RECYCLABLE NANOSORBENTS FOR

WATER AND WASTEWATER TREATMENT

USING VIBRATORY SHEARING

ENHANCED PROCESS (V-SEP) MEMBRANE

FILTRATION SYSTEM

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M.Phil

The Hong Kong

Polytechnic University

2014

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Recyclable Nanosorbents for Water and Wastewater Treatment Using Vibratory Shearing Enhanced Process (V-SEP) Membrane Filtration System

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Philosophy

September 2012

CERTIFICATE OF ORIGINALITY

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Fan Chi Ho

ABSTRACT

Rapid industrialization inevitably leads to discharging various pollutants like heavy metals into drinking water sources such as lakes and rivers. Thus the shortage of clean water has become one of the biggest problems that we are facing. Several chemical processes based on chemical precipitation, adsorption with activated carbon, and ion exchange column have been developed to treat industrial wastewater prior to discharge. However, current processes suffer from some serious drawbacks such as high material, capital, regeneration costs and low efficiency. Membrane filtration like reverse osmosis (RO) is an advanced and commerized wastewater treatment technology used in the past decades; however, it suffers from low effectiveness in treating a large volume of metal containing wastewater and high capital cost. To overcome these problems, polymer enhanced ultrafiltration technology was developed for wastewater treatment. Nevertheless, high shearing force created by the centrifuge pump during operation often causes degradation of the polymer, resulting in passage of fragmented molecules through the membrane and loss of polymer.

Vibrating Shearing Enhanced Processing (V-SEP) membrane filtration technology is an advanced system which is able to solve inherent fouling problem in traditional membrane filtration technology. A new type of amphiphilic core-shell nanoparticle which is composed of well-defined poly(methyl methacrylate) (PMMA) hydropholic core and polyethylenimine (PEI) hydrophilic polymer shell is a promising nanosorbent for heavy metal removal. It is envisioned that the core-shell particles with spherical structure and hard PMMA core can withstand high shearing force during the filtration process. The PEI polymer which is covalently attached onto PMMA hard core can effectively adsorb heavy metal ions. On the basis of these two

unique features of the V-SEP and core-shell nanosorbents, this thesis work aimed to develop a novel heavy metal treatment process using a combination of amphiphilic core-shell nanosorbent and V-SEP membrane filtration technology. The work included three major parts: 1) Scale-up synthesis of PMMA/PEI nanosorbent; 2) Purifying PMMA/PEI nanosorbent with V-SEP membrane filtration system; 3) Evaluation of heavy metal removal efficiency and nanosorbent regeneration using a combination of nanosorbent and V-SEP membrane filtration technology.

Part I : Synthesis of PMMA/PEI Nanosorbents in a Pilot Scale Reactor

PMMA/PEI nanosorbent was synthesized in a pilot scale 20L reactor via a surfactant-free emulsion polymerization by a semi-batch addition method. Particle sizes of three batches of PMMA/PEI nanosorbents were in range of 200 to 300 nm in diameter with narrow size distribution. *Zeta*-potential values of the three batches of the PMMA/PEI nanosorbents were around +40 mV and monomer conversions were up to 90%. Reaction temperature was continuously monitored during the synthesis and maintained below 85ºC. These results showed that synthesis of PMMA/PEI nanosorbent could be scaled up from laboratory quantity to 20L pilot scale based on a similar polymerization mechanism.

Part II: Purifying Nanosorbent by Membrane Filtration Process

PMMA/PEI nanosorbent can be easily purified by a high speed centrifuge in a laboratory scale, but it is not feasible to purify a large quantity of nanosorbent synthesized in Part I with the same technique. In fact, industrial scale centrifuge with such a high centrifugation speed is not available. V-SEP membrane filtration system was a suitable one for purifying PMMA/PEI nanosorbent in a pilot scale. Through systematic study of membrane types using a 6-inch membrane stirred cell. MF-03 PTFE microfiltration membrane with 0.1 um pore size was found to be the most appropriate one for purifying PMMA/PEI nanosorbent because of its low rejection percentage of unreacted PEI polymer through the membrane. Study of solid content of the nanosorbent on the flux performance suggested that appropriate solid contents for purifying nanosorbent with the V-SEP membrane filtration system were in the range of 8% to 10%. It was also found that around 240-378L of RO water was required to purify each batch of nanosorbent using diafiltration mode (continuous feeding). In order to reduce the volume of RO water used in the purifying nanosorbent, filtration of purification permeate in different types of ultrafiltration and nanofiltration membrane were conducted in a 6-inch membrane stirred cell. The result showed that NF-16 thin film composite nanofiltration membrane with 78% salt rejection gave the highest COD and conductivity rejection. Thus the NF-16 was the most appropriate membrane for recycling of purification permeate.

Part III – Application of Nanosorbent in Wastewater Treatment using V-SEP Membrane Filtration System

Application of PMMA/PEI nanosorbent in wastewater treatment was studied in two stages: preliminary study in a 6-inch membrane stirred cells and pilot study in a V-SEP membrane filtration system. The preliminary study showed that Ag (I), Cu (II) and Cr (VI) ions could be effectively removed by the nanosorbents in the 6-inch membrane stirred cell. However, Ag (I) ions were difficult to be desorbed from the nanosorbent after washing with sulphuric and nitric acid solutions, respectively. Prior to the pilot study using nanosorbent with V-SEP membrane filtration system, the optimum operation pressure and concentration of the nanosorbent have been examined since these parameters could considerably affect the removal effectiveness of contaminant with membrane filtration system. Results indicated that the optimal nanosorbent concentrations were in the range of 10.5 to 15%, and the optimum operation pressure was at 30 psi with the use of an UF-19 membrane. These optimized parameters were used in subsequent studies with V-SEP membrane filtration system. The core-shell nanosorbent is also capable of adsorbing Cu (II) ions and to be regenerated with simple pH adjustment. Adsorption of Cu (II) ions and release of the metal ions could be repeated up to three cycles using the V-SEP membrane filtration system with UF-19 membrane.

ACKNOWLEDGEMENTS

Wai Yin, Miss Wong Man Ching, Mr. Cheung King Lok, Miss Chan Yuet Siu.

I would like to show my appreciate to the staff, especially the technical staff and the general supporting of Department of Applied Biology and Chemical Technology, who have helped me in various ways.

I would especially like to thank my family for their continuing support and encouragement during the course of this study.

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ABBREVIATIONS AND SYMBOLS

Symbol	Description
PMMA/PEI	Poly(methyl methacrylate)-Polyethylenimine nanosorbent (nanoparticle)
PMMA/CTS	Poly(methyl methacrylate)–Chitosan nanosorbent (nanoparticle)
Conv. %	Monomer conversion
CTS	Chitosan
Dv	Volume-average hydrodynamic diameter
Dn	Number-average hydrodynamic diameter
PDI(Dv/Dn)	Polydispersity index of the particle size distribution
TGA	Thermogravimetry Analysis
TBHP	*Tert*-butyl hydroperoxide
SC. %	Solid content
UV-VIS	Ultraviolet-visible spectrophotometer
ζ-potential	Zeta-potential
PEI	Polyethylenimine
MMA	Methyl methacrylate
V-SEP	Vibrating Shearing Enhanced Process
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse Osmosis
GFD	Gallon per Feed per Day (Gallon/Feed/Day)
LMH	Liter per meter per Hour (Liter/Meter/Hour)

PTFE   Polytetrafluoroethylene

PVDF   Poly(vinylidene fluoride)

L V-SEP   V-SEP system with membrane area 0.4785ft^2

P V-SEP   V-SEP system with membrane area 16.44^2

RO water   Water manufactured by RO system

MWCO   Molecular Weight Cut Off

Chapter 1

Background of Heavy Metal Pollution and Its Treatments

1.1 Heavy metal pollution in the environment

Rapid industrialization and urbanization in the Pearl River Delta region in the last few decades have been almost inevitably introduced various pollutants into natural environment from different industries such as chemical and biochemical manufacturing, petrochemicals, printed circuit board, bleaching, dyeing, pulp and paper, pharmaceuticals, electroplating, food processing, battery manufacturing, stainless steel manufacturing.[2] Water and sediment pollution associated with direct discharge from industrial cannot be avoided. According to the report of the Ministry of Environmental Protection of the People's Republic of China, around twenty four thousand million tones of industrial sewage have been discharged in China in 2006, including mercury (2.6 tonnes), cadium (49.4 tonnes), chromium (VI) (96.4 tonnes), lead (339.1 tonnes) and arsenic (245.2 tonnes). Therefore, There is continuous demand in advanced and cost-effective technology to treat wastewater and sediment pollutions to address the raising water pollution problems.

Unlike organic contaminants which are capable of being decomposed into non-toxic compound by bacteria, heavy metals are non-degradable, and persist permanently in the environment. The fate of heavy metal after being discharged from industrial wastewater can be absorbed into sediment with high clay content, and eventually accumulated in benthic organisms to toxic levels. As the sediment with

high clay content is changed into acidic environment, adsorbed heavy metal in the sediment can be released and carried out by runoff water, resulting in one source of water pollution.[3] When water is polluted, aquatic organisms could accumulate trace metals from various sources in aquatic environment. The accumulation of trace metals in aquatic organisms can pose a long term burden on biogeochemical cycling in the aquatic ecosphere.[4] Once heavy metals enter the food chain in aquatic environment, they may be accumulated in aquatic organisms to dangerous levels and become harmful to human health if human consume a large quantity of aquatic organism such as fish, crab, shrimp and shellfish from the polluted environment.[4] For example, it was reported that the highest concentration of Pb in fish *Siganus oramin* collected in different regions of China was about 30 times higher than the recommended values in the China's food assessment guidelines. Concentrations of Pb in 20% fish samples were above the guideline level. In order to protect public health and prevent continuous accumulation of heavy metal in environment, different countries have implemented wastewater discharge standard to control the discharge of heavy metal from industry into natural environment. The Integrated Wastewater Discharge Standard (GB8978-1996)[5] in China is shown in Table 1.

Table 1. Integrate wastewater discharge standard (GB 8978-1996)

Contaminant	Maximum allowable discharge standard (ppm)
Total mercury	0.05
Total cadmium	0.1
Total Chromium	1.5
Total Chromium (VI)	0.5
Total arsenic	0.5
Total Lead	1.0
Total Nickel	1.0
Total Silver	0.5
Total Copper	2.0
Total Zinc	5.0

1.2 Current technologies in treating heavy-metal containing Wastewater

1.2.1 Chemical precipitation

Chemical precipitation is a well-known, common and traditional method to treat wastewater containing metal ions. The chemical precipitation methods can be divided into three major types: hydroxide precipitation; carbonate precipitation and sulfide precipitation.

Hydroxide precipitation

Hydroxide precipitation mainly uses hydroxide solution or lime to precipitate the metal ions because metal reacts with hydroxide ion to form metal hydroxide under alkaline pH as shown in the following equation:

$$X^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow X(OH)_{2(S)}$$
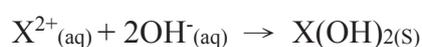
$$X^{2+} = \text{divalent metal cation}$$

Carbonate precipitation

Carbonate precipitation uses free carbonate ion to precipitate certain types of metal ion such as lead, cadmium and nickel. Chemical reaction is shown as follows:

$$X^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow XCO_{3(S)}$$
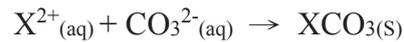
$$X^{2+} = \text{divalent metal cation}$$

Because free carbonate ion only exists under high pH condition, the solution pH is usually increased with addition of hydroxide solution. Thus, carbonate and hydroxide precipitations always occur simultaneously. This process is commonly regarded as a co-precipitation method.

Sulfide precipitation

Sulfide precipitation is based on the reaction between sulfide ion of hydrogen sulfide and metal ion to form colloidal metal sulfide. The chemical reaction is shown below:

$$X^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow XS_{(S)}$$
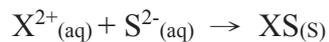
$$X^{2+} = \text{divalent metal cation}$$

The resulting sulfite precipitants usually occur under alkaline condition. The dissolved sulfide ions can be easily transformed into un-dissociated hydrogen sulfide as shown in the following equations

$$S^{2-}_{(aq)} + H_2O_{(l)} \rightarrow HS^-_{(aq)} + OH^-_{(aq)}$$

$$HS^-_{(aq)} + H_2O_{(l)} \rightarrow H_2S_{(aq)} + OH^-_{(aq)}$$

Although the chemical precipitations are simple methods to treat metal containing wastewater, consumption of precipitant lead to high material cost in a long term treatment, especially in treating wastewater with relatively low concentration of heavy metal. In addition, efficiencies of chemical precipitation methods are significantly reduced when the wastewater contains other types of contaminants such as organic compound, suspended solid, non-metallic inorganic species.

1.2.2 Activated carbon

Activated carbon is a black solid substance in a form of granular or powder charcoal which belongs to a carbonaceous material. It is a traditional type of adsorbent, and is commonly used in wastewater treatment. Activated carbon is produced from high carbon content, low inorganic and cheap carbonaceous materials such as agricultural waste products, biomass, activated groundnut husk carbon, coconut husk and palm pressed fibers, coconut shell, wood and dust coal activated carbons, coconut tree sawdust carbon, rice husk carbon, almond shell carbon, fly ash, agricultural wastes. It is manufactured through a two-stage process: carbonization followed by activation. The carbonization aims to increase carbon content and create an internal porosity. Activation process improves the pore structure of the activated carbon. There are both physical and chemical activation processes. Chemical activation is commonly used because the process is carried out at low temperature and there is no burn off char as compared to physical activation. The simple chemical activation method leads to increase in total global yield of activated carbon.[6].

High porous, large internal surface and carbon in nature of activated carbon favors the adsorption of organic compounds. Thus activated carbon is commonly and commercially utilized in removing organic compound in wastewater. However, activated carbons show relatively low removal efficiency of metal ions in wastewater. To improve its removal performance, chemical modification of inherent surface functional groups of the activated carbons is usually required. For example, activated carbon containing high amounts of acidic or polar oxygen groups present on the surface can enhance metal removal efficiency. Therefore, *in-situ* modification of activated carbon during the activation process or post-treatment of activated carbon with oxidizing agent have been developed for specific use in removal of trace toxic metals from wastewater.[7-9]

Although modified activated carbons are able to remove toxic metal ion from wastewater, the high regeneration cost of the activated carbons is one of the major drawbacks. To regenerate the activated the carbons, high temperature is generally required, thus increasing the energy coasts. The thermal treatment leads to thermal aging of the activated carbon and desorption carbonaceous residues and polymers formed from chemisorbed fraction onto the activated carbon surface.[10,11] Pelech *et al.* (2005) demonstrated that degree of desorption of chloroorganic mixtures reaching to 96% with 140 ºC superheated steam. The results suggest that high temperature is required in regenerating activated carbon. Although the regeneration process is technically feasible, it is not economically viable.

1.2.3 Electrodialysis

Electro-dialysis is a technique that combines both membrane separation and electrolysis technique. Figure.1 illustrates the principle of electro-dialysis. During the process of electro-dialysis, ionized species in the solution are passed through ion-exchange membrane under the influence of an electric field.
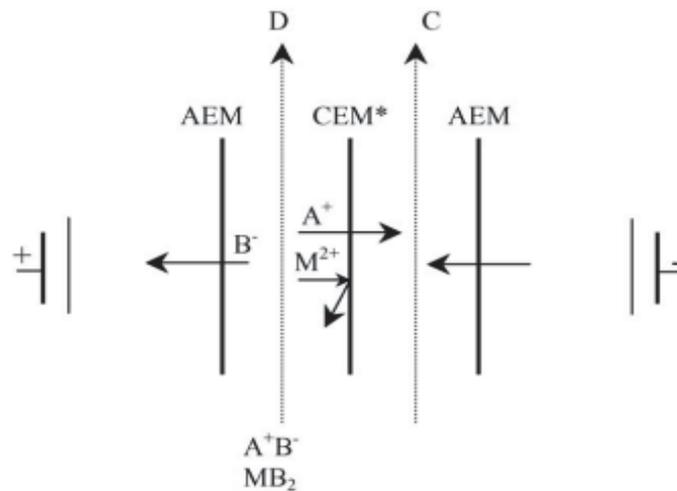
Figure 1. Electrodialysis principle (CEM: cation exchange membrane, AEM: anion exchange membrane, D: dilute, C: concentrate)[12]

Anions migrate toward the anode through anion-exchange membrane at one extremity and cations migrate toward the cathode through cation-exchange membrane at the other extremity. The electrode compartments are fed by an electrolyte. The electrochemical reactions take place between the electrodes and the solution. An alternate placement of cation and anion-exchange membranes in the electro-dialysis is to construct different cell compartments, this construction allows ionized species that are able to pass through the anion-exchange membrane to be stopped by the cation-exchange membrane and vice versa.[12-16]Thus, ionized species transport from effluent in dilute chamber to concentrate chamber under electric field force, resulting

in reduction of ionized species concentration in dilute chamber. Basis on this principle, electro-dialysis can be used in the wastewater treatment of electroplating industry. However, electro-dialysis technique has several inherent limitations. Firstly, electrolysis is most favor to remove low molecular weight ionic species from feed stream, but not suitable for non-charge, high molecular weight and less mobile species. Secondly, the removal efficiency is relatively low for effluents with extreme low salt concentration in range of 10 to 100 ppm . Since the current utilization efficiency is directly proportional to the feed salt concentration. A lower feed salt concentrations leads to fewer current-carrying ions in solution, resulting in reduction of ion transport and energy efficient. As a result, large membrane areas are required to satisfy capacity requirements for low concentration feed solutions. Thirdly, the use of electro-dialysis requires pretreatment of the feed solution in order to remove species such as calcium, magnesium hardness, suspended solids, silica and organic compounds so that they could not foul the surface of ion exchange membranes.

1.2.4 Electrowinning

Electrowinning is a process similar to the electroplating process which is able to recover metal ions from solution onto the electrode by electrolysis method. During electrowinning process, cation in solution goes toward the cathode and anion goes toward the anode. The cathode is where reduction takes place and the anode is where oxidation takes place. Therefore, positive charge metal ions move toward the cathode and reduced on the surface of cathode as shown in the following equation:

$$M^{X+}_{(aq)} + Xe^- \rightarrow M_{(s)}$$

Electrowinning process has been used in recovery of different metal ions from metal ion containing wastewater such as electroplating effluents and leaching solution. The performance of electrowinning process depends on several parameters such as current efficiency, current density, over-potential and flow rate of solution.[17,18] Thus, optimal parameters of electrowinning process in recovery of different metals from wastewater have been studied. Dutra *et al.* (2008) reported that 99.9% of copper was recovered on stainless steel mesh cathode in a 26 g/L cupper ion solution in the presence of cyanide. After electrolysis for 5 hours, 99% of cyanide was destructed under flow rate of 0.27 L/min and current density of 9.4 mA/cm^2. The major advantages of electrowinning process are that minimum quantities of sludge was produced and little amount of chemical was added during the electrowinning process. [18] Furthermore, some of electroplating companies can use remaining capacity to setup electrowinning process for their wastewater treatment when not operating at a full capacity.[18] Therefore, there is no need to consider sludge disposal, chemical and capital investment costs. Although electrowinning seems to be economical way in wastewater treatment, it has its inherent limitations in removal of metal ions from wastewater. The major drawback is the poor capability in treating relatively low concentration of metal ions in wastewater because large current or voltage is required in removing metal ions from electroplating wastewater. Thus, high energy cost is required. Furthermore, since surfactants always use in electroplating process, their presence could lower treatment efficiency of the electrowinning process because adsorbed surfactant on the cathode during electrowinning process would decrease the effective cathode area, resulting in blockage of the growing sites of metal on the cathode. In addition, the long chain length of the surfactant in solution would hinder the diffusion of metal ions from bulky solution to the surface of cathode, resulting in decreasing the mass transfer coefficient of solution at the cathode-solution interface

and the rate of electro-reduction of metal ion. As a consequence, higher energy input is required for electroreduction of metal.[19] As the applied voltage exceeds hydrogen over-voltage in electrowinning process, hydrogen is evolved from the cathode and the efficiency of electroreduction of metal is decreased.[20]

1.2.5 Ion exchange column

Ion exchange column is one of wastewater treatment technology which can be implemented to treat low concentration of metal ion in wastewater. Ion exchange column is packed with ion exchange resin which consists of two essential parts: a chelating group and a polymeric matrix. A polymeric matrix is a three-dimensional network polymer which can provide mechanical stability for ion exchange resin and chemical resistance property towards acid and base during the resin regeneration process. The cheating group which is attached to a polymeric matrix aims to adsorb metal ions from wastewater through an electrostatic interaction or/and ligand complexation. The cheating groups on the ion exchange resin can be synthesized by two different methods: 1) post-functionalization of a polymeric matrix; and 2) polymerization of a chelating group containing monomer. Functionalization of polymeric matrix means incorporating a host of ligands, such as aminocarboxylic acids, hydroxamic acids, oxines, pyridine, carboxylic acids, acid hydrazides, arsenic acids, phosphonic acids, dithiocarbamates, thiols, schiff bases, crown ethers, cryptands, iminodiacetic acid, amidoxime, aminophosphonic acid into the polymeric matrix (Table 2).

Table 2. Chemical structure of a host of ligand

Name of a host ligand	Chemical structure of a host of ligand
Aminocarboxylic acid	
Hydroxamic acids	
Oxines	
Pyridine	
Carboxylic acids	
Acid hydrazides	
Arsenic acids	
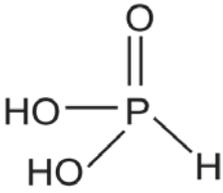
phosphonic acids	
Dithiocarbamates	
Thiols	
Schiff bases	
Crown ethers	
Cryptands	
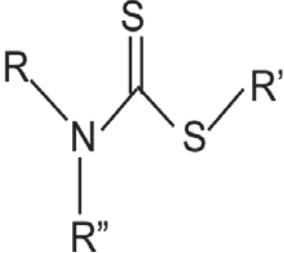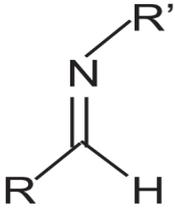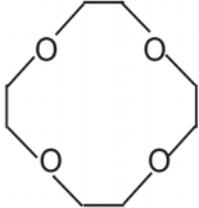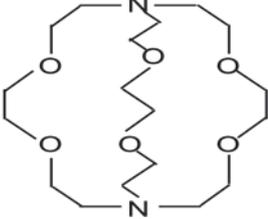
Iminodiacetic acid	
Amidoxime	
Aminophosphonic acid	

A chelating monomer can be polymerized to form polymer and then cross-linked by a cross-linking agent to prepare a chelating ion-exchange resin.[21] Types of chelating groups on the ion exchange resin can directly affect the performance of metal ion removal because chelating groups have selectivity on metal ions and optimum pH for adsorption. In addition, particle size of ion exchange resin and flow rate of wastewater in ion exchange column can also affect the performance of metal ion removal. Extensive research has been carried out to investigate the optimized operation conditions on different ion exchange resins using wastewater containing various metal ions. Panayotova *et al.* (2007) demonstrated the use of different type of trademark ion exchange resins (strong and weak acid cations) produced from Dow Chemical, Rohm & Haas Co., and Bayer to treat copper and chrome-containing water.

Results showed that using strong acid cation ion exchange resin column allows to treat 780–940 and 390–470 bed volumes of copper containing wastewater with concentration of 50 or 100 mg/L, respectively, and to treat 620-740 and 260-310 bed volumes of chrome containing wastewater with concentration of 50 or 100 mg/L respectively. The data also showed that exhausted strong and weak acid cation ion exchange column is able to concentrate heavy metal concentration up to 10-15g/L and 20-25g/L, respectively. These results indicated that the ion exchange column were effective for low concentration of copper and chrome removal. Although the use of ion exchange resin is an effective way to removal metal ions, and the resin is capable of regeneration in the column due to its porosity and good surface area, it suffers from some major drawbacks such as high capital cost in equipment, installation, operation and maintenance. As a result, majority applications using ion exchange column is in post-treatment of wastewater containing low concentration of heavy metal ion.

1.3 Membrane filtration (separation) technology

1.3.1 Introduction

1.3.1.1 Membrane filtration

Membrane filtration technology is a physical process that separate particles ranging from bacteria to atom based on the pressure difference across the membrane which is called pressure driving force. Pressure driven membrane filtration processes are commonly divided into four major categories as summarized in Figure 2 and Table 3:

Microfiltration

Microfiltration (MF): Microfiltration is a clarification process to retain the particle in the "submicron" range (suspended particles normally above 0.1um). Microfiltration is commonly used in removing bacteria and pigment, as well as suspended particles with sizes in the submicron range.

Ultrafiltration

Ultrafiltration (UF): Ultrafiltration is a process to separate macromolecules or particle with sizes larger than 0.005um (5 nm). Ultrafiltration is able to remove bacteria and viruses, and can separate macromolecules like sugar, proteins, as well as colloidal for purification, concentration, and fractionation purposes.

Nanofiltration

Nanofiltration (NF): Nanofiltration is a process that uses charged membrane with salt rejection lower than reverse osmosis (RO). It is often used in removing color, sugar and dye. It also can separate dissociated forms of compounds from their undissoicated ones such as lactic, citric and acetic acid. The dissociated form can pass through NF membrane easily at low pH, but their salts are rejected at higher pHs.

Reverse Osmosis

Reverse Osmosis (RO): RO is an opposite osmosis process that water is driven from low water potential area to high water potential through a semi-permeable membrane by applying a high pressure. The RO is commonly used in separating aqueous salt and ions with molecular weight less than 200. It can also separate heavy metal ions.
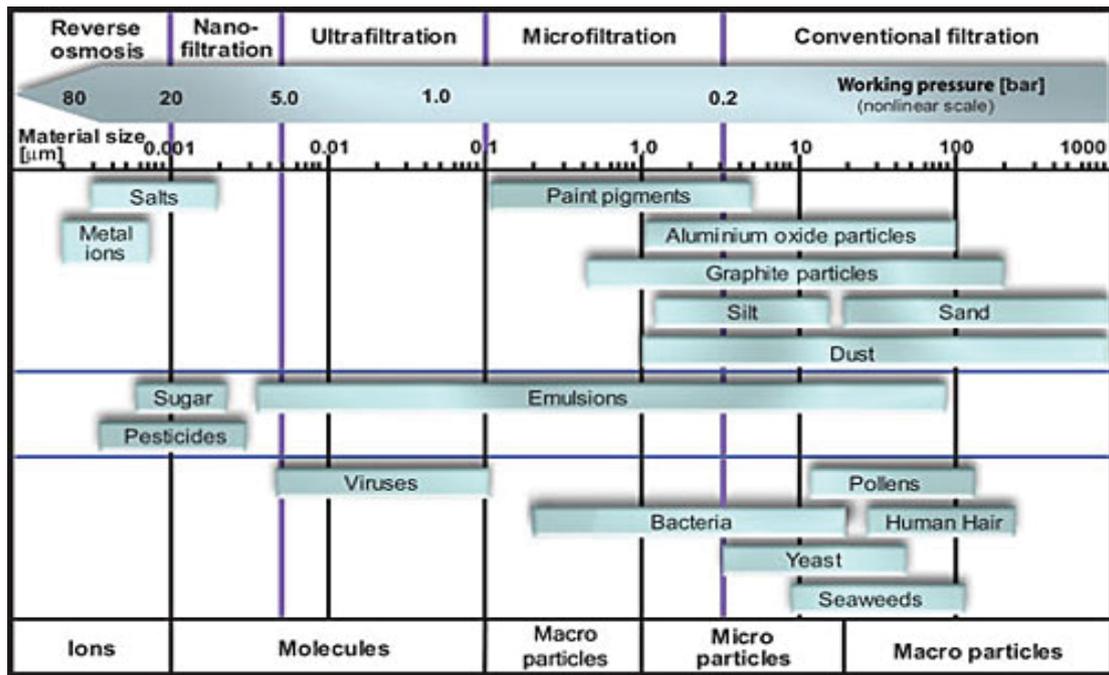
Figure 2. Membrane filtration spectrum

Table 3. Characterization of membrane processes

Process	Driving force	Retentate	Permeate
Microfiltraiton	Pressure	Suspended particles, water	Dissolved solution, water
Ultrafiltration	Pressure	Large molecules	Small molecules, water
Nanofiltration	Pressure	Small molecules, divalent salts, dissociated acids, water	Monovalent ion, undissociate acid Water
Reverse osmosis	Pressure	All Solutes, water	Water

1.3.1.2 Membrane structure

Generally, membrane is regarded as a filter, acting like filter paper or mesh. Filters are classified into two categories: depth filter and screen filters (Figure 3):
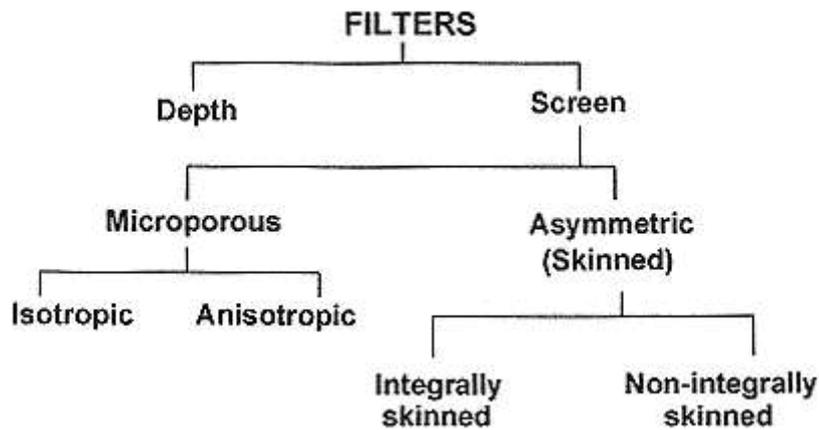
Figure 3. Classification of filters [23]

Depth filter is that particles are separated in the depths of the filter material. In contrast, screen filter removes particle on the filter surface. Membrane filter is belonged to the screen filter which can also be further classified into two types according to their structures: microporous or asymmetric (skinned membrane). There are two types of microporous membranes: isotropic and anisotriopic. The isotropic refers to the membrane with uniform pore size and anisotropic means the changing pore size along the membrane. Microporsous membrane usually has an absolute rating (pore size) that all of particles above its rating (pore size) cannot pass through the membrane. However, particle with size similar to the pore size of the membrane may probably penetrate into the pores and block them. Therefore, a rapid flux decline during first few minutes of operation is usually observed in MF membrane, arising from plugging of pores in the membrane.

Asymmetric membrane, similar to anisotriopic type microporous membrane, possess various pore sizes along the membrane, but the difference of pore size between skin layer and supporting layer is well-defined. The supporting layer consisting of many voids serves to support the skin layer in asymmetric membrane. The skin layer serves to reject or retain particle or macromolecules above the molecular weight cut-off (MWCO) to avoid entry of particle or macromolecules into supporting layer. Therefore, asymmetric membrane rarely plugs as compared with microporous membranes. On the other hand, similar to other filter, asymmetric membranes are susceptible to fouling and concentration polarization resulting in flux decline. Most of UF, NF and RO membranes have this structure, but not in most of MF membrane. Asymmetric membrane is also divided into integrally skinned and non-integrally skinned types. Integrally skinned asymmetric membrane is manufactured in one-step procedure in membrane manufacturing process with single polymer, while non-integrally skinned asymmetric membrane is made in two or more step by deposition of thin denser polymer skin solution onto a microporous support film. Thin-film composite, ultrathin, or thin-layer composite application in NF and RO belong to non-integrally skinned type.
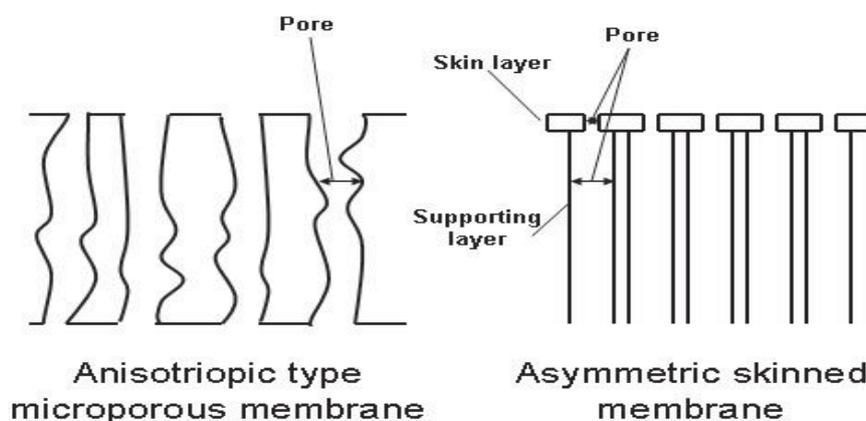
Figure 4. Anisotriopic type microporous and Asymmetric skinned membrane

1.3.1.3 Polymer used in membrane manufacturing

Membrane can be made up of different types of material, but the majority of membranes are made up from polymer. Table 4 shows a list of typical polymers used in the membrane manufacturing process. However, not all of polymers are suitable for application in pressure-driven membrane processes, thus there are only a few of commercialized polymeric membrane. Table 5 illustrates advantages and disadvantages of some commercial available polymeric membranes in pressure-driven membrane processes.

Table 4. Polymer used in membrane manufacturing[23]

Material	MF	UF	RO
Cellulose ester (mixed)	X		
Cellulose nitrate	X		
Polyamide, aliphatic e.g Nylon	X		
Polycarbonate	X		
Polyester	X		
Polypropylene (PP)	X		
Polytetrafluoroethylene (PTFE)	X		
Polyvinyl chloride (PVC)	X		
Polyvinylidene fluoride (PVDF)	X		
Cellulose (regenerated)	X	X	
Polyacrylonitrile (PAN)	X	X	
Polyvinyl alcohol (PVA)	X	X	
Polysulfone (PS)	X	X	
Polyethersulfone (PES)	X	X	
Cellulose acetate (CA)	X	X	X
Cellulose triacetate (CTA)	X	X	X
Polyamide, aromatic (PA)	X	X	X
Polyimide (PI)		X	X
Composites, Polymeric thin film			X
Polybezimidazole (PBI)			X

Table 5. Summary table of disadvantages and advantages of different polymeric membrane[23]

Membrane type	Advantage	Disadvantage
Cellulose Acetate	Low fouling due to high hydrophilicity Wide range of pore sizes with high flux Easy to manufacture Low cost	Narrow temperature range (max. temperature = 30°C) Narrow pH range (pH 2-8) Low Chlorine tolerance Creep or compaction under high pressure Poor storage properties due to highly biodegradable
Polyamide	Wider pH range	Low chlorine tolerance High biofouling tendency
Polysulfone	Wide temperature limits (75 to 125°C) Wide pH range (pH 1-13) Good chlorine resistance Wide range pore sizes available	Low pressure limit High fouling tendency due to it hydrophobility
Polyvinylidiene fluoride (PVDF)	Good resistance to common solvent Better resistance to chlorine than polysuflone	
Polytetrafluoroethylene (PTFE)	Very table to strong acid, alkalis and solvents Wide range temperature	
Polypropylene (PP)	High chemical resistance Withstand moderate high temperature	
Regenerated cellulose	Good resistance to common solvents Tolerate temperature up to 75°C	

1.3.1.4 V-SEP membrane filtration system (vibrating module)

Vibrating shearing enhanced process (V-SEP) membrane filtration system developed by New Logic Research Inc. is a vibrating module of membrane filtration system. V-SEP membrane filtration system is composed of four major components: a driving system, a membrane module (filter pack), a torsion spring (central shaft), and a system for controlling vibration. Unlike rotation module, V-SEP membrane module vibrates in a torsional oscillation similar to the action of clothes washing machine with maximum frequency of 60.75 Hz and maximum amplitude of 25.4mm (1 inch).[24,27,32,34] The vibration generated from eccentric drive motor in the driving system transfer to a membrane module through the torsion spring by the torsional oscillation motion. V-SEP membrane filtration system consists of two scales: pilot-plant and industrial scales with three categories types: I, P and L type.[24,25,26] I type V-SEP is regards as an industrial scale, and P and L type belonged to a pilot-plant scale. L type is the simplest type V-SEP membrane system because the filter pack in L type V-SEP only composes of a single membrane sheet. Therefore, ease of replacement of membrane sheet in L type V-SEP facilitates for the feasibility test and trial test in V-SEP application. In L type V-SEP membrane module, the filter pack consists of two steel plates and polypropylene clamshell acting as housing for membrane installation. A single annular membrane sheet with outer diameter 27 cm and inner diameter 9.4 cm is placed with a feed side facing downward and a tricot like drain cloth is placed on the top of membrane sheet inside polypropylene clamshell.[24,25,26,30,33,35] The feed sample is circulated by feed pump and feed into the feed inlet at one side of membrane module bottom plate and concentrates leave via concentrate outlet at the other side. The permeate is collected via permeate outlet located on the top of membrane module. If the application trial test is feasible in L

type V-SEP, P type V-SEP will be subsequently used for the same application. The external feature of P type V-SEP is similar to L type V-SEP but the major difference between the P type and L type are the internal configuration of filter pack and pipe connection (inlet and outlet).[24] In P type V-SEP, the feed inlet and permeate outlet are located on the top of filter pack. The feed inlet originated in L type V-SEP become concentrate outlet in P type V-SEP. This changing of pipe connection is arising from the difference in internal configuration of filter pack. In P type V-SEP, the feed solution is flow from the feed inlet located on the top of filter pack to horizontal parallel feed channel shown in Figure 13. Diverter grommet act as the barrier to avoid the direct passage of feed solution from the top of filter pack to concentrate outlet at the bottom of filter pack. Permeate in all of permeate channel is collected in the central tube and leave at the top of filter pack via permeate outlet. In I type V-SEP, the internal configuration of filter pack is same as P type V-SEP. Therefore, both of filter pack internal configuration in P type and I type V-SEP is same except of the process scale. In V-SEP membrane filtration system, the vibration oscillation or shear force on the membrane is mainly controlled by electronic frequency controller which is able to adjust the oscillation frequency with 0.01 Hz accuracy and the resulting amplitude was shown in Figure 14 according to the pattern of appropriate black indicator marks placed on the front of the filter pack.[24] Similar to rotary module, the major advantage of V-SEP membrane filtration system is able to create higher shear rate compared with four conventional membrane modules. In traditional cross-flow membrane filtration, high cross flow velocity across the membrane surface must be maintained to minimize the boundary layer and concentration polarization effect. However, increased cross flow velocity result in pressure drop between inlet and outlet of membrane module. This result in premature fouling and permeate flux drop to unacceptable low level. Nevertheless, V-SEP

membrane filtration system settle this drawback in traditional cross-flow membrane filtration by its high shear rate up to 150,000 sec^{-1} which is approximately 10 times than conventional cross-flow membrane system. This high shear rate can create shear wave on membrane surface to lift off solid and foulants and allow remix of these solids and foulants into bulky feed solution in feed channel. This action allows the maximum exposure of membrane pore to bulky feed solution resulting in 3-10 times permeate flux than conventional cross-flow filtration system and allows the higher feed concentration than in conventional cross-flow filtration system.
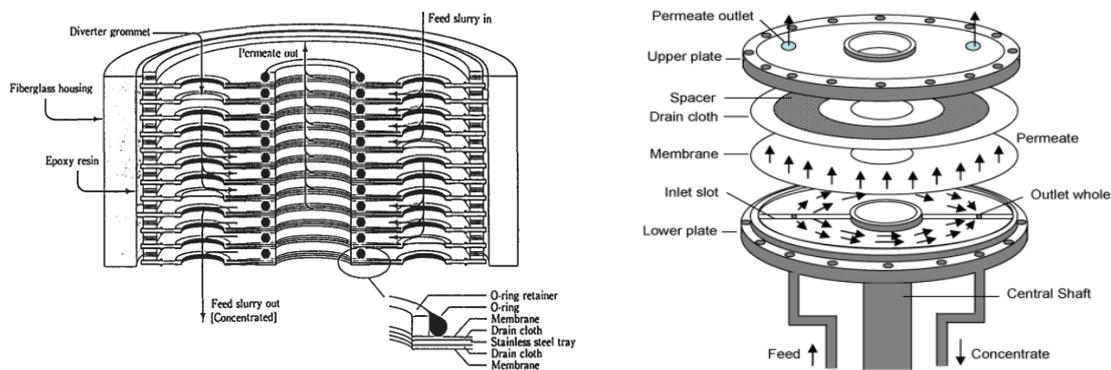
Figure 5. Internal structure of P and L types V-SEP filter packs
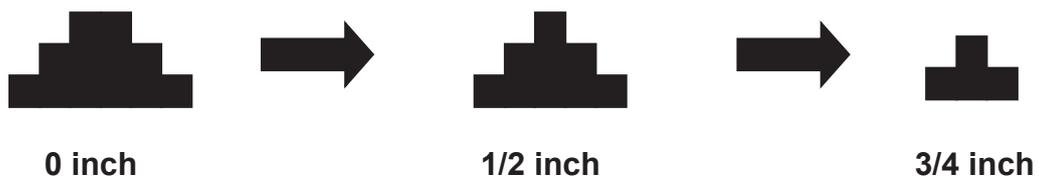
Figure 6. Black indicator marks controlling oscillation (vibration) amptitude

Table 6. Details of different scale of V-SEP membrane filtration system[25]

Model	P	I 36	I 84
Dimension include filter pack	L76cm x W61cm x H194cm	L1.2 m x W1.2m x H3.3m	L1.2m x W1.2m x H 5m
Weight	273 kg (filter pack included)	body: 1300 kg filter pack: 400 kg	body: 1600 kg filter pack: 1000 kg
Filtration area	16.6 sq ft	400 sq ft	1050 sq ft
Operating temperature	4-90°C	4-90°C	4-90°C
Operating pressure : MF	Around 30-80 psi	Around 30-80 psi	Around 30-80 psi
UF	Around 100-250 psi	Around 100-250 psi	Around 100-250 psi
NF	Around 300-500 psi	Around 300-500 psi	Around 300-500 psi
RO	Around 400-600 psi	Around 400-550 psi	Around 400-550 psi
pH tolerance	1-13	1-13	1-13
Elastomer	EPDM (optional BUNA or Viton)	EPDM (optional BUNA or Viton)	EPDM (optional BUNA or Viton)
Membrane supporting material	304L S.S. (optional 316)	304L S.S. (optional 316)	304L S.S. (optional 316)
Noise level			
Max. sound level :	80 dB	95dB	95dB
Power requirement			
voltage :	380V AC 3-phase 50Hz	380V AC 3-phase 50Hz	380V AC 3-phase 50Hz
Ambient temperature			
Operating temperature :	0-40°C	5-37°C	5-37°C
Storage temperature :	0-40°C	2-70°C	2-70°C

1.3.1.5   V-SEP membrane filtration system in wastewater treatment

Vibratory shear enhanced process (V-SEP) membrane filtration system is an advanced and proved membrane filtration system due to its increase in shear rate on membrane surface as compared to traditional membrane filtration system. Applications of V-SEP membrane filtration system in wastewater have been reported in the literature. Moulai-Mostefa *et al.* (2010) reported that using polyethersulfone (PES) ultrafiltration membrane with 50 kDa and 20 kDa in V-SEP system could effectively separate oil from metal working emulsions. Ahmed *et al.* (2010) investigated the use of V-SEP with sulfonated polyethersulfone (SPES) and polypiperzaine-amide (PPA) nanofiltration membranes for removal of arsenic (III) and arsenic (V) from drinking water. Zouboulis *et al.* (2008) investigated the performance of V-SEP vibratory membrane filtration system during the treatment of raw stabilized landfill leachate. Four different types of membrane: microfiltration PTFE membrane with mean pore size of 0.1um, ultrafiltration regenerated cellulose membrane with 100kDa and 10kDa, nanofiltration polyamide and polysulfone composite membrane with 50% salt rejection were used in this study. They concluded that V-SEP system using nanofiltration membrane could not remove organic matter in term of COD and ammonium nitrogen below discharge standards but the removal efficiency of contaminants was significantly higher as compared with removal efficiencies obtained by other conventional membrane filtration technology.

Table 7. Summary of V-SEP membrane filtration system application in wastewater

Application	Target contaminant to be removed	Max. Rej(%)	Reference
CRT picture tubes wastewater	Fine carbon	No mention	30
Ground wood mill circulation water	Organic matter	Turbidity =94 TOC = 70	31
Arsenic removal in surface water	Arsenic (III) Arsenic (V)	As(III) = 80.5 As(V) = 99.5	32
Landfill leachate	Organic matter	COD = 90	33
Water separation for metal working emulsion	Oil emulsion	Turbidity =99	34
Surface water	Organic matter	COD = 99.5	35

1.4 Water-Soluble polymer assisted membrane Filtration Technology in Wastewater

Membrane filtration technologies have been applied in different types of wastewater treatment. Uzal *et al.* (2006) reported that using microfiltration acts as a pretreatment method for color removal in indigo dyeing textile effluent under trans-membrane pressure 0.08-1 bar. Qdais *et al.* (2004) demonstrated that using reverse osmosis for treatment of wastewater containing copper and cadmium under operation pressure of 7-13 Bar. The required pressure in a reverse osmosis system is above 10 times higher than the microfiltration. Such high pressure requirement also leads to high energy consumption. On the other hand, reverse osmosis has the smallest pore size membrane in the membrane categories as described in Figure 2. Theoretically, flux performance of membrane is dependent upon its pore size. This implies that reverse osmosis membrane has the lowest flux performance among all of membrane categories. In full scale application of reverse osmosis membrane in ion removal in wastewater, such high energy consumption and lowest flux performance inevitably increase operation and equipment cost, resulting in lower economic benefit from reverse osmosis process.

In order to address this inevitable problem of reverse osmosis process in removing metal ion from wastewater, researchers have explored other membrane separation technologies with lower pressure and higher flux performance. For example, water-soluble polymers assisted membrane filtration process has been developed. This method is achieved through binding heavy metal ion by a functional group of water soluble polymer, followed by subsequent separation of the bound metals on water-soluble polymer.[96-112] Theoretically, binding of heavy metal on

functional group is based on two basic adsorption mechanisms: electrostatic interaction and liganid complexation. Water-soluble polymers contain donating groups such as amine, amides, alchols, aminoacid, pyridines, thiourea, imino. The lone pair electrons of nitrogen, sulphur, or oxygen can coordinate with heavy metal ions at specific pH as shown in the following equation:

$$nR_c\text{-}NH_2 + M^{n+} \rightarrow M(R_c\text{-}NH_2)_n^{n+} \quad M^{n+} = \text{metal cation}$$

Water-soluble polymers bear negative charge species such as carboxylic acid, phosphoric acid, sulfonic acid can bind metal ions through electrostatic interaction at specific pH as shown in the following equation:

$$nR_c\text{-}COO^- + M^{n+} \rightarrow (R_c\text{-}COO)_n M$$
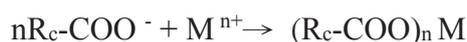
Although most of heavy metal ions bear positive charge, some of heavy metal cation bond with other species to form positive charge species such as chromate ion (CrO_4^-). As a result, water soluble polymer bear positive charge species such as protonated amine group which also can interact electrostatically with heavy metal species with positive charge shown as following equation:

$$nR_c\text{-}NH_3^+ + MO_x^{n-} \rightarrow (R_c\text{-}NH_3)_nMO_x \quad MO_x^{n-} = \text{metal negative charge species}$$

After binding heavy metal ions on the water-soluble polymer, the polymer/metal complexes are separated through membrane filtration. The bonded heavy metal ions must be desorbed from the water-soluble polymers so that the water-soluble polymer can be regenerated and the heavy metal ions are recovered. Desorption process is usually achieved through replacing other ion on the water-soluble polymer. Acid being the hydrogen ion is commonly used in the regeneration process because hydrogen ion is able to replace adsorbed heavy metal ion on water-soluble polymers

according to the following reactions:

$$M(R_c\text{-}NH_2)_n{}^{n+} + nH^+ \rightarrow (R_c\text{-}NH_3)_n{}^+ + M^{n+}$$

$$(R_c\text{-}COO)_n M + nH^+ \rightarrow (R_c\text{-}COOH)_n + M^{n+}$$
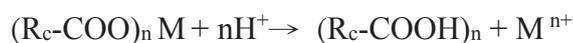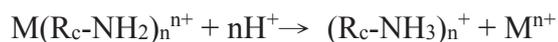
However, the regeneration process of negative charged heavy metal species loaded water-soluble polymer is different from positive charged heavy metal species loaded water-soluble polymer. In this process, hydroxide ion is commonly used because hydroxide ion is able to replace adsorbed heavy metal species on water soluble polymers and subsequently react with the hydrogen ions on water-soluble polymer to form water molecules as shown below:

$$(R_c\text{-}NH_3)_n MO_x + nOH^- \rightarrow nR_c\text{-}NH_2 + MO_x{}^{n-} + nH_2O$$
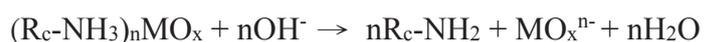
Based on the above description on adsorption and regeneration mechanism, pH adjustment plays an important role in controlling the adsorption and desorption properties of water-soluble polymer. In removal of heavy metal cation, adsorption process is mostly preferred at neutral to alkaline pH for water-soluble polymer bearing with negative charge and regeneration process is mostly preferred at acidic pH. In removal of heavy metal bonded species with negative charge, adsorption process is most preferred at acidic pH for protonation of functional group on water soluble- polymer and regeneration process is preferred under alkaline pHs.

In accordance with this mechanism, different types of water-soluble polymer and membrane filtration hybrid process have been studied in removal of heavy metal from water and wastewater. Recovery of both water-soluble polymer and heavy metal were also investigated. Polyethyleneimine (PEI) is one the most studied water-soluble polymers for wastewater treatment.
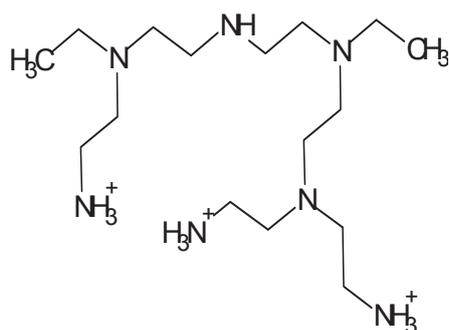
Figure 7. Chemical structure of polyethylenimine (PEI)

Aliane *et al.* (2001) investigated the use of PEI as a water-soluble macromolecule to remove chromium ion (Cr^{3+}) from wastewater. The process was assisted with tubular ultrafiltration using 15 and 50 KDa membranes. Results showed that the use of PEI increased the rejection rate of chromium ion from 30% to 80% from pH 2 to 5, while the rejection rate of chromium ion was from 5% to 20% from pH 2 to pH 5 in the absence of PEI. In addition, transmembrane pressure on permeate flux increased from 0 to $200L/hm^2$ when increasing the transmembrane pressure from 1 to 4 bar. It is evident that the water-soluble PEI polymer can complex with chromium ion and a growth of trans-membrane pressure results in increase of permeate flux.

Barron-Zambrano *et al.* (2002) demonstrated the use of PEI complexing polymer in separation of mercury from aqueous solution with ultrafiltration hybrid process, and subsequently regenerating PEI complexed polymer in a ultrafiltration process. The effect of pH and chloride on the retention rate of mercury was investigated with 15 KDa molecular weight cur-off ultrafiltration membrane under 4 bar pressure. The result showed that the retention rate reached a plateau with above 95% from pH 6 to 10 without chloride ion and with 1.0 M chloride ion. The retention rate decreased with increase in chloride ion from 0 to 1.0 M from pH 2 to 5. In subsequent

regeneration water-soluble polymer process, they discovered that the regeneration of water-soluble polymer can be performed at pH 3.5 and with a chloride ion concentration of 0.6 mol L^{-1}. They concluded that chloride ion and pH have effects on the retention rate of mercury ion using PEI water-soluble marcomolecules.

Molinari *et al.* (2004) reported that water-soluble chelating polymer PEI remove copper ions from wastewater. Five types of membrane were selected in their study: 1) Poly(ether sulphone) (PES) with molecular weight cut off of 10 kDa, 2) Fluoride-polypropylene (40 kDa), 3) Polysulphone-polypropylene (40 kDa), 4) Polyether sulphone (PES) (30 kDa), and 5) Polyacrylonitrile (PAN) (40 kDa). The effects of pH and PEI ratio on rejection percentage and polymer concentration on flux and rejection percentage were investigated. The result showed that the optimal pH is equal to 6 and the ratio of Cu^{2+} to PEI polymer is 1 to 3. Also, they discovered that the flux slightly decreased and rejection slightly decreased to 96% in the five different types of membrane as polymer concentration increased from 150 to 600 ppm. According to the results, they concluded that PAN 40 kDa is the best membrane for separation of copper ion from ultrafiltration in this investigation.
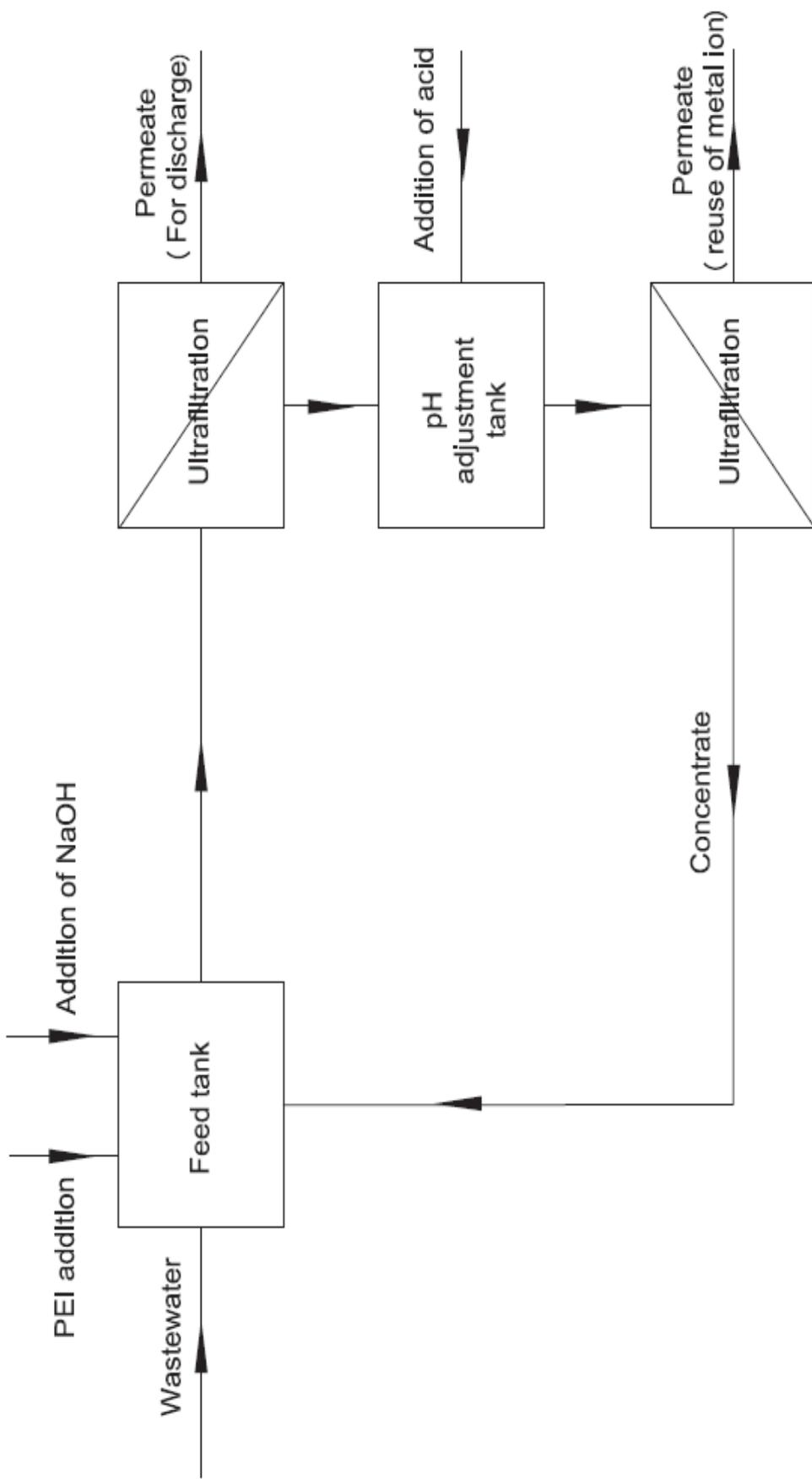
Figure 8. Water soluble polymer PEI assisted with ultrafiltration process principle diagram

Table 8. Summary of water-soluble polymer assisted membrane filtration process for heavy metal removal

Element	Species	Solution type	Polymer	pH	Max. Rej (%)	Ref.
Ca	Ca^{2+}	Pulp and paper wastewater	PEI	4.7	41	110
			PVA	4.7	52	110
Cd	Cd^{2+}	Not mention	PEI	5.59	95	103
Co	Co^{2+}	Not mention	PEI	6	~75	101
Cr	Cr^{3+}	$Cr_2(SO_4)_3$ and $CrCl_3$ solution	PEI	5	>80	104
		$Cr(NO_3)_3$ solution	PEI	6	~80	105
			Pectin	5	>80	105
	Cr^{6+}	$K_2Cr_2O_7$ solution	PEI	3-9	100	105
			Pectin	8	~50	105
Cu	Cu-EDTA	Cu^{2+}-EDTA solution	PEI	4	>90	106
	Cu-citrate	Cu^{2+}-citrate solution	PEI	5.5	99	96
	Cu^{2+}	$CuSO_4$ solution	PEI	6	>95	97
			PAA	4.6	>95	
			PAASS	4.6	>95	
			PDEHED	8	>95	
			PEI	6	>96	100
		Not mention	PEI	6	>92	107

Table 8. Summary of water-soluble polymer assisted with membrane filtration process for heavy metal removal

Element	Species	Solution type	Polymer	pH	Max. Rej (%)	Ref.
Cu	Cu^{2+}	Not mention	PEI	6	~100	101
			PAA	6	~90	101
			PMC	6	~90	101
			VBAC	6	~90	101
			VA-212	6	~25	101
Fe	Fe^{2+}	Pulp and paper wastewater	PVA	4.7	79	110
			PEI	4.7	62	110
Hg	Hg^{2+}	$Hg(NO_3)_2$ solution	PEI	6	>85	98
			CTS	6	>90	
			PEI	7-9	~100	99
Mg	Mg^{2+}	Pulp and paper wastewater	PVA	4.7	50	110
			PEI	4.7	52	110
Mn	Mn^{2+}	Pulp and paper wastewater	PVA	4.7	93	110
			PEI	4.7	64	110
Ni	Ni^{2+}	Not mention	PEI	6	~100	101
			PEI	5.88	97	103
			PEI	6	>92	107
		electroplating solution	Metal-set-Z	7	~100	102

Table 8. Summary of water-soluble polymer assisted with membrane filtration process application in heavy metal removal

Element	Species	Solution type	Polymer	pH	Max. Rej (%)	Ref.
Ni	Ni^{2+}	$NiCl_2$ solution	PEI	5	>96	108
			PC	5.2	>96	108
Pb	Pb^{2+}	Not mention	PEI	6.92	90	103
U	U^{6+}	UO_2SO_4 solution	PEI	5-9	~99	109
Zn	Zn^{2+}	Not mention	PEI	6	~90	101
		electroplating solution	Metal-set-Z	7	~100	102

Chapter 2

Development of Novel Water Treatment Methodology Using Amphiphilic Nanosorbent with V-SEP membrane filtration System

2. 1 Introduction of amphiphilic core-shell nanosorbent

Nanosorbent used in these studies is referred to a kind of amphiphilic core-shell particles that composed of hydrophobic cores and a hydrophilic shell layers. Li and coworker reported the synthesis of a range of core-shell particles using different types of water-soluble polymers including biopolymers and synthetic polymers (Figure 9). The particles were synthesized via a combination of graft copolymerization and emulsion polymerization of a monomer under 80 °C. This approach has the unique feature of combining graft polymerization, *in situ* self-assembly of the resulting amphiphilic graft copolymer and emulsion polymerization in a one-batch synthesis. This versatile and simple method enables us to prepare a wide variety of amphiphilic core-shell particles with different chemical structure, composition, size and functionality. It is also amenable to commercial production. Some distinctive advantages of this synthetic route and its products include the following:

- The particles have well-defined core-shell nanostructure with particle sizes ranging from 60 to 500 nm in diameter and narrow particle size distribution.
- The core diameter, shell thickness, and surface functionality can be easily altered through the control of reaction conditions.

- The core property can be varied from hard, soft, and temperature-sensitive to hollow.

- The shell component can use a wide range of commercially available and inexpensive amine containing water-soluble polymers, particularly biopolymers.

- The process uses aqueous-based chemistry, which is environmentally benign.

- The particles are easy to synthesize in high solids content (up to 30%) in the absence of surfactant.
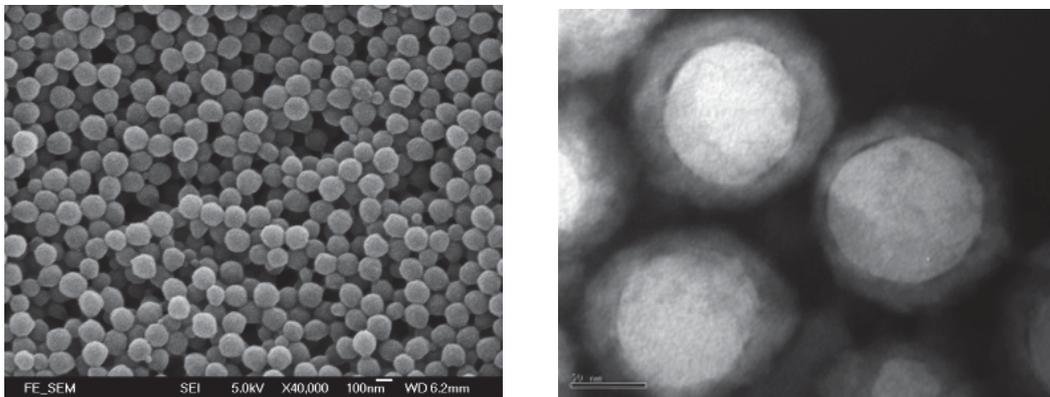
Figure 9. Morphology of particles with well-defined hydrophobic cores and hydrophilic shells

2.2 Application of PMMA/PEI nanosorbent with V-SEP membrane filtration system in water and wastewater treatment

Although water-soluble polymer assisted membrane filtration process can enhance the efficiency of membrane filtration process in removal of heavy metal ion in wastewater, Geckeler *et al.* (1996) pointed out several drawbacks about the use of water-soluble polymer in this process. Water-soluble polymers generally have flexible structure in water. Under high pressure between feed and permeate during the membrane filtration process, the shape of water-soluble polymer can change from a sphere to an ellipse or to a slim cylinder. Such change of molecular architecture under pressure results in passage of these macromolecules through the membrane. In addition, high flow centrifugal pump is commonly used in microfiltration, resulting in creating high mechanical force. Such high mechanical force under high pressure difference in membrane filtration process could cleave high molecular weight water-soluble polymer into lower molecular weight. This molecular degradation results in both loss of water-soluble polymer and heavy metal ions in permeate, and consequently decreases in heavy metal ion retention. One of solutions to overcome this drawback is to covalently link water-soluble polymer onto the surface of a strong and hard support acting as an adsorbent. Thus the adsorbent should possess the following desirable properties:

1) The adsorbent should be able to withstand strong mechanical force generated by a high flow centrifugal pump without structural deformation.

2) The adsorbents should possess high surface area to volume ratio, providing high adsorption capacity of heavy metal ions

3) The water-soluble polymer on the support cannot be detached during the treatment process.

4) The adsorbents should have uniform size for better and easy separation with selected membranes.

5) The adsorbents should have comparable efficiency as the native water-soluble polymer.

Amphiphilic core-shell particles described previously meet most of these desirable properties, thus are considered to be a promising adsorbent for water and wastewater treatment because of the following unique properties:

1) They consists of hydrophobic PMMA core which is regarded as "organic glass" with hard structure property. This property can withstand mechanical force generated by the high flow centrifugal pump under high pressure difference in membrane filtration process.

2) Core-shell particles possess particle sizes from 100 to 300 nm. The nanoscale sizes provide particles with very high surface area to volume ratio, thus giving high adsorption capacity of heavy metal ions.

3) Water soluble polymer is covalently attached onto PMMA hydrophobic core via a novel grafted co-polymerization process, giving a thick and expanded hydrophilic shell layer. This kind of core-shell nanostructure can prevent detachment of water-soluble polymer from the nanosorbent and also provide an thick hydrophilic shell for encapsulation of contaminants.

4) Active functional group for adsorption of contaminants are localized on the external polymer shell of the core-shell particles. This shell structure can provide the shortest path for encapsulation of contaminants from solution to surface of core-shell nanosorbent, resulting rapidly binding of the containments.

5) Finally, narrow particle size distribution can be controlled by surfactant-free emulsion polymerization method. The uniform size of the nanosorbents lead to

homogeneous loading of heavy metal ion onto every core-shell nanoparticle.

6) The adsorbed particles may result in slight aggregation due to lower electrostatic repulsion. The particle aggregation to micro-size allows easier membrane separation and high flow rate. Therefore, the amphiphilic core-shell particles are promising Nanosorbent to replace water-soluble polymer.

The objective of this research is to develop application of poly(methyl methacrylate)/polyethyleneimine (PMMA/PEI) nanosorbent with V-SEP membrane filtration for water and wastewater treatment. This thesis is composed of three major parts with specific objective as shown in the follows flow chart.

(1) Synthesis and characterizations of PMMA/PEI nanosorbent in pilot scale synthesis

(2) Purifying PMMA/PEI nanosorbent with V-SEP membrane filtration

(3) Development of PMMA/PEI nanosorbent in water and wastewater treatme
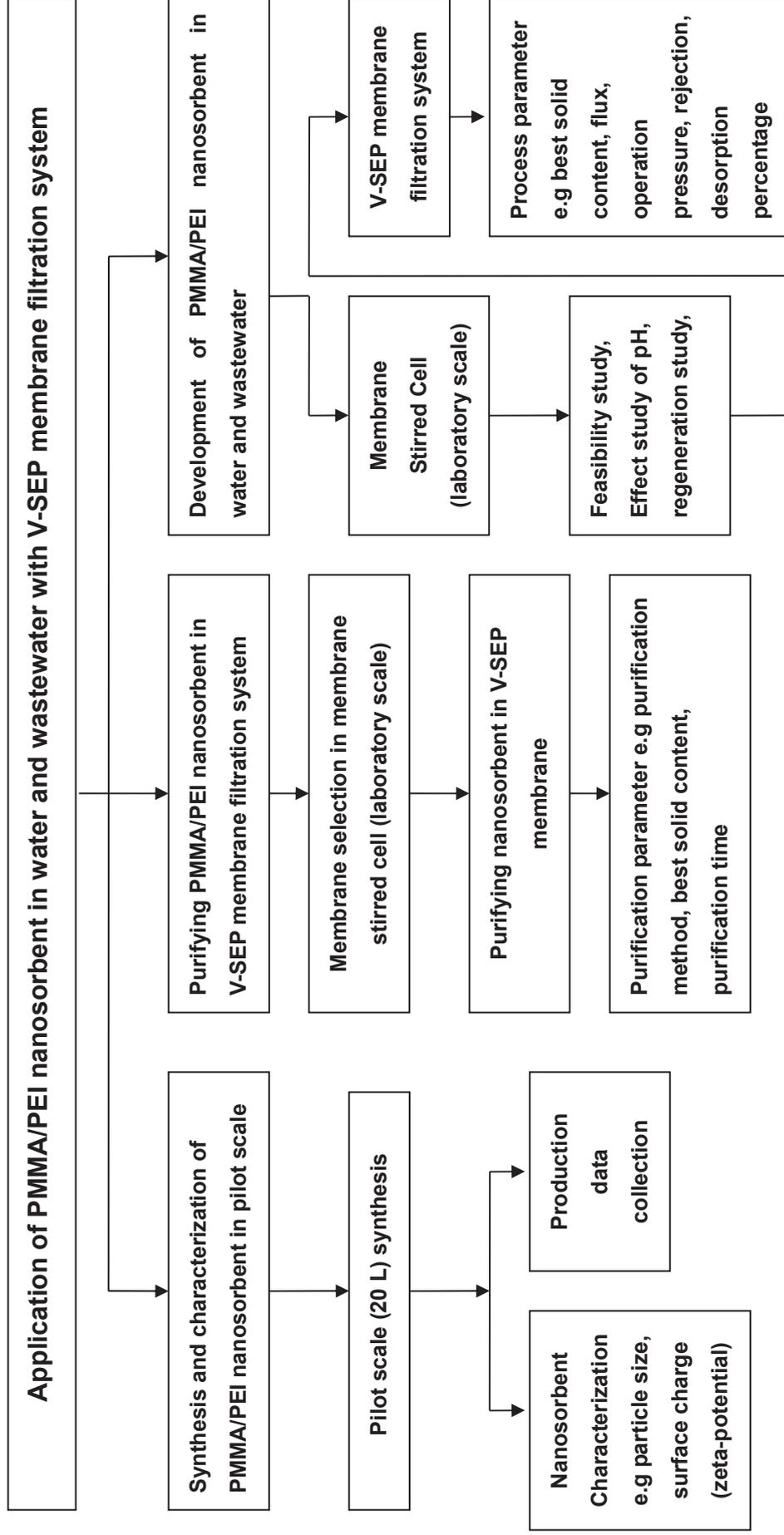
Figure 10. Flow chart of research objective

2.3 Novelty of application of PMMA/PEI nanosorbent with V-SEP membrane filtration system in water and wastewater treatment

Compared to water-soluble assisted membrane filtration process, amphiphilic core-shell PMMA/PEI nanosorbents have a great potential to replace water-soluble polymer in membrane filtration. Novel aspect this work are summarized as follows:

1) The use of amphiphilic core-shell nanosorbent in removal of heavy metal ions from wastewater treatment have never been reported in literature. Thus, this study will open up new materials and methodology for wastewater treatment.

2) Although amphiphilic core-shell nanosorbent can be synthesized up to 22% solid content in laboratory scale, synthesis of core-shell nanosorbent in the pilot scale has not yet been developed.

3) Novel and advanced V-SEP membrane filtration system has been proven to have a better flux performance than tradition membrane filtration system. There is little study on application of adsorbent with V-SEP membrane filtration in wastewater treatment.

4) Novel core-shell nanosorbent consist of hydrophilic water-soluble polymer shell can demonstrate similar adsorption and regeneration mechanisms to water-soluble polymer.

5) Core-shell nanosorbent can overcome the major inherent problems in using water- soluble polymer.

Chapter 3

Synthesis of PMMA/PEI Nanosorbents in a Pilot Scale Reactor

3.1 Introduction of the synthesis

Li's research group has developed a novel method to synthesize amphiphilic core-shell nanoparticles (nanosorbents) through graft copolymerization of vinyl monomers from water-soluble polymers containing amine groups.[115] The previous studies have demonstrated that hydrophilic biopolymers and synthetic polymers possessing primary amino groups can react with *t*-butyl hydroperoxide (TBHP) in water at 80ºC, and generate particles with well-defined core-shell nanostructure shown in Figure 9. The proposed mechanism of this process is described in Figure 10. Initially, the TBHP (t-BuOOH) initiator reacts with amine group of water-soluble polymer to generate nitrogen radical and a *tert*-butoxy (t-BuO•) radical. The resulting nitrogen radical can initiate a graft polymerization of vinyl monomer, while the *t*-BuO• radical can either initiate the homo-polymerization to form a homopolymer via route 2 or abstract hydrogen atom from the water-soluble polymer backbone. The resulting macroradical can then initiate a graft polymerization of vinyl monomer via route 3. Amphiphilic copolymer intermediates generated *in situ* are able to self-assemble to form polymeric micelle. As a result, well-defined and amphiphilic core-shell particles (nanosorbents) can be produced in the absence of surfactant.

Although PMMA/PEI core-shell nanoparticles (nanosorbents) can be produced as high as 23% solid content in laboratory scale as described by Li *et al.* (2002), synthesis of PMMA/PEI core-shell nanoparticles in a pilot-scale has not been studied previously. This chapter covers the synthesis of PMMA/PEI core-shell nanosorbents in a 20 L pilot scale production with the following objectives: (1) to prepare a large quantity of PMMA/PEI nanosorbents for further studies in wastewater treatment with pilot-scale V-SEP membrane filtration system; (2) to collect data from 20 L pilot-scale synthesis for industrial scale PMMA/PEI core-shell nanosorbent (nanoparticles) production. (3) to study properties of nanoparticles such as particles size, surface charge and monomer conversion. (4) to monitor the temperature variation in order to ensure the safe synthesis during a pilot scale production. 5) to monitor polymerization kinetic during different stages of polymerization including monomer conversion and particle size.
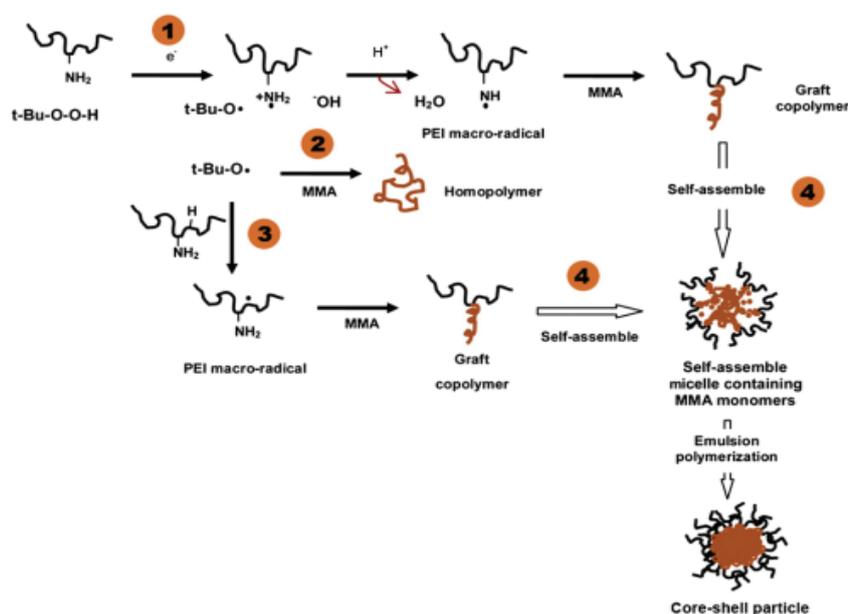
Figure 11.   Proposed nanosorbents synthesis mechanism[119]

3.2 Experimental

3.2.1 Materials

Branched polyethyleneimine (PEI) with weight average molecular weight of 750,000 (50 wt % solution in water) was obtained from Sigma Aldrich. The phenolic inhibitor in methyl methacrylate (MMA, density = 0.936 gcm^{-3}, Aldrich) was removed by washing three times with a 10 % of sodium hydroxide solution and then with deionized water until pH of the water layer dropped to 7.

3.2.2. Synthesis of PMMA/PEI nanosorbents in the 20L reactor

Acidified PEI stock solution containing 500 g of polyethylenimine was pre-adjusted to pH 7 with a 10% HCl solution according to the recipes shown in Table 10. The solution was thentransferred to a 20 L oil-jacketed reactor equipped with a thermocouple, a condenser, a mechanical stirrer and a nitrogen inlet. A fixed amount of purified water (RO water) was transferred to the reactor according to the recipes shown in Table 10. The acidified PEI solution in the reactor was purged with nitrogen for 1 hour and stirred at around 300 rpm. At the same time, the heating circulator was adjusted to 87 $^{\circ}$C. The heated oil was circulated through the jacketed reactor and heated up the solution in the reactor to 80 ^{0}C. When the solution reached 80°C, MMA (640 g) and TBHP (10mL of 200 mM) were then added into the mixture at different reaction time as shown in Table 9. Product samples were withdrawn from the reaction mixture at different reaction time.   At the end of reaction, the monomer conversion was determined gravimetrically, and solid content of the dispersion was caluculated based on the monomer conversion.

Table 9. Semi-batch Synthesis of PMMA/PEI nanosorbent . in 20 L reactor.

Addition Time[A] (min)	Addition interval time [B] (min)	Actual reaction time[C]	Material Addition		Sampling Time[D]
			MMA (g)	TBHP (mL)	
0	0	None	640 g		
10	10	0		10	45 min (sample 1)
60	50	50	640 g		105 min (sample 2)
70	10	60		10	165 min (sample 3)
120	50	110	640 g		225 min (sample 4)
130	10	120		10	285 min (sample 5)
180	50	170	640 g		360 min (sample 6)
190	10	180		10	
240	50	230	640 g		
250	10	240		10	
370	50	360			

[A]Addition time = Time measured from start of the reaction

[B]Addition interval time = Time interval between MMA addition and TBHP addition

[C] Actual reaction time = Time measured from start of addition of first batch MMA addition

[D] Sample withdrawing time is based on the actual reaction time

Table 10. Recipes used for preparation of different batchs of nanosorbents in the 20 L reactor

Batch No.	PEI (g)	HCl (g)	MMA (g)	TBHP (mL)	H_2O (g)	Theoretical % solid content
P081002	500	225	3200	50	18900	17
P081205	500	200	3200	50	15600	20
P090106	500	224	3200	50	15696	20

PEI:MMA (w/w)= 1:6.4,

TBHP at each addition = 0.1 mM

Table 11.   Reaction conditions for nanosorbents synthesis

Reaction Conditions	
Mixing speed	~ 300 rpm
Nitrogen flow rate	2.0 L/min
Initial pH of reaction medium	~7.00
Oil circulator temperature	87-87.3 ^{0}C
Monomer addition mode	Semi-batch
Reaction time	6 h

3.2.3 Measurements and characterizations

Particle size measurement

Volume-average (D_v) and number-average (D_n) diameters of PMMA/PEI nanosorbents were measured by a Particle Size Analyzer (Coulter LS 230) using a polarization intensity differential scattering (PIDS) module.

Surface charge density

All *zeta*-potential measurements of nanosorbents were determined with a Zetasizer (Malvern 3000HS). The samples concentration was around 300 ppm, and dispersed in a 1 mM NaCl aqueous solution at pH 7.

3.3 Results and discussion

3.3.1. Properties of nanosorbents synthesized in the 20L reactor

The properties of nanosorbents produced from different batches are summarized in Table 12. Particle sizes of different batches of nanosorbents synthesized in the 20 L reactor had volume-average diameters (D_v) ranging from 203 to 277 nm and number-average diameters (D_n) ranging from 184 to 233 nm. The polydispersity indexes (D_v/D_n) were between 1.10 and 1.165, indicating very narrow size distributions of the PMMA/PEI nanosorbents. Three batches of nanosorbents possess *zeta*-potential values ranging from 39.8 to 44.7mV at pH 7. These results indicated that the nanosobents contain PEI shells, which contribute to high positive surface charges. Comparing the nanosorbent properties of three batches to the properties of nanoparticles synthesized in a laboratory scale as reported by Li *et al.* (2002), properties of three batches of nanosorbents synthesized in the pilot-scale were comparable to the laboratory scale. In addition, the properties of nanosorbents produced from three batches were quite similar to each other, indicating good reproducibility of the nanosorbents.

Table 12. Summary of nanosorbents properties of different batches synthesized in the 20 L scale production

Production date	2-Oct-08	5-Dec-08	6-Jan-09
Batch No	P081002	P081205	P090106
Theoretical solid content (%)	17	20	20
Actual solid content (%)	16.1	19.1	19.3
Volume-average diameters (D_v)	277	203	230
Number-average diameters (D_n)	233	184	209
Polydispersity index (PDI)	1.165	1.103	1.100
Zeta-potential (mv) (pH = 7.00)	44.7	41.2	39.8
Final MMA conversion (%)	92.1	94.3	95.6
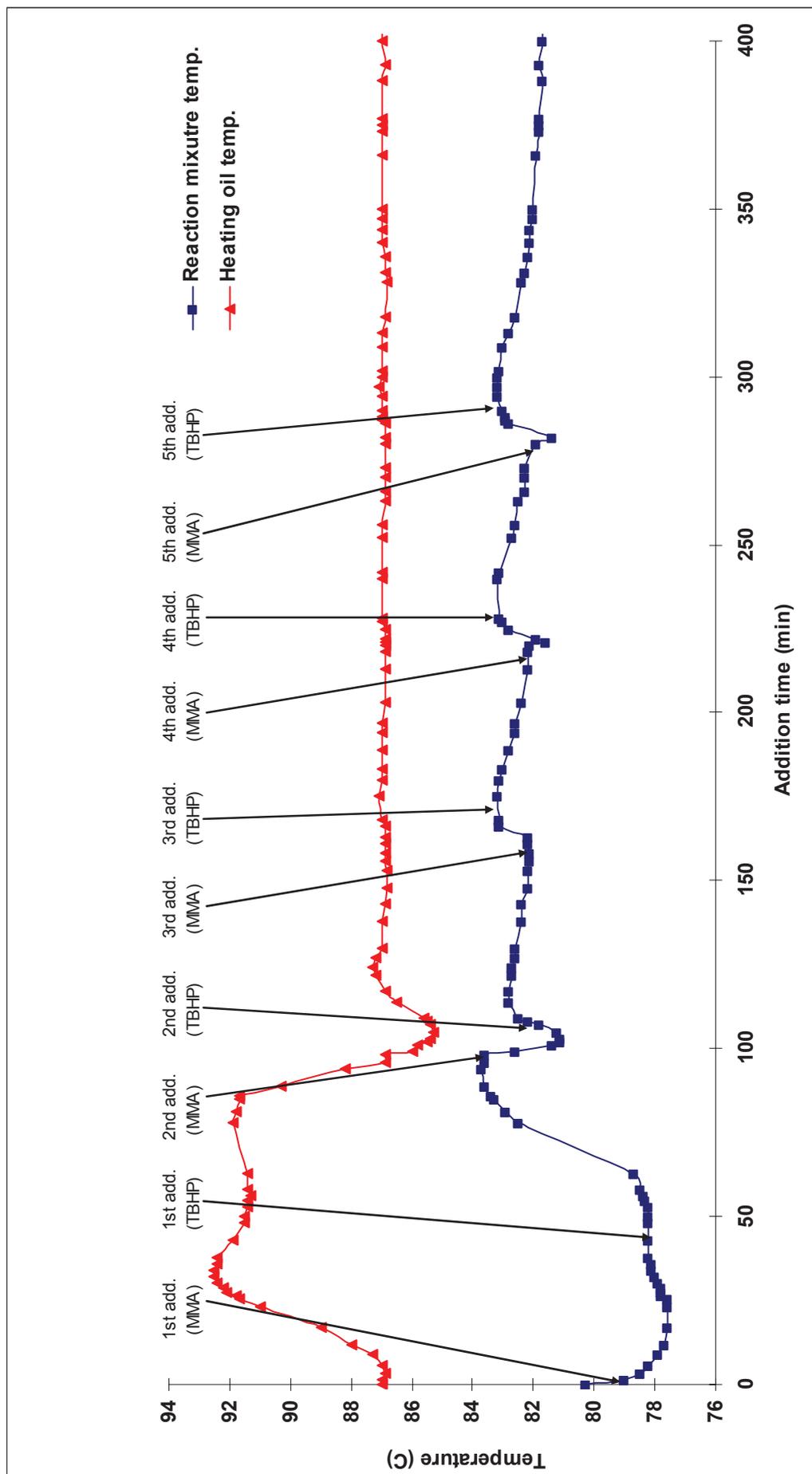
Figure 12. Reaction Temperature profile in different stages of initiator addition in a 20 L reaction (17% S.C, P081002)

50
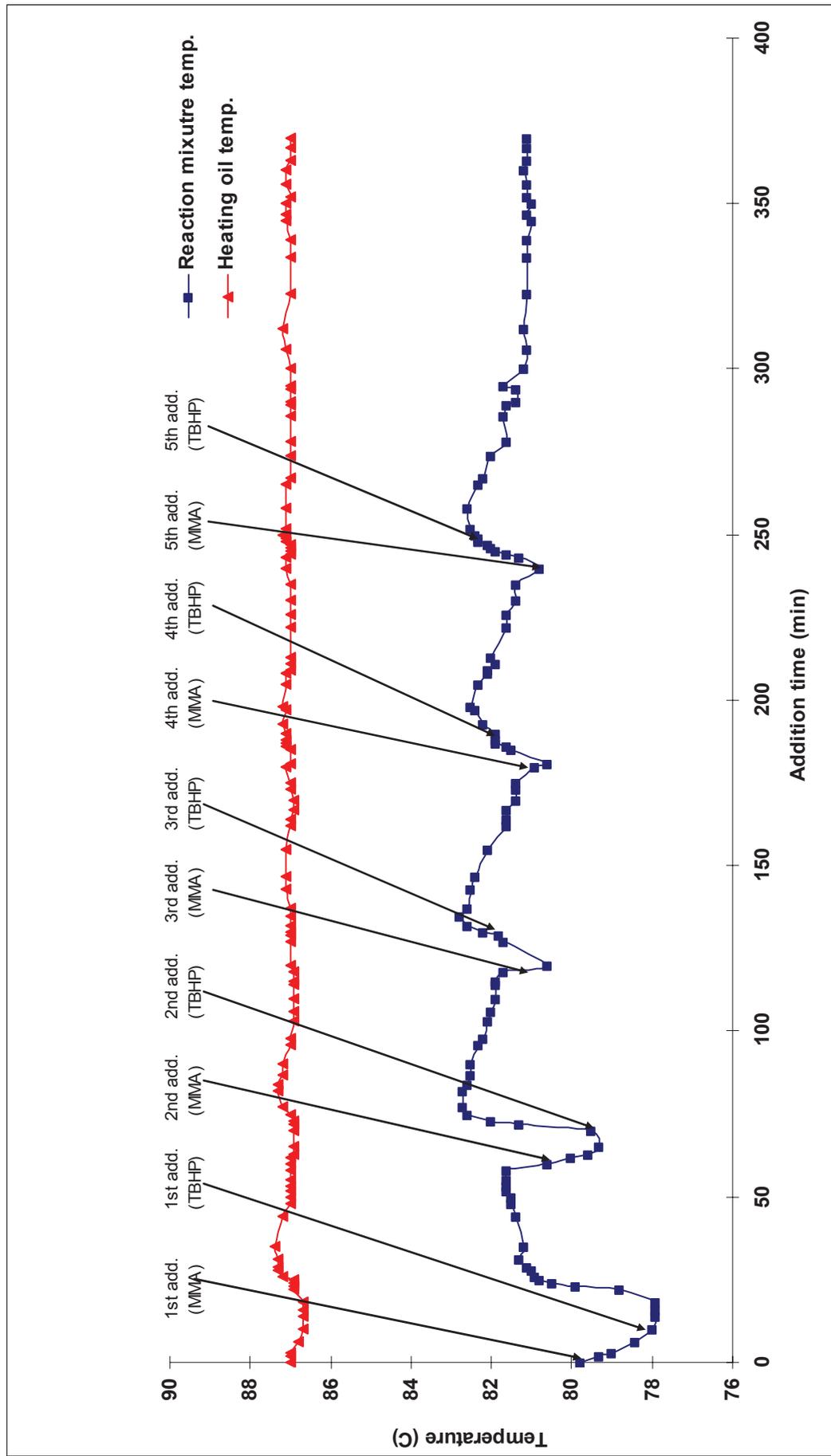
Figure 13. Reaction Temperature profile in different stages of initiator addition in a 20 L reaction (20% S.C P081205)

51
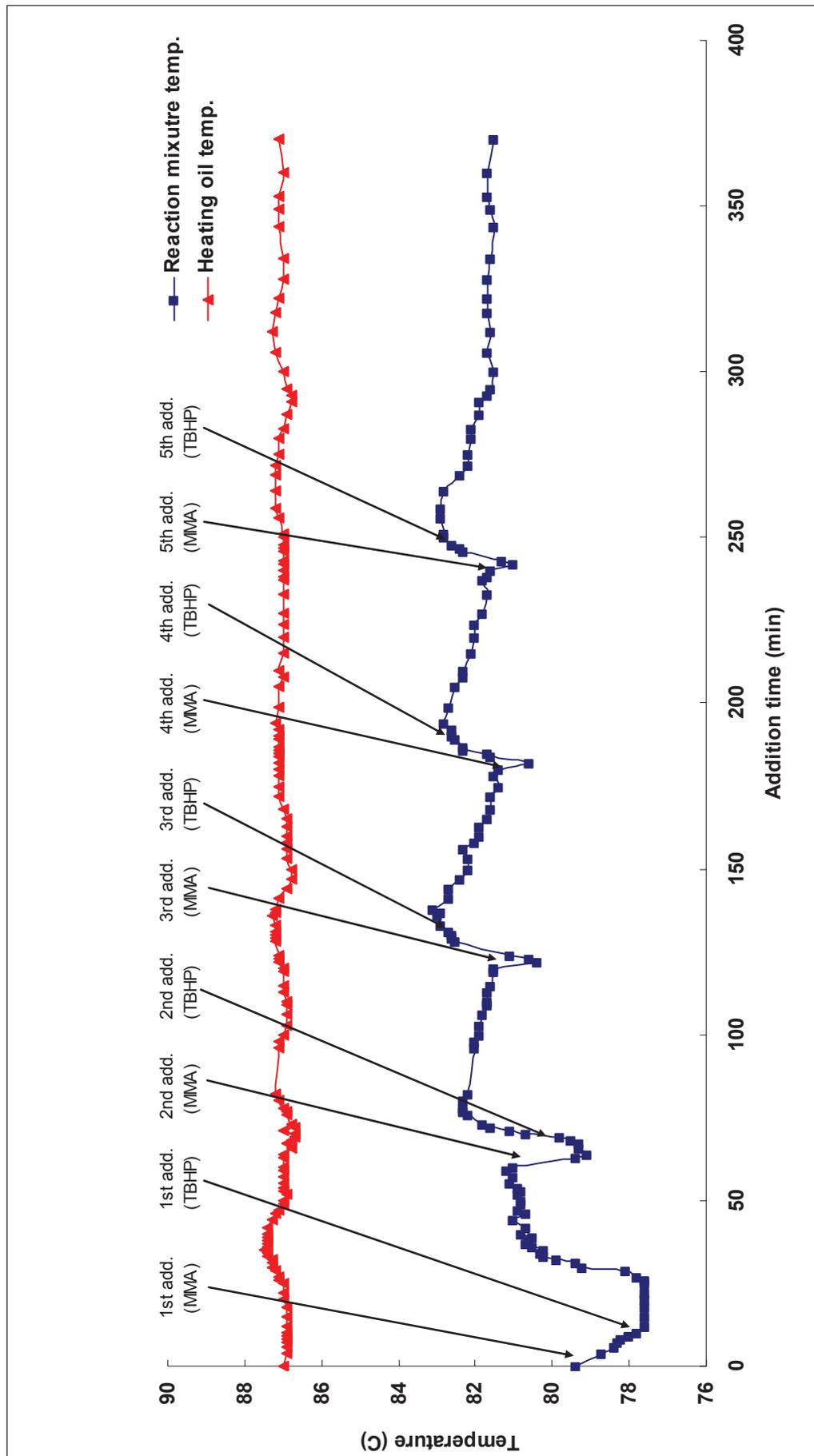
Figure 14. Reaction Temperature profile in different stages of initiator addition in a 20 L reaction (20% S.C P090106)

3.3.2. Effect of monomer and initiator addition on reaction temperature

Emulsion polymerization is an exothermic process which requires careful control. Thus, temperature monitoring during the synthetic process is necessary in order to avoid reactor overheating and subsequently risk of fire and explosion. Figure 12, 13 and 14 show changes of reaction temperature in three batches synthesis. The temperature profiles indicated that the maximum reaction temperatures only reached to 85°C when the starting reaction temperature was 80°C. Thus the polymerization only resulted in arising 5°C in the whole synthetic process. This finding suggested that the heat generated from exothermic emulsion polymerization could be sufficiently dissipated inside the 20 L reactor during whole process. Thus, the synthetic procedure for scale-up production of the nanosorbents is easy to control and safe. On the other hand, there is an interesting finding that five successive temperature rising and dropping periods occurred after addition of MMA and TBHP. The temperature dropping periods in these figures took place after each batch of MMA addition because MMA which are stored at room temperature can immediately reduce the temperature of the reaction mixture. The temperature rising periods occurred after certain time of MMA addition. The temperature rising period in the synthesis can be caused by the heat generation of exothermic emulsion polymerization reaction. It is also observed that each additional batch of monomer charging resulted in rising reaction temperature. This implies that the TBHP which is added initially could still initiate emulsion polymerization process without the need for extra feeding.

3.3.3. Monomer conversions and particle sizes

Instantaneous (monomer) conversion is defined as the ratio of MMA monomer converted to PMMA polymer in specific time to the total weight of MMA monomer addition in a specific time. Overall (monomer) conversion is defined as ratio of MMA monomer converted to PMMA polymer after complete time to the total weight of MMA monomer addition. The instantaneous MMA conversions of the three batches of nanosorbent were over 80% and overall conversions were above 90%. These suggested that majority portion of MMA monomers were consumed in each batch of MMA addition and subsequently converted to PMMA polymer in the synthesis process.

Figure 15 to 23 shows that volume and number averages diameters (Dv and Dn) increase gradually from sample 1 to sample 6 which were withdrawn during reaction (Table 9). Sample 1 to sample 6 all gave only single peaks in particle size measurements . According to proposed nanosorbent synthesis mechanism shown in Figure 10, TBHP initiators react with amine groups on a water-soluble polymer backbone, resulting in the formation of redox pairs. The subsequent nanoparticle can be formed via route 2, 3 and 4 as shown in the Figure 11. Therefore, new particle generation may take place when additional monomer was added after initial polymerization. Particle size measurement of all samples indicated that there were no bi-model particle size distribution peaks. Therefore, it can be assumed that MMA monomers in second to last batches addition could directly diffuse into the seed nanoparticles which possess radical inside the PMMA core generated in the first batch of addition. Subsequent addition of MMA monomers from second to last addition let to progressive increase of nanosorbent particle size from sample 2 to

sample 6. This assumption is in agreement with the kinetic study of particle synthesis in a laboratory scale.[119] This literature results proposed that the main locus for newly added MMA polymerization is in the core of seed nanoparticle and no secondary nanoparticles are formed with newly added MMA. This indicated that the proposed mechanism could be applied to pilot-scale synthesis, and TBHP addition from second to last batches addition are not required in the semi-batch addition of monomer.

3.4   Summary

Core-shell PMMA/PEI nanosorbents have been synthesized successfully in the 20 L pilot-scale reactor under semi-batch addition mode. The properties of three batches of PMMA/PEI nanosorbents are summarized as follows:

(1) The average number diameters of PMMA/PEI nanosorbents were ranging from 180 to 250 nm

(2) The polydispersity indexes of PMMA/PEI nanosorbents were in the range from 1.10 to 1.2, indicating quite uniform particle size distribution,

(3) The surface charge density of PMMA/PEI nanosorbent was around + 40 mV at pH 7.0, implying that the particles are highly positively charged

(4) The monomer conversions in the three batches of PMMA/PEI nanosorbent synthesis were above 90%.

(5) The maximum reaction mixture temperature only arised to 85ºC from 80ºC. Thus the exothermic polymerization process could be easily controlled.

(6)   Five successive temperature rising and dropping periods can be observed during the reaction.

(7) The instantaneous MMA conversions were over 80% and the final overall conversions reached to above 90%.

(8) Particle sizes of average number and volume diameters gradually increased from with the addition of increasing amounts of the monomer.

(9) The particle size distributions of sample 1 to sample 6 with increasing monomer charging ratio remain a single peak, but their particle size distributions (polydispersity index) became broader.

Table 13. Particles size and PDI variation in different stages in a 20 L reaction

Batch No	P081002		P081205		P090106	
	Particle size (nm)	PDI	Particle size (nm)	PDI	Particle size (nm)	PDI
Sample 1	159	142	1.120	127	118	1.076	145	137	1.058
Sample 2	157	139	1.129	156	144	1.083	178	158	1.127
Sample 3	234	213	1.099	156	144	1.083	201	180	1.117
Sample 4	257	222	1.174	187	168	1.113	215	197	1.091
Sample 5	283	241	1.174	197	177	1.113	230	211	1.090
Sample 6	283	243	1.165	203	184	1.103	230	209	1.100

* Sample 1 to sample 6 indicate the sample withdrawn from different synthesis time and the sample withdrawn time were shown in Table 9.
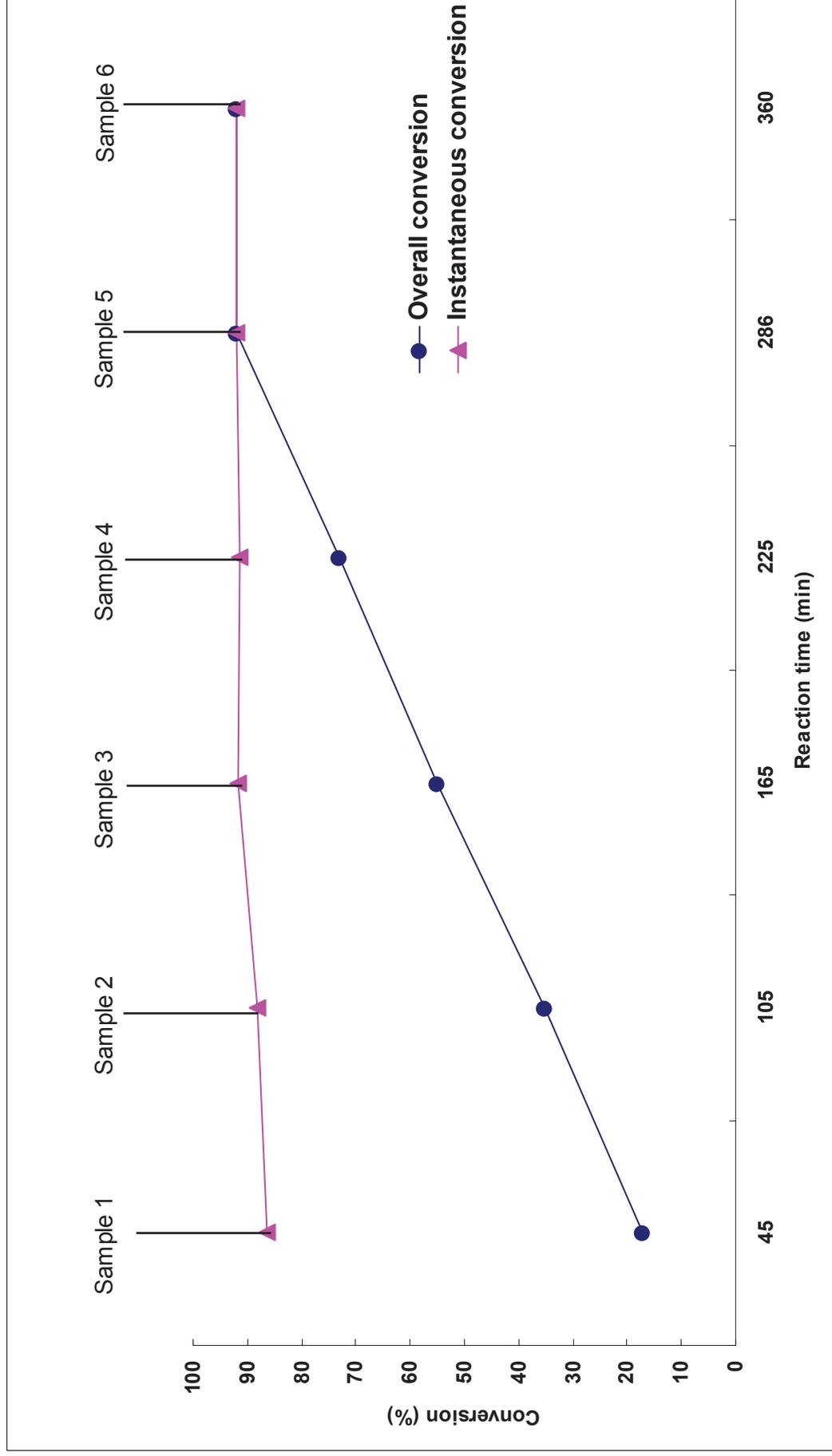
Figure 15. Conversions as a function of reaction time during the production of 17% S.C PMMA/PEI nanosorbents in the 20L reactor (P081002)
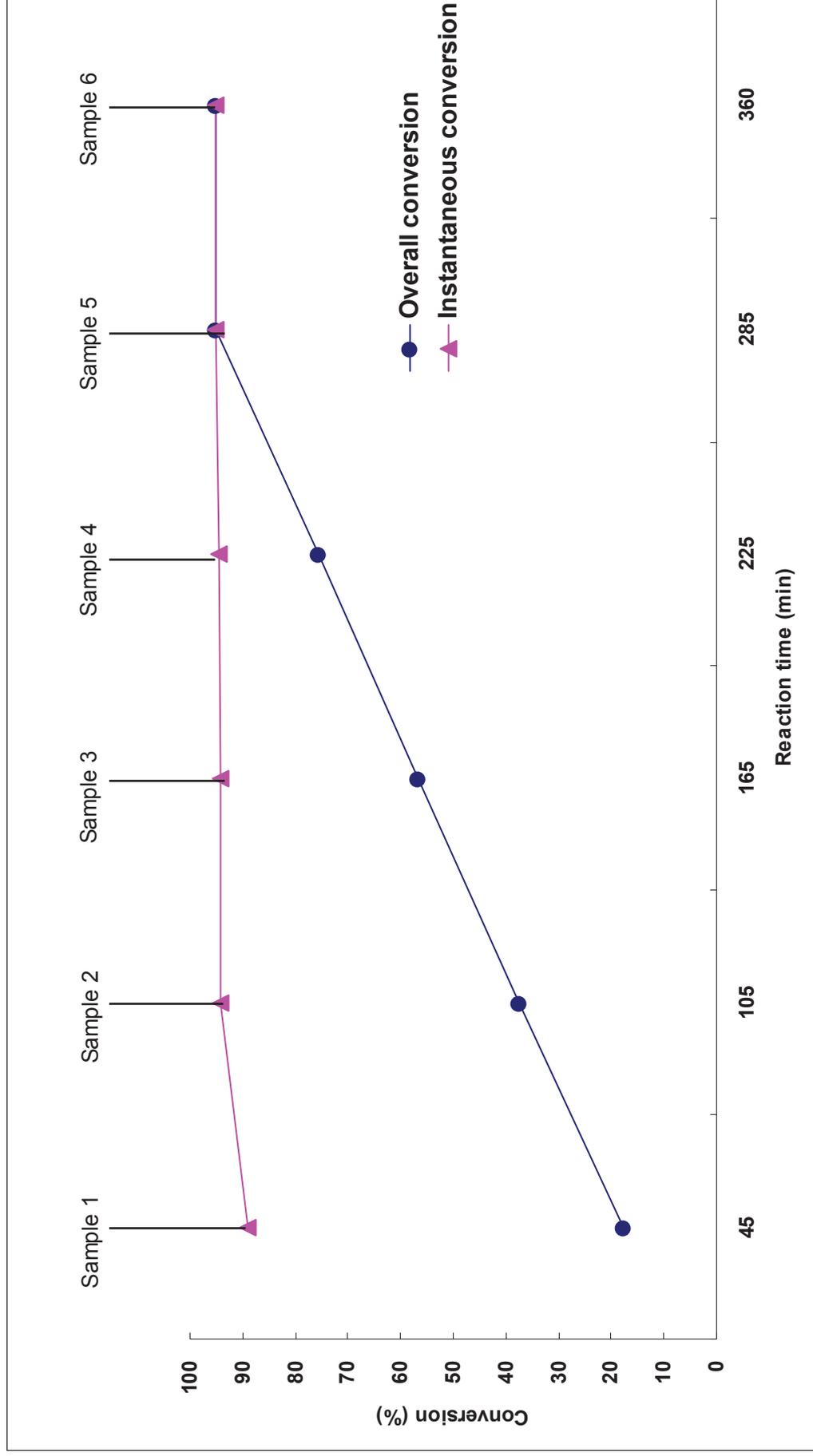
Figure 16. Conversions as a function of reaction time during the production of 20% S.C PMMA/PEI nanosorbents in the 20L reactor (P081205)
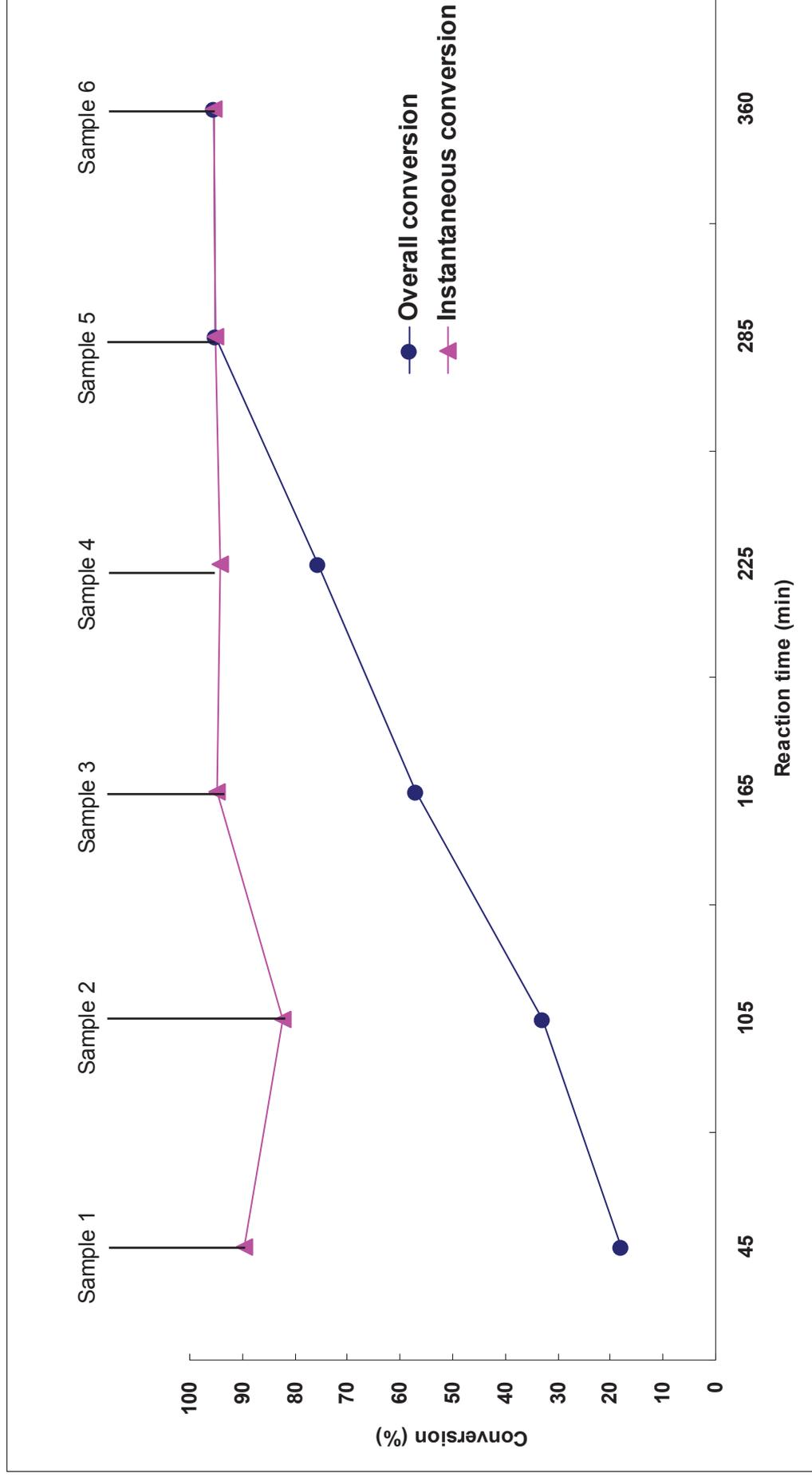
Figure 17. Conversions as a function of reaction time during the production of 20% S.C PMMA/PEI nanosorbents in the 20L reactor (P090106)
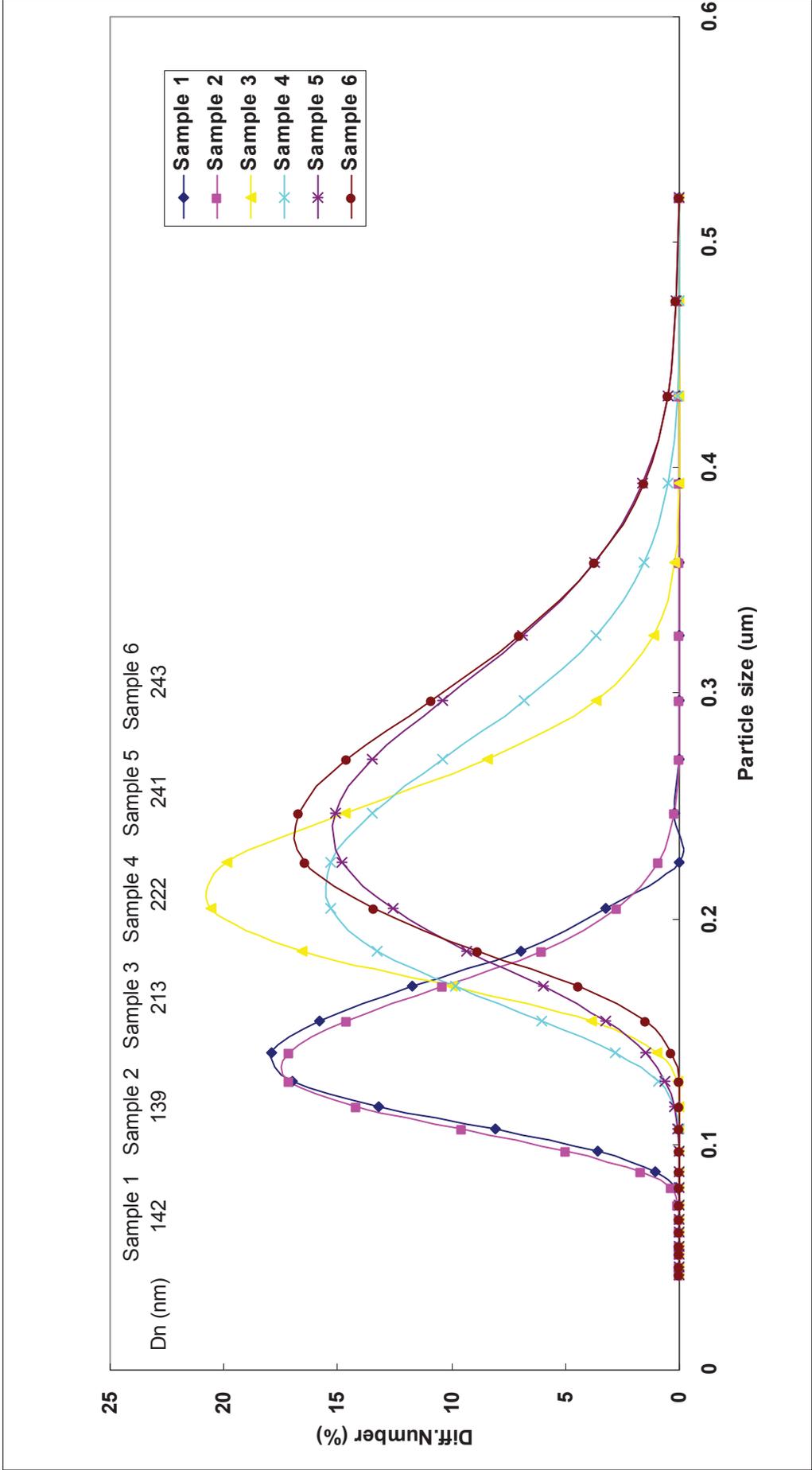
Figure 18. Particle size (Dn) variation of sample 1 to 6 withdrawn from nanosorbents production (P081002)

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Dv (nm)	159	157	234	257	283	283
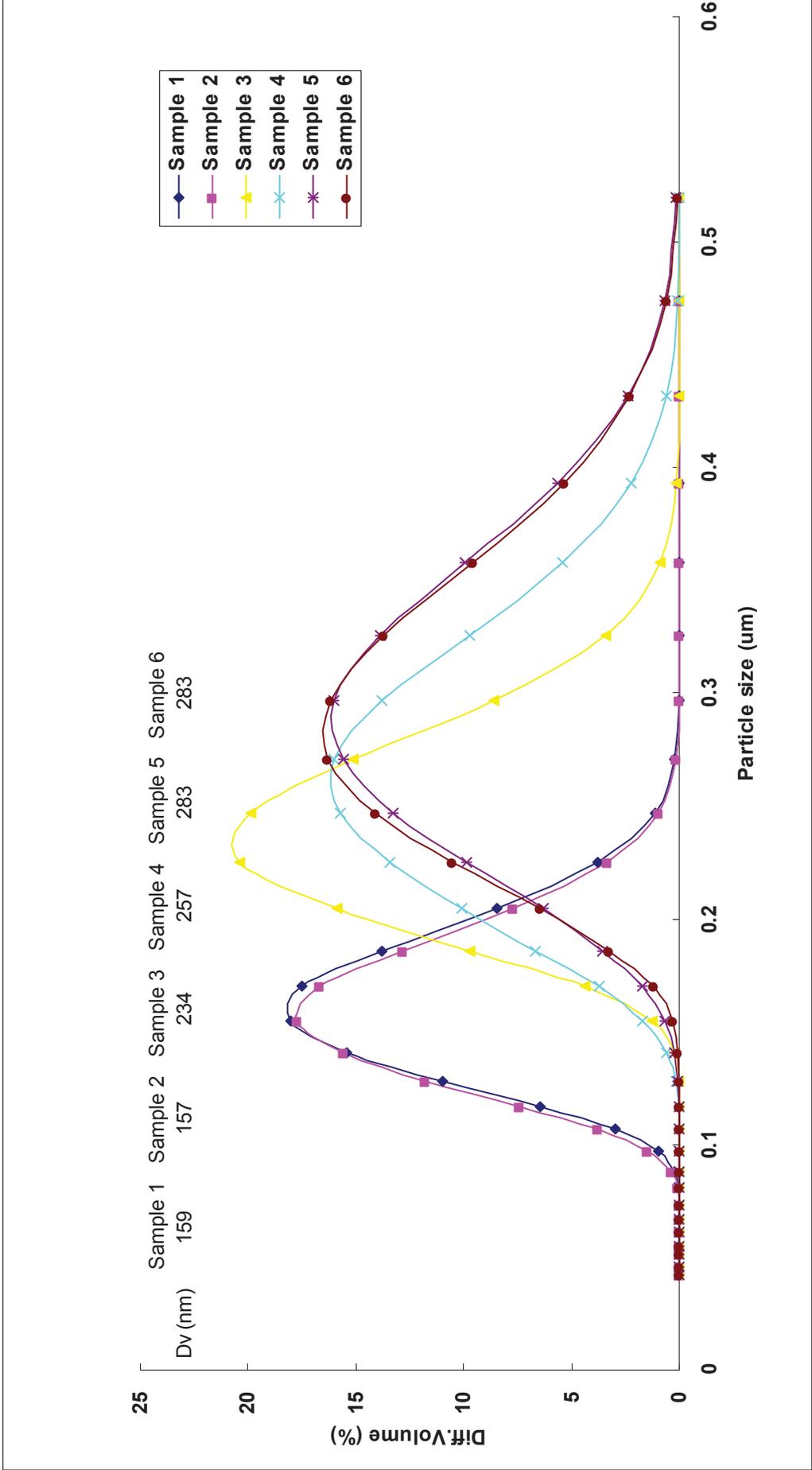
Figure 19. Particle size (Dv) variation of sample 1 to 6 withdrawn from nanosorbents production (P081002)

Dn (nm)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
	118	144	144	168	177	184
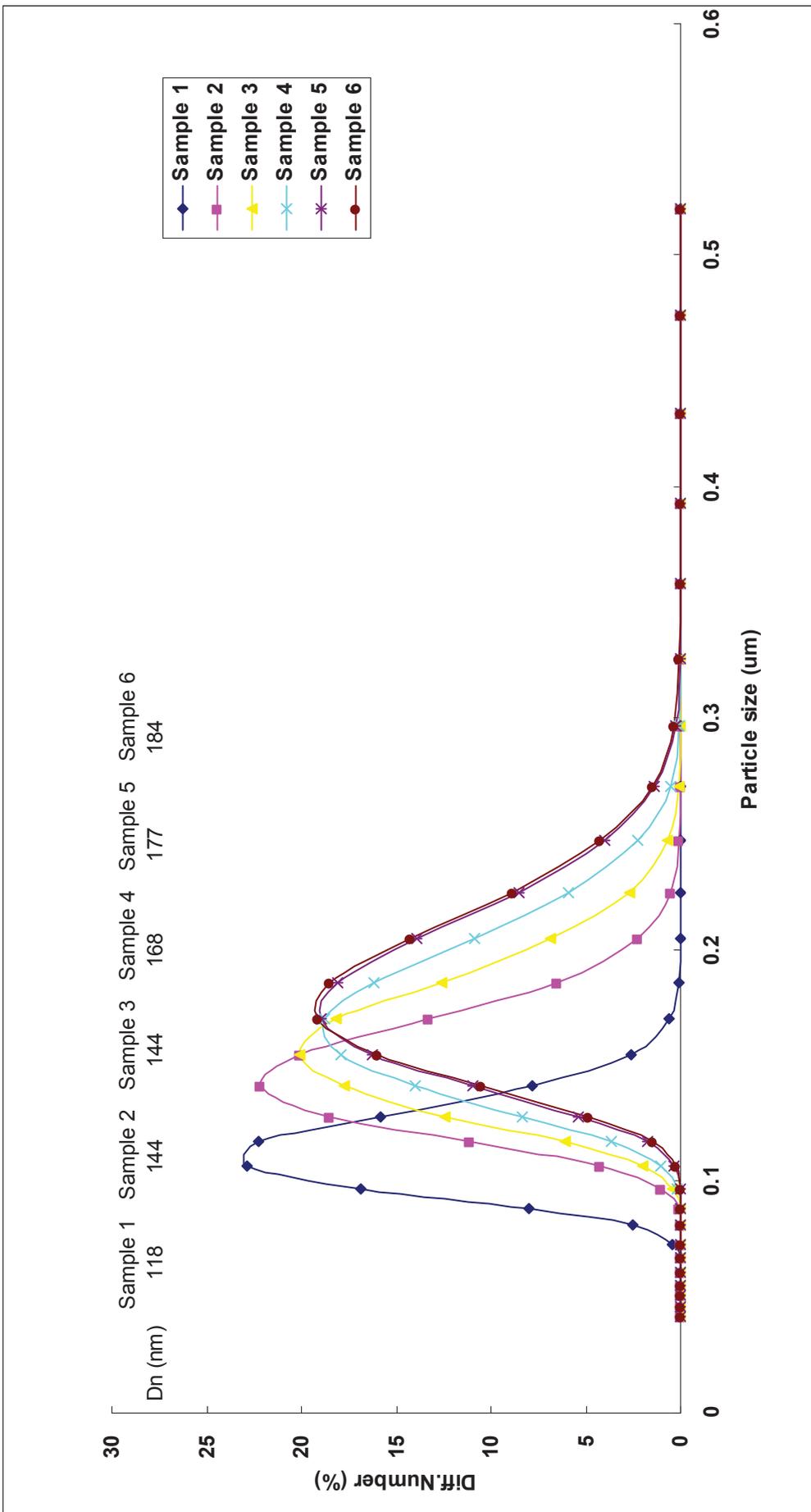
Figure 20. Particle size (Dn) variation of sample 1 to 6 withdrawn from nanosorbents production (P081205)
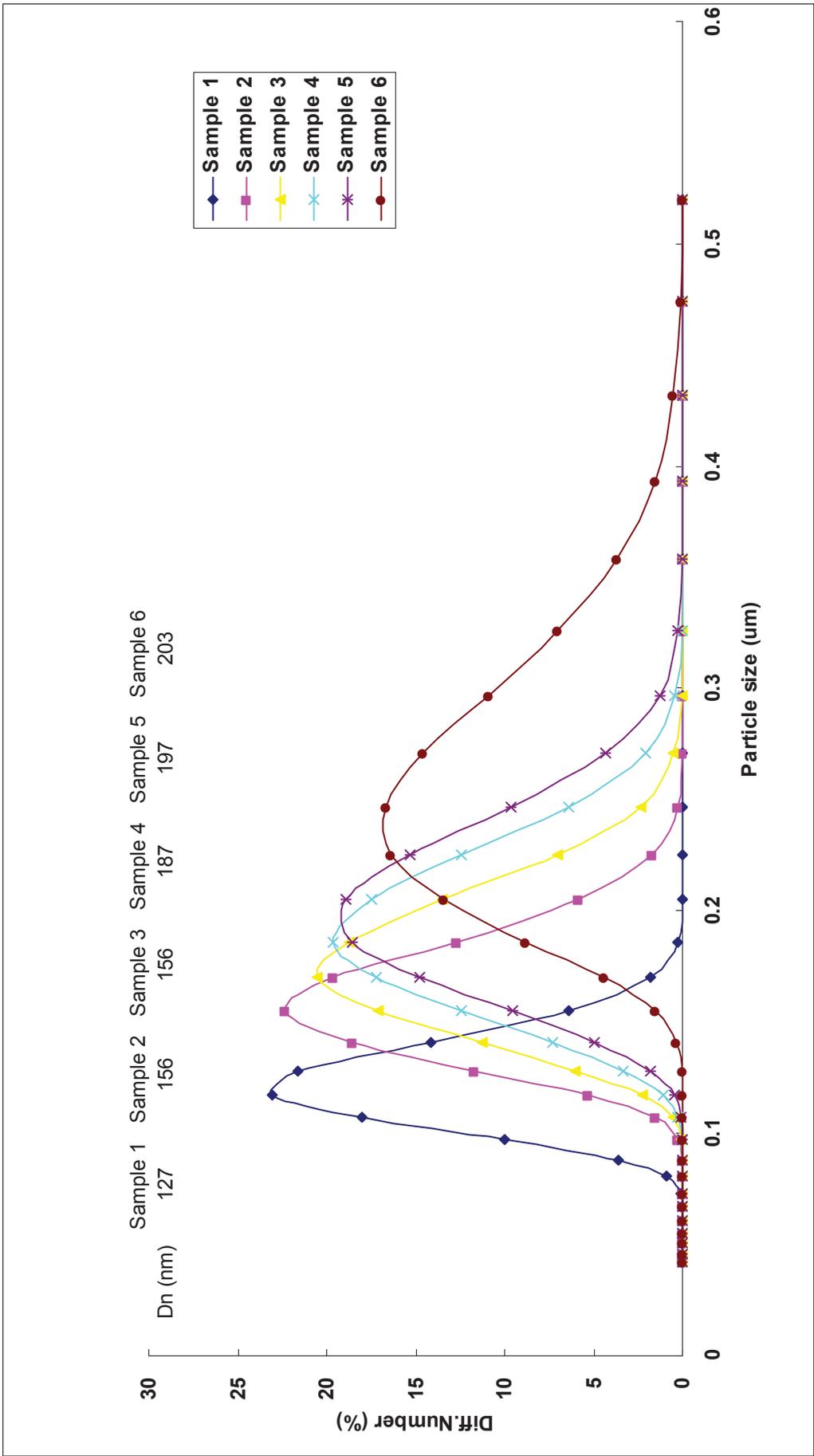
Figure 21. Particle size (Dv) variation of sample 1 to 6 withdrawn from nanosorbents production (P081205)
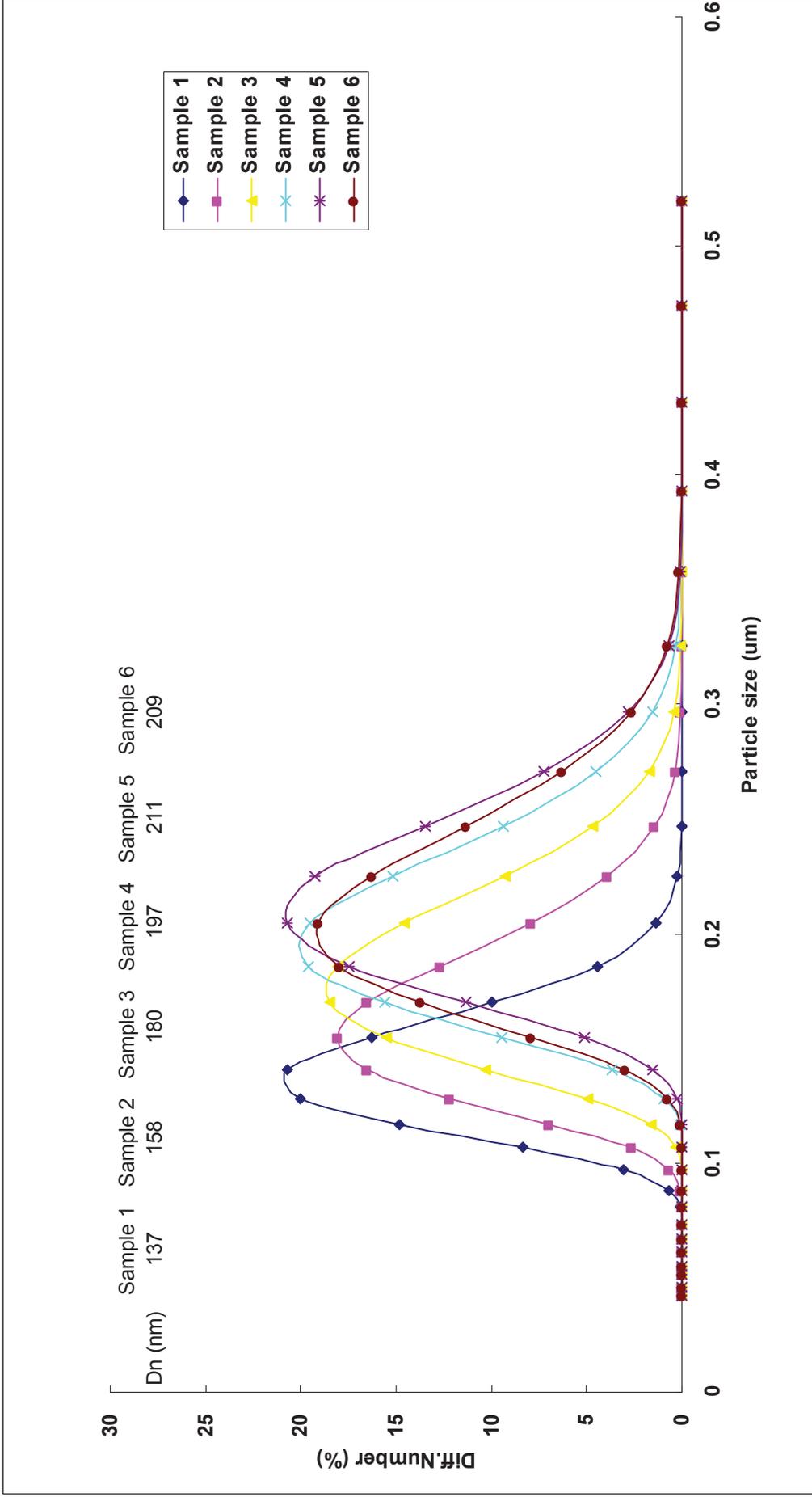
Figure 22. Particle size (Dn) variation of sample 1 to 6 withdrawn from nanosorbents production (P090106)

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Dv (nm)	145	178	201	215	230	230
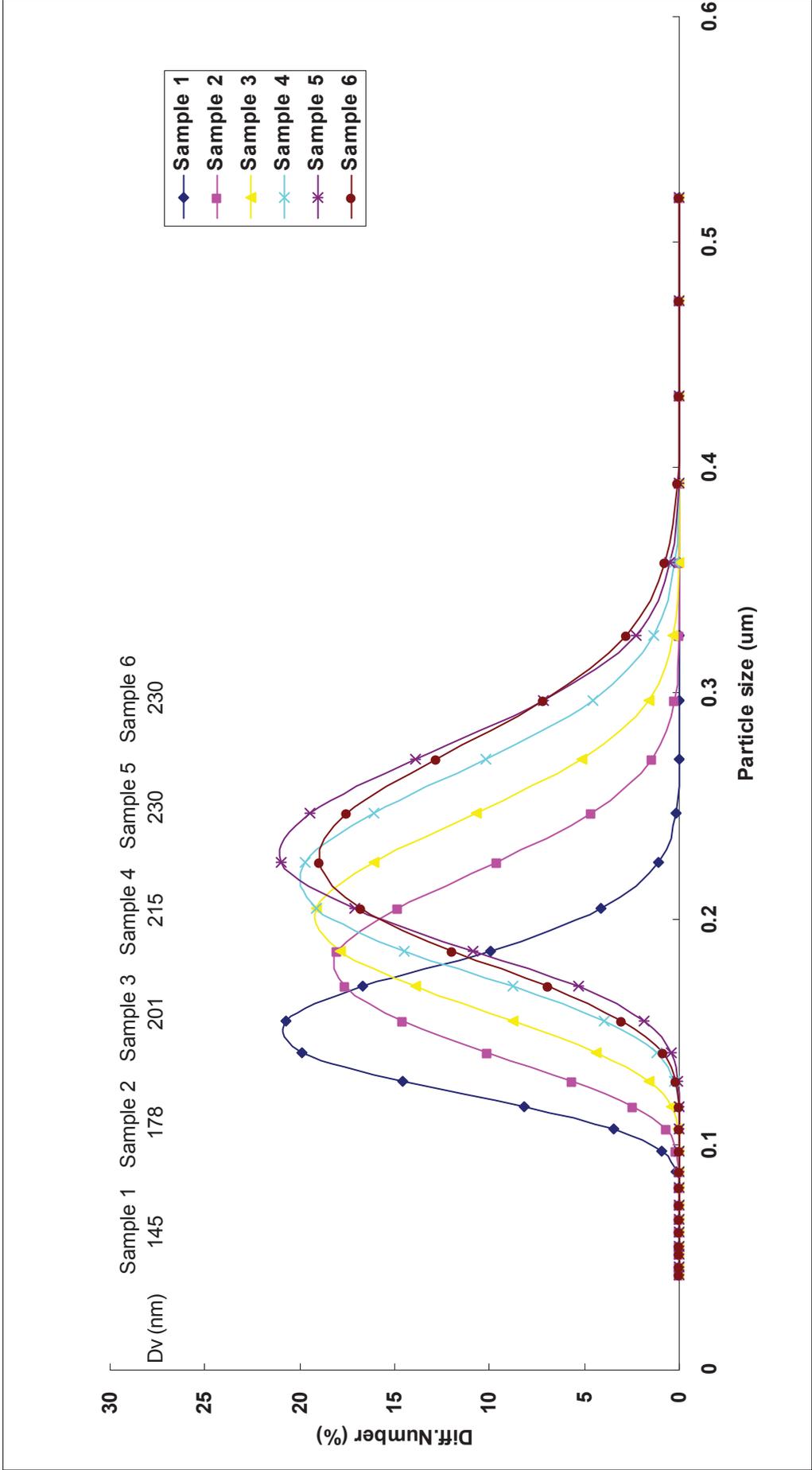
Figure 23. Particle size (DV) variation of sample 1 to 6 withdrawn from nanosorbents production (P090106)

Chapter 4

Purifying nanosorbent by the Membrane Filtration Process

4.1 Introduction

High speed centrifugation process is a method which could be used to separate unreacted PEI polymer in water from PMMA/PEI nanosorbent in a laboratory scale. After centrifugation, the PMMA/PEI nanosorbents may aggregate in the bottom. Thus the nanosorbent need to be redispered by an ultrasound treatment. Dialysis is an alternative way to purify nanosorbents in the laboratory scale, but it is time-consuming because dialysis process depends on the slow diffusion between two sides of membrane. For a large scale purification process, both centrifugation and dialysis methods are not technically and economically feasible because industrial scale high speed centrifuge is not available in the market and slow diffusion process in dialysis result in a long purification time. Using V-SEP membrane filtration is a feasible method to purify nanosorbent in pilot and industrial scale.

This chapter covers the study of using V-SEP membrane filtration system for purifying PMMA/PEI nanosorbent in a pilot plant scale. The objectives of this study include:

(1) Selection of proper membrane for purifying nanosorbent

(2) Evaluation of fouling degree of nanosorbent on selected membrane in V-SEP membrane filtration system

(3) Determination of appropriate nanosorbent solids content for optimizing flux performance in V-SEP membrane filtration system

(4) Selection of appropriate filtration mode to purify nanosorbent in V-SEP membrane filtration system

(5) Selection of appropriate membranes to recycle water from wastewater generated in purifying nanosorbent process

(6) Preparation of large batches of purified PMMA/PEI nanosorbent which are used for subsequent study in wastewater with V-SEP membrane filtration system

4.2 Experimental

4.2.1 Materials and equipment

Branched PEI with average molecular weight of 750,000 (50 wt % solution in water) obtained from Sigma Aldrich was used to prepare 500 ppm PEI solution. Six inch membrane stirred cell with membrane surface area of 0.01823 m^2 as illustrated in Figure 24 was manufactured by Dunwell New logic Ltd. (DNL) with maximum operation pressure of 40 psi. Vibratory shearing enhanced process (V-SEP) developed by New logic International Ltd. was manufactured by Dunwell New logic Ltd. (DNL). Membranes listed in Appendix Table B.1 were provided by Dunwell New logic Ltd (DNL) without the brand name due to commercial confidentiality.
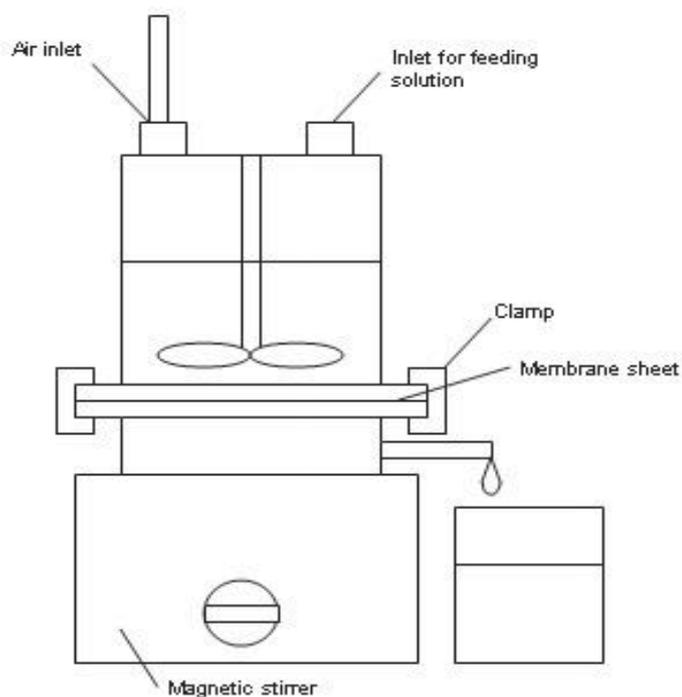
Figure 24. Outlook of 6 inch membrane stirred cell

4.2.2 Experimental procedure

4.2.2.1   Membrane selection for purifying nanosorbent in a 6 inch membrane stirred cell

200 mL of 500 ppm PEI solution were prepared and transferred into a 6 inch membrane stirred cell. The solutions were allowed to pass through different types of membranes listed in Appendix Table B1, including UF-17, UF-21, MF-16, MF-01, MF-03, MF-04 and MF-05 under 30 psi operation pressure. Final permeate samples were collected for chemical oxygen demand (COD) measurement. The rejection percentage (removal percentage) or permeable percentage of COD was used as an index for passage of PEI polymer in different types of membranes.

4.2.2.2 Fouling degree of nanosorbent in V-SEP membrane filtration system

The circulation mode of V-SEP experimental setup is shown in Figure 25. The feed tank was filled with 10 L of nanosorbent dispersion (P081205) with 4% solids content. The dispersion was charged into the V-SEP membrane filtration system with MF-03 membrane using a circulatory diaphragm pump. Through throttling control valve, the operation pressure and vibration amplitude were adjusted to 30 psi and 3/4 inch, respectively. The permeate flow rate was continually and simultaneously recorded in the experiment. A higher dispersion solid content of 13.1% was also investigated under the same operation conditions.
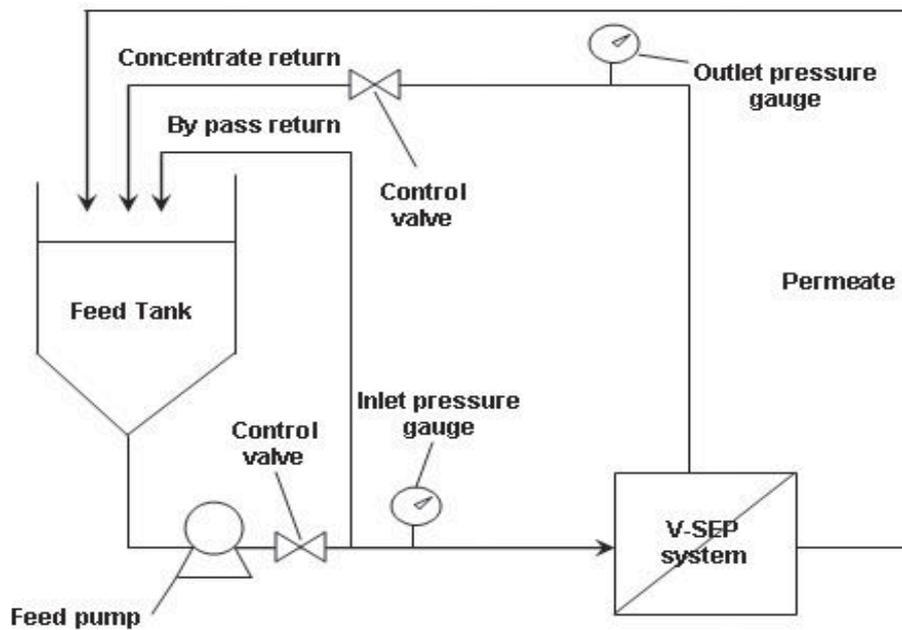
Figure 25. Schematic diagram of V-SEP experimental setup in circulation mode

4.2.2.3 **Effect study of nanosorbent solid content on flux performance in V-SEP membrane filtration system with MF-03 membrane**

Figure 26 shows the experimental setup of concentration mode of V-SEP used in this study. The feed tank was filled with 64.8 L of nanosorbent dispersion (P081205) with solid content of 1.71%. Nanosorbent dispersion (P081205) was pumped by means of a circulatory diagram pump into the V-SEP membrane filter module. By throttling control valve, the operation (outlet) pressure was adjusted to 30 psi followed by adjusting vibration amplitude to 3/4 inch. The permeate samples were continually weighted at separated permeate tank by an electronic balance to calculate nanosorbent solid content and recovery in the V-SEP membrane filtration system. The permeate flow rate was also continually and simultaneously recorded in the experiment.
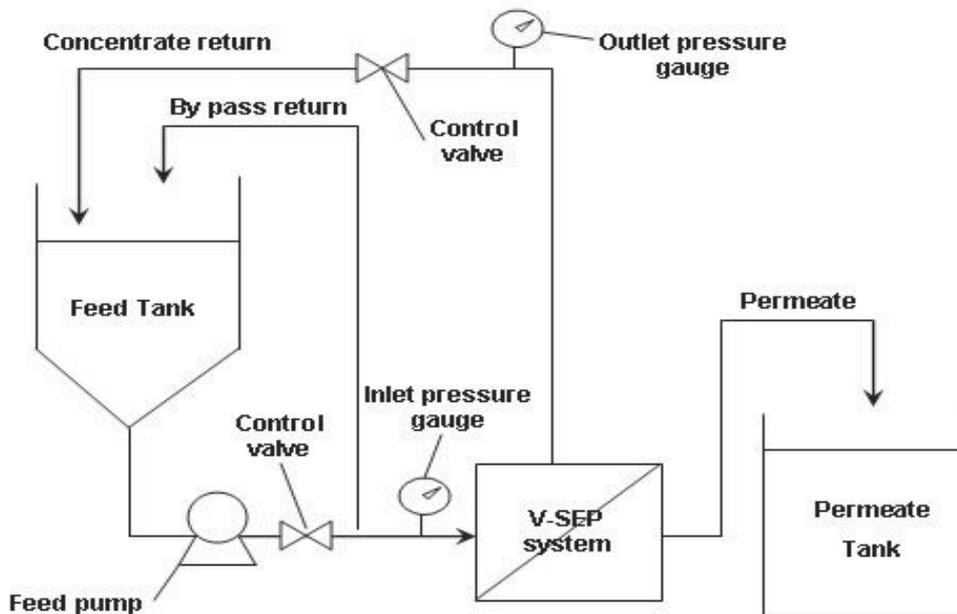
Figure 26. Schematic diagram of V-SEP experimental setup in discontinuous diafiltration mode (concentration mode)

4.2.2.4 Comparison of discontinuous and continuous diafiltration mode for purifying nanosorbent

Discontinuous diafiltration mode

The discontinuous diafiltration mode (concentration mode) of V-SEP experimental setup is schematically shown in Figure 26. The feed tank was filled with a total 35 L of nanosorbent (P081205) with solids content of 8.01%. The dispersion was pumped into the V-SEP membrane filter module using a circulatory diagram pump. Through adjusting throttling control valve, the operation (outlet) pressure and vibration amplitude were set to 30 psi and 3/4 inch, respectively. Purifying nanosorbent in a discontinuous diafiltraiton mode was performed to collect 12 kg of permeate in a separated permeate tank. The conductivity of permeate collected in the separated permeate tank was measured by a conductivity meter. Collected permeate in the separated permeate tank was re-injected into feed tank for next continuous diafiltration mode of purifying nanosorbent process experiment.

Continuous diafiltration mode

The continuous diafiltration mode of V-SEP experimental setup is schematically shown in Figure 27. Nanosorbent dispersion (P081205) was pumped into the V-SEP membrane filter module using a circulatory diagram pump. Throttling control valve, operation (outlet) pressure and vibration amplitude were set to 30 psi and 3/4 inch. The flow rate of RO water was fed into feed tank with equal permeate flow rate, aiming for performing continuous diafiltration process. Purifying nanosorbent was performed in a discontinuous diafiltraiton mode to collect 12 kg of permeate in a separated permeate tank. Conductivity of permeate

collected in permeate tank was measured by a conductivity meter.
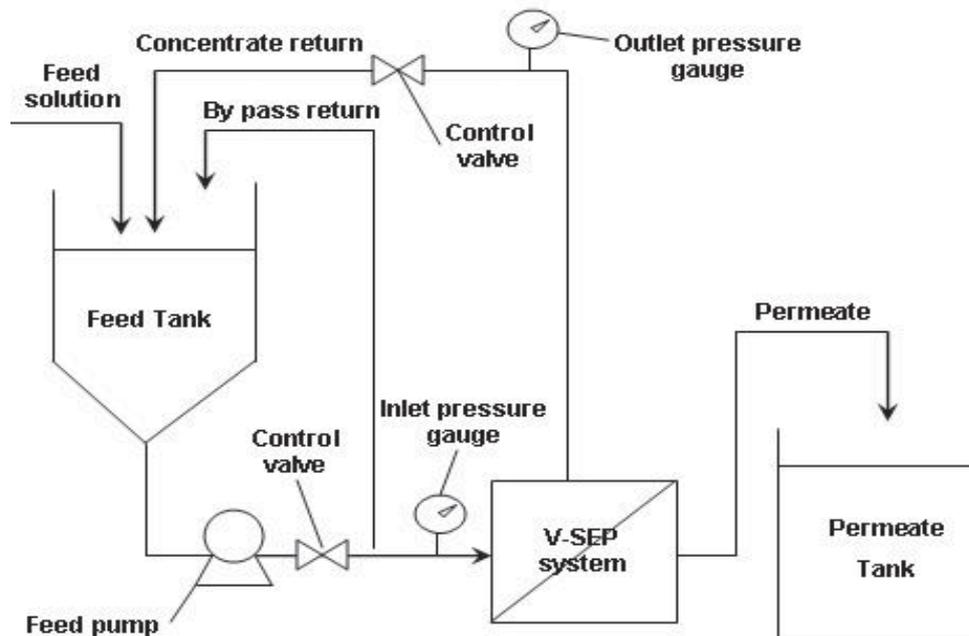
Figure 27. Schematic diagram of V-SEP experimental setup in continuous diafitration mode

4.2.2.5 Purifying nanosorbent in the V-SEP membrane filtration system

The continuous diafiltration mode of V-SEP experimental setup is schematically shown in Figure 27. Nanosorbent dispersion (P081205) was pumped into the V-SEP membrane filter module using a circulatory diagram pump. Throttling control valve, operation (outlet) pressure and vibration amplitude were set to 30 psi and 3/4 inch, respectively. The flow rate of RO water was fed into the feed tank and subsequently was adjusted to equal flow rate of permeate, aiming for performing continuous diafiltration process. Purifying nanosorbent was performed in a continuous diafiltraiton mode. The conductivities of collected permeate in different processing times were measured by a conductivity meter and total water

consumption for purifying nanosorbent was also recorded. The experiments were repeated three times using other two batches of 35 L nanosorbents (P081002 and P090106)) with solids contents of 7.76% and 8.41%, respectively.

4.2.2.6 Membrane selection to recycle water from purifying nanosorbent wastewater

200 mL of nanosorbent dispersion (P081205) previously obtained was first transferred into a 6 inch membrane stirred cell. The permeate was passed through a selected membrane (UF-07, NF-11, NF-05, NF-16 as listed in Appendix Table B1) with an operation pressure of 40 psi. The conductivity and chemical oxygen demand (COD) of final collected permeate were measured for calculation of rejection percentage in different selected membrane.

4.2.2.7 Measurements

Solid content

Solid content was measured gravimetrically.

Conductivity

Conductivity was measured by a conductivity meter (Hanna HI 8733).

Chemical oxygen demand

Chemical oxygen demand was measured by a Hach 8086 method. Chemical oxygen demand solution and COD reactor was obtained from Hach.

4.3 Results and discussion

4.3.1 Membrane selection for purifying nanosorbent in 6 inch membrane stirred cell

The main purpose of PMMA/PEI purifying nanosorbent is to remove unreacted PEI and other residues in water from particle dispersion using a membrane filtration process. The main criteria of membrane selection are that a selected membrane must allow the passage of unreacted PEI and other smaller molecules through the membrane and to reject nanosorbent simultaneously. A range of microfiltration and ultrafiltration membranes have been used to study PEI polymer permeable percentage or rejection percentage. Permeable percentage represents percentage of raw PEI polymer passing through the membrane. Conversely, removal percentage (rejection percentage) of PEI represents raw PEI molecule rejected by the membrane.

Figure 28 summarizes results of PEI polymer rejection percentages or permable percentage in UF-16, UF-17, UF-21, MF-01, MF-03, MF-04, MF-05 and MF-16 membrane under 30 psi operation pressure in a 6-inch membrane stirred cell. This operation pressure is equal to the minimum operation pressure of V-SEP membrane filtration system in ultrafiltration and microfiltration. Cake formation or concentration polarization effect of nanosorbent in V-SEP membrane filtration system can be minimized, giving maximized passage of unreacted PEI polymer through membrane. Thus, this operation pressure of 30 psi was selected for purifying nanosorbent in a 6-inch membrane stirred cell.
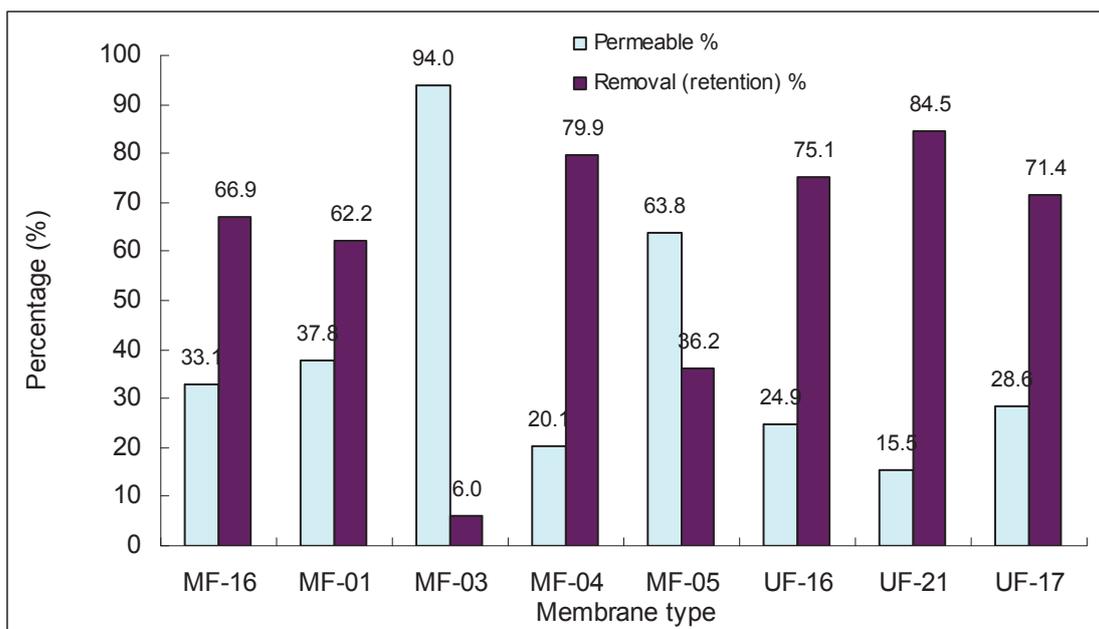
Figure 28. Membrane selection for purifying nanosorbent using 500 ppm PEI solution (Operation pressure 30 psi)

Results showed that reject percentage of the PEI polymer with UF-16, UF-17 and UF-21 ultrafiltration membrane are in range of 71 to 85%. The molecular weight cut-off of UF-16 and UF-17 are 100 kDa, while the UF-21 is 200 kDa as listed in Appendix Table B1, and also the average molecular weight of PEI polymer is 750 kDa. Since molecular weight cut-off of UF-16, UF-17 and UF-21 are 2 to 8 times less that the average molecular weight of PEI polymer, high rejection percentage of PEI polymer in these ultrafiltration membranes are expected.

Because large portion of PEI polymer cannot pass through these UF membranes, other microfiltration membranes including MF-01, MF-03, MF-16, MF-04 and MF-05 membranes were also investigated. The results shown in Figure 28 illustrates that the PEI polymer rejection percentage are 66.9% in MF-16 membrane, 62.2% in MF-01, 6.0% in MF-03 membrane, 79.9% in MF-04 membrane and 36.2% in MF-05 membrane. According to Appendix Table B1, pore size of MF-16 membrane is 0.03um, MF-01 is 0.05 um and MF-03 is 0.1 um and these membrane are made up of

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hydrophobic PTFE (Teflon). This indicated that PEI polymer rejection decreases with increasing the pore size of these PTFE microfiltration membranes. Because PEI polymer rejection percentage is only 6% in MF-03 membrane, MF-03 membrane meets one of the criteria in purifying nanosorbent. On the other hand, the average number particle diameter and volume particle diameter of the nanosorbents are in the range of 184 to 233 nm and 203 to 277 nm as mentioned in Chapter 3. The average particle size of PMMA/PEI nanosorbent is approximately 2 to 3 times greater than the pore size of MF-03 membrane. Theoretically, PMMA/PEI nanosorbents could be separated by the MF-03 membrane. Therefore, MF-03 membrane was firstly selected to be used for purifying nanosorbent.

4.3.2   Fouling degree of nanosorbent on MF-03 membrane in V-SEP membrane filtration system

Fouling degree measurement plays an important role in membrane filtration process because fouling degree on membrane affects the membrane filtration period, cleaning frequency of membrane module and replacement of membrane module. Figures 29 (a) and (b) shows that the permeate flux trend is steady between 160 and 180 GFD at 40 °C, and between 140 and 160 GFD at 30 °C at 4.0% nanosorbent solids content. At 13.1% solids content, the flux trend is steady between 40 and 50 GFD at 40 °C, and between 30 and 40 GFD at 30 °C. The steady fluxes in two different nanosorbent solids content indicate that fouling of nanosorbent on PTFE MF-03 is relatively low. This effect may be due to the fact that PMMA/PEI nanosorbents are highly positive charges ranging from + 40 to 45 mv at pH 7. Since PTFE (Teflon) is a neutral polymer ($-C_2F_2-$). there is little electrostatic interaction between the nanosorbents and PTFE MF-03 membrane. Thus rapid drop in flux was

not observed at initial stage of membrane filtration in this study. A rapid drop in flux at initial stage of membrane filtration is a common phenomenon in microfiltration indicating that pores on the membrane are physically blocked by the solutes in the feed sample. Microfiltration membrane normally has a wide pore distribution so that portion of large pores on microfiltration membrane must firstly plugged resulting in a steep drop in flux at initial stage of membrane filtration. However, this phenomenon was not observed in this study. Comparing the particle size of nanosorbents and average pore size of MF-03 membrane, the particle sizes of PMMA/PEI nanosorbents were 2 times greater than the average pore size of MF-03 membrane. Furthermore, since the nanosorbents had very narrow size distribution, majority of particles could not go into the pores of the membranes. Thus they were not physically blocked by the pores on MF-03 membrane surface resulting in steady fluxes even at two different nanosorbent solids content.

On the other hand, these steady fluxes in this study imply a great advantage on PMMA/PEI purifying nanosorbent in V-SEP membrane filtration system. Operation cost e.g membrane filtration period, membrane cleaning frequency and membrane replacement cost largely depends on fouling degree of membrane. These steady fluxes indicate that membrane filtration rate in the purification process can be maintained in last long membrane filtration process and membrane cleaning frequency and membrane replacement cost can be greatly reduced arising from no fouling phenomenon observed in this study. Inevitably, operation cost can be greatly reduced in this purification process. Therefore, MF-03 membrane is a proper membrane for purifying nanosorbent in V-SEP membrane filtration system.
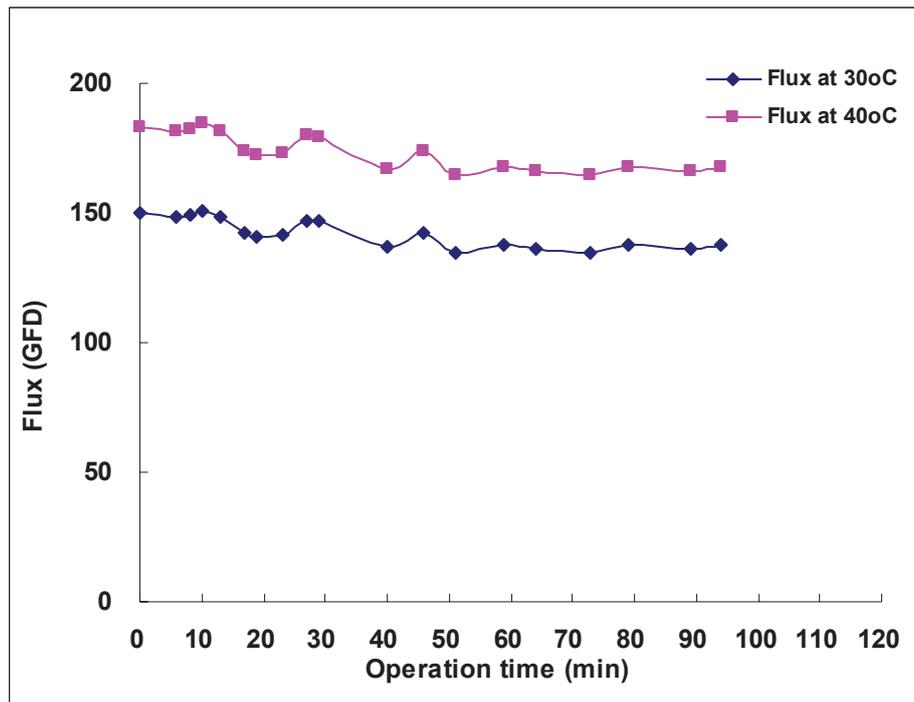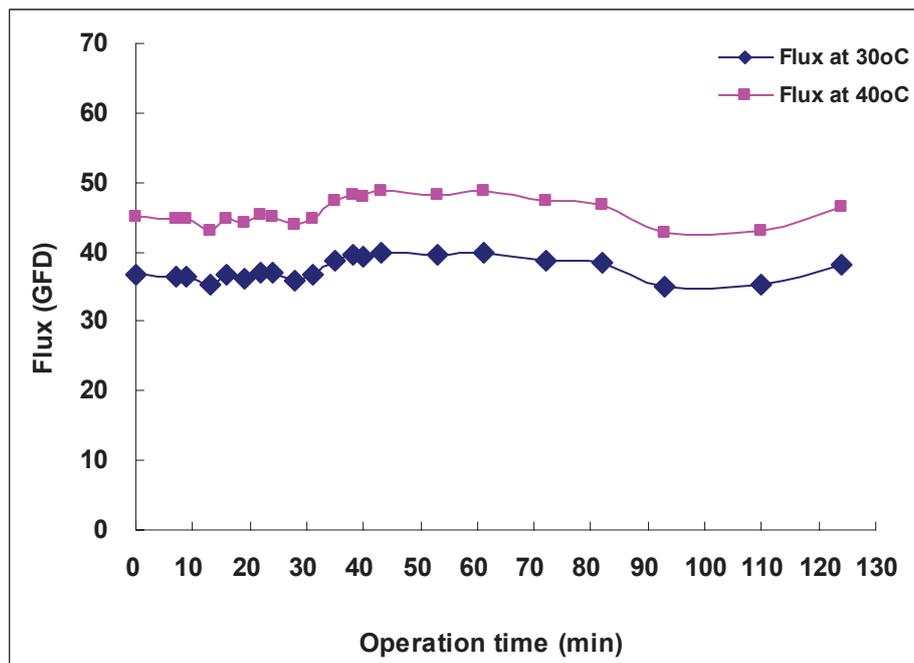
Figure 29. Fouling degree of nanosorbent on MF-03 membrane in V-SEP membranefiltration system at (a) 4.0% solids content; and (b) 13.1% solids content. The operation pressure was at 30 psi.

4.3.3 Effect study of nanosorbent solids content on flux performance in V-SEP membrane filtration system with MF-03 membrane

Variation of nanosorbent solids content on permeate flux performance in V-SEP membrane filtration system with MF-03 membrane in concentration mode was studied and the result was shown in Figure 30. Theoretically, the permeate flux decline is an inevitable tendency as the solid content increase in solution in membrane filtration process. Figure 30 shows that permeate flux decreased from 31 to 8.5 GFD with increasing solids contents from 1.74% to 12.81%. This deceasing trend is a good indicator to evaluate purification efficiency of nanosorbent in V-SEP membrane filtration system because permeate flux is low at high nanosorbent solid content and vice versa. Thus, an optimized solid content with permeate flux could be selected.

Preliminary estimation of purification time using various nanosorbent solid contents was calculated and shown in Table 14. The calculation is based on the several assumptions and results from Figure 30. The calculation results indicate that the appropriate nanosorbent solid content for purifying nanosorbent is in the range of 8% to 10%.
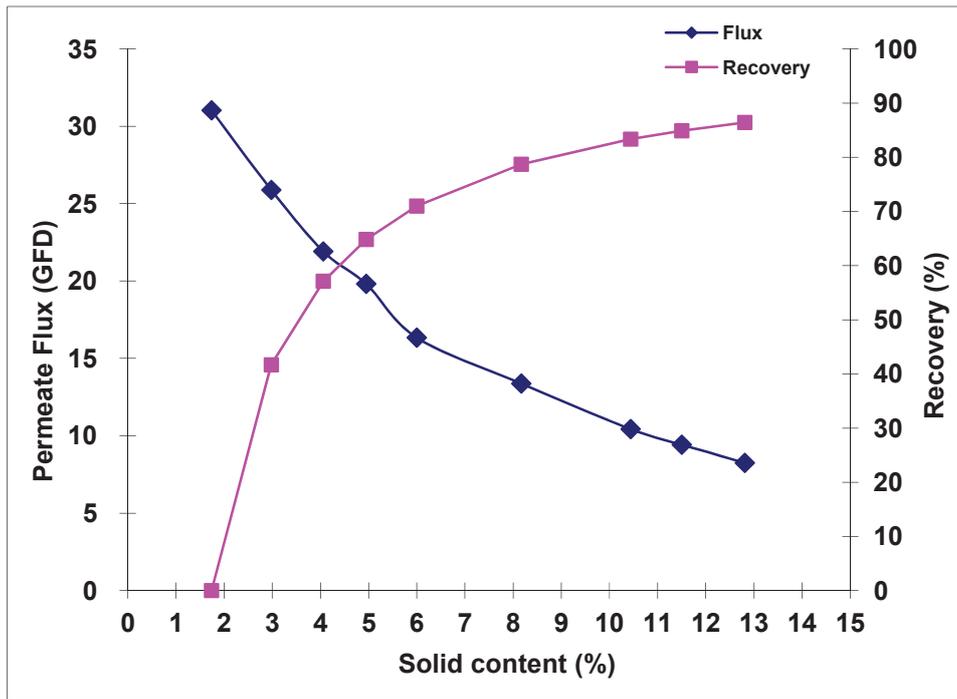
Figure 30. Effect study of nanosorbent solid content on permeate flux performance in V-SEP membrane filtration system with MF-03 membrane in concentration mode (Operation pressure 30 psi)

Table 14. Preliminary estimation of optimum solid content for purifying nanosorbent in pilot scale

Solid content (%)	Flux (GFD)	Permeate flowrate (mL/min)	Total volume in tank (L)	Purification times for each batch	Time for each purification (min)	Total purification time for each batch (min)
4.06	21.91	828	49.26	2	59.49	59.49 X 2 = 118.99
4.95	19.81	768	40.40	2	52.61	52.61 X 2 = 105.22
6.00	16.34	648	33.33	2	51.44	51.44 X 2 = 102.88
8.17	13.37	552	48.96	1	88.69	88.69
10.44	10.43	444	38.31	1	86.29	86.29

Assumption:

1. Max Feed tank volume is 70L

2. Volume of each batch nanosorbent is 20L

3. Solid content of each batch nanosorbent is 20%

4. All of unreacted PEI is removed if equivalent volume (total volume of nanosorbent in tank) of RO water is used in purification

4.3.4 Comparison of discontinuous and continuous diafiltration modes for purifying nanosorbent

The process operation of discontinuous diafiltration and continuous diafiltration modes were previously described in section 4.2.2.4. The major difference between the continuous and discontinuous diafiltration modes is that nanosorbent solid content in feed tank keeps constant in continuous diafiltration mode and nanosorbent solid content in feed tank gradually increase due to continuously loss of water in the feed tank in purification process. Figure 31 illustrates that the conductivity of permeate in continuous diafiltration mode is higher than that in discontinuous mode. The possibility of this variation in discontinuous and continuous diafiltration modes is that unreacted PEI polymer or other residues is easily dispersed in low nanosorbent solid content rather than high nanosorbent solid. Although nanosorbent solid content in feed tank in these two continuous modes were equal at initial stage of purifying nanosorbent, unreacted PEI polymer or other residues was more difficult to disperse as increase in nanosorbent soild content in discontinuous diafiltration mode. As a result, purifying nanosorbent in V-SEP membrane filtration system can be performed in continuous filtration mode rather than discontinuous filtration mode.
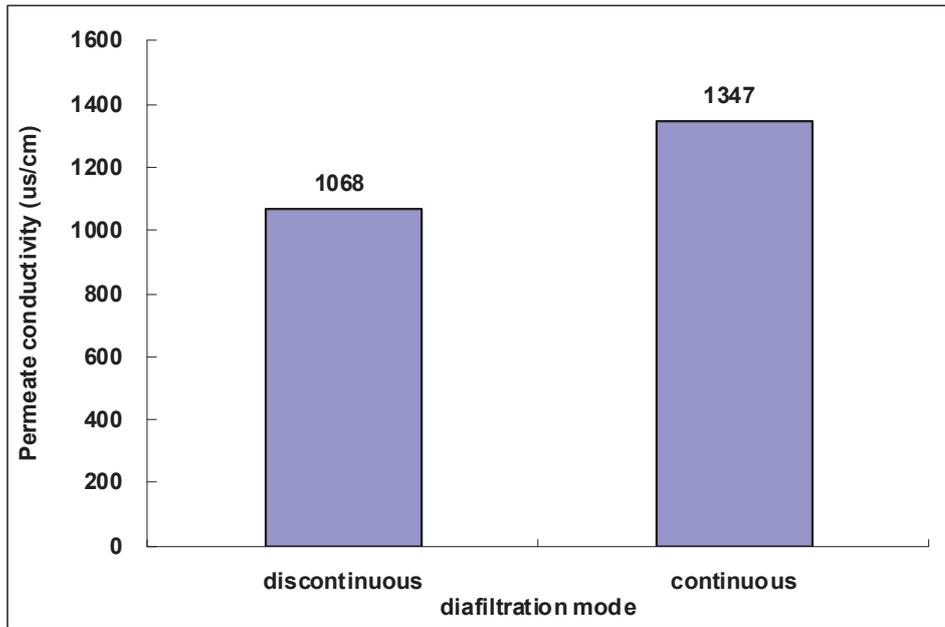
Figure 31. Comparison of discontinuous and continuous diafiltration mode for nanosorbent (P081205) purification (Operation pressure 30 psi)

4.3.5 Purifying nanosorbent in V-SEP membrane filtration system

According to the results in previous section 4.3.3 and 4.3.4, three batches of PMMA/PEI nanosorbent synthesized in Chapter 3 were purified in V-SEP membrane filtration system in continuous filtration mode. Conductivity was used as an indicator to determint the concentration of unreacted PEI in permeate during purifying nanosorbent process because branched PEI polymer water-soluble cationic polymer which composed of cationic primary, secondary and tertiary amine group bearing .high positive charges in water. Figure 32 shows that the permeate conductivity of three batches nanosorbent were measured during purifying nanosorbent process. Three trends in Figure 32 shows that permeate conductivity drastically declined at the initial stage of purification process and subsequently slightly decreased and finally almost constant until the end of purification process. These trends suggest that majority of unreacted PEI in the three batches of

nanosorbent can pass through MF-03 membrane at the initial stage of purifying nanosorbent process.

On the other hand, processing time of purifying nanosorbent is highly concerned because the processing time is directly related to purifying nanosorbent efficiency in V-SEP membrane filtration system. As a result, an optimized purifying nanosorbent time must be determined according to the trends in Figure 32. Three trends in Figure 32 shows that the permeate conductivity decreased from high level to a low level and subsequently remained constant until the end of purification process and thus the optimized purifying nanosorbent processing time can be determined at a point which the permeate conductivity started to remain constant. According to Figure 32, optimized purification processing time of nanosorbent (P081002) is 420 min, nanosorbent (P081205) is 510 min and nanosorbent (P090106) is 780 min. The optimized purification processing time of each batch nanosorbent is different because the solids content of nanosorbent (P081002) is 7.76,nanosorbent (P081205) is 8.01 and nanosorbent (P090106) is 8.41. As the volume of three batches of nanosorbent is fixed in the purification process, the optimized purification processing time is expected to be longer as the nanosorbent solids content rise arising from difficulty of unreacted PEI polymer dispersed in higher nanosorbent solid content discussed previously in section 4.3.4.

It is noted in table 15 that RO water consumption at optimized purification process time for the three batches nanosorbent is around 5 to 8 times to the initial volume of nanosorbent in purification process. Hence, large amount of RO water were required in the purifying nanosorbent process and subsequently large amount of permeate containing unreacted PEI polymer were generated resulting in wastewater

from purifying nanosorbent process. In order to minimize wastewater generated in purifying nanosorbent process, recycling of water from purifying nanosorbent process wastewater (permeate) is necessary.
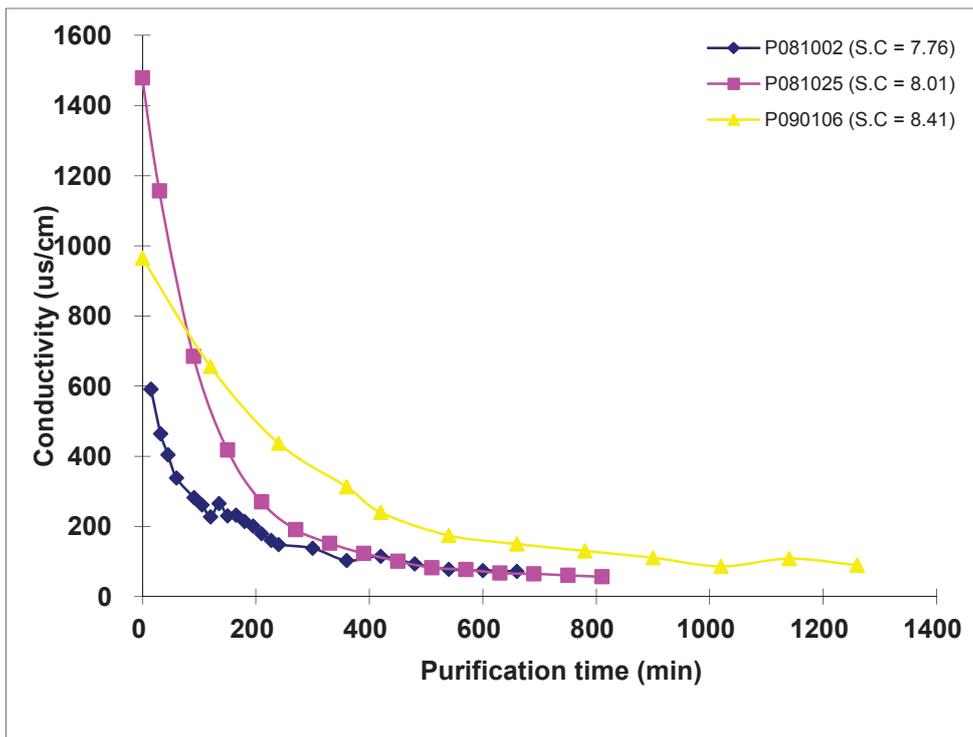
Figure 32. Conductivity in purifying nanosorbent permeate versus purification time

Table 15. Summary table of purification time and total RO water consumption for different batches of nanosorbent in purification

Batch No	P081002	P081205	P090106
Solid content[1] (%)	7.76	8.01	8.41
Optimized purification processing time (min)	420	510	780
RO water consumption at optimized processing time (L)	168	247	266
Total RO water consumption (L)	264	393	430
Total purification time (min)	660	810	1260
Ratio of RO water consumption at optimized processing time to initial volume of nanosorbent in purification process	4.8	7.1	7.6

[1] Solid content = Solid content of nanosorbent in purification process in V-SEP membrane filtration system

4.3.6 Membrane selection to recycle water from purifying nanosorbent wastewater

In order to recycle water from purifying nanosorbent wastewater, membrane filtration process was also used subsequently. Figure 33 illustrates that the conductivity and COD rejection percentage of purifying nanosorbent wastewater (permeate) in range of ultrafiltration and nanofiltration membranes. UF-07 membrane was firstly selected to recycle water from purifying nanosorbent wasteater because the molecular weight cut off of UF-07 membrane is 10,000 Da according to membrane listed in Appendix Table B1 and the average molecular weight of PEI polymer is 750kDa. Since the molecular weight of unreacted PEI is 75 times higher than the molecular weight cut off of UF-07 membrane, majority of

unreacted PEI in the wastewater is expected to be rejected by UF-07 membrane. Other nanofiltration membranes such as NF-11, NF05 and NF-16 were subsequently selected for recycling water from purifying nanosorbent wastewater (permeate) because their pore sizes are smaller than UF-07 membrane. Theoretically, the rejection percentage of COD and conductivity must be higher than that of UF-07 membrane so that these nanofiltration membranes can also be selected.

Figure 33 shows that conductivity and COD were simultaneously increased from UF-07 to NF-16 membranes. These results are in close agreement with the pore size of UF-07 to NF-16 membranes as listed in Appendix Table B1. It is also noted that the rejection percentage of conductivity suddenly increases from 49.4% to 88.2% from NF-05 to NF-16 membrane because the salt (sodium chloride) rejection percentage of NF-05 is 40-60% and NF-16 is 78% mentioned in Appendix Table B1.

According to Figure 33, COD and conductivity rejection of NF-16 nanofiltration membrane are highest in the four selected membranes. Therefore, NF-16 nanofiltration membrane is an applicable membrane to produce high quality of recycled water for purifying nanosorbent.
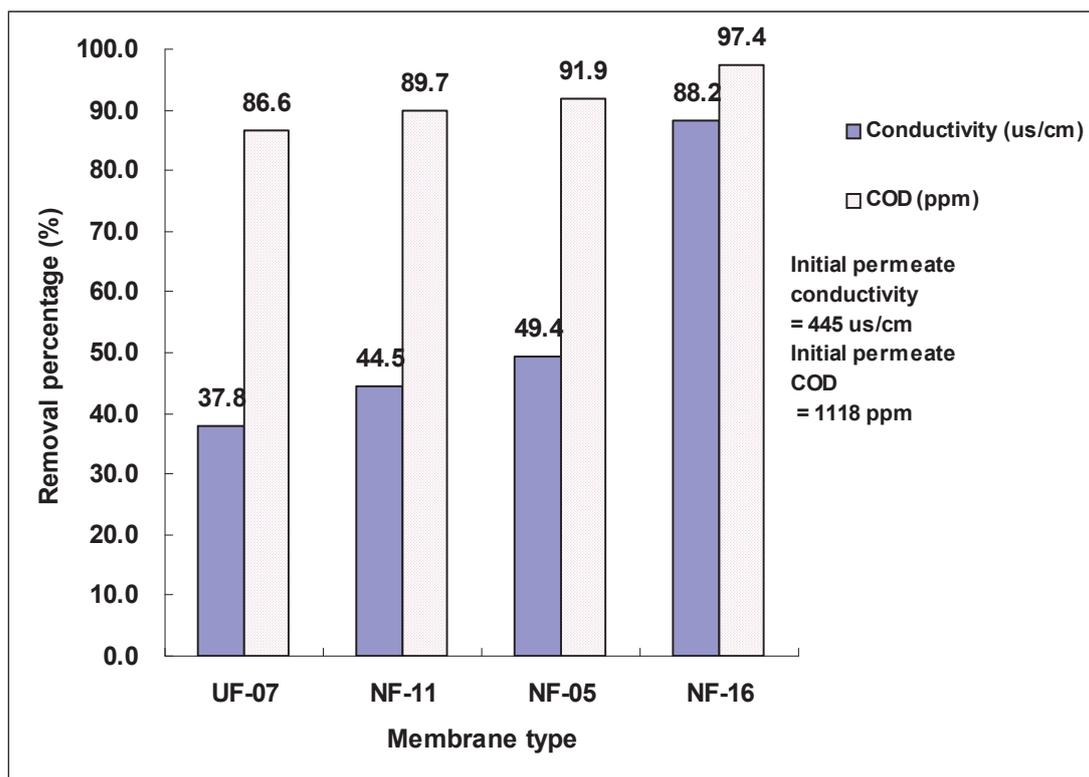
Figure 33. Membrane selection to recycle waster from purifying nanosorbent
wastewater

4.4 Finding and summary

The PMMA/PEI nanosorbent has been purified using V-SEP membrane filtration system. Several keys findings are summarized as follows:

(1)   Only MF-03 membrane meets two criteria in purifying PMMA/PEI nanosorbent with V-SEP membrane filtration system.

(2)   Fouling degree of PMMA/PEI nanosorbent on MF-03 membrane in V-SEP filtration system is relatively low. Thus purifying nanosorbent is achievable with V-SEP with a low operation cost.

(3)   Continuous diafiltration mode is better than discontinuous diafiltration mode in purifying nanosorbent with V-SEP membrane filtration system.

(4)   Appropriate solids content range for purifying nanosorbents is around 8-10%.

(5)   The processing time for purifying nanosorbent increases with increase in

nanosorbent solids content.

(6) The optimal time for purifying nanosorbent process is in range of 420 to 780 min with the nanosorbent solids content between 7.8% and 8.4 %.

(7) The most appropriate membrane for producing high quality recycled water from purifying nanosorbent wastewater is the NF-16 membrane.

Chapter 5

Application of Nanosorbent in Wastewater Treatment using Vibratory Shearing Enhanced Process (V-SEP) Membrane Filtration System

5.1 Introduction

This chapter covers the application of PMMA/PEI nanosorbents in water and wastewater treatments using vibratory shearing enhanced process (V-SEP) membrane filtration system with UF-19 membrane. UF-19 was selected for this study because of its suitability for a wide pH and temperature ranges as well as chloride tolerant (Appendix Table B1). Two parts of research have been carried out: 1) Study of nanosorbent regenerability in a 6-inch membrane stirred cell with a dead end filtration mode. 2) Evaluation of performance of nanosorbents in wastewater treatment in a pilot scale V-SEP membrane filtration system using continuous diafiltration mode.

5.2 Experimental

5.2.1 Materials and equipment

Nanosorbents (P081205) synthesized (described in Chapter 3) and subsequently purified (described in Chapter 4) were used for this study. Copper

sulphate (CuSO$_4$) obtained from Uni-Chem was used to prepare 133.5 and 90 ppm stock Cu(II) ion solutions. Chromium oxide (CrO$_3$) obtained from Uni-Chem was used to prepare 400 ppm stock Cr (VI) ion solution. Cu(II) ion solution (133.5 ppm) and Cr(VI) ion solution (400 ppm) were used for study in the 6 inch membrane stirred cell, while 90 ppm stock Cu(II) ion solution was used in V-SEP membrane filtration system. Silver nitrate solution was obtained from Defond electroplating company. It was diluted 100 times to form a stock Ag(I) ion solution (218 ppm) for study in a 6 inch membrane stirred cell. The stirred cell was manufactured by Dunwell New Logic Ltd. The vibratory shearing enhanced process (V-SEP) developed by the New logic International Ltd. was manufactured by Dunwell New logic Ltd (DNL). Membrane properties as listed in Appendix Table B.1 are provided by Dunwell New logic Ltd (DNL) without brand name due to commercial confidentiality.

5.2.2 Experimental procedure

5.2.2.1 Feasibility and renewability of nanosorbents in removal of Ag (I) ions using UF-19 membrane in the 6 inch membrane stirred cell

Effect of pH on Ag(I) ion removal by UF-19 membrane

100 mL of 218 ppm stock Ag(I) ion solutions were firstly adjusted to pH 4, 5, 7 and 9 with 1% nitric acid and 1% sodium hydroxide. The pH pre-adjusted Ag(I) ion solution was transferred into a 6-inch membrane stirred cell and filtration was performed under 30 psi operation pressure. Permeate was collected for analysis of silver ion concentration.

Effect of pH on Ag(I) ion removal with nanosorbent using UF-19 membrane

A 100 mL of 218 ppm stock Ag(I) ion solution was mixed with 3.66 mL nanosorbent dispersion (solids content of 5.46%, P081205). The mixturewas adjusted to pH 4, 5, 7 and pH 9 with 1% nitric acid and 1% sodium hydroxide respectively. The pH pre-adjusted mixture was transferred into the a 6-inch membrane stirred cell and filtrations was performed under 30 psi operation pressure. Permeate was collected for silver concentration analysis.

Ag(I) ion adsorbed nanosorbent regeneration by sulphuric acid or nitric acid with UF-19 membrane

A 100 mL of 218 ppm stock Ag(I) ion solution was firstly mixed with 3.66 mL (solids content of 5.46%) of nanosorbent dispersion (P081205) and subsequently adjusted the solution pH to 5. The pre-adjusted mixture was transferred into the 6-inch membrane stirred cell, and filtration was performed under 30 psi operation. 90 mL of permeate was collected for silver concentration analysis. 90 mL of pH 2 HNO_3 solution was added to 10 mL of concentrate (Ag(I) ion loaded nanosorbent solution). The mixture was fed into the 6-inch membrane stirred cell for regeneration process. Permeate was collected for silver concentration analysis. The experiments were duplicated using 1M H_2SO_4 solution and 1M HNO_3 as the regeneration agents.

5.2.2.2 Feasibility and renewability of nanosorbents in removal of Cu (II) ions using UF-19 membrane in the 6 inch membrane stirred cell

Effect of pH on Cu (II) ion removal using only the UF-19 membrane

A 135 mL of 133.5 ppm stock Cu(II) ion solution was first diluted to a total volume of 200 mL with 90 ppm Cu(II) ion solution. This solution was used to prepare solutions of pH 2, 3, 4, 5, 6 and 7   using 1 % sulphuric acid and 1% sodium hydroxide to adjust the solution pH.. The pH pre-adjusted 90 ppm Cu(II) ion solutions were transferred into the 6-inch membrane stirred cell, and filtration was performed under 30 psi operation pressure. Permeate was collected for analysis of copper ion concentration.

Effect of pH on Cu(II) ion removal by nanosorbent using UF-19 membrane

A 135 mL of 133.5 ppm Cu(II) ion solution was firstly mixed with 9.86 mL (solids content of 8.27%) nanosorbent dispersion,   and subsequently diluted to a total volume of 200 mL solution containing 90 ppm Cu(II) ions. The mixtures were subsequently adjusted to pH 2, 3, 4, 5 using 1 % sulphuric acid and 1% sodium hydroxide, respectively. The pH pre-adjusted mixtures were transferred into the 6-inch membrane stirred cell and filtrations were performed under 30 psi operation pressure. Permeate was collected for analysis of copper concentration.

Study of removal efficiency of Cu(II) ion by nanosorbent with UF-19 membrane in five successive adsorption and regeneration cycles

A 135 mL of 133.5 ppm Cu(II) ion solution was firstly mixed with 9.86 mL (solids content of 8.27%) of nanosorbent dispersion, and then diluted to a total volume of 200 mL containing 90 ppm Cu(II) ions. The mixture was adjusted to pH 5 by a 1% sodium hydroxide and a 1% sulphuric acid,. The pre-adjusted solution was transferred into the 6-inch membrane stirred cell. The filtration process was performed under 30 psi operation pressure. 90mL of permeate was collected for copper concentration analysis. 90 mL of pH 2.5 H_2SO_4 solution was added to 10 mL of concentrate (Cu(II) ion loaded nanosorbent solution). The mixture was fed into the 6-inch membrane stirred cell for regeneration process. Permeate was also collected for analysis of copper ion concentration. The adsorption and regeneration cycles were duplicated for four times to study nanosorbent regenerability. 90mL of 90 ppm Cu(II) ion solution in adsorption process and pH 2.5 H_2SO_4 solution in regeneration process were fed into 6 inch membrane stirred cell respectively. The volume of collected permeate, Cu (II) ion solution used in adsorption process and pH 2.5 H_2SO_4 solution in regeneration process are equal in order to maintain constant mixture volume in the membrane stirred cell.

5.2.2.3 Feasibility and renewability of nanosorbents in removal of Cr (VI) ions using UF-19 membrane in the 6 inch membrane stirred cell

Effect of pH on Cr(VI) ion removal by only the UF-19 membrane

A 45 mL of stock Cr(VI) ion solution (400 ppm) was diluted to 200 mL, giving a 90 ppm Cr(VI) ion solution. The solutions was then adjusted to pH 2, 4, 6, 8 and 10 with a 1% sulphuric acid and 1% sodium hydroxide, respectively. Different pH pre-adjusted 90 ppm Cr(VI) ion solutions were transferred into the

6-inch membrane stirred cell, and filtrations were performed under 30 psi operation pressure. Permeate was collected for chromium concentration analysis.

Effect of pH on Cr(VI) ion removal by nanosorbents with UF-19 membrane

The procedure is the same as above except the Cr VI) ion solution was mixed with 9.86 mL (solids content 8.27%) of nanosorbents.

Study of removal efficiency of Cr(VI) ion by nanosorbent with UF-19 membrane in five successive adsorption and regeneration cycles

A 45 mL of Cr(VI) ion solution (400 ppm) was mixed with 9.86 mL (solids content of 8.27%) of nanosorbent dispersion, and then diluted to a total volume of 200 mL, giving a 90 ppm Cr(VI) ion solution. The mixture was adjusted to pH 3 with 1% sodium hydroxide and 1% sulphuric acid, and subsequently transferred into the 6-inch membrane stirred cell. The filtration process was performed under 30 psi operation pressure. Permeate was collected for chromium concentration analysis. 90 mL of pH 10 NaOH solution was added to 10 mL of concentrate (Cr(VI) ion loaded nanosorbent solution). The mixture was fed into the 6-inch membrane stirred cell for regeneration process. Permeate was also collected for analysis of copper ion concentration. The adsorption and regeneration cycles were duplicated for four times to study nanosorbent regenerability. 90mL of 90 ppm Cr(VI) ion solution in adsorption process and pH 10 NaOH solution in regeneration process were fed into 6 inch membrane stirred cell respectively. The volume of collected permeate, Cr (VI) ion solution used in adsorption process and pH 10 NaOH solution in regeneration process are equal in order to maintain constant mixture volume in the membrane stirred cell.

5.2.2.4 Fouling degree test and pressure study of nanosorbent in UF-19 membrane in V-SEP membrane filtration system

The feed tank was filled with total 10 L of nanosorbent (P081205) dispersion with solids content of 7.5 %. Nanosorbent solution (P081205) was pumped into the V-SEP membrane filter module using a circulatory diagram pump and both of permeate and concentration were returned to feed tank. Through throttling control valve, the operation (outlet) pressure was adjusted to 30 psi, and the vibration amplitude to 3/4 inch. The permeate flow rate was continually recorded for calculation of permeate flux. The experiments were duplicated under operation pressures of 60 and 120 psi, respectively.

5.2.2.5 Effect of nanosorbent solids content in flux performance using UF-19 membrane in the V-SEP membrane filtration system

The feed tank was filled with a total 21.9 L of nanosorbent (P081205, solid content 3.31%) dispersion. Nanosorbent (P081205) was pumped into the V-SEP membrane filter module using a circulatory diagram pump. Through throttling control valve, the operation (outlet) pressure was adjusted to 30 psi and the vibration amplitude to 3/4 inch. Concentrate was returned to feed tank and permeate collected in a separated permeate tank was continually weighted with an electronic balance to calculate nanosobent solids content and recovery percentage in the V-SEP membrane filtration system. Permeate flow rate was continually recorded during the process.

5.2.2.6 Feasibility and renewability of nanosorbents in removal of Cu (II) ions using UF-19 membrane in V-SEP membrane filtration system

Cu(II) ion removal with nanosorbent using UF-19 membrane in V-SEP membrane filtration system

A 200 L of 90 ppm Cu(II) ion solution was firstly adjusted to pH 5 with a 10% sulphuric acid. A 5.45 L of 15% nanosorbent dispersion was also adjusted to pH 5 in the feed tank, and then pumped into the V-SEP UF-19 membrane filter module using a circulatory diagram pump. The operation (outlet) pressure was adjusted to 30 psi, and vibration amplitude to 3/4 inch in a continuous diafiltration mode as mentioned in section 1.3.2.4. At the same time, a 200 L of pH 5 solution containing 90 ppm Cu (II) ions was directly fed into feed tank with flow rate equal to permeate flow rate. The permeate flow rate was continuously recorded and samples were collected at 30 min interval in order to determine Cu(II) ion concentration in permeate.

Regeneration of Cu(II) ion adsorbed nanosorbents in the V-SEP membrane filtration system

A 5.45 L of nanosorbent (15 % solids) which previously treated with 200 L of 90 ppm Cu(II) ion was adjusted to pH 2.5 using 10% sulphuric acid, followed by transferring 34.55 L this solution into a feed tank. By throttling control valve, operation pressure was adjusted to 30 psi, and vibration amplitude was adjusted to 3/4 inch in a concentration mode. The volume of collected permeate in permeate tank was continuously monitored with an electronic balance until 34.55 L of permeate was collected. Simultaneously, the permeate flow rate was recorded and

permeate was collected at 15, 25 and 34.55 L for Cu(II) ion analysis. Finally, 5.45 L of 15% regenerated nanosorbent was adjusted to pH 5 with a 10% sodium hydroxide in the feed tank for next adsorption cycle.
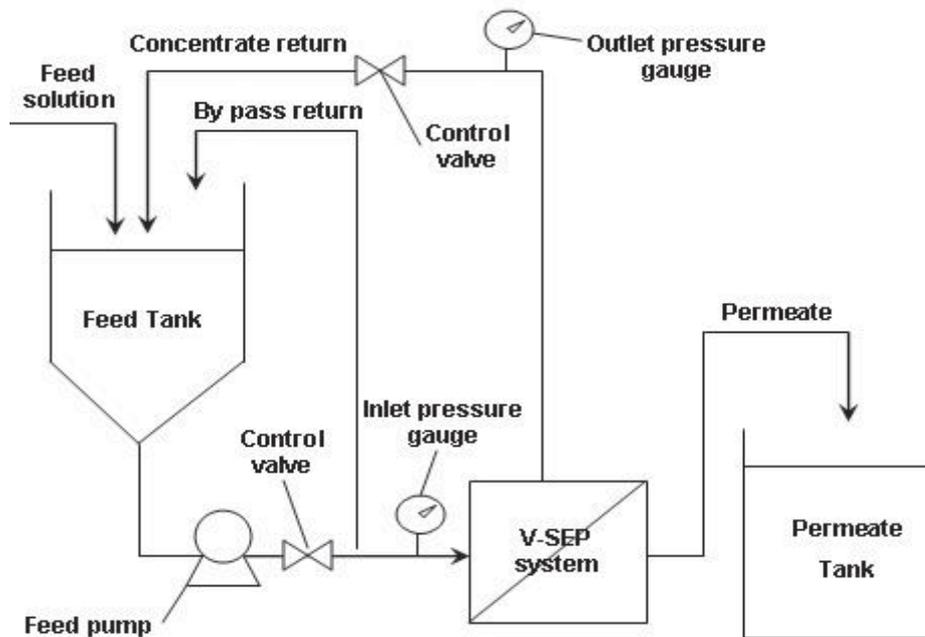
Figure 34. Schematic diagram of V-SEP experimental setup in a continuous diafiltration mode

5.2.2.7 Measurements

Cu (II) and Cr(VI) ion concentrations were determined by the Hach 8117 and 8023 methods, respectively. Ag(I) ion concentration was measured by an atomic absorption spectrometer (Pekin Elmer analyst 100).

5.3 Result and discussion

5.3.1 Feasibility and renewability of nanosorbents in removal of Ag (I) ions using UF-19 membrane in the 6 inch membrane stirred cell

Figure 35 compares removal percentage of Ag(I) ions at different solution pHs in the absence and presence of nanosorbents. The experiments were performed in a 6-inch membrane stirred cell with UF-19 membrane. The removal percentage of Ag (I) ions by UF-19 membrane is 3.3% at pH 4, 1.6% at pH 5, 1.5% at pH 7 and 6.4% at pH 9. These results suggested that the Ag(I) ions cannot rejected by ultrafiltration membrane, resulting in passage of most of metal ions through ultrafiltration membrane. In other words, most of the Ag(I) ions can pass through UF-19 membrane, At pH 9, the removal percentage was slightly higher than lower pHs. This effect may be attributed to the fact that Ag(I) ion are able to react with hydroxide ion to form unstable and insoluble silver hydroxide. The silver hydroxide could subsequently form insoluble silver oxide as shown in the following equation.

$$2Ag^+_{(aq)} + 2OH^-_{(aq)} \rightarrow 2AgOH_{(s)} \rightarrow Ag_2O_{(s)} + H_2O_{(l)}$$

As a result, a small portion of insoluble siver oxide in the solution can be rejected by UF-19 membrane resulting in higher removal percentage of Ag(I) ion with UF-19 membrane in alkaline conditions.
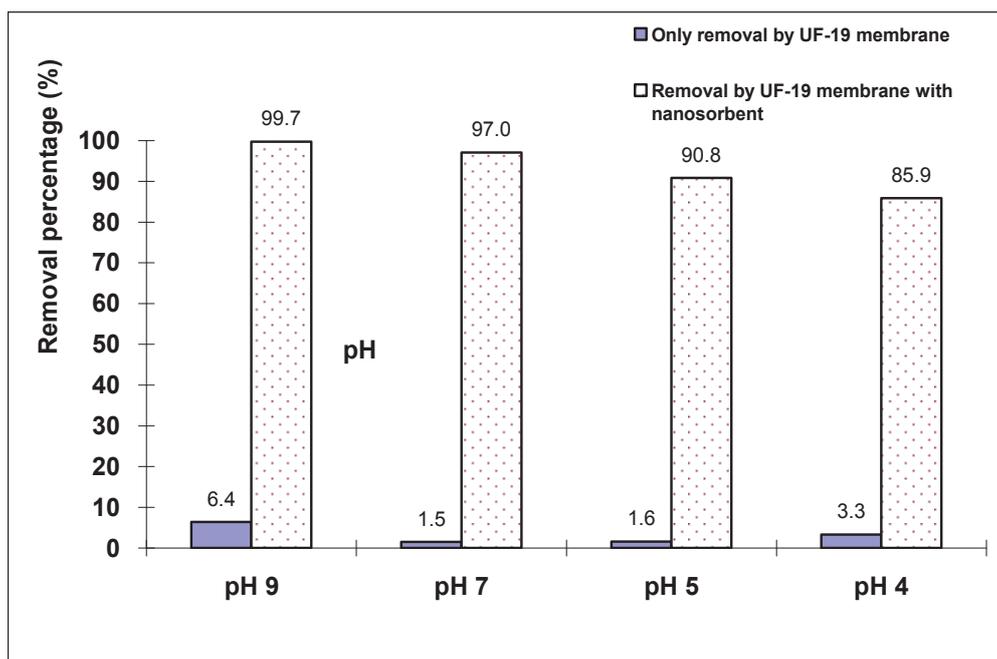
Figure 35. Effect study of pH on Ag (I) ion removal by nanosorbent with UF-19 membrane

Results shown in Figure 35 exhibits that removal percentage of Ag(I) ions with UF-19 membrane is significantly enhanced in the presence of nanosorbent from pH 4 to 9. These great improvement in Ag(I) ion removal percentage indicates that adsorption of Ag(I) ions effectively took place between pH 4 to 9. The nanosorbent containing adsorbed Ag(I) ions can be effectively separated by the UF-19 membrane. It was also noted that removal percentage of Ag(I) ions with UF-19 membrane in the presence of nanosorbent increased with rising pH from 4 to 9. This effect is attributed to the ligand complexation mechanism. Adsorption of Ag(I) ions onto nanosorbent is based on the ligand complexation mechanism between Ag(I) ion and amine group on nanosorbent. Araising solution pH lead to increasing the number of available amine groups on nanosorbent, thus enhancing the loading capacity. As a result, removal percentage of Ag(I) ions with UF-19 membrane in the presence of nanosorbent is increased from 85% to 99% with rising pH from 4 to 9.
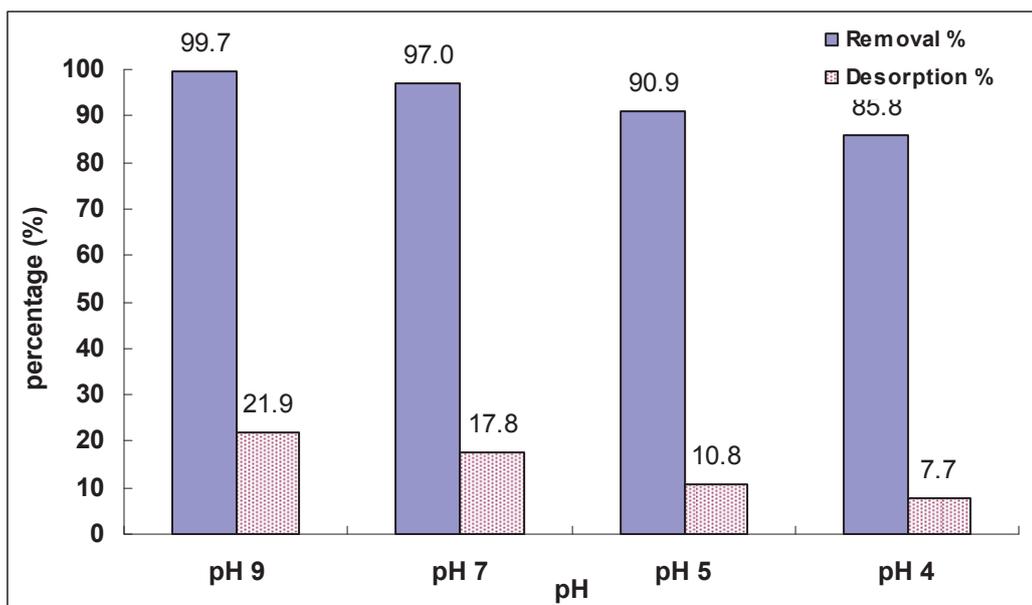
Figure 36. Effect study of pH on Ag (I) ion removal by nanosorbent and desorption
efficiency of Ag (I) ion from adsorbed nanosorbent using 1M HNO₃ with
UF-19 membrane

Regeneration of Ag-loaded nanosorbent for reuse was attempted with acid
treatment process according to the following desorption reaction mechanism:

$$\text{Nano-NH}_2\ \text{Ag}^+_{(s)} + \text{H}^+_{(aq)} \rightarrow \text{Nano-NH}_3^+_{(s)} + \text{Ag}^+_{(aq)}$$
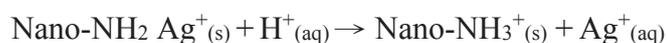
Figure 36 shows that desorption percentages of Ag(I) ions from various
Ag-loaded nanosorbents using 1M HNO₃ as regeneration agent are very low,
ranging from 7% to 22% . Figure 36 shows that the desorption percentage of Ag I)
ions from Ag-loaded nanosorbent is 7% at adsorption pH 5 using pH 2 HNO₃
solution as regeneration agent. These results suggest that Ag(I) ions loaded on
nanosorbent cannot be completely desorbed from nanosorbent by 1M HNO₃ and pH
2 HNO₃ solution. These results are in close agreement with Asem *et al.*(2005)
proposed reaction mechanism. They suggested that complex Ag(NO₃)₂⁻ anions may
be formed in acidic condition and subsquently these negatively charged anions may
interact electrostatically with amine group on the resin shown as following equation:

$$R_3NH_3^+NO_3^-{}_{(s)} + Ag(NO_3)_2^-{}_{(aq)} \rightarrow R_3NH_3^+Ag(NO_3)_2^-{}_{(s)} + NO_3^-{}_{(aq)}$$

Hence, strong electrostatic interaction between $Ag(NO_3)_2^-$ and protonated amine group on nanosorbent may hinder desorption of Ag (I) ions from nanosorbent.
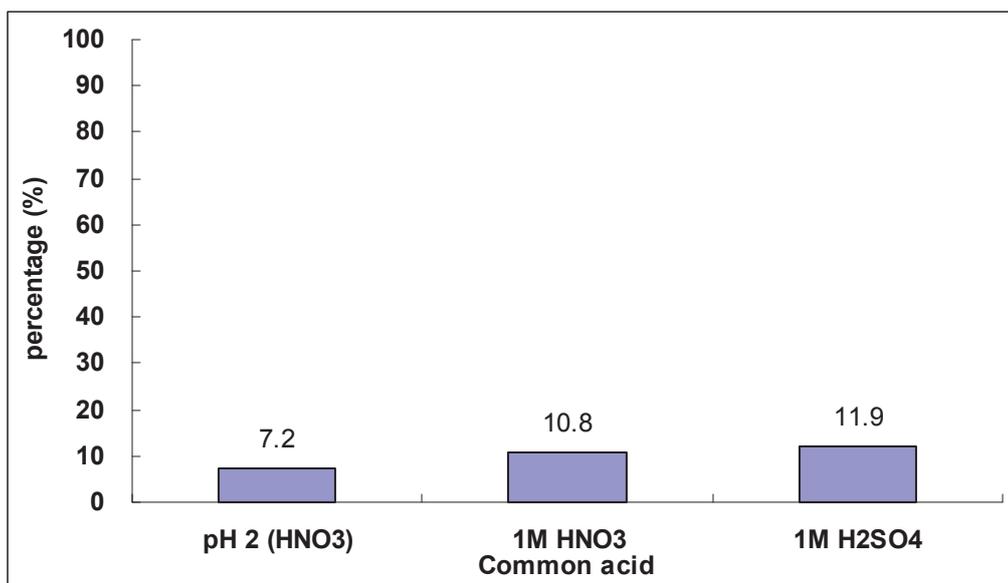
Figure 37. Desorption efficiency of Ag (I) ion from adsorbed nanosorbent using 1M sulphuric acid, 1M nitric acid and pH 2 solution adjusted by nitric acid

In order to increase desorption percentage of Ag (I) ion from nanosorbents, 1M of sulphuric acid was used instead of 1M of nitric acid as regeneration agent. Results shown in Figure 37 indicate that desorption percentage of Ag(I) ions using 1M H_2SO_4 as regeneration agent is comparable with the 1M HNO_3. This reflects that ligand complexation interaction between Ag(I) ions and amine group on nanosorbent is much stronger than interaction between hydrogen ions and amine group. Therefore, regeneration of Ag(I) loaded nanosorbent is not feasible due to strong ligand complexation between Ag(I) ions and amine group on nanosorbent.

5.3.2 Feasibility and renewability of nanosorbents in removal of Cu (II) ions using UF-19 membrane in the 6 inch membrane stirred cell

Effect of pH on Cu(II) ion removal using the UF-19 membrane only was studied. Figure 38 shows that removal percentage of Cu(II) ions is slightly increased from 2.2% to 12.8% as pH rises from 2 to 6, and is significantly increased from 12.8% to 99% at pH 7. This means that majority of Cu(II) ions can pass through UF-19 membrane at pH below 6 but are almost removed at pH 7. This effect is due to the formation of insoluble copper hydroxide as shown in the following equation.

$$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Cu(OH)_{2\,(s)}$$
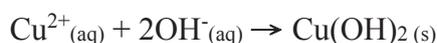
Therefore, formation of insoluble copper hydroxide increases with rising pH, resulting in higher removal percentage of Cu(II) ions..

Figure 38. Effect study of pH on Cu(II) ion removal by nanosorbent with UF-19 membrane and Cu(II) ion only removal by UF-19 membrane

Effect of pH on Cu (II) ion removal in the presence of nanosorbent with UF-19 membrane was also studied. Figure 38 demonstrates that removal percentage of Cu (II) ions in the presence of nanosorbents is significantly higher than without the nanosorbents from pH 3 to 5. These results obviously indicate that Cu(II) ions can be loaded onto nanosorbent arising from ligand complexation between Cu(II) ions and amine groups on the nanosorbents. Since the removal percentage of Cu(II) ions with the nanosorbents could achieved 96.6% at pH 5 with UF-19 membrane, the optimal pH for Cu(II) ions removal by nanosorbent with UF-19 membrane was set at pH 5.

In order to investigate the recyclability of nanosorbents in Cu (II) ions removal , removal efficiencies of Cu(II) ions by the same batch of nanosorbents in successive adsorption and regeneration cycles were studied with UF-19 membrane. Figure 39 illustrate that the removal percentage of Cu(II) ions drastically decrease from 96% to 46% from the first to the second adsorption and regeneration cycles and the removal percentage of Cu(II) ions maintain around 40-46% in afterwards adsorption and regeneration cycles. The decrease in removal percentage of Cu(II) ions in first to second adsorption and regeneration cycles maybe caused by incomplete desorption of Cu(II) ions from the nanosorbents in first regeneration process with two possible reasons: 1) Insufficient hydrogen ion for desorption of Cu(II) ions on nansorbent in the first regeneration process. and 2) Strong metal-ligand complexation between amine groups and Cu(II) ions. Permanent adsorption of Cu (II) ions with theamine groups on nanosorbent hinder adsorption of Cu(II) ions onto nanosorbent in the second to subsequent adsorption and regeneration cycles. As a result, comparable removal percentages of Cu(II) ions in second to fifth adsorption and regeneration cycles were achieved.
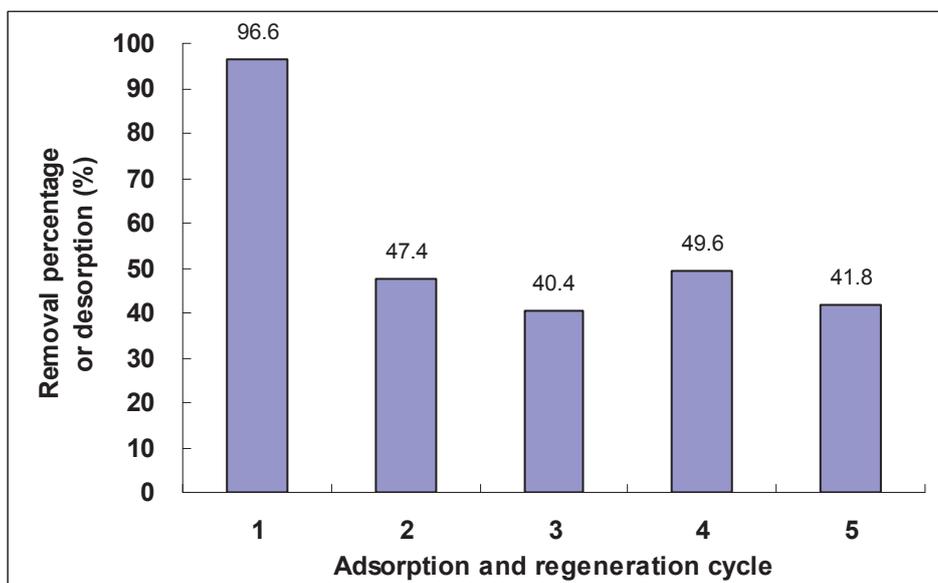
Figure 39. Removal efficiency of Cu(II) ion by nanosorbent with UF-19 membrane in five successive adsorption and regeneration cycles

5.3.3 Feasibility and renewability of nanosorbents in removal of Cr (VI) ions using UF-19 membrane in the 6 inch membrane stirred cell

Effect of pH on Cr(VI) ions removal was firstly studied using UF-19 membrane. Figure 40 shows that removal percentages of Cr(VI) ions are in the range of 0 to 6.7% in range of pH 2 to 10. In fact, Cr(VI) ions can exist in the form of CrO_4^{2-} and $HCrO_4^-$ in all pHs. Theoretically, these ions can only be separated by the reverse osmosis membrane, but not by the ultrafiltration membrane. Therefore, majority of CrO_4^{2-} and $HCrO_4^-$ ions passed through UF-19 membrane resulting in low removal percentages of Cr (VI) ion in range of pH 2 to 10.
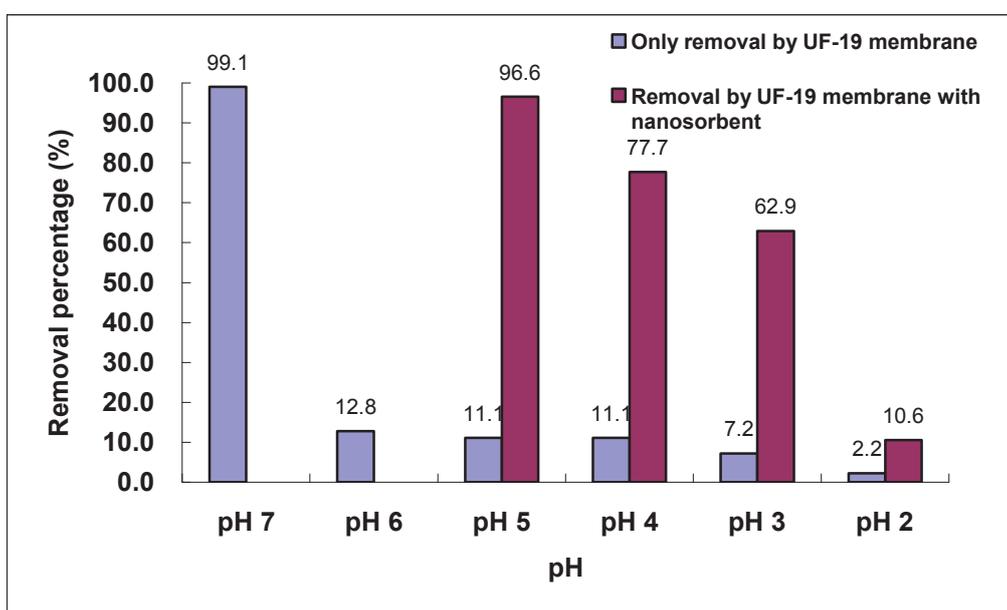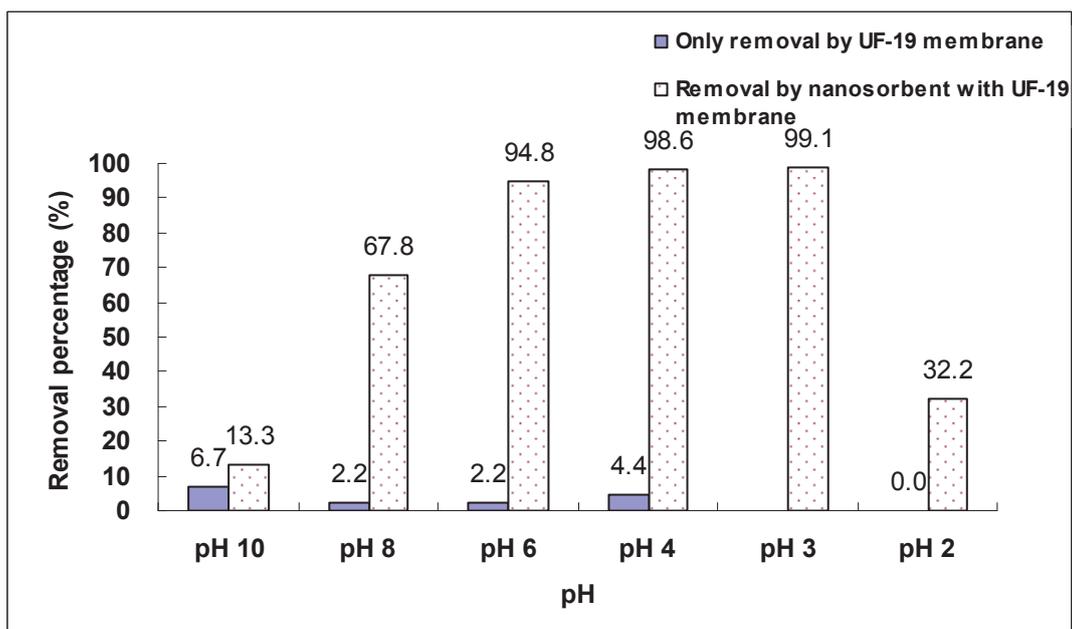
Figure 40. Effect study of pH on Cr(VI) ion removal by nanosorbent with UF-19 membrane and Cr(VI) ion only removal by UF-19 membrane

Effect of pH on Cr(VI) ions removal in presence of nanosorbent with UF-19 membrane was also investigated. Figure 40 shows that the removal percentages of Cr(VI) ions in the presence of nanosorbents are significantly higher than that in the absence of nanosorbent at pH 3, pH 4, pH 6 and pH 8. This implies that nanosorbent is able to absorb anionic Cr(VI) species. The Cr(VI)-loaded nanosorbents were separated by UF-19 membrane. The adsorption of anionic Cr(VI) species onto nanosorbent is due to the electrostatic interaction between anionic Cr(VI) species and protonated amine groups on nanosorbents according to the following reaction:

$$Nano\text{-}NH_3^+{}_{(aq)} + HCrO_4^-{}_{(aq)} \rightarrow Nano\text{-}NH_3^+ HCrO_4^-{}_{(s)}$$
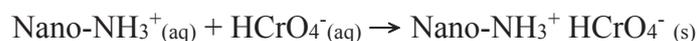
It was also found that removal percentage of Cr(VI) ions in the presence of nanosorbents is slightly reduced from 99 to 94% as solution pH changed from pH 3 to pH 6, and then drastically decreased from 94 to 13% when pH changed from 6 to 10. This effect is caused by the fact that increasing solution pH lowers protonation

degree of amine group of the nanosorbent, thus reducing the electrostatic interaction between anionic Cr(VI) species and amine groups on nanosorbent.

$$\text{Nano-NH}_3{}^+{}_{(aq)} + \text{OH}^-{}_{(aq)} \rightarrow \text{Nano-NH}_{2(s)} + \text{H}_2\text{O }_{(l)}$$
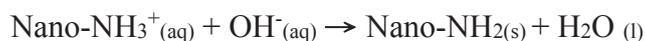
It is also noted that removal percentage of Cr(VI) ions in the presence of nanosorbents at pH 2 is significantly lower than that at pH 3. In previous discussion, decreasing pH increases protonation degree of amine groups on nanosorbent, and thus removal percentage of Cr (VI) ions in the presence of nanosorbents at pH 2 should be higher or close to at pH 3. However, the result at pH 2 contradicts with theoretical prediction. This may due to the presence of excessive sulphate ions from the sulphuric acid. The sulphate ions are capable of partially adsorbed onto protonated amine groups on nanosorbent as shown in the following equation.

At pH 3, concentration of anionic Cr (VI) ions in solution is much higher than that of sulphate ions and thus majority of anionic Cr(VI) ions in solution can be adsorbed onto protonated amine groups on nanosorbent.

$$2\text{Nano-NH}_3{}^+{}_{(S)} + \text{SO}_4{}^{2-}{}_{(aq)} \rightarrow (\text{Nano-NH}_3{}^+)_2\text{SO}_4{}^{2-}{}_{(s)}$$
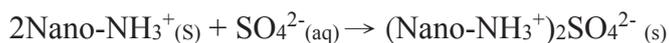
Thus, some of protonated amine group on nanosorbent occupied by sulphate ions hinder the adsorption of anionic Cr(VI) species onto amine group on nanosorbent at pH 2, resulting in competing adsorption between sulphate ions from sulphuric acid and anionic Cr(VI) species onto nanosorbent.

To study nanosorbent recyclability in Cr(VI) ions removal, removal efficiency of Cr(VI) ions in the presence of nanosorbents in five successive adsorption and regeneration cycles was investigated with UF-19 membrane . Figure

40 illustrates that removal percentage of Cr(VI) ions in the presence of nanosorbents drastically decrease from 99% to 22% from first to third adsorption and regeneration cycles and subsequently removal percentage of Cr(VI) ions maintain in a similar range of 17-20% from fourth to fifth adsorption and regeneration cycles. There may be two possible reasons for this effect: 1) Insufficient hydroxide ion for desorption of Cr(VI) ions on nanosorbents in the first and second regeneration process; and 2) strong electrostatic interaction between protonated amine groups and anionic Cr(VI) ions. As a result, permanent adsorption of anionic Cr(VI) ions on protonated amine groups on nanosorbent hinder adsorption of Cr(VI) ions onto the nanosorbents in the third to fifth adsorption cycle.
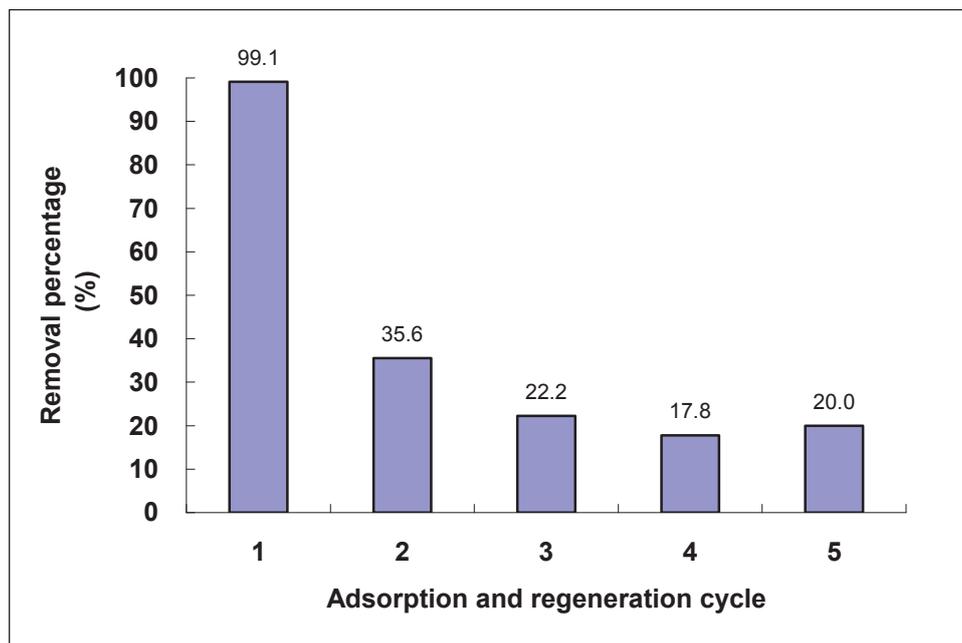
Figure 41. Removal efficiency of Cr(VI) ion by nanosorbent with UF-19 membrane in five successive adsorption and regeneration cycle

5.3.4 Fouling degree test and pressure study of nanosorbent in UF-19 membrane in V-SEP membrane filtration system

The objective of this investigation is to determine the fouling degree of nanosorbent on UF-19 membrane and to determine the effect of pressure on flux performance in UF-19 membrane. The study was firstly performed at 30 psi operation pressure and this operation pressure is equal to the minimum operation pressure of V-SEP membrane filtration system in ultrafiltration. The results shows that the permeate flux gradually decrease from 64 GFD to 43 GFD at initial stage of filtration to 330 min operation time and subsequently almost constant after 330 min operation time. Since PMMA/PEI nanosorbents are highly positive charges ranging from +40 to 45 mv at pH 7 and ether (-O-) and sulphone (-SO_2-) group on polyethersulphone (PES) membrane are netural group, there is little electrostatic interaction between the nanosorbent and PES UF-19 membrane. The steady flux can be observed after 330 min operation time indicating relatively low fouling of the nanosorbents on UF-19 membrane.
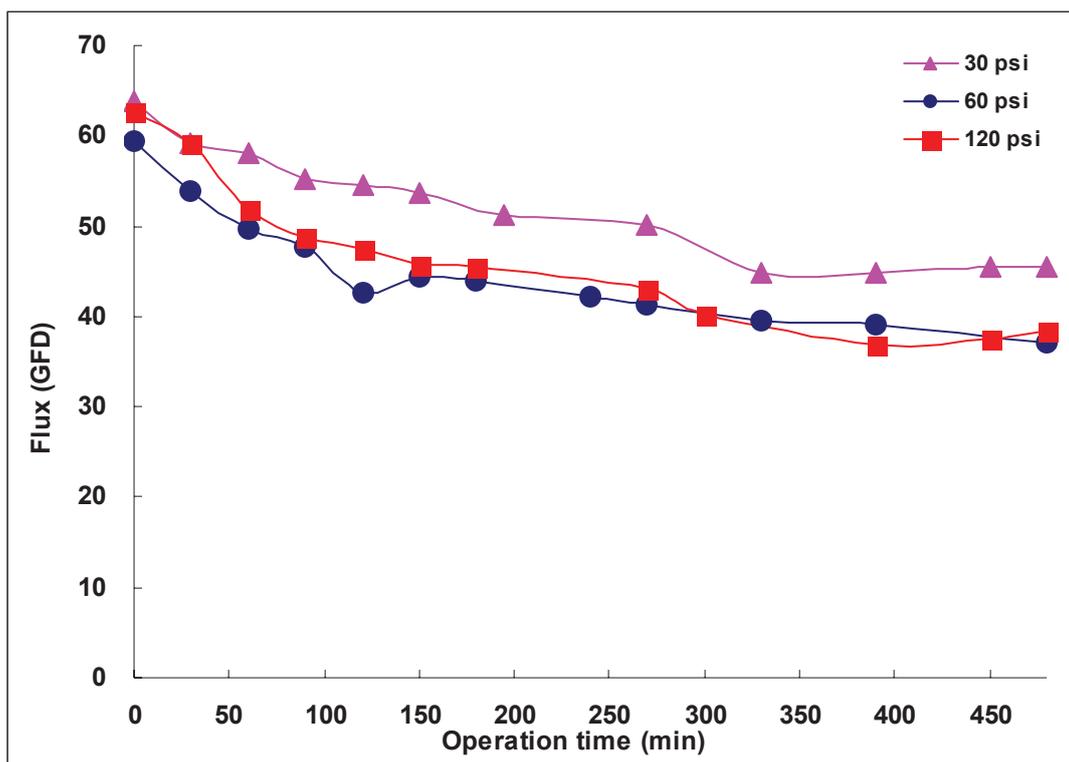
Figure 42. Fouling degree test and effect study of pressure on the permeate flux
performance of nanosorbent in UF-19 membrane at 7.5% solid content

Effect of pressure on flux performance of nanosorbent in UF-19 membrane
was subsequently studied at 60 and 120 psi operation pressure respectively. The
result shows that the permeate fluxes at 60 and 120 psi operation pressure were
slightly lower than that at 30 psi operation pressure. This can be attributed to
concentration polarization effect. Concentration polarization is an effect that
hydrocolloids, marcromolecules, large solutes or particle rejected by the
membrane and subsequently a cake (polarization) layer was formed on UF-19
membrane surface. This layer can act as secondary layer to resist permeate flow.
Although permeate flux theoretically increase with increasing operation pressure,
concentration polarization effect also simultaneously increase. As peremate flux
decline attributed by concentration polarization effect is greater than permeate
flux increase with rising operation pressure, the overall permeate flux decrease

with increasing operation pressure. As a result, slightly permeate flux decline were observed in Figure 42 and thus 30 psi is an optimum operation pressure application of nanosorbent in wastewater treatment using V-SEP membrane filtration system.

5.3.5 Effect study of nanosorbent solid content on permeate flux performance in V-SEP membrane filtration system with UF-19 membrane

Variation of nanosorbent solids content on permeate flux performance in V-SEP membrane filtration system with UF-19 membrane in concentration mode was studied similar to section 4.3.3 and the result was shown in Figure 43. Theoretically, the permeate flux decline is an inevitable tendency as the solid content increase in solution in membrane filtration process. Figure 43 shows that permeate flux decreased from 105 to 55 GFD with increasing solids contents from 3.3% to 4.3% and subsequently gradually decreased from 55 to 24 GFD with increasing solids contents from 4.3% to 10.% and finally almost constant at 23 GFD with increasing solids contents from 10% to 15%. This deceasing trend is a good indicator to evaluate optimum nanosorbent solids contents for metal ions removal in V-SEP membrane filtration system because permeate flux is low at high nanosorbent solid content and vice versa. Thus, 15% nanosorbent solid content was firstly selected for application of nanosorbent for metal ions removal in V-SEP membrane filtration system. Although permeate flux decline with increasing nanosorbent solids contents, metal ions can be concentrated to high concentration at high nanosorbent concentration after desorption of metal ions loaded nanosorbent in the process. As a result, high concentration of metal ions

can be collected in permeate after membrane filtration process.
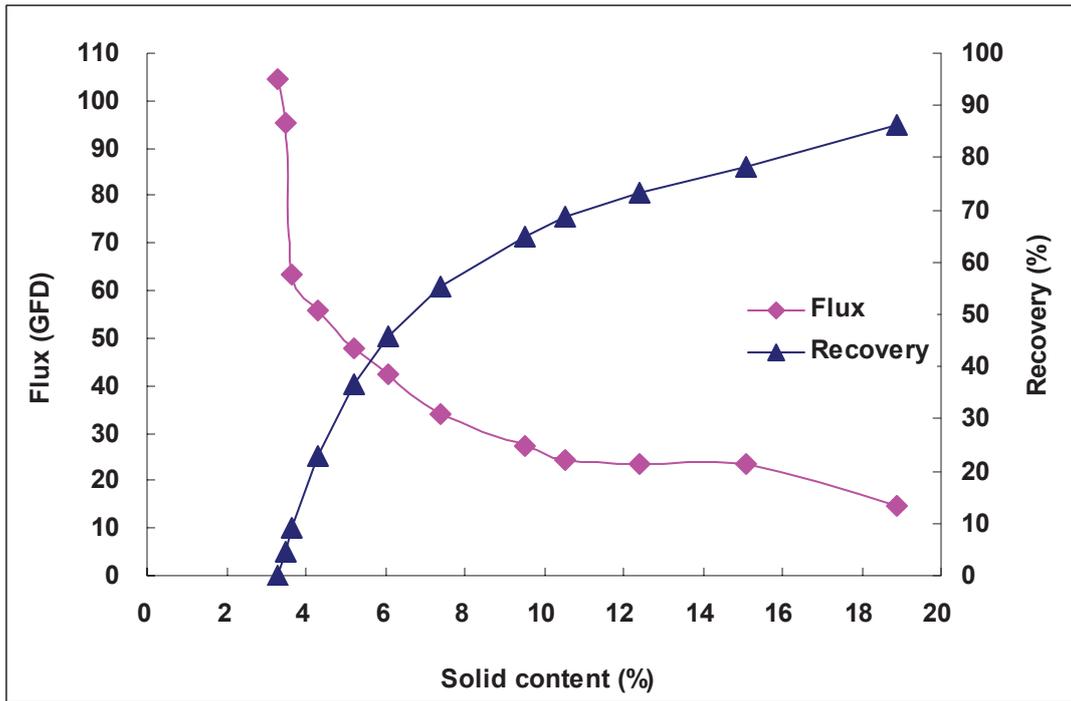
Figure 43. Effect study of nanosorbent solid content on permeate flux performance in V-SEP membrane filtration system with UF-19 membrane in concentration mode

5.3.6 Feasibility and renewability of nanosorbents in removal of Cu (II) ions using UF-19 membrane in V-SEP membrane filtration systm

Figure 44 illustrates that removal percentage of Cu(II) ions slightly decease from 100% to 90% as Cu(II) ions to nanosorbent dosage gradually increase from 0 to 21 mg/g in the first adsorption cycle. Continuous diafiltration mode filtration was performed in this study with feeding flow rate of simulated 90 ppm Cu(II) ions to feed tank equal to permeate flow rate. This reflects that Cu(II) ion concentration was gradually increased in the system and nanosorbent solids contents was almost constant in the process. So, Cu (II) ions to nanosorbent dosage increase in the process. In addition, vacant adsorption sites (amine groups) on nanosorbent were

gradually occupied by Cu (II) ions as continuous feeding of simulated 90 ppm Cu (II) ions to the system. Therefore, slight decline in removal percentage of Cu(II) ions in the system is observed and removal percentage of Cu(II) ions is inversely proportional to Cu (II) ions to nanosorbent dosage shown in Figure 54.
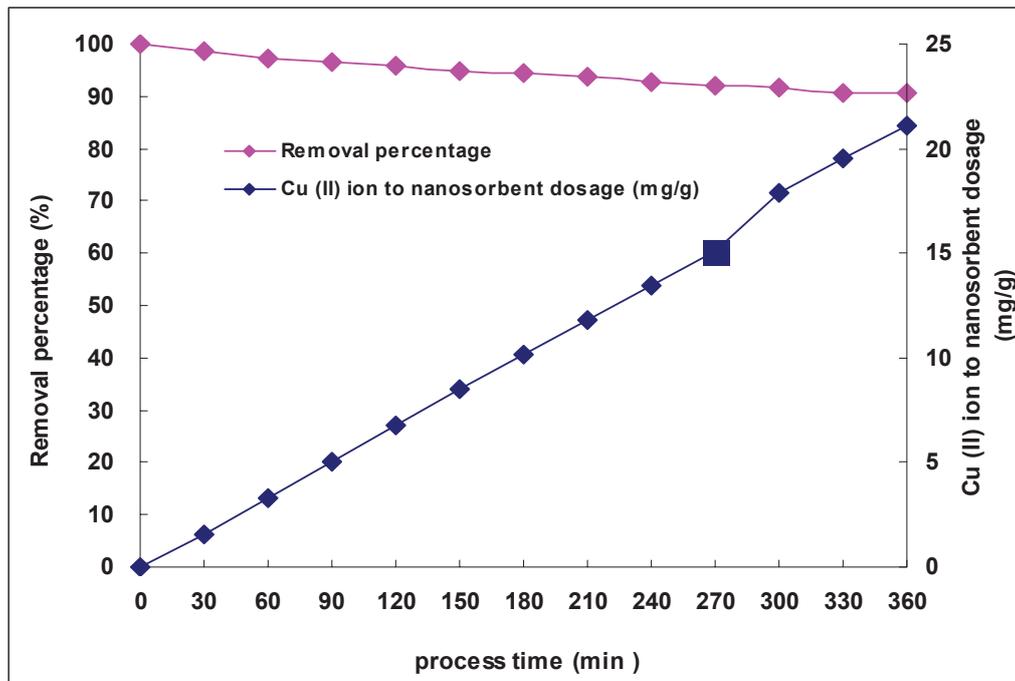
Figure 44. Effect study of nanosorbent dosage in Cu (II) ion removal with UF-19 membrane in V-SEP membrane filtration system in first adsorption cycle

On the other hand, Figure 44 plays an important role to evaluate nanosorbent dosage in Cu(II) ion containing wastewater treatment with V-SEP membrane filtration system. In reality, Cu(II) ions concentration in wastewater is varied from different manufacturing processes, sources and wastewater discharge standards is varied from different nations. Therefore, as feeding wastewater Cu(II) ions concentration, daily wastewater treated volume, wastewater discharge standards (Cu(II) ion concentration in permeate) are known, volume of nanosorbent (15% solids content) used to treat Cu (II) ion containing wasteweater and membrane filtration processing time can be evaluated according to Figure 44.
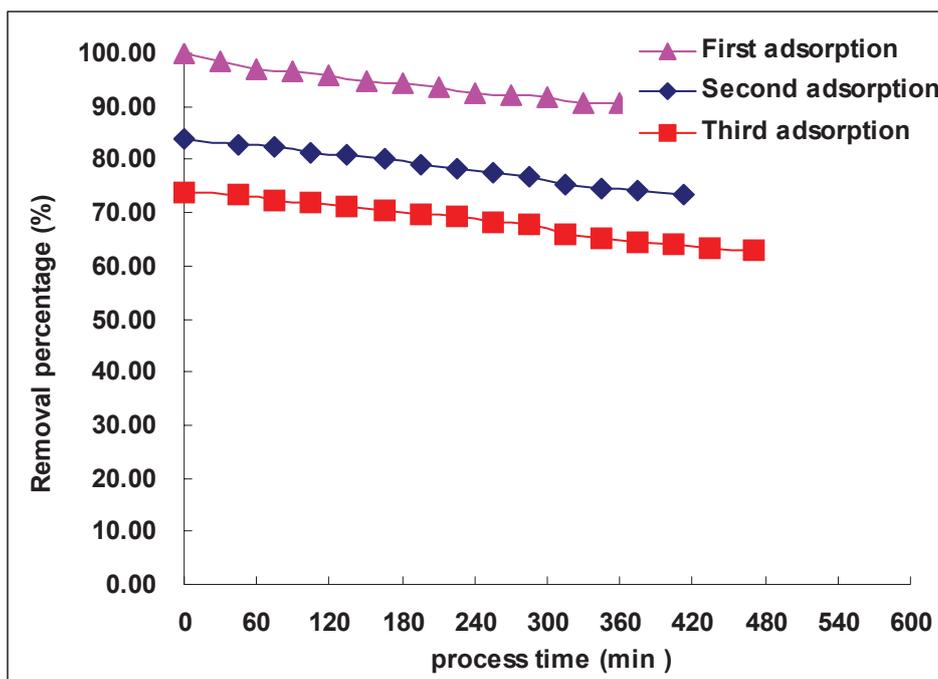
Figure 45. Removal percentage of Cu(II) ion by nanosorbent with UF-19 membrane in V-SEP membrane filtration system in three adsorption cycles

Figure 45 demonstrates that Cu(II) ion removal percentage by nanosorbent in V-SEP membrane filtration system in each adsorption cycle. The results shows that removal percentage of Cu(II) ions slightly decease 100% to 90% in first adsorption cycle, removal percentage of Cu(II) ions slightly decrease from 84% to 74% in second adsorption cycle and removal percentage of Cu(II) ions slightly decrease from 74% to 63% in third adsorption cycle. The decreasing trends of removal percentage of Cu(II) ions in second and third adsorption cycle are similar to first adsorption cycle and can be attributed to same explaination of first adsorption cycle previously discussed in above.

However, removal percentage of Cu(II) ions by nanosorbent is 90% at the end of membrane filtration process in first adsorption cycle and removal percentage of Cu (II) ions is 63% at the end of membrane filtration process in

third adsorption cycles. This reflects that adsorption efficiency of Cu(II) ions by nanosorbent decrease from first to third adsorption cycle as regenerated nanosorbent reused. This can be clearly explained by the result presented in Figure 46. Figure 46 exhibits that desorption percentage of Cu(II) ions from nanosorbent decreases from 70% to 50% from first to third desorption cycle. The result obviously indicates that Cu(II) ions cannot be completely desorbed from nanosorbent due to permanent ligand complexation interaction between Cu(II) ions and adsorption sites (amine groups) on nanosorbent. As a result, removal percentage of Cu(II) ions by nanosorbent decrease from first to third adsorption cycles
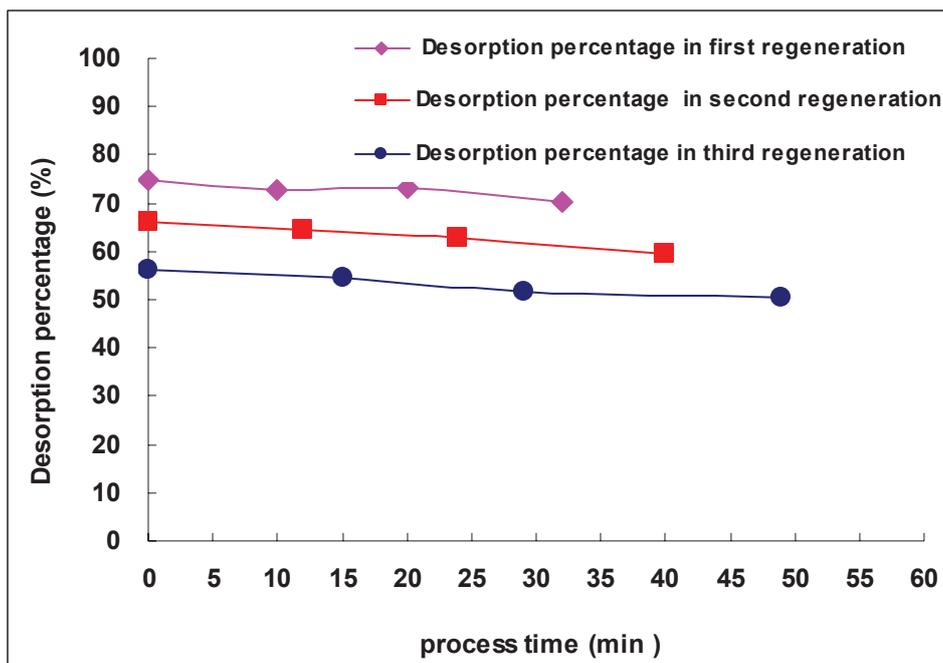
Figure 46. Desorption efficiency of Cu(II) ion from adsorbed nanosorbent with UF-19 membrane in V-SEP membrane filtration system in three regeneration cycles
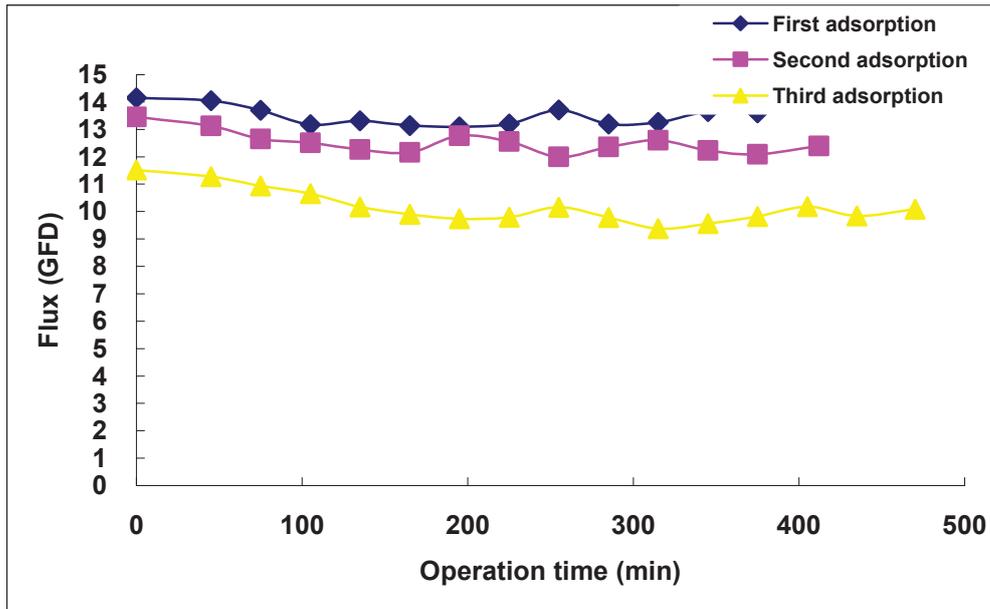
Figure 47. Flux performance of Cu (II) ion removal by nanosorbent with UF-19 membrane in V-SEP membrane filtration system in three adsorption cycles

Flux performance of Cu(II) ions removal by nanosorbent in V-SEP membrane filtration system is presented in Figure 47. The result demonstrates that the flux in each adsorption cycle is steady from initial stage to end of membrane filtration process. This result is good agreement with the result of fouling degree study of nanosorbent on UF-19 membrane in section 5.3.4 and can be clearly explained in previous discussion in section 5.3.4.

On the other hand, the steady flux observed in each adsorption cycle indicates that flux in removal of Cu(II) ions by nanosorbent in V-SEP membrane filtration system can be maintained in long membrane filtration process. This means that membrane cleaning and membrane module replacement frequency aiming in flux recovery in the process is greatly reduced. In addition, steady flux in the process implies that treatment volume of Cu(II) ions containing feeding wastewater can be

maintained in this process Inevitably, overall operation cost of removal of Cu(II) ions by nanosorbent in V-SEP membrane filtration system can be greatly reduced and the treatment efficiency can be maintained.
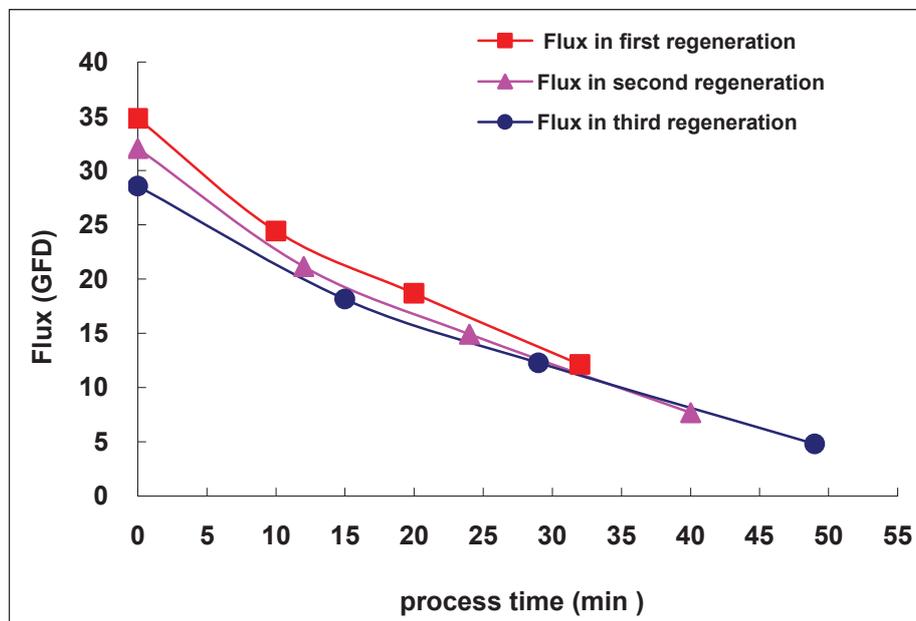
Figure 48. Flux performance of desorption of Cu(II) ion from adsorbed nanosorbent with UF-19 membrane in V-SEP membrane filtration system in three regeneration cycles

Figure 48 demonstrates that flux is gradually decreasing in every regeneration cycles. 34.55 L of pH 2.5 solutions was fed into feed tank in regeneration process to make up 40L of mixture before regeneration process and subsequently nanosorbent concentration in the tank was decreased from 15% to 2.04%. In addition, regeneration process was performed in concentration mode and permeate was continuously collected in separated permeate tank. As a result, nanosorbent concentration was increased from 2.04% to 15% from initial stage to end of regeneration process. Flux decline is an inevitably tendency as solution concentration increase in membrane filtration process. Hence, flux decline in every regeneration cycles can be observed.

5.4 Summary

Development of PMMA/PEI nanosorbent in water and wastewater has been performed in the 6-inch membrane stirred cell prior to the V-SEP membrane filtration system. Several findings in removal of Ag(I), Cu(II) and Cr(VI) ions in the presence and absence of nanosorbent in the 6-inch membrane stirred cell are summarized as follows:

Removal of Ag(I) ions by nanosorbent in the 6-inch membrane stirred cell

(1) Minor of Ag(I) ions could be rejected by UF-19 membrane from pH 4 to pH 9 due to formation of insoluble silver oxide.

(2) Removal percentage of Ag(I) ions in the presence of nanosorbent with UF-19 membrane is significantly higher than that absence of nanosorbent from pH 4 to pH 9.

(3) Removal percentage of Ag(I) ions in presence of nanosorbent with UF-19 membrane is slightly increased as pH changed from 4 to 9.

(4) Desorption percentage of Ag(I) ions from the nanosorbent is quite low using pre-adjusted pH 2 solution of HNO_3, 1M HNO_3 and 1M H_2SO_4 as regeneration agent resulting in difficulty in regeneration of Ag(I) loaded nanosorbents for further reuse.

Removal of Cu(II) ions by nanosorbent in the 6- inch membrane stirred cell

(1) Removal percentage of Cu(II) ions in the absence of nanosorbent with UF-19 membrane gradually increases as pH changed from 2 to 6 due to formation of insoluble copper hydroxide from part of Cu(II) ions.

(2) The optimum pH of Cu(II) ions removal by UF -19 membrane is pH 7 due to formation of insoluble copper hydroxide from majority of Cu(II) ions.

(2) Optimum adsorption pH of Cu(II) ion removal in the presence of nanosorbent with UF-19 membrane is pH 5.

(3) In five successive adsorption and regeneration cycle of Cu(II) ion removal by nanosorbent with UF-19 membrane, the removal percentages of Cu(II) ions are maintained in the range of 40-50% from second to fifth adsorption and regeneration cycles.

Removal of Cr(VI) ion with nanosorbent in 6 inch membrane stirred cell

(1) Removal percentage of Cr(VI) ions in absence of nanosorbent with UF-19 membrane are low from pH 2 to 10.

(2) Removal percentage of Cr(VI) ions in presence of nanosorbent with UF-19 membrane is significantly higher than that of without nanosorent with UF-19 membrane.

(3) Removal percentage of Cr(VI) ions in presence of nanosorbent with UF-19 membrane gradually decrease from pH 3 to pH 10 and drastically decline from pH 3 to pH 2.

(4) Optimum adsorption pH of Cr(VI) ion removal in presence of using UF-19 membrane is around pH 3.

(5) In five successive adsorption and regeneration cycle of Cr(VI) ions removal by nanosorbent with UF-19 membrane, the removal percentage of Cr(VI) ions is reduced from 36 to 30% from second to fifth adsorption and regeneration cycles

Development of PMMA/PEI nanosorbent in Cu(II) ion removal has been performed in V-SEP membrane filtration system with UF-19 membrane, several key findings were summarized as follows:

(1) Steady flux can be observed in membrane fouling study of nanosorbent on UF-19 membrane in V-SEP membrane filtration system at 30 psi, 60 psi and 120 psi operation pressure indicating low level membrane fouling of nanosorbent on UF-19 membrane.

(2) The optimal operation pressure for application of nanosorbent in wastewater with V-SEP membrane filtration system is 30 psi.

(3 The optimal nanosorbent concentration for application of nanosorbent in water and wastewater V-SEP membrane filtration system is ranging from 10.5 to 15%.

(4) The removal percentage of Cu(II) ions by nanosorbent in V-SEP membrane filtration system decrease from 90 to 75% from first to second adsorption cycle and subsequently decrease to 63% in third adsorption cycle.

(5) The desorption percentages of Cu(II) ions from nanosorbent in V-SEP membrane filtration system decrease from 70 to 60% from first to second regeneration cycle and subsequently decrease to 50% in third regeneration cycle.

(6) Steady flux in each adsorption cycle of Cu(II) ion removal by nanosorbent in V-SEP membrane filtration system can be observed and flux decline in each regeneration also be observed.

Chapter 6 Conclusion

Part I: Synthesis of PMMA/PEI Nanosorbents in a Pliot ScaleReactor

Our study has demonstrated that PMMA/PEI nanosorbent were successfully synthesized in the 20L pilot scale reactor under semi-batch addition mode. The result showed that the nanosorbent properties of synthesized in 20L pilot scale reactors are quite similar to the nanosorbent properties synthesized in laboratory scale. According to reaction temperature change, particle size change, monomer conversions change, observed single peak of the particle size in PMMA/PEI nanosorbent synthesis process, these observations are quite similar to PMMA/PEI nanosorbent synthesized in laboratory scale described in Ho *et al.* (2010) and also this observation can be explained by emulsion polymerization reaction mechanism mentioned in Ho *et al.* 2010. This confirms that the emulsion polymerization reaction mechanism in 20L pilot scale synthesis is equal to laboratory scale synthesis. On the other hand, risk of overheating and explosion is highly concerned in PMMA/PEI nanosorbent synthesis in 20L pilot scaler eactor because emulsion polymerization is an exothermic reaction. The result showed that the maximum reaction temperature in the 20L reactor synthesis was only 5ºC above intial synthesis temperature. This implies that risk of overheating and explosion can be minimized and the reaction temperature can be well controlled under an acceptable temperature.

In conclusion, synthesis of PMMA/PEI nanosorbent was successfully up-scaled from laboratory scale to 20L pilot scale with similar resultant

PMMA/PEI nanosorbent properties and equal emulsion polymerization reaction mechanism. Also, PMMA/PEI nanosorbent synthesized in 20L pilot scale reactor is a safe manufacturing process without risk of overheating and explosion problems.

Part II: Purifying Nanosorbent by Membrane Filtration Process

PMMA/PEI nanosorbent has been successfully purified by V-SEP membrane filtration system with MF-03 membrane in this study. The study shows that nanosorbent can be purified by V-SEP membrane filtration system with MF-03 membrane in continuous diafiltration mode nearly 8% solids contents and the optimized purifying nanosorbent processing time is from 420 to 780 min. On the other hand, the flux is steady on the study of fouling degree of PMMA/PEI nanosorbent on MF-03. This observation represents that membrane cleaning frequency and membrane replacement frequency can be reduced. Low overall operation cost of purifying nanosorbent process in V-SEP membrane filtration system can be predicted. However, this process generates a large quantity of wastewater resulting in secondary water pollution so different types of ultrafiltration and nanofiltration were selected to treat the wastewater. The result shows that NF-16 membrane from a range of ultrafiltration and nanofiltration membrane is a proper membrane to treat the wasterwater so that the treated wastewater can be recycled and resued in the purifying nanosorbent process.

In conclusion, PMMA/PEI nanosorbent were sucessfully purified by V-SEP membrane system with MF-03 membrane under 30 psi operation pressure in continuous diafiltration mode with low operation cost and NF-16 is a proper

membrane to recycle water from the purifying nanosorbent wastewater for reuse. Future process design of purifying nanosorbent in V-SEP membrane filtration system and reused of purifying nanosorbent wastewater is described in Figure 49.
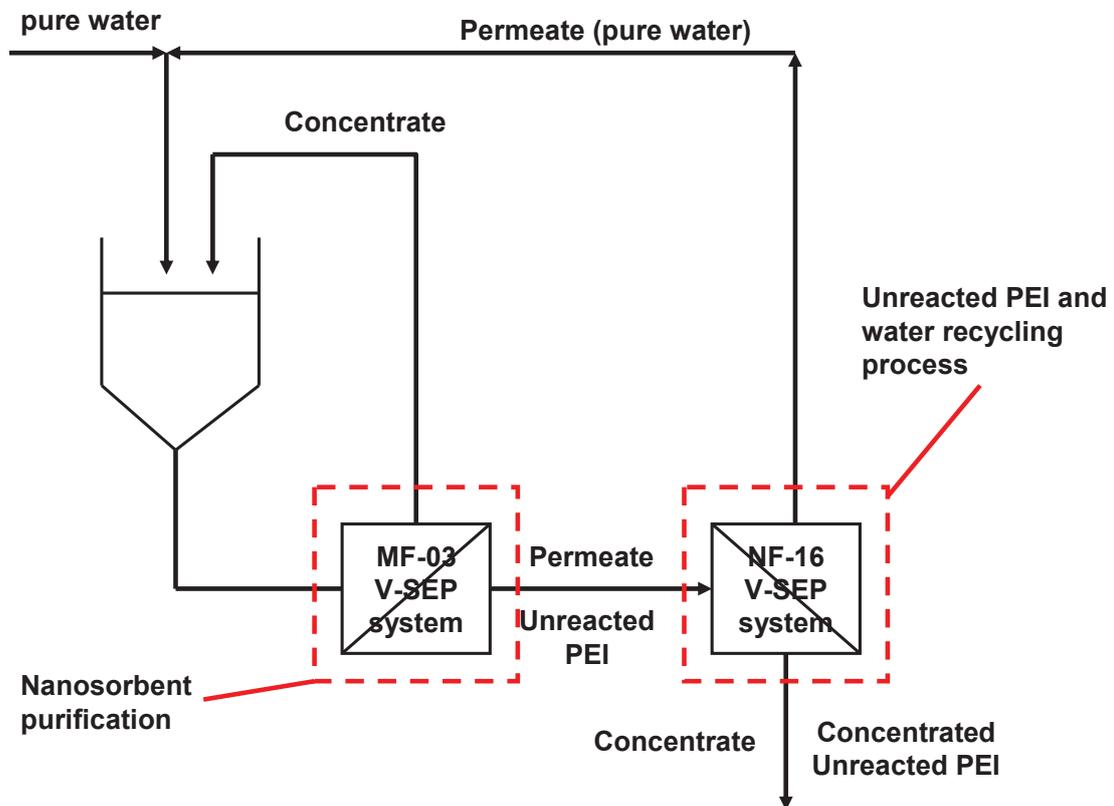
Figure 49. Future process design of purifying nanosorbent with V-SEP membrane filtration system

Application of Nanosorbent in Wastewater Treatment using Vibratory Shearing Enhanced Process (V-SEP) Membrane Filtration System

Application development of PMMA/PEI nanosorbent in water and wastewater has been firstly exploited in the 6-inch membrane stirred cell prior to in V-SEP membrane filtration system. Removal of Ag(I) ion, Cu(II) ion and Cr(VI) ions by nanosorbents were studied. The result showed that only minority of Ag (I) ions desorbed from Ag-loaded nanosorbent using sulphuric acid and nitric acid as regeneration agent and thus we can conclude that removal of Ag(I) ion by regenerated nanosorbent is technically infeasible. However, it is found that 40% to 50% of Cu(II) ions can be removed by regenerated nanosorbent from second to fifth adsorption cycles at optimal pH 5 and 20 to 35% of Cr(VI) ion can be removed by regenerated nanosorbent at optimal pH 2,. In conclusion, nanosorbent in removal of Cu(II) ion and Cr(VI) ion in the 6 inch membrane cell were successfully regenerated so application of nanosorbent in removal of Cu(II) ion using V-SEP membrane filtration system was subsequently and firstly studied.

Development of PMMA/PEI nanosorbent in Cu(II) ion removal has been firstly selected and performed in the V-SEP membrane filtration system with UF-19 membrane. In the effect of operation pressure on flux performance and effect of nanosorbent concentration on flux performance, the result showed that the optimal operation pressure is 30 psi and the optimal nanosorbent concentration is in range from 10% to 15%. In the study of removal of Cu(II) ions by nansorbent in V-SEP membrane filtration system, removal percentages of Cu(II) ions were reduced from 90 to 75% from first to third adsorption cycle and desorption percentage of Cu(II) ions declined from 70 to 50% from first to third desorption cycle under optimized

30 psi operation pressure and 15% nanosorbent solids contents. This demonstrated that regenerated nanosorbent can be recyled in removal of Cu(II) ions with V-SEP membrane filtration system. On the other hand, the study of fouling degree of PMMA/PEI nanosorbent on UF-19 and the flux performance of removal of Cu (II) ions by nanosorbent in V-SEP membrane filtration system showed that steady fluxes were observed. This indicates that membrane cleaning frequency and membrane replacement frequency can be greatly reduced resulting in lower overall operation cost of nanosorbent in wastewater treatment using V-SEP membrane filtration system.

Therefore, patented V-SEP membrane filtration technology used with patented amphiphilic core-shell nanosorbent in removal of Cu(II) ions containing wastewater is technically feasible process with low overall membrane filtration operation cost. This innovative wastewater treatment technology can be further developed to be a commercial wastewater treatment technology for removal of metal containing wastewater. Future process design of removal of Cu (II) ions by PMMA/PEI nanosorbent in V-SEP membrane filtration system is described in Figure 50.
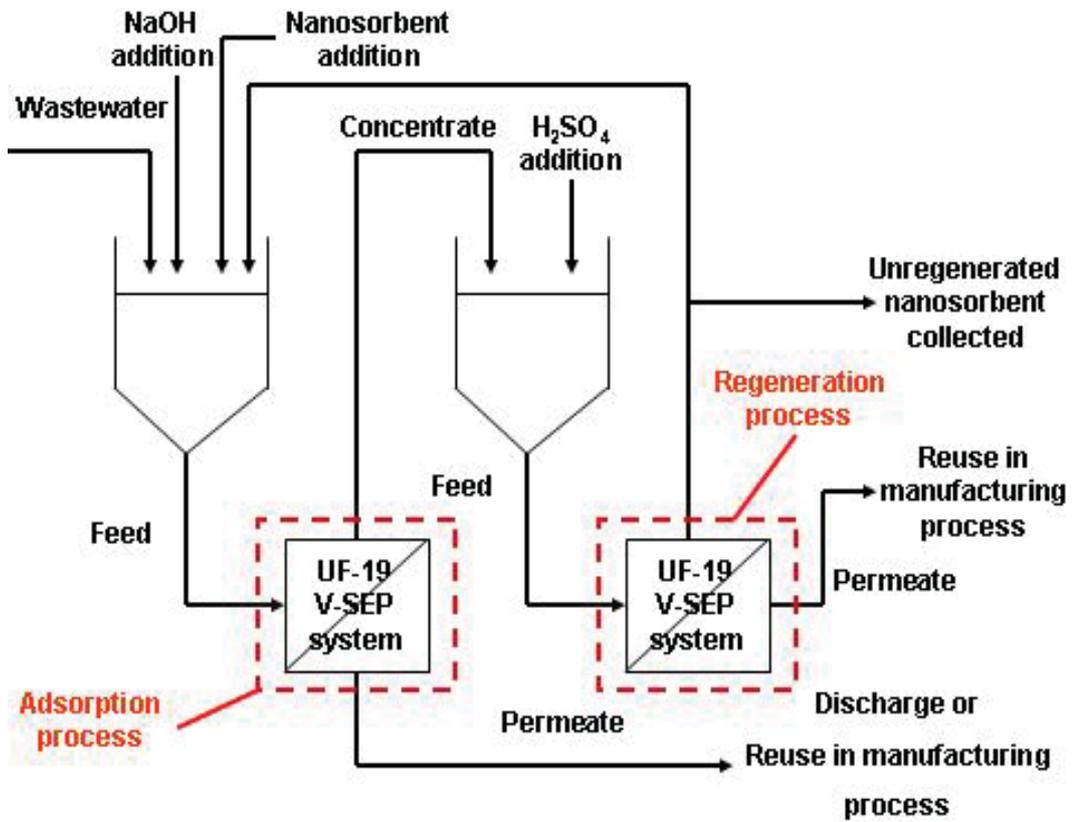
Figure 50. Continuous process flow of removal of Cu (II) ion with nanosorbent in V-SEP membrane filtration system

Chapter 7 Recommendation for future study

__Synthesis of PMMA/PEI Nanosorbents in a Pilot scale Reactor__

Although synthesis of PMMA/PEI nanosorbent was successfully up-scaled from laboratory scale to 20L pilot scale, the study of synthesis of PMMA/PEI nanosorbent 100L pilot scale or in 1000L (1 tons) industrial scale can be conducted in the future.

__Purifying Nanosorbent by Membrane Filtration Process__

Nanosorbent were sucessfully purified by V-SEP membrane system with MF-03 membrane under 30 psi operation pressure in continuous diafiltration mode and the purifying nanosorbent wastewater was successfully and preliminarily treated by NF-16 membrane in 6 inch membrane stirred cell. In order to complete further process design in Figure 59, the treatment of purifying nanosorbent wastewater can be performed in V-SEP membrane filtration system with NF-16 membrane.

__Application of Nanosorbent in Wastewater Treatment using Vibratory Shearing Enhanced Process (V-SEP) Membrane Filtration System__

To apply the nanosorbent in removal of metal ion in real wastewater with V-SEP membrane filtration system in future, several studies will be further conducted as follows:

(1) Application of nanosorbent in Cr (VI) ion removal and nanosorbent regeneration will be performed in V-SEP membrane filtration system with UF-19 membrane.

(2) Feasibility test of removal of other metal ions by nanosorbent and nanosorbent regeneration will be performed in the 6-in membrane stirred cell

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Appendix

Table A.1 Conversions and particle size variation in 17% S.C PMMA/PEI nanosorbent production (P081002) in the 20L reactor

Sample No	Reaction time (min)	Solid content (%)	Weight of MMA Addition (g)	Instantaneous conversion (%)	Overall conversion (%)	Particle size (nm)		PDI
						Dv	Dn	
1	45	6.31	640 g	86.5	17.3	159	142	1.120
2	105	8.86	640 g	88.1	35.2	157	139	1.129
3	165	11.55	640 g	91.8	55.1	234	213	1.099
4	225	13.83	640 g	91.5	73.2	257	222	1.174
5	286	16.09	640 g	92.1	92.1	283	241	1.174
6 (Product)	360	16.09	3200	92.1	92.1	283	243	1.165

$$\text{Instantaneous conversion} = \frac{\text{Solid Content x (Water + MMA + PEI} \bullet \text{HCI) - PEI} \bullet \text{HCI}}{\text{MMA added}} \text{X100\%} = \frac{11.55\% \text{ X } (18900 + 640 + 640 + 640 + 725) - 725}{640 + 640 + 640} \text{X100\%} = 91.8\%$$

$$\text{Overall conversion} = \frac{\text{Solid Content x (Water + MMA + PEI} \bullet \text{HCI) - PEI} \bullet \text{HCI}}{\text{Total MMA added}} \text{X100\%} = \frac{11.55\% \text{ x } (18900 + 640 + 640 + 640 + 725) - 725}{3200} \text{X100\%} = 55.1\%$$

Table A.2 Conversions and particle size variation in 20% S.C PMMA/PEI nanosorbent production (P081205) in the 20L reactor

Sample No	Reaction time (min)	Solid content (%)	Weight of MMA Addition (g)	Instantaneous conversion (%)	Overall conversion (%)	Particle size (nm) Dv	Dn	PDI
1	45	7.50	640 g	89.1	17.8	127	118	1.076
2	105	10.83	640 g	94.1	37.6	156	144	1.083
3	165	13.78	640 g	94.3	56.6	156	144	1.083
4	225	16.54	640 g	94.5	75.6	187	168	1.113
5	286	19.19	640 g	95.1	95.1	197	177	1.113
6 (Product)	360	19.20	3200	95.1	95.1	203	184	1.103

Table A.3 Conversions and particle size variation in 20% S.C PMMA/PEI nanosorbent product (P090106) in the 20L reactor

Sample No	Reaction time	Solid content	Weight of MMA	Instantaneous	Overall	Particle size (nm)		PDI
	(min)	(%)	Addition (g)	conversion (%)	conversion (%)	Dv	Dn	
1	45	7.61	640 g	89.7	17.9	145	137	1.058
2	105	10.05	640 g	82.4	33.0	178	158	1.127
3	165	13.87	640 g	94.8	56.9	201	180	1.117
4	225	16.54	640 g	94.3	75.5	215	197	1.091
5	286	19.22	640 g	95.2	95.2	230	211	1.090
6 (Product)	360	19.26	3200	95.5	95.5	230	209	1.100

Table B.1   Membrane list

Membrane	Pore size[1]	% rej NaCl[2]	Type	Membrane material	pH Tol[3]	Temp Tol[4]	Chlorine Tol[5]	Best pressure
RO-06		96.00%	RO	Thin film composite	2-11	70°C	1000 ppm hours	400-600 psi
NF-16		78.00%	NF	Thin film composite	3-10	70°C	NiL	NiL
NF-05		40-60%	NF	Thin film composite	3-10	60°C	<0.1ppm	350-500 psi
NF-11		10.00%	NF	Polyethersulfone	1-14	90°C	5000 ppm	200-400 psi
UF-07	10,000da		UF	Polyethersulfone	1-14	90°C	5000 ppm	100-250 psi
UF-16	100,000da		UF	Regenerated cellulose	1-11	55°C	20 ppm	30-150 psi
UF-17	100,000da		UF	Polysulfone	1-14	90°C	200 ppm	30-150 psi
UF-19	150,000da		UF	Polyethersulfone	1-14	90°C	5000 ppm	30-150 psi

[1] *Pore size = Pore size in form of molecular cut off or pore size*   [2] *rej NaCl = Rejection percentage of sodium chloride*

[3] *pH Tol = membrane tolerant pH*   [4] *TempTol = membrane tolerant temperature*

[5] *Chlorine Tol = membrane tolerant chlorine concentration*

Table B.1 Membrane list

Membrane	Pore size[1]	% rej NaCl[2]	Type	Membrane material	pH Tol[3]	Temp Tol[4]	Chlorine Tol[5]	Best pressure
UF-21	200,000da		UF	Polyethersulfone	2-11	70°C	100 ppm	30-150 psi
*MF-16	0.03um		MF	PTFE on Polyester	1-14	110°C	No effect	30-50 psi
*MF-01	0.05um		MF	PTFE on Polyester	1-13	110°C	No effect	30-50 psi
*MF-03	0.1um		MF	PTFE on Polyester	1-13	110°C	No effect	30-50 psi
MF-04	0.1-0.2mm		MF	Polyethersulfone	2-11	70°C	100 ppm	30-50 psi
*MF-05	0.1-0.2mm		MF	Kynar PVDF	1-13	50°C	1000 ppm hours	30-50 psi

Membrane belonged to hydrophobic type. Ethanol is essential to wet these membranes before filtration of aqueous feed.

Table B.2 Membrane selection for purifying nanosorbent using PEI solution

Membrane	PEI Feed COD	Permeate COD	Removal (Retention) %[1]	Permeable %[2]
MF-16	978	324	33.1	66.9
MF-01	978	370	37.8	62.2
MF-03	978	919	94.0	6.0
MF-04	978	197	20.1	79.9
MF-05	978	624	63.8	36.2
UF-16	978	244	24.9	75.1
UF-21	978	152	15.5	84.5
UF-17	978	280	28.6	71.4

[1] *Removal (Retention) % = (PEI Feed COD − Permeate COD)/PEI Feed COD X 100%*

[2] *Permable% = Permeate COD/PEI Feed COD X 100%*

Table B.3   Effect of nanosorbent solid content in flux performance in V-SEP

membrane filtration system

Solid content (%)	Flux at 30ºC (GFD)	Recovery[1] (%)
1.74	31.0	0.00
2.98	25.9	41.7
4.06	21.9	57.1
4.95	19.8	64.8
6.00	16.3	71.0
8.17	13.4	78.7
10.44	10.4	83.3
11.50	9.4	84.9
12.81	8.3	86.4

[1]*Recovery* = Volume of permeate collected / Initial volume of mixture in the V-SEP system X 100%

Table B.4 Purifying nanosorbent data

P081002		P081205		P090106	
Purification time (min)	**Conductivity (us/cm)**	**Purification time (min)**	**Conductivity (us/cm)**	**Purification time (min)**	**Conductivity (us/cm)**
15	591.0	0.0	1479.0	0.0	965.0
32	464.0	30.0	1157.0	120.0	656.0
45	404.0	90.0	685.0	360.0	313.0
60	338.0	150.0	418.0	420.0	240.0
91	282.0	210.0	270.0	540.0	174.0
105	261.0	270.0	191.0	660.0	150.0
120	227.0	330.0	152.0	780.0	130.0
135	265.0	390.0	123.0	900.0	110.7
150	230.0	450.0	101.0	1020.0	85.9
165	232.0	510.0	82.2	1140.0	108.0
180	214.0	630.0	67.0	1260.0	89.5
195	201.0	690.0	64.9		
210	179.0	750.0	60.6		
227	160.0	810.0	56.5		
240	148.0				
300	137.6				
360	102.7				
420.00	114.60				
480.00	93.20				
540.00	77.50				
600.00	74.00				
660.00	71.70				

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Table B.5 Membrane selection for unreacted PEI and water recycling of permeate from purifying nanosorbent

Sample	Cond.[1] (us/cm)	Removal % of Cond.[1](%)	COD (ppm)	Removal % of COD (%)
Permeate from purification[2]	445		1118	
Permeate pass through UF-07	277	37.8	150	86.6
Permeate pass through NF-11	247	44.5	115	89.7
Permeate pass through NF-05	225	49.4	91	91.9
Permeate pass through NF-16	52.4	88.2	29	97.4

[1]Cond. = Conductivity

[2]Permeate from purification = Permeate collected from PMMA/PEI purifying nanosorbent

Table C.1 Feasibility test of Ag (I) ion removal by nanosorbent and Ag (I) ion adsorbed nanosorbent regeneration with UF-19 membrane in 6 inch membrane stirred cell

Sample pH	Only removal by UF-19 membrane		Removal by UF-19 membrane with nanosorbent			
	Average permeate concentration (ppm)	Removal percentage[1] (%)	Average permeate concentration (ppm)	Removal percentage[1] (%)	Average permeate concentration (ppm)	Desorption percentage[1] (%)
pH 9	204.4	6.4	99.1	0.6	99.7	21.7
pH 7	215.0	1.5	11.8	6.4	97.1	17.6
pH 5	214.8	1.6	10.1	20.1	90.8	10.7
pH 4	211.0	3.3	10.1	30.8	85.9	7.7

Regeneration agent	Average permeate concentration (ppm)	Desorption percentage (%)
pH 2 (HNO$_3$)	14.4	7.3
1M HNO$_3$	21.2	10.8
1M H$_2$SO$_4$	22.4	11.8

* Initial Ag(I) solution concentration = 218 ppm

[1] Removal percentage (%) = (Initial Ag(I) solution concentration – average permeate concentration)/ Initial Ag(I) solution concentration X 100

[2] Desorption percentage (%) = Average permeate concentration in regeneration/ (Initial Cu(II) solution concentration –average permeate concentration in adsorption) x 100

Table C.2 Effect of pH on Cu (II) ion removal by nanosorbent with UF-19 membrane and Cu (II) ion only removal by UF-19 membrane

Sample pH	Only removal by UF-19 membrane		Removal by UF-19 membrane with nanosorbent	
	Average permeate concentration (ppm)	Removal percentage[1] (%)	Average permeate concentration (ppm)	Removal percentage[1] (%)
pH 7	0.8	99.1	NiL	NiL
pH 6	78.5	12.8	NiL	NiL
pH 5	80.0	11.1	3.1	96.6
pH 4	80.0	11.1	20.1	77.7
pH 3	83.5	7.2	33.4	62.9
pH 2	88.0	2.2	80.5	10.6

* Initial Cu(II) solution concentration = 90 ppm

[1] Removal percentage (%) = (Initial Cu(II) solution concentration – average permeate concentration)/ Initial Cu(II) solution concentration X 100

Table C.3 Removal efficiency of Cu (II) ion by nanosorbent and desorption efficiency of Cu (II) ion from adsorbed nanosorbent with UF-19 membrane in five successive adsorption and regeneration cycle

Cycle	Average permeate concentration (ppm)	Removal percentage[1] (%)
1	3.1	96.6
2	47.3	47.4
3	53.6	40.4
4	45.4	49.6
5	52.4	41.8

* Initial Cu(II) solution concentration = 90 ppm

[1] Removal percentage (%) = (Initial Cu(II) solution concentration – average permeate concentration)/ Initial Cu(II) solution concentration x 100

Table C.4 Effect of pH on Cr (VI) ion removal by nanosorbent with UF-19 membrane and Cr (VI) ion only removal by UF-19 membrane

Sample pH	Only removal by UF-19 membrane		Removal by UF-19 membrane with nanosorbent	
	Average permeate concentration (ppm)	Removal percentage[1] (%)	Average permeate concentration (ppm)	Removal Percentage[1] (%)
pH 10	84	6.7	78	13.3
pH 8	88	2.2	29	67.8
pH 6	88	2.2	4.7	94.8
pH 4	86	4.4	1.3	98.6
pH 3	NiL	NiL	0.8	99.1
pH 2	90	0.0	61	32.2

* Initial Cr(VI) solution concentration = 90 ppm

[1] Removal percentage (%) = (Initial Cr(VI) solution concentration – average permeate concentration)/ Initial Cr(VI) solution concentration x 100

Table C.5 Removal efficiency of Cr (VI) ion by nanosorbent with UF-19 membrane in five successive adsorption and regeneration cycle

Cycle	Average permeate concentration (ppm)	Removal percentage[1] (%)
1	0.8	99.1
2	5.8	35.6
3	70	22.2
4	74	17.8
5	72	20.0

* Initial Cr (VI) solution concentration = 90 ppm

[1] Removal percentage (%) = (Initial Cr(VI) solution concentration – average permeate concentration)/ Initial Cr(VI) solution concentration x 100

Table C.6 Fouling degree test and effect study of pressure on the permeate flux
performance of nanosorbent in UF-19 membrane at 7.5% solid content

Process Time (Min)	Flux at 30ºC (GFD) at 30 psi	Flux at 30ºC (GFD) at 60 psi	Flux at 30ºC (GFD) at 120 psi
0	63.8	59.4	62.8
30	59.1	54.0	59.2
60	58.1	49.7	51.9
90	55.3	47.6	48.9
120	54.4	42.7	47.4
150	53.6	44.5	45.8
180	51.3	43.9	45.5
270	50.2	41.3	43.1
300			40.2
330	44.9	39.5	
390	44.9	39.1	37.0
450	45.5		37.6
480	45.4	37.2	38.3

Table C.7 Effect study of nanosorbent solid content on permeate flux performance in V-SEP membrane filtration system with UF-19 membrane in concentration mode

Solid content (%)	Flux at 30ºC (GFD)	Recovery[1] (%)
3.31	104.6	0.0
3.47	95.1	4.6
3.46	63.3	9.1
4.29	55.7	22.9
5.21	48.0	36.6
6.10	42.5	45.7
7.41	33.8	55.3
9.54	27.1	64.8
10.53	24.5	68.6
12.41	23.3	73.3
15.11	23.7	78.1
18.90	14.7	86.4

[1]*Recovery* = Volume of permeate collected / Initial volume of mixture in the V-SEP system X 100%

Table C.8 Flux performance, Cu (II) ion removal percentage and Cu (II) ion to nanosorbent ratio in removal of Cu (II) ion by nanosorbent in V-SEP membrane filtration system in first adsorption cycle

Process time (min)	Flux at 30ºC (GFD)	Cu (II) ion in permeate (ppm)	Removal percentage (%)	Cu (II) ion to nanosorbent dosage (mg/g)
0	14.2	0.0	100.0	0.0
30	14.0	0.5	98.6	1.6
60	13.7	2.5	97.2	3.3
90	13.2	3.2	96.5	5.1
120	13.3	3.8	95.8	6.8
150	13.1	4.8	94.7	8.5
180	13.1	5.1	94.4	10.2
210	13.2	5.8	93.6	11.8
240	13.7	6.7	92.6	13.5
270	13.2	7.1	92.1	15.2
300	13.3	7.5	91.6	17.9
330	13.7	8.3	90.8	19.5
360	13.6	8.5	90.6	21.1

Table C.9 Flux performance, Cu (II) ion removal percentage in removal of Cu (II) ion by nanosorbent in V-SEP membrane filtration system in second adsorption cycle

Process time (min)	Flux at 30°C (GFD)	Cu (II) ion in permeate (ppm)	Removal percentage (%)
0	13.5	14.6	83.8
45	13.1	15.3	83.0
75	12.7	16.0	82.2
105	12.5	16.8	81.4
135	12.3	17.3	80.8
165	12.2	18.0	80.0
195	12.7	18.8	79.1
225	12.6	19.6	78.3
255	12.0	20.1	77.6
285	12.4	21.1	76.6
315	12.6	22.3	75.2
345	12.2	22.8	74.7
375	12.1	23.1	74.3
412	12.4	24.0	73.4

Table C.10 Flux performance, Cu (II) ion removal percentage in removal of Cu (II) ion by nanosorbent in V-SEP membrane filtration system in third adsorption cycle

Process time (min)	Flux at 30ºC (GFD)	Cu (II) ion in permeate (ppm)	Removal percentage (%)
0	11.5	23.6	73.8
45	11.3	24.0	73.4
75	10.9	24.8	72.5
105	10.7	25.4	71.5
135	10.2	26.0	71.1
165	9.9	26.7	70.3
195	9.7	27.3	69.6
225	9.8	27.7	69.2
255	10.2	28.7	68.2
285	9.8	29.1	67.7
315	9.4	30.7	65.9
345	9.5	31.2	65.3
375	9.8	31.9	64.6
405	10.2	32.5	63.9
435	9.9	32.9	63.4
470	10.1	33.5	62.8

Table C.11 Flux performance, Cu (II) ion desorption percentage in removal of Cu (II) ion by nanosorbent in V-SEP membrane filtration system in three regeneration cycles

First regeneration			
Process time (min)	Flux at 30ºC (GFD)	Cu (II) ion in permeate (ppm)	Desorption percentage (%)
0	34.8	319.0	74.7
10	24.4	310.0	72.6
20	18.7	312.0	73.1
32	12.1	300.0	70.3

Second regeneration			
Process time (min)	Flux at 30ºC (GFD)	Cu (II) ion in permeate (ppm)	Desorption Percentage (%)
0	32.0	236.0	66.3
14	21.2	229.0	64.3
24	14.9	223.0	62.7
40	7.7	212.0	59.6

Third regeneration			
Process time (min)	Flux at 30ºC (GFD)	Cu (II) ion in permeate (ppm)	Desorption Percentage (%)
0	28.6	174.0	56.2
15	18.2	169.0	54.6
29	12.3	160.0	51.7
49	4.8	156.0	50.4