

***Low pressure driven multilayered polyelectrolyte membranes:
A sustainable tool for Phosphate recovery***

The subject of phosphate (P) recovery from various sources is in the forefront in recent years since its natural resources are alarmingly going down raising a threat to the agricultural sector. On the other hand eutrophication is a leading environmental issue for aquatic sources desired to be cut down. Non-renewability of phosphate mines, geological imbalance and steep increase in fertilizer price point out the significance of protocol development for its recovery. Over fertilization together with the modern agricultural practices leads to excess run off of nutrients to water bodies eventually causing dead zones in oceans that is ever increasing in number. The global P-flow analysis indicates that two sectors represent the major flow into surface water. Non-point source soil erosion and run off that has relatively low P concentrations and high volumetric flow. The other being flow of animal waste with high P content and low volumetric flow. Once it reaches the water source, it can get easily settled together with the particulate matter making the recovery almost impossible. The P removal/recovery technologies from aqueous streams still have many drawbacks, the major being energy intensive. Ultrafiltration (UF) is a low pressure driven membrane separation method used for the removal of inorganic micro pollutants. Membrane separation methods which include nanofiltration (NF) and UF are the most preferred physical processes for the treatment of wastewater. The attraction about membrane separation is that it can be conveniently incorporated in a process and separation can be carried out at room temperature. These methods look even more versatile today by the use of nanostructured membranes fabricated via layer by layer (LbL) assembly of polyelectrolytes (PE). It affords a porous support and a self assembled skin. The skin thickness mainly depends on deposition parameters. Separation characteristics of membrane can be formulated by controlling the charge density, hydrophilicity, and pore size (composition, pH, supporting salt, etc.). Here we propose a low energy route for the effective recovery of phosphate from aqueous solution at low concentration range (100 ppm).

Organization of the thesis

The thesis comprises of five chapters. The first chapter discusses the importance of phosphate recovery and the sustainability issues of this nutrient. The state-of-art of nanoskinned composite membranes in analytical separation with special emphasis on ion separation is also discussed in this chapter. Chapter 2 presents an exclusive coverage on the

experimental methods/protocols followed for multilayer membrane fabrication, its characterization, and membrane filtration. Chapter 3 presents some preliminary investigations for a suitable polyelectrolyte pair for coating on membrane substrates that may impart ion selective property for the membrane at low pressure end, particularly suitable for selective phosphate recovery from aquatic system at low ppm level. Chapter 4 illustrates the potential use of PEI/PSS bilayers assembled via layer by layer (LbL) method on nylon microfiltration membrane for the recovery of phosphate from water in the presence of chloride under ultrafiltration conditions at highly charged state of PEI. Chapter 5 describes the influence of deposition pH of PEI in multilayer formation and in the transport profile of $\text{Cl}^-/\text{H}_2\text{PO}_4^-$ pair. More attention is paid to the influence of ionic strength in the growth mechanism of PEI/PSS multilayer in low and highly charged state of PEI.

Chapter 1

Introduction and objectives

This chapter describes the need for the recovery of phosphorous from water from an environmental as well as energy point of view. Phosphorous recovery from industrial and municipal waste streams drew more attention recently due to the depletion of phosphorous resources and the eutrophication of water bodies. Various techniques used for P recovery were discussed and among them an overview of membrane technology is highlighted. A description of various pressure driven membrane separation processes, its energy requirement and role in separation process are discussed. Conferring a suitable surface that respond to external stimuli cut down the energy requirements separation process.

Chapter 2

Materials and methods

The details of the materials used and the experimental methods adopted for the investigation have been presented in this chapter. Techniques such as Fourier Transform Infrared Spectroscopy in the Attenuated Total Reflection mode (ATR-FTIR), Ellipsometry, Scanning Electron Microscopy (SEM) with EDS, Ion Chromatography (IC), and ultrafiltration cell were used. A brief description of various techniques employed is presented in this chapter.

Chapter 3

Search of suitable polyelectrolyte pair for chloride/phosphate separation.

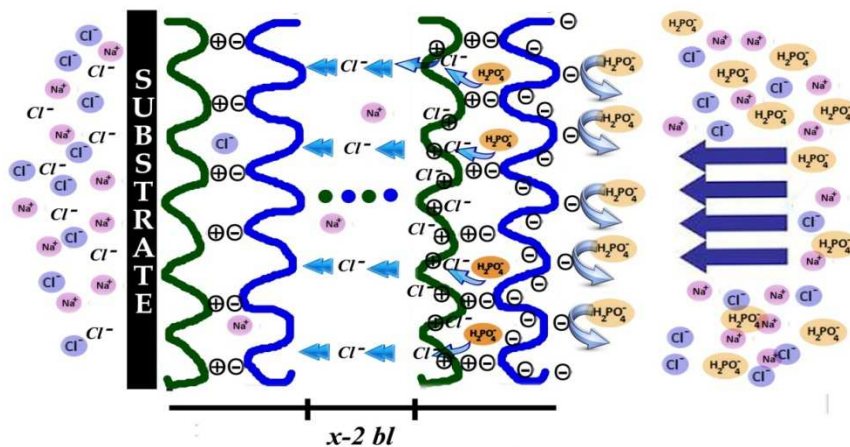
This chapter presents some preliminary investigations for a suitable polyelectrolyte pair for coating on membrane substrates that may impart ion selective property for the membrane at low pressure end, particularly suitable for selective phosphate recovery from aquatic system at low ppm level. A wide range of polyelectrolytes from strong to weak having different charge density were used for LbL assembly on various substrates. Substrates used were mainly polyether sulfone (supor) and nylon microfiltration membranes having pore size 0.45 μm . Polycations selected for the study were poly(diallyl-dimethyl ammonium chloride), poly(2-dimethyl aminoethyl methacrylate methyl chloride quarternary salt, chitosan, poly(dimethylamine-co-epichlorohydrin-co-ethylene diamine), Trimethyl chitosan, and polyetheleneimine. Polyanions used were poly (styrene sulfonate), humic acid, polyvinyl sulphate, dextran sulphate, chondroitin sulphate, and poly (acrylic acid). LbL formation was also studied using macrocyclic compound 1,4,7,10,13,16-hexaazacyclooctadecane (aza 6). Nanoparticle (ZnO) and single charged species (pyrene sulfonic acid sodium salt) were introduced in LbL assembly of PDAC/PSS to enhance permselectivity. The influence of various combinations of polyelectrolyte multilayers on the transport characteristics of chloride/phosphate pair is discussed in this chapter. More attention is paid to PDAC/PSS pair with respect to single ion transport (Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-}) and mixed ion transport (Cl^- & PO_4^{3-} , NO_3^- & PO_4^{3-} , and SO_4^{2-} & PO_4^{3-}). Recovery status of phosphate from laundry waste water using PDAC/PSS is also included. Specifically, this work examines the potential of PSS/PDADMAC deposited on polyether sulfone microfiltration membranes for the recovery of phosphate from laundry water as a function of the number of adsorbed layers as well as charge density of bilayer. PEI/PSS deposited on nylon gave better results and in the forthcoming chapters the filtration characteristics as well as membrane chemistry of PEI/PSS multilayer is explored.

Chapter 4

Phosphate recovery using PEI/PSS multilayered membranes constructed from highly ionised PEI

This work illustrates the potential use of PEI/PSS bilayers assembled via layer by layer (LbL) method on nylon microfiltration membrane for the recovery of phosphate from

water in the presence of chloride under ultrafiltration conditions. The buildup pH is maintained at 5.9 so that PEI is deposited in highly charged state. Bilayers were constructed from polyelectrolyte solutions of varying ionic strength (0-1 M of NaCl). The selected pH for deposition of PEI (5.9) and the presence of supporting salt in the polyelectrolyte solution is expected to provide membranes with high permeability and high charge density. This particular combination of bilayers yielded high flux membranes that allowed selective removal of H_2PO_4^- in the presence of Cl^- at low pressure (0.28 bar). The magnitude of negative solute rejection of chloride showed increasing trend with the number of bilayer for a particular salt concentration. Whereas the increase in magnitude with ionic strength is so high (-6.18 to -269.17 at 0.5 M NaCl for 9 bl) that gave the best observed $\text{Cl}^-/\text{H}_2\text{PO}_4^-$ selectivity (310.23, flux $13.53 \text{ m}^3/\text{m}^2\text{-day}$). To the best of our knowledge, this is the first time a multilayer polyelectrolyte system with such a high selectivity and rejection for H_2PO_4^- is reported. The solution flux decreased with number of bilayers and ionic strength. The suitability of this polyelectrolyte pair for the recovery of phosphate in presence of nitrate and humic acid were tested. The role of buildup polyelectrolyte concentration, feed concentration and the composition of membrane support on rejection of phosphate were investigated. An ion exchange mechanism is suggested for the selective recovery of phosphorous and is schematically represented below.



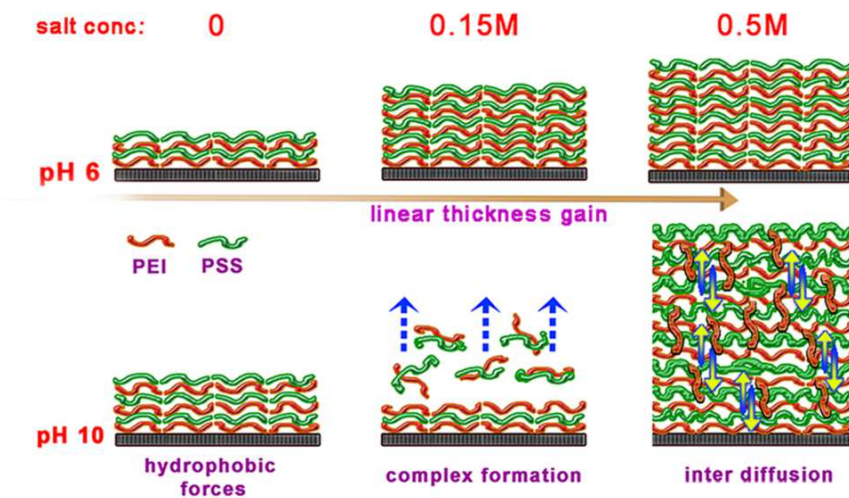
Scheme 1: Schematic representation of transport of $\text{Cl}^-/\text{H}_2\text{PO}_4^-$ through PEI/PSS multilayers.

CHAPTER 5

Phosphate recovery using low ionisation state of PEI in PEI/PSS multilayers

The influence of deposition pH of PEI in multilayer formation and in the transport profile of $\text{Cl}^-/\text{H}_2\text{PO}_4^-$ has been investigated. PEI being a weak polyelectrolyte, the degree of ionisation varies according to the pH in which it is dissolved. In this study, pH of deposition

is varied between 4-10 (4, 6, 8, and 10) for PEI and PSS. With the progress in pH from acidic to alkaline region, the adhesive force shifts from strongly electrostatic to weakly electrostatic form. The presence of nonionized segments towards alkaline region has a negative impact on the selectivity factor of $\text{Cl}^-/\text{H}_2\text{PO}_4^-$. The selectivity and flux shifts from 310.23 and 13.05 $\text{m}^3/\text{m}^2\text{-day}$ to 3.58 and 5.65 $\text{m}^3/\text{m}^2\text{-day}$, respectively. Ion exchange mechanism seems to be nonoperative at higher deposition pH of PEI. The multilayer formation is evaluated by ellipsometry, ATR and SEM at each deposition pH. In order to have further insight into the role of ionic strength (0 – 0.5 M NaCl) in multilayer formation at the low ionised state of PEI a detailed study is carried out using ATR. Besides this the transport characteristics are also evaluated. Primarily salt addition (0.05 and 0.15 M NaCl) resulted in thin layer formation, indicating partial desorption of PEI/PSS complexes. This observation is supported by the rejection (34.82 and 35.67%) and flux (10.45 and 8.32 $\text{m}^3/\text{m}^2\text{-day}$) data of $\text{Cl}^-/\text{H}_2\text{PO}_4^-$ for 9th bilayer. Further addition of salt (0.20 – 0.50 M) to the buildup medium resulted in large thickness gain (80.05 nm). However the rejection and selectivity value remained low compared to the strongly ionised state of PEI (98.81%, and 310.23 at pH 5.9 and 54.96 and 3.58 at pH 10 for 9th bilayer). The transport data points out the involvement of secondary forces in the multilayer build up in a region beyond the salt concentration of 0.15 M NaCl. The interplay of buildup pH and ionic strength is depicted in scheme 2.



Scheme 2. Schematic representation of interplay of salt and buildup pH

In addition to these studies, transport characteristics are also evaluated at various feed pH (2.0-11.5). The observation of rejection pattern indicates that PEI is more selective towards monovalent phosphate. The stability of multilayer build up at pH 6 as a function of ionic strength of deposition medium was also investigated. Stability of multilayer membranes