal wastewater and polluted

water[12–14].

The objective of this work is to investigate the effectiveness of alkaline filtration for removal of cadmium from waters under different conditions. Using different types of membranes and alkaline additives, the effects of feed pH on the permeate cadmium concentration, permeate pH and permeate flux were studied in a systematic manner.

4.2. Material and Method

4.2.1. Material

Three commercial membranes, MV020 (microfiltration membrane), UH050 (ultrafiltration membrane) and NF270 (nanofiltration membrane) kindly supplied by Sterlitech Corporation (WA, USA) were used in this work.

Cadmium (II) nitrate with the purity of 99% (ACS) was purchased from Strem Chemical Inc. (MA, USA). Nitric acid with purity of 68%-70% ACS and sodium hydroxide with purity of 98.9% ACS were purchased from Fisher Scientific (Fair Lawn, NJ). Sodium carbonate with purity of 99.5% ACS was obtained from Sigma Aldrich Inc. (St. Louis, MO). N-butanol was purchased from Fisher Scientific (Fair Lawn, NJ).

4.2.2. Preparation of Feed Solution

The cadmium nitrate solution with Cd^{2+} ion concentration of 100,000 ppm was first

prepared and then diluted to 5 ppm by adding deionized water of 17 MΩ·cm^{-1} resistivity. The pH of the feed was further adjusted to 7, 8.5 and 10 by adding NaOH (0.5 M) or Na_2CO_3 (0.5 M). In particular, when the solution of Na_2CO_3 was added, the volume of the solution added to 1 L of the feed $Cd(NO_3)_2$ solution was measured using a micropipette to know the total dissolved ion concentration (DIC) in the feed. The volumes of the added solutions and the corresponding DICs are summarized in Table 4-1.

Table 4-1 Volume of sodium carbonate solution into feed solution at different pH

pH	Volume of Alkaline added into Feed (μL)	Initial DIC Concentration in Feed (mol·L^{-1})
7	66.7	3.34×10^{-5}
8.5	110	5.5×10^{-5}
10	816.7	4.08×10^{-4}

4.2.3. The Solubility of Cadmium Ions in Feed

Ion concentrations in the feed solution were calculated using the available solubility products and dissociation constants as follows.

For adding NaOH, Cd^{2+} in feed has the following equilibrium.

$$Cd^{2+} + 2 \cdot OH^- \xleftrightarrow{k_{sp,Cd(OH)_2}} Cd(OH)_2 \quad (4\text{-}1)$$

Where $k_{sp,Cd(OH)_2}$ is the solubility product constant (k_{sp}) of $Cd(OH)_2$ which is 7.2×10^{-15} mol^{-3}·L^{-3} at 25°C[15]. Thus, the cadmium concentration at a given pH can be calculated by the following equations.

$$k_{sp,Cd(OH)_2} = [Cd^{2+}] \cdot [OH^-]^2 \quad (4\text{-}2)$$

$$[Cd^{2+}] = \frac{k_{sp,Cd(OH)_2}}{[OH^-]^2} \quad (4\text{-}3)$$

Where $[OH^-]$ and $[Cd^{2+}]$ are the concentration of OH^- and Cd^{2+}. The concentration of OH^-, $[OH^-]$ can be calculated by ionization balance of water.

$$H^+ + OH^- \overset{k_{sp,H_2O}}{\longleftrightarrow} H_2O \quad (4\text{-}4)$$

$$k_{sp,H_2O} = [H^+] \cdot [OH^-] \quad (4\text{-}5)$$

$$[H^+] = 10^{-pH} \quad (4\text{-}6)$$

$$[OH^-] = \frac{k_{sp,H_2O}}{[H^+]} = \frac{k_{sp,H_2O}}{10^{-pH}} = 10^{pH} \cdot k_{sp,H_2O} \quad (4\text{-}7)$$

Where k_{sp,H_2O} is solubility product constant of water which is 1.01×10^{-14} $mol^{-2}\cdot L^{-2}$ at 25°C[15]. Combining equations (4-3) and (4-7), the saturation concentration of Cd^{2+} can be calculated for a given pH.

$$[Cd^{2+}] = \frac{k_{sp,Cd(OH)_2}}{[OH^-]^2} = \frac{k_{sp,Cd(OH)_2}}{\left(10^{pH}\cdot k_{sp,H_2O}\right)^2} \quad (4\text{-}8)$$

Solubility of $CdCO_3$ is described by the following equilibrium:

$$Cd^{2+} + CO_3^{2-} \overset{k_{sp,CdCO_3}}{\longleftrightarrow} CdCO_3 \quad (4\text{-}9)$$

$$k_{sp,CdCO_3} = [Cd^{2+}] \cdot [CO_3^{2-}] \quad (4\text{-}10)$$

Where $k_{sp,CdCO_3}$ is solubility product constant (K_{sp}) of $CdCO_3$ which is 1.0×10^{-12} $mol^{-2}\cdot L^{-2}$ at 25°C[15]. $[Cd^{2+}]$ and $[CO_3^{2-}]$ are the concentration of Cd^{2+} and CO_3^{2-}.

Among DICs the following dissociation equilibriums are maintained[16]. For the

dissociation equilibrium of H_2CO_3:

$$H_2CO_3 \overset{k_{a1}}{\longleftrightarrow} H^+ + HCO_3^- \tag{4-11}$$

$$k_{a1} = \frac{[H^+]\cdot[HCO_3^-]}{[H_2CO_3]} \tag{4-12}$$

For the dissociation equilibrium of HCO_3^-

$$H^+ + HCO_3^- \overset{k_{a2}}{\longleftrightarrow} 2\cdot H^+ + CO_3^{2-} \tag{4-13}$$

$$k_{a2} = \frac{[H^+]^2\cdot[CO_3^{2-}]}{[H^+]\cdot[HCO_3^-]} = \frac{[H^+]\cdot[CO_3^{2-}]}{[HCO_3^-]} \tag{4-14}$$

Where the acid dissociation constant of H_2CO_3 and HCO_3^- are k_{a1} (4.3×10^{-7} mol L^{-1} at 25°C) and k_{a2} (4.8×10^{-11} mol L^{-1} at 25°C)[15]. $[H_2CO_3]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ are the concentration of H_2CO_3, HCO_3^- and CO_3^{2-}. Respectively, and the sum of these concentrations is the concentration of dissolved inorganic carbon [DIC]. Hence,

$$[DIC] = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \tag{4-15}$$

$$1 = \frac{[H_2CO_3]}{[DIC]} + \frac{[HCO_3^-]}{[DIC]} + \frac{[CO_3^{2-}]}{[DIC]} \tag{4-16}$$

Combine the equation (4-13), (4-14) and (4-15), and using pH instead of $[H^+]$[16].

$$[HCO_3^-] = \frac{[DIC]}{1+\frac{[10^{-pH}]}{k_{a1}}+\frac{k_{a2}}{[10^{-pH}]}} \tag{4-17}$$

$$[CO_3^{2-}] = \frac{[DIC]}{1+\frac{[10^{-pH}]}{k_{a2}}+\frac{[10^{-pH}]^2}{k_{a1}\cdot k_{a2}}} \tag{4-18}$$

When precipitation occurs [*DIC*] is no longer the initial DIC, which is called $[DIC]_{start}$, since CO_3^{2-} co-precipitates with cadmium and [*DIC*] decreases. [*DIC*] after the

cadmium ion precipitation, which is called $[DIC]_{final}$ is therefore smaller than $[DIC]_{start}$. Considering that the decrease of the molar concentration of CO_3^{2-} by precipitation is equal to the decrease of the molar concentration of Cd^{2+} according to (4-9), $[DIC]_{final}$ becomes:

$$[DIC]_{final} = [DIC]_{start} - [Cd^{2+}]_{precipitate} \quad (4\text{-}19)$$

$$[DIC]_{final} = [DIC]_{start} - \left([Cd^{2+}]_{start} - [Cd^{2+}]_{final}\right) \quad (4\text{-}20)$$

Where $[Cd^{2+}]_{precipitate}$, $[Cd^{2+}]_{start}$ and $[Cd^{2+}]_{final}$, respectively, denote the decrease of Cd^{2+} concentration due to precipitation, initial Cd^{2+} concentration in the feed, and finial Cd^{2+} concentration in the feed.

It should be noted that, in the case of the addition of Na_2CO_3 or the mixture of Na_2CO_3 and $NaHCO_3$, two solutions for $[Cd^{2+}]$s are obtained either via equation (4-8) or via equations (4-10), (4-17) and (4-18). The smaller value is adopted as the dissolved Cadmium concentration.

4.2.4. Alkaline Filtration

The dead-end filtration cell with a feed capacity of 325 mL was used for filtration experiments at 25°C. The effective area of membrane was 0.0013 m^2. The membrane was placed on the membrane support made of sintered metal, which was at the bottom of the filtration feed chamber. The pressure to drive filtration was from nitrogen

cylinder via pressure regulator. The operating pressure for NF270 (NF membrane) and UH050 (UF membrane) membranes is 43.5 psig. The operating pressure for MV020 (MF membrane) membranes was 15 psig, since the MV020 has much bigger flux. The permeate weight was automatically recorded by computer every ten seconds in this filtration system.

The membrane was washed by deionized water before filtration. After assembling the filtration system, 300 mL of feed solution was loaded into the feed chamber and pressurized to a predetermined value. Upon starting filtration, the initial 10 g of permeate was collected and discarded. Then, 10 g of permeate was collected and its cadmium ion concentration was measured by Flame Atomic Absorption Spectrometer (FAAS, Thermo Fisher Scientific) after adding 0.2 mL of HNO_3 (68%-70%) to stabilize the cadmium ion, which was followed by the collection of 3 g of permeate to measure pH by a pH meter (Fisher Scientific).

After collecting the above samples, the permeate was collected into a container placed on a balance, and the permeate weight was automatically recorded by a computer every 10 seconds until the amount of permeate collected became 100 g. The used membrane was then removed from the filtration cell, rinsed with deionized water, and the surface was cleaned with a rubber scraper. The membrane was rinsed again with deionized water before storage in deionized water.

The average flux of the membranes can be calculated by the following equation[17].

$$J = \frac{w}{\rho t A} \tag{4-21}$$

Where J is the flux ($m^3 \cdot h^{-1} \cdot m^{-2}$) of the membrane, w is the weight (kg) of permeate collected during filtration time t (h), ρ is the permeate density (kg m^{-3}) and A is s the effective area (m^2) membrane, which is 0.0013 m^2.

4.3. Result and Discussion

4.3.1. Cadmium Rejection by Alkaline Filtration

Figure 4-1 shows the effect of feed solution pH on permeate cadmium concentration in alkaline flirtation with different membranes when NaOH or Na_2CO_3 was used for pH adjustment.

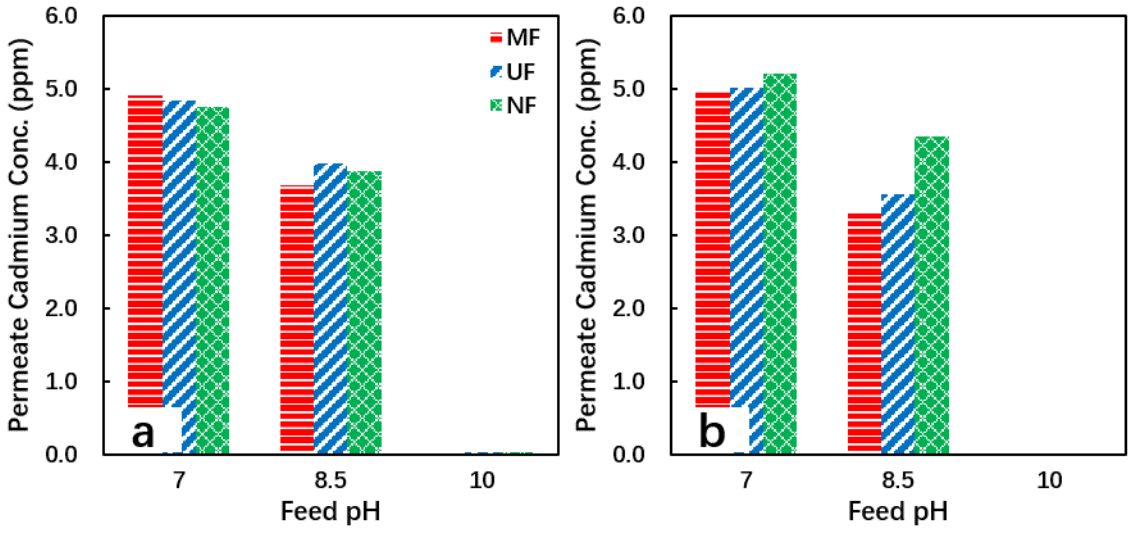

Figure 4-1 Effect of pH on permeate cadmium concentration in alkaline filtration with different membranes when NaOH (a) or Na_2CO_3 (b) was used as the alkali

Compared to the previous results of lead removal (Table 3-1), it is noticed that the cadmium removal efficiency is not as high as lead removal at the same alkaline filtration conditions. This is because of the higher solubility of $Cd(OH)_2$ and $CdCO_3$ than those of $Pb(OH)_2$ and $PbCO_3$.

The saturation solubility of Cd^{2+} ions has the following equilibrium with solid $Cd(OH)_2$.

$$Cd^{2+} + 2 \cdot OH^{-} \leftrightarrow Cd(OH)_2 \tag{4-22}$$

whose solubility product $k_{sp,Cd(OH)_2}$ is 7.2×10^{-15} $mol^3 \cdot L^{-3}$ at 25°C[15]. When the saturation concentration of Cd^{2+} is calculated by equation (4-8). $[Cd^{2+}]$ is 80773.6 ppm, at pH 7; $[Cd^{2+}]$ is 80.77 ppm, at pH 8.5 and $[Cd^{2+}]$ is 8.077×10^{-2} ppm, at pH 10. Thus, the saturation concentration of Cd^{2+} ions decreases dramatically when pH increases from 7 to 10.

The experiment results given in Figure 4-1-a show that no membranes can reject cadmium when pH is 7. This is because the saturation cadmium concentration (80773.6 ppm) is much higher than feed Cd concentration (5 ppm) at pH 7.0, meaning all added cadmium was present in the feed as Cd^{2+}. Thus, the cadmium can pass the MF and UF membranes as ions. Even NF membranes with smaller pores and negative charges could not reject cadmium ions this pH.

With the increase of feed pH, the permeate cadmium concentration tends to decrease. At pH 8.5 the permeate cadmium concentration was lower than the feed cadmium concentration of 5 ppm. This is because solubility of cadmium was lowered with the pH increase. Even though the saturated cadmium concentration at pH 8.5 is 80.77 ppm that is far above the feed cadmium concentration of 5 ppm, it is three orders of magnitude lower than that at pH 7, indicating higher precipitation tendency of $Cd(OH)_2$. At pH 10, the saturation concentration of Cd^{2+} was far lower than the feed Cd^{2+} concentration. Therefore, most of cadmium precipitated as $Cd(OH)_2$, enabling high cadmium removal.

When Na_2CO_3 was used as the alkali for pH adjustment, there was also a decreasing trend of cadmium concentration in the permeate as pH increased and the permeate cadmium concentration was below 0.5 ppm even when pH was 7.

$$Cd(OH)_2 \leftrightarrow Cd^{2+} + 2(OH^-) \quad (4\text{-}23)$$

$$Cd(CO_3) \leftrightarrow Cd^{2+} + CO_3^{2-} \quad (4\text{-}24)$$

When adding Na_2CO_3, the solubility of cadmium ion was mainly controlled by the equilibrium as described by equations (4-23) and (4-24). In this case, $[Cd^{2+}]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ are calculated from equations (4-10), (4-17) and (4-18) and $[Cd^{2+}]$ values so calculated are shown for different pH values in Table 4-2.

Table 4-2 Effect of pH on equilibrium cadmium ions concentration for adding sodium carbonate by different calculation method

pH	Equilibrium cadmium ions concentration (ppm)	
	Calculate by OH^-	Calculate by CO_3^{2-}
7	80773.5	1.28
8.5	80.77	7.21×10^{-4}
10	8.07×10^{-2}	9.55×10^{-7}

The concentration of HCO_3^- and CO_3^{2-} show in Table 4-3.

Table 4-3 Effect of pH on carbonate concentration in feed for adding sodium carbonate

pH	Adding Na_2CO_3 ($mol\cdot L^{-1}$)	
	HCO_3^-	CO_3^{2-}
7	1.84×10^{-7}	8.81×10^{-11}
8.5	1.03×10^{-5}	1.56×10^{-7}
10	2.46×10^{-4}	1.18×10^{-4}

Compared with adding NaOH, adding Na_2CO_3 will have smaller saturation concentration of Cd^{2+} ions in feed, but unlike the result of lead (adding Na_2CO_3 are more effectively than adding NaOH to remove lead),the result of cadmium shows that adding Na_2CO_3 can not increase the removal of cadmium. In some cases, the addition Na_2CO_3 will reduce the removal of cadmium.

Although when pH is 7, the concentration of Cd^{2+} ions and Pb^{2+} ions in the feed were the same, i.e., 5 ppm, the membranes could reject lead more effectively than reject cadmium. The permeate metal concentration were 0.32 to 0.41 ppm for lead, but, 4.76 to 4.91 ppm for cadmium at this pH. When pH was 8.5, the permeate concentration were 0.01 to 0.04 ppm for lead and 3.99 to 3.68 ppm for cadmium.

Figure 4-2-a is the diagram of Cd^{2+} ions solubility at different pH with no DIC. The Cd^{2+} ions concentration in $Cd(NO_3)_2$ saturation solution at 25°C is 1.65×10^5 ppm[15], which is sets the maximum value of the Cd^{2+} when NaOH was used as the Cd^{2+} ions solubility at different pH and DIC concentration. Comparing with the case of adding NaOH as the alkali, the existence of DIC could dramatically decrease the solubility of Cd^{2+} ions.

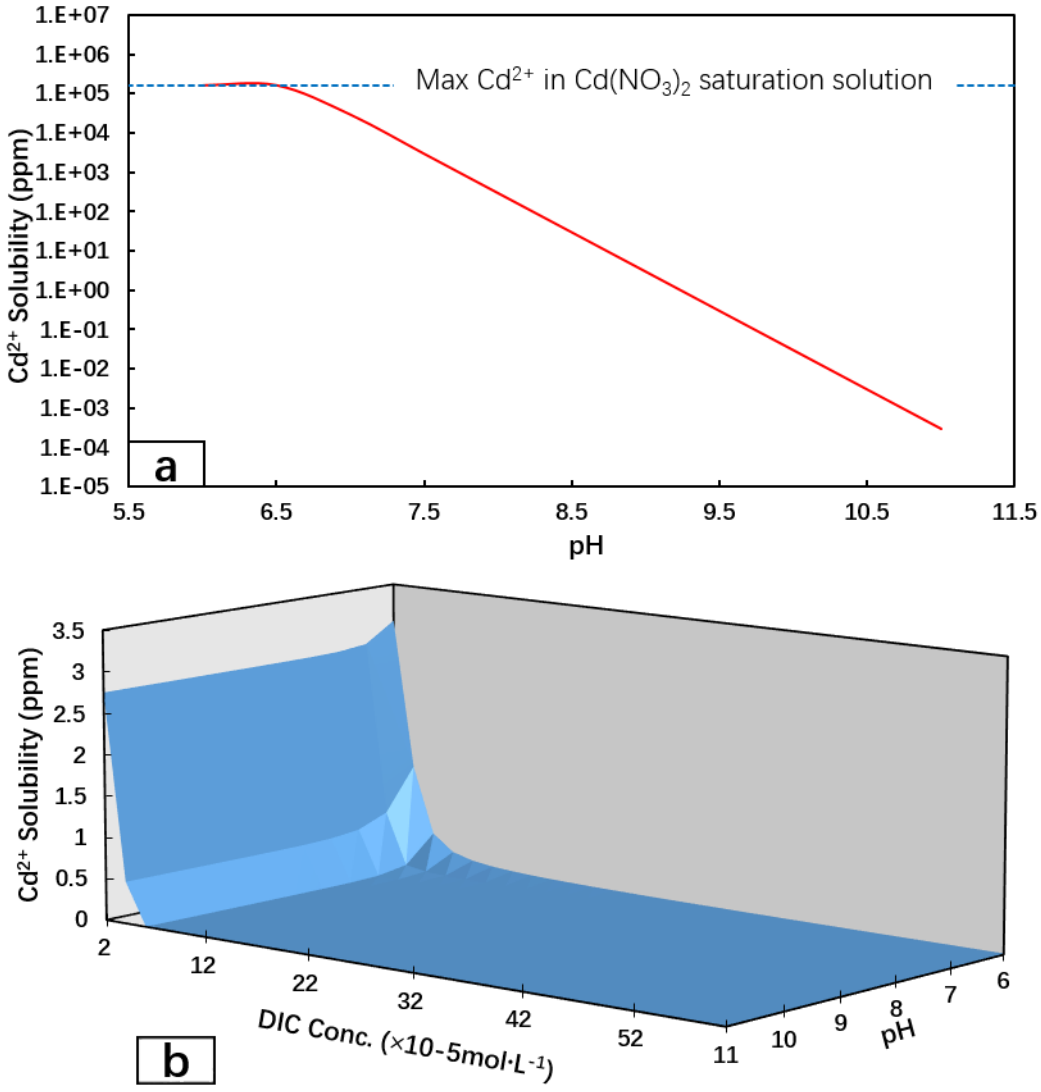

Figure 4-2 Cd^{2+} ions solubility at different pH and different DIC concentration, (a) is with zero DIC

(NaOH); (b) is with DIC concentration from 2×10^{-5} to 6×10^{-4} mol·L^{-1}

Figure 4-2-b shows that the increase of DIC concentration can effectively decrease the Cd^{2+} ions at $CrCO_3$ saturated aqueous solution and the change of pH does not have significant influence on the saturation concertation of Cd^{2+} ions when pH is between 6 and 11.

4.3.2. Permeate pH

Figure 4-3 shows the effect of feed pH on the permeate pH for MF, UF and NF membrane, respectively. The blue line marked as Feed* indicates the pH of feed standing still 2 hours. The initial feed pH was shown as Feed(i) which is black dash line in diagram. It shows that the permeate pH of MF, UF and NF membranes is approximately equal to feed pH standing still 2 hours. It means that those membranes cannot reject OH^- ions effectively.

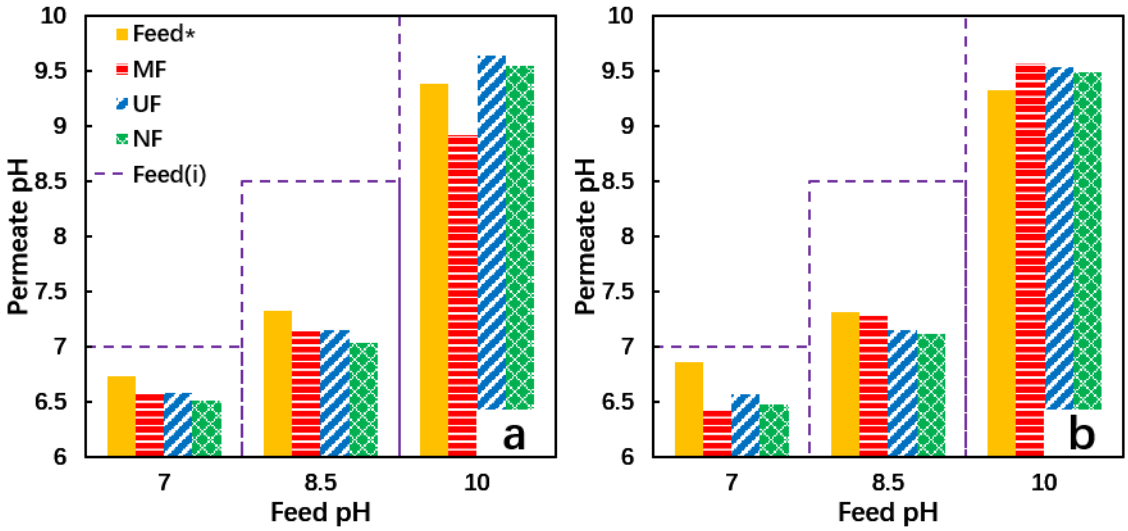

Figure 4-3 Effect of initial feed pH on permeate pH when alkaline filtration was carried out with three different types of membranes, i.e., MF, UF, and NF when the alkali was: (a), NaOH and (b), Na_2CO_3.

4.3.3. Flux and Fouling

Figure 4-4-a shows the effect of pH on the flux of the MF membrane. With the increase of initial feed pH the flux exhibited a decreasing trend with both NaOH and Na_2CO_3 and the flux dropped faster with NaOH.

As shown in Figure 4-4-b, the flux of UF membrane was smaller when NaOH was the alkali in comparison to Na_2CO_3 at all pH levels. With the increase of feed pH, the flux of UF alkaline filtration decreased when either NaOH or Na_2CO_3 was the alkali and the flux decreased faster from pH 8.5 to pH 10 than from pH 7 to 8.5 in both cases.

Figure 4-4-c shows that the flux did not have a clear trend either with pH increase nor with different types of alkalis, indicating other factors (e.g., pore size and charge of the

NF membrane) might be controlling the process.

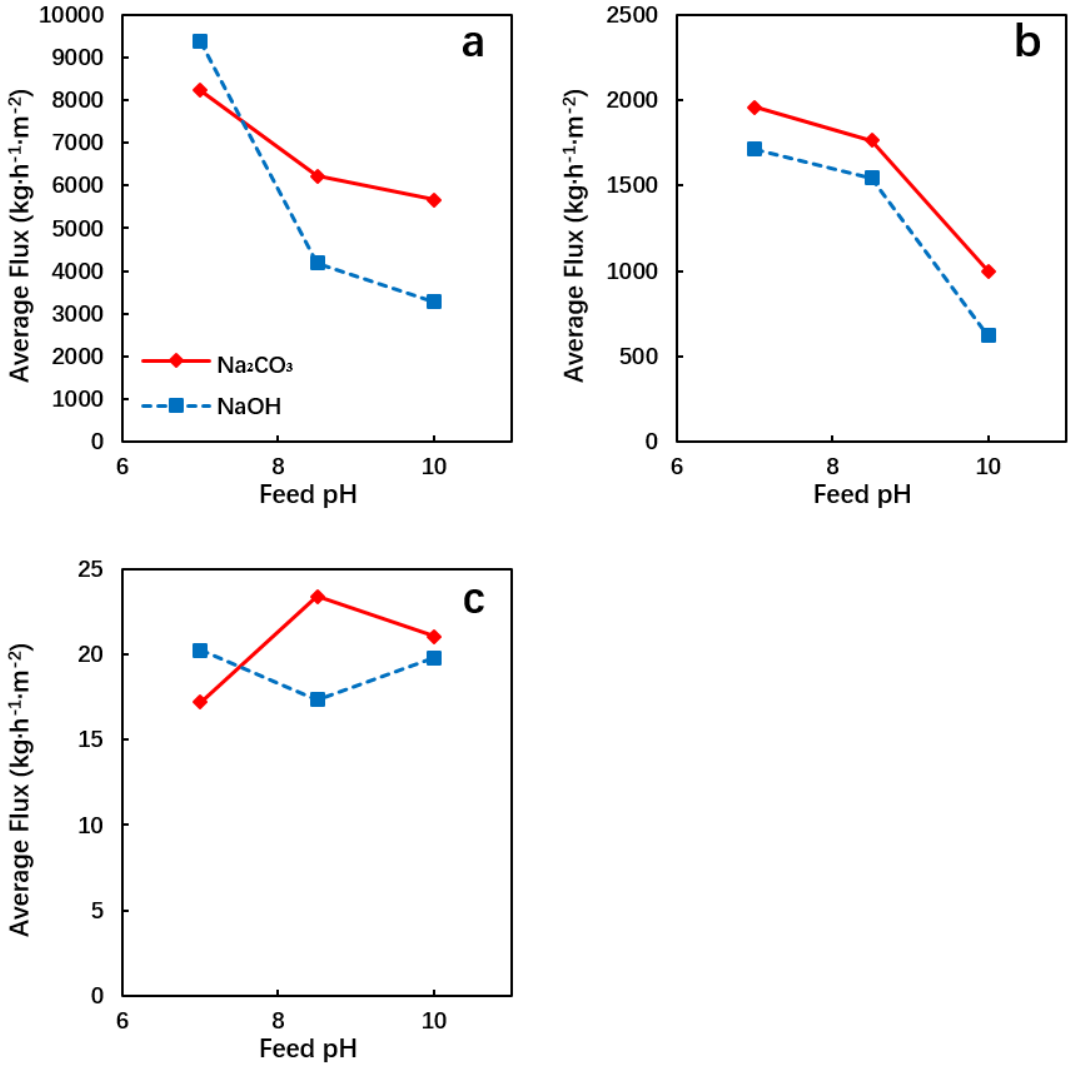

Figure 4-4 Effect of pH on flux for different alkaline solutions, (a) is for MF membrane; (b) is for UF membrane; (c) is for NF membrane

It is likely that fine particles whose size was between the pore size of UF and NF membrane were formed in alkaline filtration and the amount of these fine particles increased with feed pH. As a result, the flux of MF and UF alkaline filtration decreased with pH increase but that of NF alkaline filtration did not change significantly. However,

this hypothesis needs to be verified experimentally.

4.4. Conclusion

In this study the removal of cadmium by alkaline filtration was investigated with three different membranes, i.e., MF, UF, and NF, and two alkalis, i.e., NaOH and Na_2CO_3. There is no significant difference in permeate cadmium concentration between adding NaOH and Na_2CO_3. It was demonstrated that the three different membranes had no significant effect on permeate cadmium concentration, indicating that the rejection of cadmium was controlled by factors other than membrane properties, which is similar to that observed with lead alkaline filtration. Furthermore, cadmium removal efficiency increased with pH of the feed. However, the type of alkali did not show significant impact on cadmium removal, which is different from that observed with the lead alkaline filtration. The best condition for cadmium removal was MF alkaline filtration at pH 10 with Na_2CO_3 as the alkali, which allowed a permeate cadmium concentration of 0.015 ppm at a flux of 6,000 kg m^{-2} h^{-1}.

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Chapter 5. Conclusions and Recommendations

5.1. Conclusion

The removal of two different heavy metal ions, i.e., lead and cadmium, by alkaline filtration was investigated at three different pH levels (i.e., 7.0, 8.5, and 10.0), with three membranes (i.e., MF, UF, and MF) and three different alkalis (i.e., NaOH, Na_2CO_3, and Na_2CO_3/$NaHCO_3$ equal molar mixture. The following are concluded based on the experimental data and theoretical analysis.

1. Lead could be effectively removed by alkaline filtration when feed pH was 8.5 and 10 to a level that satisfy drinking water standards. The removal of lead increases as feed pH increase.
2. DIC can decrease the solubility of lead dramatically and increase the removal of lead effectively at same feed pH.
3. Different membranes have no significant effect on lead reject and therefore permeate lead concentration at the same feed concentration (i.e., 5 ppm), since the fouling layer on the membrane surface dominate the lead removal of alkaline filtration;
4. Drastic reduction of flux was observed when initial feed pH increased from 8.5 to 10.0 in MF alkaline filtration and UF alkaline filtration with NaOH as the

alkali but absent from NF alkaline filtration or carbonate alkali filtration with any of three membranes. This is explained by the adsorption of fine $Pb(OH)_2$ particles, which were of relatively small negativity, by the nonpolar intraporous surfaces of UF and MF membranes but rejected by the nano-scale NF membrane pores that carried negative charges at pH 10. $PbCO_3$ particles formed in carbonate alkaline filtration were believed not to be able to plug the UF and MF pores due to the expulsion among these particles themselves, which were shown to have large negative zeta potentials.

5. A hypothesis is proposed to explain the mechanism of alkaline filtration based on experimental data, which involves the formation of negatively charged $Pb(OH)_2$ particles in alkaline filtration and $PbCO_3$ particles in carbonate alkaline filtration with the size of most particles larger than the pore size of the MF membrane and therefore the UF and NF membranes. As a result, a fouling layer would be formed on the surface of the membrane by these large particles, which would help enhance lead removal by either retaining fine particles of the same charge or adsorbing Pb^{2+} ions of opposite charge.
6. For cadmium, unlike lead, the carbonate alkaline filtration did not show significant advantage over alkaline filtration on cadmium removal even though the solubility of $CdCO_3$ is much smaller than that $Cd(OH)_2$ at the same pH.
7. With increase of feed pH, although the solubility of cadmium decrease

dramatically, the alkaline filtration can not remove cadmium more efficiently. More studies are needed to remove cadmium efficiently.

5.2. Recommendations

1. Given the great potential for efficient and cost-effective removal of heavy metal ions such as lead and cadmium from aqueous solutions by alkaline filtration as demonstrated in this thesis, it is worth to further investigate this technology using real industrial wastewaters or contaminated waters containing high levels of lead, cadmium, or other heavy metal ions;
2. Laboratory studies should be expanded to other important heavy metal contaminants such as mercury and arsenic;
3. More systematic studies should be carried out to further our understanding to the mechanism of alkaline filtration. For instance, experiments could be carried with feed of a serious of constant DIC concentration at varied pH levels to better characterize the effects of DIC on particle formation and particle properties, as well as the rejection of metal ions and permeate flux;
4. Studies on the interferences of common metal ions such as Na^+ and K^+ and common anions such as Cl^- and SO_4^{2-} are warranted;
5. Investigate the performance of alkaline filtration with real wastewater and the

interferences of organic substance;

6. Screen of commercial MF and UF membranes for best performance should also be carried out for commercialization readiness;
7. Investigate the removal of Mg^{2+} and Ca^{2+} ions in sea water by alkaline filtration which is as pre-treatment for desalination by RO filtration to reduce the fouling.